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Determination of a silane intermolecular force field potential model from an *ab initio* calculation

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Intermolecular interaction potentials of the silane dimer in 12 orientations have been calculated by using the Hartree-Fock (HF) self-consistent theory and the second-order Møller-Plesset (MP2) perturbation theory. We employed basis sets from Pople's medium-size basis sets [up to 6-311++$G(3df, 3pd)$] and Dunning's correlation consistent basis sets (up to the triply augmented correlation-consistent polarized valence quadruple-zeta basis set). We found that the minimum energy orientations were the G and H conformers. We have suggested that the Si-H attractions, the central silicon atom size, and electronegativity play essential roles in weakly binding of a silane dimer. The calculated MP2 potential data were employed to parametrize a five-site force field for molecular simulations. The Si-Si, Si-H, and H-H interaction parameters in a pairwise-additive, site-site potential model for silane molecules were regressed from the *ab initio* energies.

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I. INTRODUCTION

The determination the intermolecular interaction potentials or the van der Waals interactions has become very important in materials chemistry research as well as in the optoelectronic or semiconductor industry. These interactions are crucial for understanding and predicting the thermodynamic properties of liquids and solids [1], the energy and charge transfers among molecular complexes [2], and the conformational tertiary structures of nanostructures. In our previous studies, we have calculated thoroughly the interaction potentials of the methane and carbon tetrachloride dimers [3–8] and studied the dispersion energy. The silane (SiH_4) structure is similar to the methane structure and is a candidate to perform a prototype study. In the semiconductor and optoelectronic industry [9–12], silane is widely used for the chemical vapor deposition of silicon and silicon dioxide thin layers. There has been great interest in downscaling of optoelectronic devices and their structural properties. Most of the studies previously focused on the intramolecular potential energies, but only a few have calculated the intermolecular potential energies of the silane dimer in the recent years [13–16]. Govender, Rootman, and Ford [13] calculated a single-point geometry optimization at the second-order Møller-Plesset (MP2)/6-311++G(d,p) level. Sakiyama, Takagi, and Matsumoto [14] calculated the interaction energies of the silane dimer for nine relative orientations at the MP2 augmented correlation-consistent polarized valence triple-zeta basis set (aug-cc-pVTZ) level with 162 different spatial configurations. From our previous conclusions, they all have shown that the low-level basis sets did not systematically converge to the expected potential curve. Those previous low-level *ab initio* calculations are a good starting point to investigate the various factors affecting the contributions to the interaction energy, such as electrostatic, induction, dispersion, and exchange terms. Although the interaction potentials of the methane dimer have been studied extensively, there were relatively few *ab initio* studies on the interaction potentials of the structurally similar silane dimer.

In this paper, we performed high-level *ab initio* calculations of potential energies of the silane dimer in terms of the Hartree-Fock (HF) and MP2 methods, up to aug-cc-pV5Z, and we also construct full intermolecular potential curves and potential energy surfaces. To understand this system, the aim of the present study is to determine Si-Si, Si-H, and H-H force field parameters from *ab initio* potential energies to obtain an accurate representation of minimum structures. In addition, a Lennard-Jones (LJ) five-site potential [17] was parametrized to give excellent fits to both the repulsive and attractive regions of the potential energy curves.

This paper is organized as follows. In Sec. II, we present details of the calculations. In Sec. III the results are presented and discussed. In Sec. IV, a summary and a brief perspective are given.

II. METHODS AND CALCULATIONS

All the quantum chemistry calculations have been performed by using the GAUSSIAN03 program package [18]. As to the uncertainty estimates for our calculations, we used the Tight convergence with the GAUSSIAN package. It sets the convergence threshold as 0.0006 kcal/mol. As we have included the numerical data only to the third decimal, the largest uncertain estimates for each potential data are at most ±0.001 kcal/mol. We therefore did not include uncertainty estimates for our calculated data. Similar to the methane dimer, a large part of the exchange-repulsion interactions of the silane dimer can be calculated by the HF method. The calculation of electron correlation energies depends on the level of the correlation-corrected method, the size of the basis set, and the correction of the basis set superposition error (BSSE). The state-of-the-art choice for the correlation-corrected method is the Møller-Plesset (MPx, $x = 2$–4) perturbation method [19]. The isolated silane molecule was first optimized with the MP2 theory with a 6-311++$G(3df,3pd)$ basis set and was found to be of a tetrahedral configuration (T_d symmetry) with a Si-H bond length of 1.47 Å, which is consistent with the experimental data by Kattenberg and Oskam (Si-H bond length = 1.4806 ± 0.0008 Å) [20] and by Willetts and Jones

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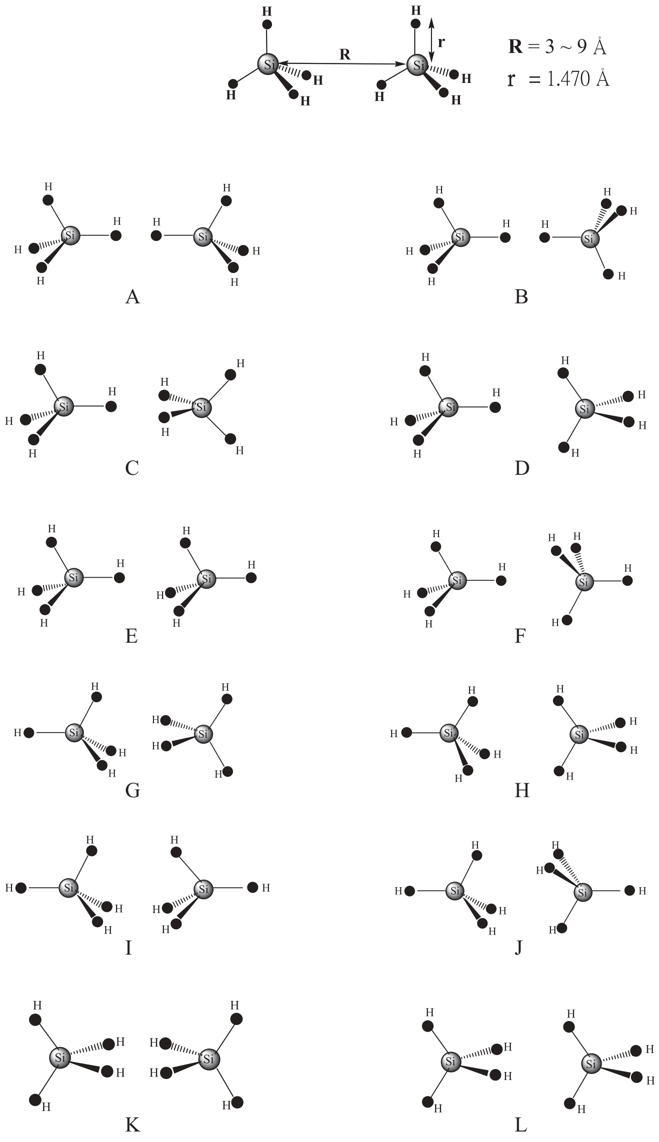

FIG. 1. The 12 symmetric conformers of the silane dimer. We designate each conformer by a representative capital letter from *A* to *L*.

(Si-H bond length = 1.482 Å) [21], and with average value given by Duncan (Si-H bond length = 1.4813 ± 0.0006 Å) [22] and the linear fitting prediction data found by Duncan, Harvie, and McKean (Si-H bond length = 1.479 ± 0.003 Å) [23]. The 12 symmetric conformers chosen to sample the orientational dependence are depicted in Fig. 1. Because of the high symmetry of the dimer configuration, the angular sampling should be wide enough to model the rotational dynamics in normal thermodynamic conditions. The MP2 method [19] has been used to treat the correlation effect. Pople's medium-size basis sets [up to 6-311++$G(3df,3pd)$] [24] and Dunning's correlation-consistent basis sets (aug-cc-pVXZ, $X = \mathrm{D, T, Q, 5}$) [25] were employed in the calculations. The BSSEs were corrected by the counterpoise method of Boys and Bernardi [26]. Subsequently, the Si-Si distance, denoted as R, was sampled for a large range of 3.0–9.0 Å, with 31 configuration points for each conformer. A total of 372 configuration points were actually sampled and the energies calculated. During the scan we used rigid and symmetric conformer assumptions. The MP2 interaction energies at the basis set limit have been estimated by using the methods of Martin [27] and Helgaker *et al.* [28], and a numerical extrapolation scheme based on the Lagrange formula [29] is adopted. The G and H conformer potential data with some basis sets are shown in Table I.

III. RESULTS AND DISCUSSIONS

A. HF self-consistent field calculations

The BSSE-corrected HF interaction potentials of the silane dimer in 12 symmetric conformers are shown in Fig. 2. The HF calculations for all conformers yield purely repulsive potentials without minima for all the basis sets used. This can be attributed to the rather weak electrostatic interactions for the silane dimer. In the short range, the strong exchange-repulsion interaction dominates with little alternation from the electrostatic and induction attractions.

B. MP2 calculations

In Fig. 3 we shown the MP2 potentials for the 12 conformers by using a high-level aug-cc-pV5Z basis set. We can see that the potentials become deeper when there are more inner hydrogen atoms and close on-distance contacts between the monomers. It was found that the minimum-energy conformation corresponds to the C_s symmetry configuration (the G and H conformers). It is interesting to analyze the orientational dependence from the repulsive and the attractive components of the potentials separately. SiH_4 is a nonpolar molecule and the dominant long-range attraction is thus owing to the London dispersion force. On the other hand, the strong

TABLE I. The basis set dependence of MP2 potentials for the G and H conformers.

	MP2					
	G conformer			H conformer		
Basis set	R_0 (Å)	R_m (Å)	E_b (kcal/mol)	R_0 (Å)	R_m (Å)	E_b (kcal/mol)
aug-cc-pVDZ	3.98	4.45	−0.484	3.98	4.46	−0.482
aug-cc-pVTZ	3.86	4.33	−0.594	3.87	4.34	−0.590
aug-cc-pVQZ	3.84	4.31	−0.622	3.85	4.31	−0.622
aug-cc-pV5Z	3.82	4.30	−0.651	3.83	4.30	−0.646
Basis set limit	3.78	4.28	−0.712	3.79	4.29	−0.692

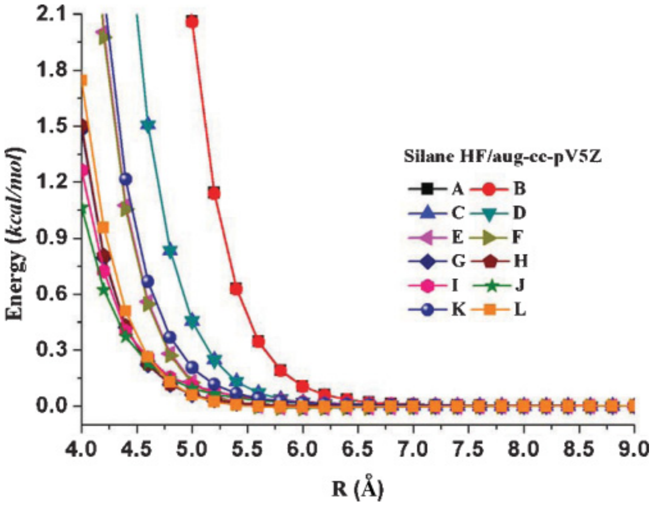

FIG. 2. (Color online) The HF potentials for the 12 orientations using the aug-cc-pV5Z basis set.

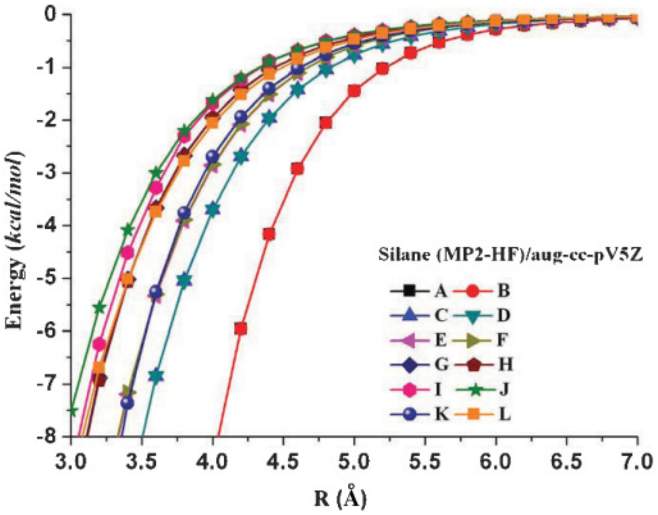

FIG. 4. (Color online) The MP2-HF potentials for the 12 orientations using the aug-cc-pV5Z basis set.

repulsive force almost comes from the exchange-repulsion interaction. In contrast with the HF, the MP2 potential thus helps to delineate the relative importance of the dispersion energy in the intermolecular interactions overall. In Fig. 4 we show the MP2 potentials subtracting the corresponding HF potentials, dubbed as MP2-HF, for the 12 conformers. The MP2-HF potentials largely represent the dispersion curves that are purely attractive. The dispersion interaction between molecules is a weak attraction owing to an instantaneous dipole moment in one molecule inducing a dipole moment in another molecule. The dispersion energy (V_{disp}) can be roughly represented by the form [30,31]

$$V_{\mathrm{disp}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} \cdots, \qquad (1)$$

where C_6, C_8, C_{10},... are the dispersion coefficients. We have completed a nonlinear fitting to the MP2 potential data by using Eq. (1) and obtained $C_6 = 342.35$ eV Å^6 (for the G conformer), which is consistent with literature value [31–33]. However, it is important to mention that the C_6 coefficient depends on the configurations of the molecule. For example, for conformers A–L, we obtained a wide range (283.73–1507.97 eV Å^6) of the C_6 coefficient. In addition, the higher-order dispersion coefficients C_8, C_{10}, etc., are also important contributions for the total interaction [31], and here we only do a simple approach of calculation to compare to the well-known literature value (343.0 eV Å^6) [31–33].

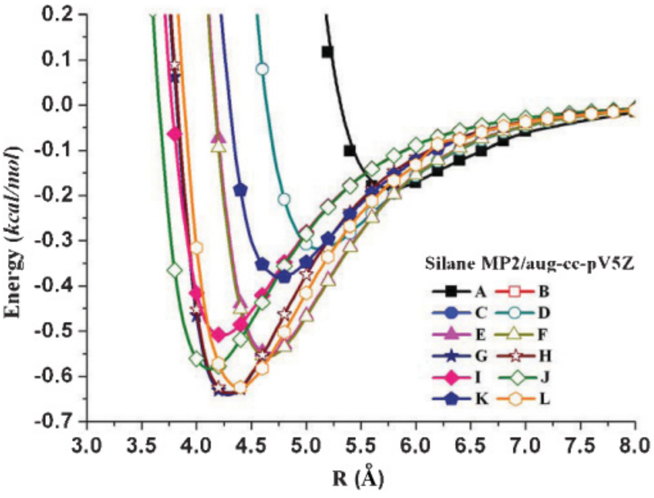

FIG. 3. (Color online) The MP2 potentials for the 12 orientations using the aug-cc-pV5Z basis set.

In Table I we present the G and H conformers of several basis sets with the MP2 method. R_0 is the distance at which the potential is zero and can be obtained from a two-point interpolation of the calculated data. The bond length R_m and the binding energy E_b can be obtained through a harmonic modeling of the three lowest potential data near equilibrium regions. With increasing basis size, the equilibrium bond length converges at the aug-cc-pVTZ basis set to a 0.02-Å accuracy, while a fairly large basis set, aug-cc-pV5Z, is required to converge the binding energy at a chemical accuracy (~0.03 kcal/mol). It is clear from Table I that the aug-cc-pVTZ basis set still underestimates the binding energy by ~33%, and is consistent with previous papers [14]. The strong dependence on the basis set and the slow convergence on the binding energy require an estimation of the potential features at the complete basis set (CBS) limit. The CBS binding energies can be obtained by an extrapolation scheme with Dunning's basis sets. We consider the methods of Martin [27] and Helgaker *et al.* [28], and a numerical extrapolation scheme based on the three-term Lagrange formula [29] and the MP2/CBS results are listed in Table II. We see that by using the aug-cc-pVXZ data, the three extrapolation methods yield similar CBS values.

C. Analytical site-site pair potential model

Unlike the methane dimer [11–15], in Fig. 3, we see that the 12 orientation potential energy curves of silane dimer are not systematically arranged in order. The G and H conformer energies are relatively lower than the I and J conformers. This

TABLE II. The estimated MP2/CBS binding energies for the *G* conformer using the three extrapolation methods described in the text.

		aDZ[a]	aTZ[a]	aQZ[a]	a5Z[a]
Number of basis function		126	284	536	902
		Extrapolation			
Methods	aDT[b]	aTQ[c]	aQ5[d]	aDTQ[e]	aTQ5[f]
Martin	−0.633	−0.638	−0.675	NA[g]	NA[g]
Helgaker	−0.640	−0.642	−0.681	NA[g]	NA[g]
Numerical	−0.682	−0.654	−0.693	−0.645	−0.712

[a] Number of basis function with the MP2/aug-cc-pVXZ (X = D, T, Q, and 5).

[b] Basis set limit estimation with the aug-cc-pVXZ (X = D and T).

[c] Basis set limit estimation with the aug-cc-pVXZ (X = T and Q).

[d] Basis set limit estimation with the aug-cc-pVXZ (X = Q and 5).

[e] Basis set limit estimation with the aug-cc-pVXZ (X = D, T, and Q).

[f] Basis set limit estimation with the aug-cc-pVXZ (X = T, Q, and 5).

[g] Not available.

indicates that not only the inner silicon-silicon interactions play a major role but also the interchange of influence of silicon-hydrogen interactions is very important. Besides, the central silicon atom size is larger than that of carbon atom ($r_{\rm Si}$ = 110 pm, r_C = 70 pm) and silicon Pauling electronegativity is smaller than the carbon atom (silicon = 1.90, carbon = 2.55), which would play an important role. For those reasons, the calculated results show that the *G* and *H* potential curves may be more favorable toward stabilization than others. Therefore, we conclude that the inner silicon interactions, the interplay of silicon-hydrogen interactions, silicon atom size, and electronegativity are also major components contributing to the potential anisotropy.

Based on these observations, an analytical five-site model was proposed to represent the MP2/aug-cc-pV5Z potential data. The site-site interaction is represented by a LJ function [33]:

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], \qquad (2)$$

where the indices i and j denote the atoms in separated monomers, respectively, and r_{ij} represents the silicon-silicon distance for a pair of monomers. In this model σ_{ij} and ε_{ij} are the potential parameters to be determined in the nonlinear regression. No bias weights were put on specific configurations, except that we excluded from the nonlinear fitting some of the largest repulsive energy points in the regression to prevent their dominance in the least-squares cost function [34]. However, this latter constraint could effectively put more weight on deeper wells. For the five-site model, the best-fitting parameters we obtained are $\sigma_{\rm HH} = 2.754$ Å, $e_{\rm HH} = 0.100$ kcal/mol, $\sigma_{\rm SiH} = 3.070$ Å, $\varepsilon_{\rm SiH} = 0.006$ kcal/mol, $\sigma_{\rm SiSi} = 4.150$ Å, and $\varepsilon_{\rm SiSi} = 0.072$ kcal/mol. In Figs. 5(a) and 5(b) we present the fitting curves and the *ab initio* data. We note that, although Eq. (2) has been used often to model dispersion bound dimers, the higher-order dispersion terms may be important also. The inverse-six-power term used here takes these interactions effectively, and a careful examination on the long-range part interaction should be performed [31]. To obtain accurate long-range interactions, a higher-level theory (higher than MP2) has to be used, but this approach is currently beyond our calculation capacity for this system.

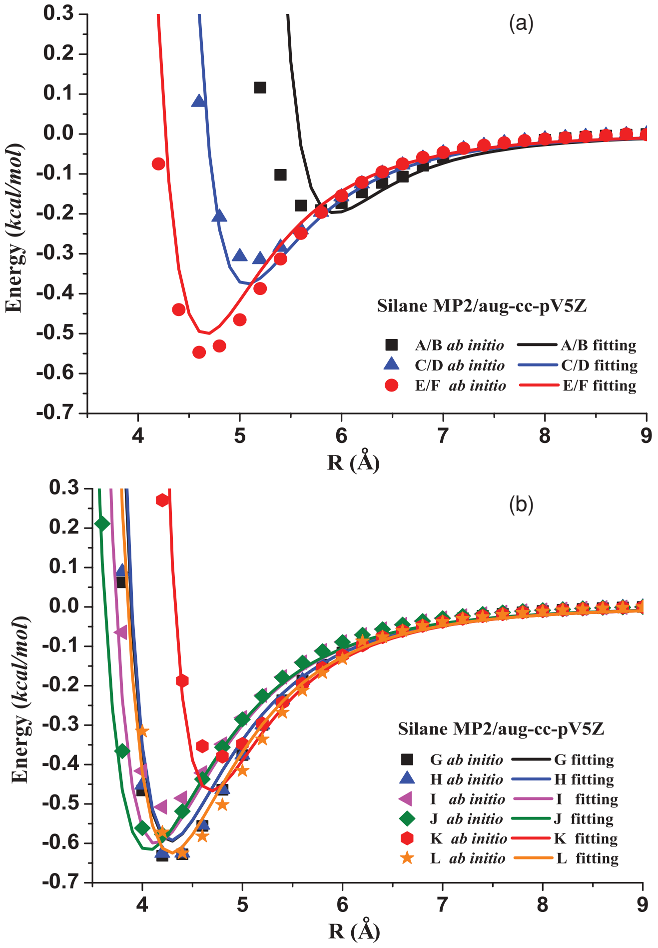

FIG. 5. (Color online) Comparison of the fitting curves (line) and the potential data (symbol).

IV. CONCLUSION

The present work extends our previous work [11–16] for calculating intermolecular potential energies with state-of-the-art methodology. We have systematically analyzed the intermolecular potential of silane dimer in 12 conformers. We also employed a high-level quantum chemistry calculation to obtain the potential data, which are consistent with previous literature for *G* and *H* conformers. Although the inner silicon interactions and interplay silicon-hydrogen interactions are decisive for the most stable conformer, the central silicon atom size and electronegativity also play a very important role in this system. The potentials exhibit significant anisotropy, which is analyzed and considered in the five-site force field model used to fit the potential data and determines the accuracy of the potential curve-fitting parameters.

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