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# Structure and dynamic properties of neutral and ionized $\text{SiH}_5$ and $\text{Si}_2\text{H}_3$

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## Abstract

The equilibrium structures and dynamical properties of neutral and ionized  $\text{SiH}_5$  and  $\text{Si}_2\text{H}_3$  have been studied using the *ab initio* molecular dynamics method. The obtained equilibrium structures are in good agreement with other highly precise methods. In  $\text{SiH}_5^+$ , we have clearly observed that  $\text{H}_2$  rotates about the  $\text{C}_3$  axis. In  $\text{Si}_2\text{H}_3^+$ , we have found that H atoms can interchange positions frequently and also the structure changes. The different dynamical behaviors of the Si–H and C–H molecules has been addressed. © 1997 Published by Elsevier Science B.V.

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## 1. Introduction

There is a growing interest in the study of small silicon molecules, since these systems are known to play a key role in the plasma-enhanced chemical vapor deposition of thin films and nano-materials, which is an important but not a well-understood process [1]. Also some siliconium ions with unsaturated bonds, like  $\text{SiH}_5^+$  and  $\text{Si}_2\text{H}_3^+$ , are of considerable interest in understanding the nature of nonclassical bonding [2]. Recently, the conventionally accepted concept, that the structure of a molecule can be identified as the lowest in energy although many isomers may exist, is becoming doubtful. A typical

example is protonated methane  $\text{CH}_5^+$  which has nearly isoenergetic classical and non-classical ionic structures; both theoretical and experimental results show that an equilibrium geometry can hardly be assigned to  $\text{CH}_5^+$  [3]. There is a lot of excellent theoretical work on the geometric structures of small silicon-hydrogen molecules based on quantum chemistry. It is also known that the ground state properties of unsaturated silicon molecules are different from those of unsaturated carbon molecules, but few studies have been performed on these small unsaturated Si–H molecules at finite temperature, which is crucial to understanding the dynamical properties of these molecules and the process of chemical vapor deposition.

Density functional theory has gained acceptance in recent years as it provides a reliable and economical method for calculating the structures and binding

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energies of molecules and solids. Moreover, combined molecular dynamics and density functional theory, i.e. the *ab initio* molecular dynamics (Car–Parrinello) [4] method, can be used not only to study the equilibrium structures of molecules in a sophisticated way by simulated annealing [5], but also to precisely study dynamical properties at finite temperature which is difficult for other methods. Recently, *ab initio* molecular dynamics simulations have been performed for small hydrogenated carbon molecules [6,7], and a large amplitude pseudorotational motion for hydrogen and structure changes have been observed [6]. Although silicon and carbon atoms have similar electronic structures, it is known that there are a lot of differences in the cluster and solid phases. In small pure atomic clusters, silicon clusters prefer to have compact structures with large coordination number, while small carbon clusters are known to have ring structures with fewer coordination number. In hydrogenated silicon and carbon molecules, some of the molecules, like  $\text{SiH}_3^+$  and  $\text{CH}_3^+$  [8], are believed to have similar structures, but many of them, like  $\text{SiH}_7^+$  ( $\text{CH}_7^+$ ) [9] and  $\text{Si}_2\text{H}_2(\text{C}_2\text{H}_2)$  [10], have clearly different structures. In this Letter, by performing *ab initio* molecular dynamics simulations, we study the structure and dynamical behavior of neutral and ionized  $\text{SiH}_5$  and  $\text{Si}_2\text{H}_3$ . We also try to address some differences in the dynamical properties between small Si–H and C–H molecules.

## 2. Calculation details

Our calculations are based on the *ab initio* molecular dynamics method [4], in which density functional theory [11] with the local density approximation [12] is used. The energy functional is minimized by the conjugate gradient method. The Kohn–Sham orbitals for the valence electrons are expanded by plane waves in a face-centered-cubic unit cell with lattice constant of  $25.0 a_0$ . This cell size is sufficiently large to make dispersion effects negligible. The interaction between core and valence electrons is described by the first-principles norm-conserving pseudopotentials of Bachelet–Hamman–Schluter [13] type with *s* and *p* non-locality in all the calculations, which is proved to have a high precision for silicon

and hydrogen in the condensed phase [14]. An energy cut-off of 16 Ry has been used in the plane-wave expansion of the pseudo-wavefunctions. With this energy cut-off, we can get a bond length of  $2.92 a_0$  for SiH, about 1% overestimated compared to the experimental result of  $2.88 a_0$  [15]. We have used the simulated annealing techniques to obtain the equilibrium structures. The obtained ground state structures are in good agreement with the results of highly precise configuration interaction calculations (CI) and also with the experimental results. To make a more detailed comparison with the results of CI, we have performed a steepest descent on some structures predicted by CI. Generally, we have got the same energy sequence as found by CI, although the energy difference might be different in some cases. However, we find that some isomers are not stable and the structure is changed immediately against the steepest descent.

## 3. Results

The presence of  $\text{SiH}_5$  had been postulated in various matrices [16], but experimental and theoretical studies on its structures and properties were quite limited. The lowest energy structure obtained from our simulated annealing has  $D_{3h}$  symmetry (see Fig. 1a), which is in agreement with the results of experiments and also theoretical calculations [17]. The apical and equatorial Si–H bond lengths are  $3.10$  and  $2.92 a_0$  respectively, which are close to the results of  $3.11$  and  $2.87 a_0$  obtained in Ref. [17]. The suggested isomer with  $C_{4v}$  symmetry [16,17] was found to be unstable. However, we have obtained a similar structure with  $C_{2v}$  symmetry (see Fig. 1b); in fact it has almost the same energy as the ground state structure. There are three kinds of Si–H bond lengths:  $2.88 a_0$  for one apical bond,  $2.98 a_0$  for two equatorial bonds and  $3.08 a_0$  for two basal bonds. We have identified another isomer for  $\text{SiH}_5$  which was not reported before, it is only  $0.05$  eV higher in energy than the lowest energy structure. From Fig. 1c, it can be seen that the structure of the isomer can be easily considered as  $\text{SiH}_3 + \text{H}_2$ ; the distance between Si and the closest H atom in  $\text{H}_2$  is about  $5.17 a_0$ , which is much longer than the Si–H distance  $2.90 a_0$  in

$\text{SiH}_3$ . The distance between H and H in  $\text{H}_2$  is about  $1.50 a_0$  which is close to the equilibrium distance of  $\text{H}_2$  in other LDA calculations [18]. Since the distance between  $\text{SiH}_3$  and  $\text{H}_2$  is large, the interaction between  $\text{SiH}_3$  and  $\text{H}_2$  would be weak, so this isomer of  $\text{SiH}_5$  will probably be one of the transition states from  $\text{SiH}_5$  to  $\text{SiH}_3$  plus  $\text{H}_2$ .

Much attention has been paid to  $\text{SiH}_5^+$ , since it can be easily identified in experiments and its properties had been measured recently [19]. Our obtained equilibrium structure for  $\text{SiH}_5^+$  is similar to the ground state as predicted by CI (see Fig. 1d) [20]. The equatorial and apical Si–H bond lengths are  $2.86$  and  $3.57 a_0$  respectively, which is in agreement with  $2.75$  and  $3.61 a_0$  from CI calculations. This structure is essentially composed of weakly bonded  $\text{SiH}_3^+$  and  $\text{H}_2$  groups. We have performed a steepest descent calculation starting at  $D_{3h}$  symmetry and we find that it is not stable for  $\text{SiH}_3^+$ . These results

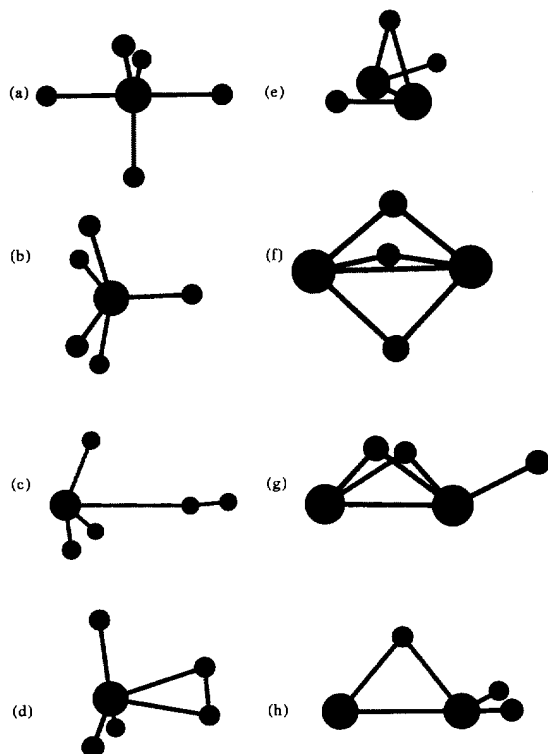


Fig. 1. Structures for  $\text{SiH}_5(\text{SiH}_5^+)$  and  $\text{Si}_2\text{H}_3(\text{Si}_2\text{H}_3^+)$ . Big circles denote silicon atoms and small circles denote hydrogen atoms.

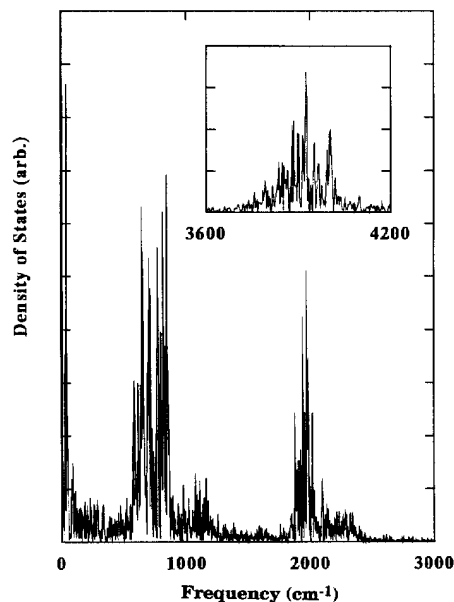


Fig. 2. Vibrational density of states for  $\text{SiH}_5^+$ . The inset shows the spectrum of the scaled H–H mode.

suggest that the ionization might completely change the atomic structure.

Usually, conventional quantum mechanical methods can be used to calculate the harmonic frequencies at the equilibrium geometry. Because the ab initio molecular dynamics method can precisely simulate the system at finite temperature, the vibrational density of states can be evaluated from the Fourier transformation of the velocity autocorrelation function of atoms. Generally, all the selection rules are relaxed and anharmonic effects have been explicitly included, which is particularly important in a shallow PES. We have studied the dynamical properties of  $\text{SiH}_5^+$ , starting with the lowest energy structure shown in Fig. 1d. By given a random displacement to each atom, the system is equilibrated at 110, 300 and 800 K. The time step is chosen as  $8.0 a_0$  ( $\sim 1.93 \times 10^{-16}$  s) and the simulation is performed for  $\sim 7$  ps at each temperature. The obtained vibrational density of states is shown in Fig. 2. There are two bands in the spectrum. The band at around  $2000 \text{ cm}^{-1}$  corresponds to stretching of the Si–H bond, and the strong band at  $\sim 900 \text{ cm}^{-1}$  is associated with the

H–Si–H bending mode. As shown in the insert of Fig. 2, the H–H stretch mode in  $H_2$  is also clearly identified at  $3800\text{ cm}^{-1}$ , which is in agreement with recent experimental results [19]. When heating the molecule from 110 to 800 K, the peaks in the vibrational density of states are smeared out gradually, but the essential feature remains and more details will be published elsewhere [21].

Analysis of the Si–H bonds shows that the H atoms are always attached to the Si atom even at 800 K. The H atoms in the  $SiH_3^+$  group, which are close to the Si atom, vibrate with an average bond length of  $2.9\ a_0$  and a fluctuation amplitude of  $0.2 \sim 0.3\ a_0$  at low temperature. At  $T = 800\text{ K}$ , the changes in the average bond length is small, but the amplitude of vibration increases significantly up to  $0.6 \sim 0.7\ a_0$ . The H atoms in the  $H_2$  group vibrate with an average bond length of  $3.6\ a_0$  and a fluctuation amplitude of  $0.5 \sim 0.6\ a_0$  at low temperature and  $0.7 \sim 0.8\ a_0$  at high temperature (800 K).

Since there are two bonded H atoms which weakly interact with  $SiH_3^+$  (see Fig. 1d), we have carefully analyzed the motion of  $H_2$  relative to the other three H atoms and the Si atom. These two H atoms are found to rotate around the  $C_3$  axis. In Fig. 3, we show the distances, R1 (solid line) and R2 (dotted line), between one H atom in  $H_2$  and the other two H atoms in  $SiH_3^+$  at  $T = 110\text{ K}$ . To make the figure clear, only the results for the first two picosecond are presented. We can see that in at the first  $\sim 0.7\text{ ps}$

the dashed line is always lower than the solid line, i.e. R1 is larger than R2. From the structure of  $SiH_5^+$  as shown in Fig. 1d, this indicates that there is no rotation around the  $C_3$  axis in  $SiH_3^+$ . After  $\sim 0.7\text{ ps}$ , R1 and R2 change their relative magnitude periodically, which suggests that  $H_2$  begins to rotate about the  $C_3$  axis. From Fig. 3, this rotation frequency can be roughly estimated to be  $5 \sim 6\text{ THz}$ , which is only about one tenth of the frequency in the Si–H stretch mode.

Since it was suggested that H would scramble involving a  $C_{2v}$  transition state structure [22], we have tried to clarify this kind of motion in our simulation. In the  $C_{2v}$  structure, the two atoms in  $H_2$  move close to Si while the distance between them increases significantly. We have observed the distance changes for more than 6 ps, but the average distance between the Si and H remains unchanged with only some fluctuations. Thus our calculations up to 800 K show that a scrambling motion involving a  $C_{2v}$  transition state structure would be difficult.

It is interesting to compare the dynamical structure of  $SiH_5^+$  with  $CH_5^+$  at finite temperature, although the structure difference at zero temperature is well identified. Dynamical simulation found that [6] temporal  $H_2$  can be formed in  $CH_5^+$  and the time averaged structure for  $CH_5^+$  can be recognized as a strongly interacted  $CH_3^+ + H_2$ . In  $SiH_5^+$ ,  $H_2$  is always there interacting with  $SiH_3^+$  weakly, and it also has a specific rotation around the  $C_3$  axis of  $SiH_3^+$ . Thus, although the ground state structures for  $SiH_5^+$  and  $CH_5^+$  are different and  $H_2$  does not exist in the ground state of  $CH_5^+$ , the dynamical structures for  $CH_5^+$  and  $SiH_5^+$  are analogous, in the sense that both of them can be considered as  $MH_3^+ + H_2$  ( $M = \text{Si}, \text{C}$ ).

The structure and dynamics of protonated disilyne have been a subject of interest. The minimum energy conformations of  $Si_2H_3^+$  were located by conventional SCF and CI methods [23–25]. By using the simulated annealing method, the structures of  $Si_2H_3$  and  $Si_2H_3^+$  have been calculated. We have found that the lowest energy structure of  $Si_2H_3$ , shown in Fig. 1e, is  $HSiHSiH$ -like with  $C_2$  symmetry, while the  $H_2SiHSi$ -like structure is an isomer only 0.04 eV higher in energy. The  $H_2SiHSi$ -like structure is about 0.10 eV higher. The  $H_3SiSi$ -like structure, which was predicted to be the ground state [23], is found to be 0.39 eV higher in energy. We have also studied

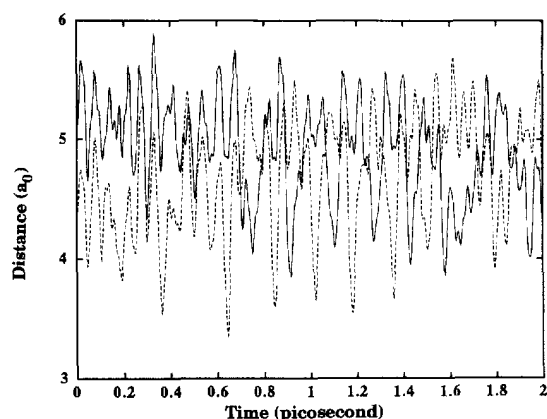


Fig. 3. Temporal atomic distances between one H atom in  $H_2$  and two other H atoms in the  $SiH_3^+$  group.

the  $\text{SiH}_3\text{Si}$ -like structure. It is significantly higher in energy ( $\sim 0.64$  eV) than the bridged structure. For  $\text{Si}_2\text{H}_3^+$ , we find that the  $\text{SiH}_3\text{Si}$ -like structure has the lowest energy (see Fig. 1f), consistent with the result of CI calculations [24]. Moreover, we find that the  $\text{H}_3\text{SiSi}$ -like structure has a high energy, 0.97 eV relative to the ground state. Compared to the results of the CI calculation, two isomers, whose energies are close in energy to the ground state structure,  $\text{HSiH}_2\text{Si}$  (Fig. 1g) and  $\text{H}_2\text{SiHSi}$  (Fig. 1f), have been correctly identified. Our calculations also show that the structure with  $C_2$  symmetry for  $\text{Si}_2\text{H}_3^+$  is not stable, although an  $\text{HSiHSiH}$ -like isomer (with  $C_{2v}$ ) was identified. This isomer is 0.89 eV higher in energy than the  $\text{SiH}_3\text{Si}$ -like structure. Generally, as can be seen from Table 1, our calculated structures are in better agreement with the results of the CI method than the SCF method.

Dynamical simulations on  $\text{Si}_2\text{H}_3^+$ , starting with the  $\text{HSiH}_2\text{Si}$ -like structure have been performed at low temperature (120 K), room temperature (300 K) and high temperature (1050 K). At each temperature, the system is observed up to 7 ps after equilibration. Fig. 5 shows the vibrational density of states obtained at low temperature. Essentially, there are four bands in the whole spectrum. We find that the band at  $\sim 2000$   $\text{cm}^{-1}$  is associated with the Si–H stretch

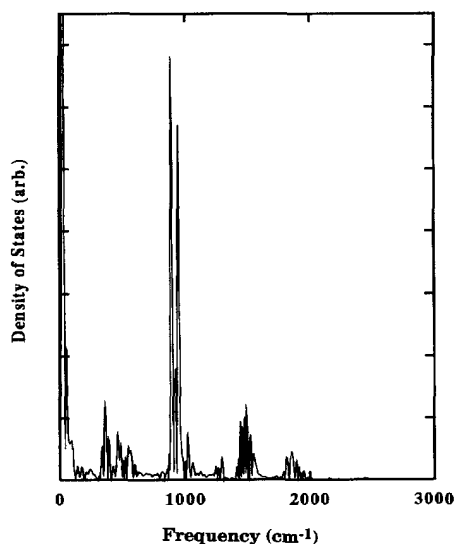


Fig. 4. Vibrational density of states for  $\text{Si}_2\text{H}_3^+$ .

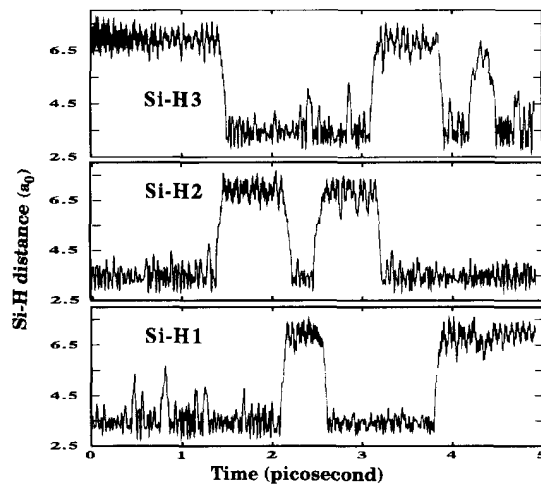


Fig. 5. Temporal atomic distances between one Si atom and three H atoms in  $\text{Si}_2\text{H}_3^+$ .

mode, the band at about  $1000$   $\text{cm}^{-1}$  is associated with the H–Si–H and Si–Si–H bend modes. The band at  $500$   $\text{cm}^{-1}$  can be attributed to the Si–Si stretch, and the band at  $1500$   $\text{cm}^{-1}$  comes from the Si–H stretch for those H atoms at the bridge site. The increasing temperature would bring some changes in the spectrum, but no essential changes have been found.

It is also interesting to look at the structural properties for  $\text{Si}_2\text{H}_3^+$  at finite temperature. At low temperature and room temperature, it seems that all the atoms are only vibrating at the equilibrium positions in our observed time. At high temperature, we find that the H atoms jump from one position to another and also the structure changes have been identified. In Fig. 5, we show the instantaneous atomic distances between one Si(1) and three H atoms, H1, H2, H3, at high temperature. At the beginning, there are two H atoms at the bridge position ( $R_{\text{Si-H}} \sim 3.5$   $a_0$ ) and the H3 atom is only strongly attached to the Si(2) atom. For  $\sim 1.2$  ps, all the H atoms are vibrating at the equilibrium positions with an amplitude of  $1.0$   $a_0$ . At  $1.2$  ps, the H2 atom at the bridge position interchanges position with the H3 atom, then H2 becomes more strongly bonded to Si(2). At  $\sim 2.1$  ps, H1 and H2 interchange position and about half a picosecond later, H1 and H2 move back. At  $\sim 3.2$  ps, H2 inter-

changes position with H3. At  $\sim 3.8$  ps, the H3 atom moves back to the bridge position, at the same time, H1 moves away from the bridge position. Up to 4.1 ps, only the H atoms interchange the position and the structure remains the same. However, at 4.2 ps, the H3 atom moves away from the bridge position and the H1 atom does not move back; consequently, the structure changes from HSiH<sub>2</sub>Si-like to H<sub>2</sub>SiHSi-like. Afterwards, H3 atom comes back and the structure becomes HSiH<sub>2</sub>Si-like again.

In C<sub>2</sub>H<sub>3</sub><sup>+</sup>, the H atom at the bridge site was found to change position and move to one C atom and the other, which is in agreement with experimental observations. In Si<sub>2</sub>H<sub>3</sub><sup>+</sup>, it is also observed that the H atoms can interchange position. Since the energy of the HSiHSiH-like structure is high, the H atom can only jump from the bridge site to one of the two silicon atoms and the HSiHSiH-like structure is not observed in our limited observed time at 1050 K.

#### 4. Summary

In this work, we have performed ab initio molecular dynamics on SiH<sub>5</sub> and Si<sub>2</sub>H<sub>3</sub> and their ions. The obtained equilibrium structures are in good agreement with the results of the CI method. An interesting isomer for SiH<sub>5</sub> has been identified, which might be one of the possible transition states from SiH<sub>5</sub> to SiH<sub>3</sub> + H<sub>2</sub>. Our dynamical studies have provided direct information on the structural properties of these Si–H molecules; internal rotation and structure

changes have been clearly observed. The similarities and differences between the dynamical properties for Si–H and C–H molecules have been discussed.

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Table 1

The relative energies of the isomers of Si<sub>2</sub>H<sub>3</sub> and Si<sub>2</sub>H<sub>3</sub><sup>+</sup>. The SCF results for neutral Si<sub>2</sub>H<sub>3</sub> are from Ref. [23]. Both the SCF and CI results for ionized Si<sub>2</sub>H<sub>3</sub><sup>+</sup> are from Ref. [24]

		Present	SCF	CI
Si <sub>2</sub> H <sub>3</sub>	HSiHSiH	0.00		
	H <sub>2</sub> SiHSi	0.04		
	H <sub>2</sub> SiSiH	0.09	0.05	
	H <sub>3</sub> SiSi	0.39	0.00	
	SiH <sub>3</sub> Si	0.64		
Si <sub>2</sub> H <sub>3</sub> <sup>+</sup>	SiH <sub>3</sub> Si	0.000	0.01	0.00
	HSiH <sub>2</sub> Si	0.360	0.50	0.56
	H <sub>2</sub> SiHSi	0.672	0.14	0.57
	HSiHSiH	0.891	1.00	0.99
	H <sub>3</sub> SiSi	0.971	0.00	0.71

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