Quantum Chemistry Investigation on the Dihydrogen Bond between Silicane and Ammonium

Wei-Liang Zhu,[†,‡] Chum Mok Puah,*[,†] Xiao-Jian Tan,[‡] Hua-Liang Jiang,*[,‡] and Kai-Xian Chen[‡]

Department of Chemical Process & Biotechnology, Singapore Polytechnic, 500 Dover Road, Singapore 139651, Singapore and Center for Drug Discovery & Design and State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences, 294 Taiyuan Road, Shanghai 200031, People's Republic of China

Received: May 31, 2000; In Final Form: October 30, 2000

Quantum chemical calculations are performed on the complex formed by silicane and ammonium in order to investigate the binding characteristics and nature of the dihydrogen bond. The calculation results using B3LYP and MP2 methods with the basis sets from 6-31G* to 6-311++G(2df,2pd) reveal that the dihydrogen-bond angle is ∼180.0° and that the bond length is ∼1.60 Å. The calculated enthalpies of formation of this complex using B3LYP/6-311++G(2df,2pd) and MP2/6-311++G(d,p) methods, corrected by basis-set superposition error (BSSE) and thermal energy, are −5.595 and −4.465 kcal/mol, respectively. Taking into account our CCSD(T)/6-311++G(2df,2p) and G2 results, we suggest that the binding strength between SiH_4 and NH_4^+ is ∼5.0 ± 0.5 kcal/mol. The BSSE released from the B3LYP method seems to converge at the basis set 6-311++G(d,p). In addition, charge distribution, electrostatic interaction energy, and the molecular-orbital coefficient analysis on all molecular orbitals of this complex show that s−s orbital interaction plays a key role in their bindings. Three intrinsic vibrational bands of this complex are identified by the normal-mode analysis on the calculated vibration spectra. The thermodynamic parameters of the possible reaction between SiH_4 and NH_4^+ are also calculated, which show that the equilibrium constants of this reaction are about 4.34×10^6 and 1.78×10^7 for the B3LYP/6-311++G(2df,2pd) and MP2/6-311++G(d,p) methods, respectively. All of these results are helpful for us to better understand the nature and the characteristics of the dihydrogen bond and exploit its application.

1. Introduction

A hydrogen bond is one of the most important noncovalent interactions in chemistry and biology. It is responsible for the functions and properties of many materials, such as the binding of a substrate to its enzyme, the base pairing in nucleic acids, and the selectivity of a catalyst. A typical hydrogen bond, known for over 50 years, stands for the binding interaction between the protonic hydrogen atom and an oxygen or nitrogen atom. In the last 15 years or so, extensive experimental and theoretical efforts have been expended in an attempt to clearly understand the noncovalent interaction. The investigation results revealed many interesting and attractive nonbonding interactions. One of them is the H···H interaction, or dihydrogen bond.[1−4] Similar to a hydrogen bond, the dihydrogen bond could exist in both intermolecular and intramolecular cases. One of these two dihydrogen bond hydrogen atoms is always attached to an electronegative atom, such as oxygen or nitrogen, and the other one is always linked to an electropositive atom, such as a transition metal or boron.[5−7] The distance between these two hydrogen atoms is, in general, shorter than 2.0 Å, and the strength is normally 4−6 kcal/mol, much the same as a classical hydrogen bond of average strength.[2,6,8]

The field of dihydrogen-bonding research is developing quite rapidly.[5] The challenge now is to apply dihydrogen bonding in some useful way. It is possible to envisage future applications of the dihydrogen bond extending to many different areas, e.g., developing new catalysts.[9] As a complement to the experiment, quantum chemical calculations on the dihydrogen bond will provide much useful information at atomic and electronic levels, such as geometry, charge distribution, thermodynamic parameters, and vibrational mode. These data are useful for further study of the dihydrogen bond, for example, in developing new force fields to reproduce dihydrogen bonds. Hence, quantum chemical calculation results will not only help us to better understand the nature and characteristics of the dihydrogen bond but also help us to exploit its application.

In this study, we present a quantum chemical study on the interaction between silicane and ammonium. To the best of our knowledge, the possible dihydrogen-bond interactions and reaction between silicane (SiH_4) and ammonium (NH_4^+) have not been studied either by an experimental or a theoretical method. Although many dihydrogen bonds are found to be related to transition-metal complexes,[7−9] those complexes are too big to be studied using a quantum chemistry method with a large basis set, which is essential to produce a reliable calculation result for noncovalent interactions. It has been shown that a simplified model could be used to represent the nature and characteristics of the noncovalent interaction.[10] Hence, we adopt the SiH_4−NH_4^+ complex as a model system to investigate the nature and characteristics of the dihydrogen bond. We did some investigations before on the noncovalent interaction between NH_4^+ and aromatics using both MP2 and DFT-B3LYP

---

* To whom correspondence should be addressed. E-mail: Puah@sp.edu.sg. Fax: 65-7721976.

[†] Singapore Polytechnic.

[‡] Chinese Academy of Sciences.

10.1021/jp001977t CCC: $20.00

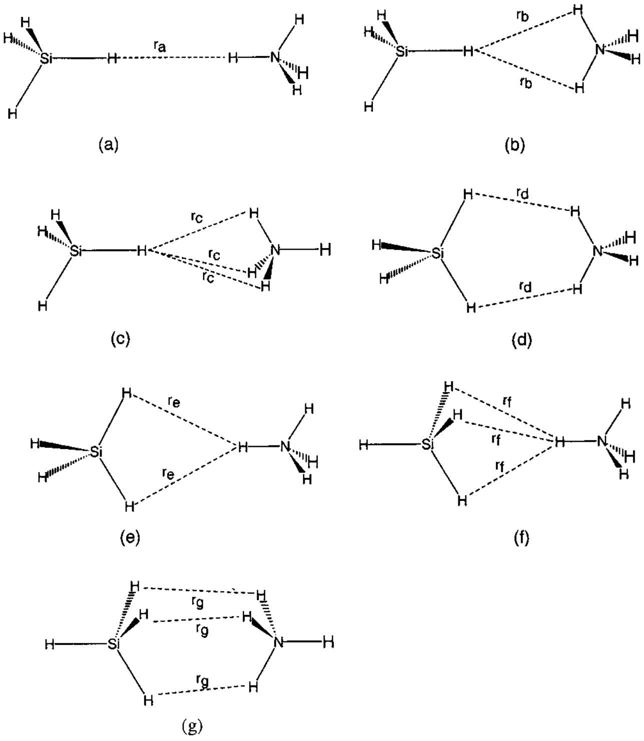


Figure 1. Initial structures of the complexes formed by SiH_4 and NH_4^+.

methods,[11,12] which showed that B3LYP results were satisfactory in comparison with MP2 and experimental results.[13−15] Hence, B3LYP and MP2 methods are used throughout this study. The basis sets used are from 6-31G* to 6-311++G(2df,2pd) for the B3LYP method and from 6-31G* to 6-311++G(d,p) for the MP2 method. We do not perform an MP2/6-311++G(2df,2pd) calculation because it needs too much disk space. Basis-set superposition error[16] (BSSE) and zero-point vibration energy (ZPVE) are also estimated so that an unambiguous result could be reached. In addition, we also perform a calculation on the electrostatic (ES) energy between SiH_4 and NH_4^+ in order to estimate the importance of the ES energy for the binding of SiH_4 to NH_4^+. It is possible that SiH_4 reacts with NH_4^+. In an attempt to investigate the thermodynamic parameters of this possible reaction, a quantum chemical calculation on this reaction is also performed in this study using B3LYP and MP2 methods with the basis sets from 6-31G* to 6-311++G(2df,2pd).

The goals of this work are to reveal the geometrical characteristics of the SiH_4−NH_4^+ complex, to investigate the binding strength between SiH_4 and NH_4^+, to get further insight into the interactive nature of the dihydrogen bond, to find out the intrinsic vibrational bands of the complex formed by SiH_4 and NH_4^+, and to provide the thermodynamic parameters of the reaction of SiH_4 and NH_4^+. This information will help us to develop a noncovalent interaction force field with a view to exploit the application of the dihydrogen bond.

2. Computational Details

To look for the global minimum energy structure of this complex, seven different initial structures are designed for the complex, which are shown in Figure 1. The frequency calculations are performed on the basis of the optimized structure with the lowest energy at the same level. For the geometry with an imaginary frequency, geometrical reoptimization is carried out until the imaginary frequency is removed by reading force constant.

With regard to the reaction of SiH_4 and NH_4^+, SiH_3−NH_3^+ and H_2 are assigned as their products. Geometry and frequency calculations are also performed on the products of this reaction for the sake of revealing its thermodynamic parameters.

$$SiH_4 + NH_4^+ \rightarrow SiH_3{-}NH_3^+ + H_2$$

All of the calculations are carried out on a Power Challenge R10000 supercomputer with the Gaussian98 program.[17]

3. Results and Discussion

3.1. Geometry of the SiH_4−NH_4^+ Complex. The optimization on all initial structures leads to the same geometry regardless of whichever method or basis set is used. Figure 2 depicts the optimized geometry, which suggests that, energetically, the geometry with one dihydrogen bond is the favorable structure of the complex formed by silicane and ammonium. Table 1 summarizes some important geometrical parameters. The optimized interactive distance between hydrogen atoms H2 and H7 using both B3LYP and MP2 methods with the basis sets from 6-31G* to 6-311++G(2df,2pd) is ∼1.6 Å (Table 1 and Figure 2). This distance is obviously shorter than the normal H···H contact of 2.4 Å, suggesting that silicane could interact with ammonium to form a stable complex. This optimized interaction distance is in agreement with the common dihydrogen-bond length that has been observed experimentally in dihydrogen complexes.[2,6,8]

Table 1 also shows that the complexation of SiH_4 and NH_4^+ results in the lengthening of both of the Si1−H2 and N6−H7 bonds (Figure 2). However, this interaction gives rise to the shortening of other Si−H or N−H bonds. These results reveal that the binding between silicane and ammonium weakens the strength of the Si1−H2 and N6−H7 bonds and strengthens that of the other bonds.

The optimized bond lengths of the B3LYP method are always slightly longer than those based on the MP2 method (Table 1), whereas the optimized dihydrogen binding distance is always shorter with the former method than with the latter method. Furthermore, unlike the B3LYP binding distance that is almost unaffected by the basis set, the addition of diffusion and polarization functions to the basis set of the MP2 method obviously results in a decrease of the interaction distance. Therefore, the MP2 distance is approaching the B3LYP distance, while the basis set increases. However, further calculations using much bigger basis sets are needed to confirm this supposition.

All of the calculated dihydrogen-bond angles are 179.9°, which is different from what has been revealed from the experimental data, 90−120°.[7−9] Therefore, linear dihydrogen-bond geometry is also possible besides a bent one, according to our calculation results. Hence, we think that the angle of 90−120° is not a prerequisite for the formation of a stable dihydrogen-bond complex.

3.2. Charge Distribution. Table 2 shows the CHelpG[18] and natural orbital (NO)[19] atomic charges calculated at B3LYP/6-31G** and MP2/6-31G** levels. We divide the whole complex into two parts, SiH_4 and NH_4^+, respectively. The calculated atomic charges with these two methods show that more than 0.9 units of positive charge is still located at NH_4^+ (Table 2). This result shows that charge transfer may not play an important role in dihydrogen binding.

The calculated result also suggests that a great shift of the atomic charge distribution in SiH_4 takes place during the complexation. Here, H2 is found to be more negatively charged than the other three hydrogen atoms attached to Si. Actually,

TABLE 1: Some Optimized Geometrical Parameters[a]

	$SiH_4-NH_4^+$ (complex)			SiH_4 or NH_4^+ (free state)		
	6-31G*	6-31G**	6-311++G(2df,2pd)	6-31G*	6-31G**	6-311++G(2df,2pd)
			(a) B3LYP Method			
R1−2	1.519	1.519	1.512	1.487	1.485	1.480
R1−3	1.478	1.477	1.473	1.487	1.485	1.480
R6−7	1.049	1.048	1.044	1.029	1.027	1.024
R6−8	1.028	1.026	1.022	1.029	1.027	1.024
R2−7	1.574	1.572	1.573			
Si1−H2−N6	179.9	179.9	179.9			
			(b) MP2 Method			
R1−2	1.511	1.503	1.502	1.484	1.474	1.475
R1−3	1.476	1.466	1.468	1.484	1.474	1.475
R6−7	1.038	1.033	1.034	1.029	1.023	1.021
R6−8	1.028	1.022	1.020	1.029	1.023	1.021
R2−7	1.717	1.676	1.613			
Si1−H2−N6	179.9	179.9	179.9			

[a] Refer to Figure 2 for the atomic numbering. The distances are in Å, and the angles are in deg.

TABLE 2: Atomic Charges (*Q*/*e*) of the $SiH_4-NH_4^+$ Complex with the 6-31G Basis Set**[a]

	part of SiH_4						part of NH_4^+					
	Si1	H2	H3	H4	H5	total	N6	H7	H8	H9	H10	total
						B3LYP						
CHelpG	0.550	−0.270	−0.076	−0.076	−0.076	0.052	−0.733	0.422	0.420	0.420	0.420	0.949
NO	0.434	−0.210	−0.040	−0.040	−0.040	0.093	−0.609	0.359	0.386	0.386	0.386	0.907
						MP2						
CHelpG	0.717	−0.309	−0.128	−0.128	−0.128	0.024	−0.817	0.460	0.444	0.444	0.444	0.975
NO	0.756	−0.343	−0.125	−0.125	−0.125	0.038	−0.684	0.425	0.407	0.407	0.407	0.962

[a]Refer to Figure 2 for the atomic numbering.

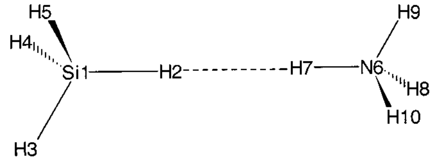


Figure 2. Optimized geometry of the complex formed by SiH_4 and NH_4^+.

in a free state, all of these four hydrogen atoms should be charged equally. The difference in charges could be caused by the attraction of the positively charged NH_4^+.

3.3. Molecular-Orbital Analysis. The analysis on all calculated molecular-orbital coefficients using B3LYP/6-31G** and MP2/6-31G** methods shows that there are only two molecular orbitals, nos. 10 and 14, which correspond to the atomic orbitals of H2 and H7. In the case of the related atomic orbitals of H2 and H7 which are s orbital in nature, we conclude that the orbital interaction between these two hydrogen atoms is due to an s−s interaction. Figure 3 depicts the contours of these two molecular orbitals.

3.4. Thermodynamic Parameters. Parts a and b of Table 3 summarize the calculated thermodynamic parameters of the B3LYP and MP2 methods, respectively. The change of thermal energy ($\Delta E_{\mathrm{thermal}}$) during the complexation ranges from 1.52 to 1.35 kcal/mol and from 1.67 to 1.56 kcal/mol for the B3LYP and MP2 methods, respectively. In the case of the BSSE, the larger the basis set, the smaller the BSSE released from the B3LYP method. Table 3a shows that the B3LYP BSSE seems to converge at the basis set 6-311++G(d,p). However, there is no such tendency for the MP2 BSSE; therefore, a larger basis set should be tested.

The calculated enthalpy of formation corrected by thermal energy and the BSSE, ΔH^{corr}, ranges from −5.17 to −5.60 kcal/mol and from −3.80 to −4.46 kcal/mol for the B3LYP and MP2 methods, respectively. It is known that modern density-functional theory (DFT) approaches are lacking in terms of accounting for the dispersion.[20] Normally the dispersion is ∼−0.5 kcal/mol for one atomic pair of period I elements. Hence, B3LYP binding strength should be weaker than that for the MP2 result. However, although less dispersion contributions could be expected for the dihydrogen-bond system because the atomic pair is a H···H pair, it is strange that the binding strength released from B3LYP is stronger than that of MP2 (Table 3). This result might suggest that dispersion is not important in the binding, and again, a much larger basis set might be needed for the MP2 method.

To further check the binding enthalpy, we performed CCSD(T)/6-311++G(2df,2p) and G2 calculations on this system.[21,22] The binding energy ($\Delta E_{\mathrm{inter}}$) released from CCSD(T)/6-311++G(2df,2p) is −6.029 kcal/mol, which is stronger than that for the MP2 results but still weaker than that for the B3LYP result. However, its BSSE is 0.375. Thus, we suggest that a larger basis set should be tested to accommodate this discrepancy. The G2 method's binding enthalpy is −4.858 kcal/mol. Taking into account all of these calculated results, we suggest that the binding strength between SiH_4 and NH_4^+ is ∼5.0 ± 0.5 kcal/mol.

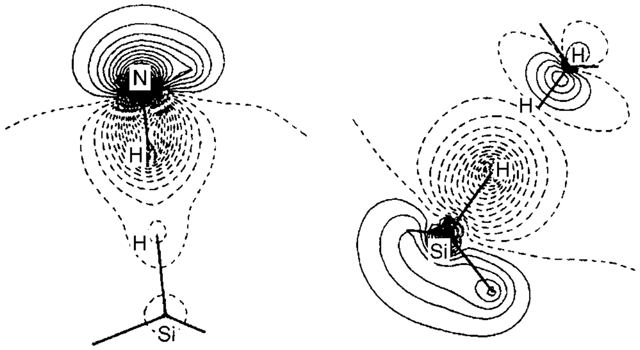
The calculated changes of free energy using the B3LYP method are positive in nature when a small basis set is used. In contrast, when the basis sets with polarization and diffusion functions are used, the results are always negative. These results suggest that diffusion and polarization functions have a significant effect on the calculated change of free energy of the B3LYP method. Hence, considering the calculated BSSEs, we suggest that the basis set 6-311++G** should be used when B3LYP is employed to investigate dihydrogen bonding.

3.5. ES Interaction between SiH_4 and NH_4^+. The ES interaction between SiH_4 and NH_4^+ is calculated using CHelpG atomic charge in place of NH_4^+. The calculated results show that the ES energy is 0.729 and 0.732 kcal/mol for B3LYP/6-

TABLE 3: Thermodynamic Parameters of the Complex Formed by SiH_4 and NH_4^+[a]

	6-31G(d)	6-31G(d,p)	6-31+G(d,p)	6-31++G(d,p)	6-311++G(d,p)	6-311++G(2df,2pd)
			(a) B3LYP Method			
ΔE_{inter}[b]	−6.654	−6.621	−6.246	−6.317	−6.304	−6.445
$\Delta E_{thermal}$[c]	1.524	1.433	1.410	1.496	1.384	1.347
ΔS[d]	−20.223	−19.247	−14.035	−15.429	−13.892	−14.038
ΔH[e]	−5.722	−5.780	−5.428	−5.413	−5.512	−5.690
ΔG[f]	0.307	−0.042	−1.243	−0.813	−1.370	−1.505
ZPVE[g]	0.915	0.743	0.674	0.856	0.596	0.532
BSSE[h]	0.289	0.230	0.155	0.239	0.108	0.095
ΔE_{corr}[i]	−6.365	−6.391	−6.091	−6.208	−6.196	−6.350
ΔH_{corr}[j]	−5.433	−5.550	−5.273	−5.174	−5.404	−5.595
ΔG_{corr}[k]	0.596	0.188	−1.088	−0.574	−1.262	−1.410
			(b) MP2 Method			
ΔE_{inter}[l]	−5.333	−5.449	−5.428	−5.693	−5.946	
$\Delta E_{thermal}$	1.672	1.569	1.583	1.563	1.578	
ΔS	−12.479	−13.500	−13.509	−13.789	−14.834	
ΔH	−4.253	−4.472	−4.437	−4.722	−4.960	
ΔG	−0.532	−0.447	−0.409	−0.611	−0.537	
ZPVE	0.835	0.700	0.728	0.710	0.800	
BSSE	0.454	0.362	0.488	0.643	0.495	
ΔE_{corr}	−4.879	−5.087	−4.940	−5.050	−5.451	
ΔH_{corr}	−3.799	−4.110	−3.949	−4.079	−4.465	
ΔG_{corr}	−0.078	−0.085	0.079	0.032	−0.042	

[a] All of the calculated values are presented in units of kcal/mol except $^{\Delta}S$, which is presented in units of cal/mol/K. [b] B3LYP energy change: $\Delta E_{inter} = E(\text{complex}) - E(SiH_4) - E(NH_4^+)$. [c] Thermal energy change: $\Delta E_{thermal} = E_{thermal}(\text{complex}) - E_{thermal}(SiH_4) - E_{thermal}(NH_4^+)$. [d] Entropy change: $\Delta S = S(\text{complex}) - S(SiH_4) - S(NH_4^+)$. [e] Enthalpy of formation: $\Delta H = \Delta E_{inter} + \Delta E_{thermal} + \Delta(PV)$. [f] Free energy change: $\Delta G = \Delta H - T\Delta S$. [g] ZPVE correction: $\text{ZPVE} = E_{ZPVE}(\text{complex}) - E_{ZPVE}(SiH_4) - E_{ZPVE}(NH_4^+)$. [h] BSSE correction: $\text{BSSE} = [E_A - E_{A(AB)}] + [E_B - E_{B(AB)}]$, where $E_{A(AB)}$ (or $E_{B(AB)}$) is the energy of fragment A (or B), based on the geometry extracted from the optimized complex structure, with its own basis set augmented by the basis set of B (or A). E_A (or E_B) is the energy of the isolated fragment A (or B), with just its own basis set. [i] BSSE- and ZPVE-corrected binding energy: $\Delta E_{corr} = \Delta E_{inter} + \text{BSSE}$. [j] BSSE- and ZPVE-corrected enthalpy of formation: $\Delta H_{corr} = \Delta H + \text{BSSE}$. [k] BSSE- and ZPVE-corrected change of free energy: $\Delta G_{corr} = \Delta G + \text{BSSE}$. [l] MP2 energy change.



a. Molecular orbital No. 10 b. Molecular orbital No. 12

Figure 3. Molecular-orbital contours of molecular orbitals nos. 10 and 12.

31G** and MP2/6-31G** methods, respectively, with ∼14 and ∼18% of their corrected binding enthalpy. Both of these results suggest that the ES interaction is not the dominant component of the binding of SiH_4 to NH_4^+. Hence, electronic or orbital interactions should play a key role for this binding. We have demonstrated that the orbital interaction is an s−s interaction by molecular-orbital analysis. Therefore, we conclude that the s−s orbital interaction, rather than the ES interaction, is the main component of the binding in the SiH_4−NH_4^+ complex.

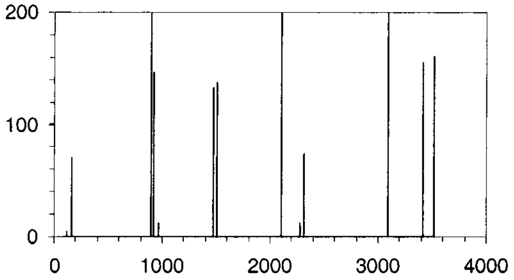
3.6. Vibrational Spectrum and Normal-Mode Analysis. Normal-mode analysis is performed on all of the calculated vibrational bands at the B3LYP/6-31++G** level. Figure 4 depicts the calculated spectra of SiH_4, NH_4^+, and their complex. With regard to free SiH_4, there are two bands, which are located at 921 and 2252 cm^{-1}, respectively (Figure 4b). For free NH_4^+, there are also two bands with wavenumbers of 1494 and 3494 cm^{-1} (Figure 4c). However, their complex has 19 normal modes with intensity larger than 1.0 km/mol (Figure 4a). That means some new vibrational modes appear after the complexation of SiH_4 and NH_4^+. By comparison of parts a−c of Figure 4, three new bands are identified, which are located at ∼160, ∼2100, and ∼3089 cm^{-1}. According to our experience, a scaling of the B3LYP/6-31G** frequency by 0.96 makes the theoretical band perfectly agree with the experimental result.[23,24] After the scaling, these bands are at 154, 2016, and 2965 cm^{-1}, respectively. In addition, the bands at 2106 and 2965 cm^{-1} have the highest IR intensities, 1056.2 and 1063.3 km/mol, respectively. Therefore, the IR spectrum of the complex is significantly different from those of its monomers. Thus, these three bands should be the intrinsic vibrational bands of the newly formed complex. Figure 5 shows our normal-mode analysis results on these intrinsic modes. The band at 154 cm^{-1} is caused by the stretching of the dihydrogen bond (Figure 5a). The band at 2016 cm^{-1} results from the stretching of the Si1−H2 bond (Figure 5b). The band at 2965 cm^{-1} belongs to the stretching of the N6−H7 bond (Figure 5c). Obviously, all three of these vibrations result in a change of the interactive distance between SiH_4 and NH_4^+. This information also demonstrates that these three new bands belong to the intrinsic bands of the complex SiH_4−NH_4^+.

The normal-mode analysis result also shows that the deformation mode of SiH_4, 921 cm^{-1} at the free state, is split into three bands, 893, 922, and 969 cm^{-1} (unscaled hereinafter in this paragraph), after it complexes with NH_4^+. The stretching of the Si−H bond, 2252 cm^{-1} at the free state, is also split into three bands, 2100, 2278, and 2304 cm^{-1}. The normal mode of the band 2100 cm^{-1} is depicted in Figure 5b. The other two bands correspond to the coupling of the stretching of the Si−H3, Si−H4, and Si−H5 bonds. The deformation mode of NH_4^+, 1494 cm^{-1} at the free state, cleaves into 1511 and 1733 cm^{-1} after complexation. This obvious blue shift suggests a quite strong interaction between NH_4^+ and SiH_4, which is different

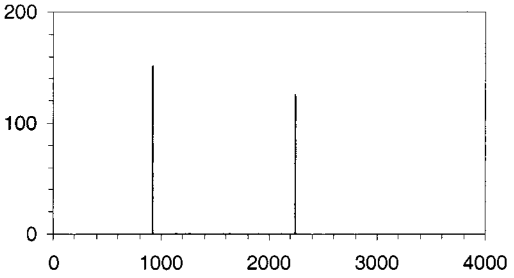
TABLE 4: Thermodynamic Parameters of the Reaction of SiH_4 and NH_4^{+a}

	6-31G(d)	6-31G(d,p)	6-31+G(d,p)	6-31++G(d,p)	6-311++G(d,p)	6-311++G(2df,2pd)
			(a) B3LYP Method			
$\Delta E_{inter}{}^{b}$	−7.165	6.765	−6.385	−6.697	−6.525	−7.158
$\Delta E_{thermal}{}^{c}$	−3.020	−2.976	−3.000	−3.303	−2.998	−3.039
ΔS^{d}	−6.088	−5.978	−3.885	−3.974	−3.958	−3.829
ZPVE[e]	−3.452	−3.421	−3.438	−3.431	−3.429	−3.479
ΔH^{f}	−10.185	−9.741	−9.385	−10.000	−9.523	−10.197
ΔG^{g}	−8.370	−7.959	−8.227	−8.815	−8.343	−9.055
			(b) MP2 Method			
$\Delta E_{inter}{}^{h}$	−10.575	−8.971	−9.110	−9.308	−8.838	
$\Delta E_{thermal}$	−3.167	−3.234	−3.267	−3.255	−3.267	
ΔS	−3.958	−3.841	−4.010	−4.086	−4.067	
ZPVE	−3.591	−3.671	−3.690	−3.668	−3.685	
ΔH	−13.742	−12.205	−12.377	−12.563	−12.105	
ΔG	−12.562	−11.060	−10.381	−10.345	−9.892	

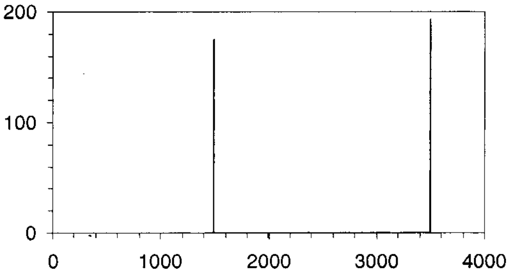
[a] All of the calculated values are presented in units of kcal/mol expect ΔS, which is presented in units of cal/mol/K. [b] B3LYP energy change: $\Delta E_{inter} = E(SiH_3NH_3^+) + E(H_2) - E(SiH_4) - E(NH_4^+)$. [c] Thermal energy change: $\Delta E_{therm} = E_{thermal}(SiH_3NH_3^+) + E_{thermal}(H_2) - E_{thermal}(SiH_4) - E_{thermal}(NH_4^+)$. [d] Entropy change: $\Delta S = S(SiH_3NH_3^+) + S(H_2) - S(SiH_4) - S(NH_4^+)$. [e] ZPVE correction: $ZPVE = \sum E_{ZPVE}(\text{reactant}) - \sum E_{ZPVE}(\text{product})$. [f] Enthalpy of formation: $\Delta H = \Delta E_{inter} + \Delta E_{thermal} + \Delta(PV)$. [g] Change of free energy: $\Delta G = \Delta H - T\Delta S$. [h] MP2 energy change.



a. Complex formed by SiH_4 and NH_4^+



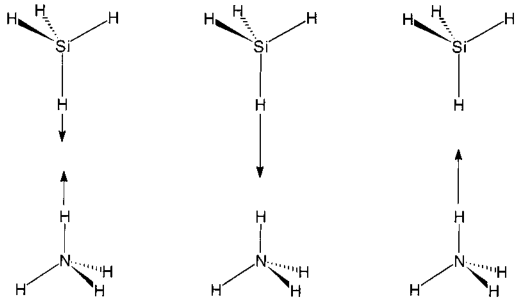
b. SiH_4 at free state



c. NH_4^+ at free state
(The x axis is in cm^{-1}, y axis is in KM/mol)

Figure 4. Calculated IR spectra at the B3LYP/6-31++G** level.

from the complex formed by SiH_4 and NH_3.[25] The stretching of the N−H bonds of NH_4^+, 3494 cm^{-1} at the free state, is split into three bands, 3089, 3418, and 3514 cm^{-1}. The normal mode of the band at 3089 cm^{-1} is shown in Figure 5c. The other two bands are contributed by the coupling of the N−H7, N−H8, and N−H9 bonds. These identified intrinsic vibrational bands and assigned normal modes could help us in investigating the SiH_4−NH_4^+ complex experimentally.



a. 154 cm^{-1}, 70.3 KM/mol b. 2016 cm^{-1}, 1056.2 KM/mol c. 2965 cm^{-1}, 1063.3 KM/mol

Figure 5. Normal-mode analysis result of intrinsic vibrational bands of the SiH_4−NH_4^+ complex at the B3LYP/6-31++G** level.

3.7. Reaction between SiH_4 and NH_4^+. Parts a and b of Table 4 summarize the calculated result of the reaction of SiH_4 and NH_4^+ with B3LYP and MP2 methods, respectively. The calculated ΔE_{inter}, ΔH, and ΔG values of the reaction in terms of the absolute value with the MP2 method are larger than those with the B3LYP method. This is different from those in the case of the formation of their complex, in which the MP2 binding strength is weaker than that of the B3LYP result.

Table 4 also shows that the effect of the basis set on the thermodynamic parameters of the B3LYP method is smaller than that of the MP2 method. For example, the calculated free energy of the reaction ranges from −7.96 to −9.06 kcal/mol for the B3LYP method. However, it ranges from −9.89 to −12.56 kcal/mol for the MP2 method. Obviously, the change of free energy from B3LYP is less affected by basis sets. However, the change of free energy from the MP2 method decreases as the basis set scale increases. It seems that the MP2 result converges to the B3LYP result. Therefore, further calculation is needed to ensure that the MP2 and B3LYP results converge to each other when a much larger basis set is used.

According to the calculated change of free energy, the equivalent constants of this reaction under standard conditions could be estimated as 4.34×10^6 and 1.78×10^7 using B3LYP/6-311++G(2df,2pd) and MP2/6-311++G(d,p) methods, respectively. Obviously this reaction might be carried out completely.

4. Conclusion

In this study, quantum chemistry methods, viz., B3LYP and MP2, are employed to study the complex formed by silicane and ammonium with basis sets from 6-31G* to 6-311++G(2df,2pd) in order to explore the binding nature and characteristics of dihydrogen bonds. The calculated results show that the BSSE released from the B3LYP method seems to converge at the basis set 6-311++G(d,p). The B3LYP/6-311++G(2df,2pd) enthalpy of formation of this complex, corrected by the BSSE and thermal energy, is −5.595 kcal/mol, which is very close to the common value of the dihydrogen strength, −4 to −6 kcal/mol, estimated experimentally. However, the MP2/6-311++G(d,p) method reveals a lower value of −4.465 kcal/mol. The optimized structures using both B3LYP and MP2 methods with the basis sets from 6-31G* to 6-311++G(2df,2pd) suggest that the dihydrogen bond may adopt the angle of 180.0°, which is energetically favorable but different from the data released from the Cambridge X-ray crystal structure database, 90−120°. Also, the optimized bond length is ∼1.60 Å. The calculated total atomic charges do not show significant charge transfer between SiH_4 and NH_4^+ while they complexed with each other. On the basis of our calculated charge distribution, the ES interaction energy, and the molecular-orbital analysis results, we find that the s−s orbital interaction plays a vital role in the binding of SiH_4 to NH_4^+. We also identify three intrinsic vibrational bands of this complex by normal-mode analysis on all calculated vibration normal modes, which are located at ∼154, 2016, and 2965 cm^{-1} (scaled by 0.96). These three vibrational modes are related to the vibration, resulting in the change of dihydrogen-bond length. The normal-mode analysis results also show that some vibrational bands of free SiH_4 and NH_4^+ are split and carry out a blue shift after complexation. The calculated change of enthalpy and change of free energy of the reaction of silicane and ammonium using the B3LYP method with the basis sets from 6-31G* to 6-311++G(2df,2pd), corrected by thermal energy, are -9.78 ± 0.40 and -8.51 ± 0.55 kcal/mol, respectively. Results obtained using the MP2 method with the basis set from 6-31G* to 6-311++G** are -12.92 ± 0.82 and -11.23 ± 1.34 kcal/mol, respectively. The estimated equilibrium constants of this reaction are about 4.34×10^6 and 1.78×10^7 with B3LYP/6-311++G(2df,2pd) and MP2/6-311++G(d,p) methods, respectively.

All of these calculated results including complex geometry, charge distribution, binding strength, interaction nature, intrinsic vibrational bands, and reaction parameters are helpful for us to better understand the interaction between silicane and ammonium. They could prove useful in developing a new dihydrogen-bond force field as well as in exploiting the applications of the dihydrogen bond.

Acknowledgment. We gratefully acknowledge financial support from the National Natural Science Foundation of China (Grant 29725203), the "863" High-Tech Program of China (Grant 863-103-04-01), and the State Key Program of Basic Research of China (Grant 1998051115). The quantum chemistry calculations were performed on Power Challenge R10000 at the Network Information Center, Chinese Academy of Sciences, Beijing, People's Republic of China.

References and Notes

(1) Stevens, R. C.; Milstein, R.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429.
(2) Van der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831.
(3) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rherngold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348.
(4) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356.
(5) Kulkarni, S. A. *J. Phys. Chem. A* **1999**, *103*, 9330.
(6) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337.
(7) Luther, T. A.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 6688.
(8) Crabtree, R. H. *Science* **1998**, *282*, 2000.
(9) Kelly, P.; Loza, M. *Chem. Br.* **1999**, *11*, 26−28.
(10) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.
(11) Becke, D. *J. Chem. Phys.* **1993**, *98*, 5648.
(12) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281.
(13) Zhu, W.-L.; Jiang, H.-L.; Puah, C. M.; Tan, X.-J.; Chen, K.-X.; Cao, Y.; Ji, R. Y. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2615−2622.
(14) Tan, X. J.; Jiang, H. L.; Zhu, W.-L.; Chen, K. X.; Ji, R. Y. *J. Chem. Soc., Perkin Trans. 2* **1999**, 107−111.
(15) Zhu, W.-L.; Tan, X.-J.; Puah, C. M.; Gu, J.-D.; Jiang, H.-L.; Chen, K.-X.; Felder, C. E.; Silman, I.; Sussman, J. *J. Phys. Chem. A* **2000**, *104*, 9573−9580.
(16) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(17) *Gaussian98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.
(18) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.
(19) Reed, E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(20) Kappé, A. K.; Bernstein, E. R. *J. Phys. Chem. A* **2000**, *104*, 6117.
(21) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
(22) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.
(23) Zhu, W.-L.; Jiang, H.-L.; Gu, J.-D.; Chen, J.-Z.; Shen, J.-K.; Chen, K.-X.; Ji, R.-Y.; Cao, Y. *THEOCHEM* **1999**, *488*, 21.
(24) Zhu, W.-L.; Puah, C.-K.; Tan, X.-J.; Jiang, H.-L.; Chen, K.-X.; Ji, R.-Y. *THEOCHEM* **2000**, *528*, 193.
(25) Meininger, D. R.; Ault, B. S. *J. Phys. Chem. A* **2000**, *104*, 3481.