

Structure and Dynamic Properties of Neutral and Ionized SiH_5 and Si_2H_3

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Abstract

The equilibrium structures and dynamical properties of neutral and ionized SiH_5 and Si_2H_3 have been studied by using *ab-initio* molecular-dynamics method. The obtained equilibrium structures are in very good agreement with other highly precise methods. In SiH_5^+ , we have clearly observed that H_2 rotates about the C_3 axis. In Si_2H_3^+ , we have found that H atoms can interchange the positions frequently and also the structure changes. The different dynamical behavior for Si-H and C-H molecules has been addressed.

Key-words: Neutral – ionized SiH_5 .

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There is presently a growing interest in 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 very important but not a well-understood process[1], and also some siliconium ions with unsaturated bonds, like SiH_5^+ and Si_2H_3^+ , are of considerable interest in understanding the nature of nonclassical bonding[2]. Recently, the conventionally accepted concept, that a structure of molecule can be identified as the lowest in energy although many isomers may exist, is becoming doubtful. The typical example is protonated methane CH_5^+ which has nearly isoenergetic classical and non-classical ionic structures, both of the theoretical and experimental results show that an equilibrium geometry can be hardly assigned to CH_5^+ [3]. There are a lot of excellent theoretical work on the geometric structures of small silicon-hydrogen molecules based on the theory of quantum chemistry. It is also known that the ground state properties of unsaturated silicon molecules are different from that of unsaturated carbon molecules, but few studies have been performed on these small unsaturated Si-H molecules at finite temperature, which is crucial to understand the dynamical properties of these molecules and the process of chemical vapor deposition.

The density functional theory has gained acceptance in recent years as it provided a reliable and economical method for calculating structure and binding energy of molecules and solids. Moreover, the combined molecular-dynamics and density functional theory, i.e. *ab-initio* molecular-dynamics (Car-Parrinello)[4] method, can be used not only to study the equilibrium structures of molecules in sophisticated way by simulated annealing[5], but also to precisely study the dynamical properties at finite temperature which is very difficult for other methods. Recently, *ab-initio* molecular-dynamics simulations have been performed for small hydrogenated carbon molecules[6,7], a large amplitude pseudorotational motions for hydrogen and also 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 cluster and solid phases. In the 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 SiH_3^+ and CH_3^+ [8], are believed to have similar structures, but many of them, like SiH_7^+ (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 simulation, we study the structure and dynamical behavior of neutral and ionized SiH_5 , and Si_2H_3 , we also try to address some differences in dynamical properties between small Si-H and C-H molecules.

Our calculations are based on *ab-initio* molecular-dynamics method[4], in which the

density functional theory[11] with the local density approximation[12] is used. The energy functional is minimized by conjugate gradient method. The Kohn-Sham orbitals for the valence electrons are expanded by the plane waves in a face-centered-cubic unit cell with lattice constant of 25.0 a.u.. This cell size is sufficiently large to make dispersion effects negligible. The interaction between core and valence electrons is described by the first principle 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 condensed phase[14]. An energy cut-off 16 Ry has been used in the plane-wave expansion of the pseudo-wavefunctions. With this energy cut-off, we can get the bond length of 2.92 a.u. for SiH, about 1% overestimated comparing to the experimental results of 2.88 a.u.[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 the highly precise configuration interaction(CI) and also with the experimental results. To make a more detailed comparison with the results of CI, we have performed the 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.

The presence of SiH₅ 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 calculation[17]. The apical and equatorial Si-H bond length are 3.10 a.u. and 2.92 a.u. respectively, which are very close to the results of 3.11 a.u. and 2.87 a.u. obtained in Ref. [17]. The suggested isomer with C_{4v} symmetry[16,17] was found to be unstable. But 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.u. for one apical bond, 2.98 a.u. for two equatorial bonds and 3.08 a.u. for two basal bonds. We have identified another isomer for SiH₅ 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 SiH₃+H₂, the distance between Si and the closest H atom in H₂ is about 5.17 a.u., which is much longer than the Si-H distance 2.90 a.u. in SiH₃. The distance between H and H in H₂ is about 1.50 a.u. which is close to the equilibrium distance of H₂ in other LDA calculation[18]. Since the distance between the SiH₃ and H₂ is very large, the interaction between SiH₃ and H₂ would be very weak, so this isomer of SiH₅ will probably be one of the transition state from SiH₅ to SiH₃ plus

H₂.

People paid much attention to SiH₅⁺, since it can be easily identified in the experiment and its properties had been measured recently[19]. Our obtained equilibrium structure for SiH₅⁺ 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 a.u., and 3.57 a.u. respectively, which is in agreement with 2.75 a.u. and 3.61 a.u. from CI calculations. This structure is essentially composed of weakly bonded SiH₃⁺ and H₂ groups. We have performed a steepest descent calculation started at D_{3h} symmetry and we find that it is not stable for SiH₃⁺. These results suggest that the ionization might completely change the atomic structure.

Usually the conventional quantum mechanical methods can be used to calculate the harmonic frequencies at the equilibrium geometry. Because *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 velocity auto correlation function of atoms. Generally, all the selection rules are relaxed, and the anharmonic effects have been explicitly included, which is particularly important in shallow PES. We have studied the dynamical properties of SiH₅⁺, started with the lowest energy structure shown in Fig. 1d. By given a random displacement to each atom, the system is equilibrated at 110 K, 300 K and 800 K. The time step is chosen as 8.0 a.u.($\sim 1.93 \times 10^{-16}$ sec.), and the simulation is performed for ~ 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 cm⁻¹ is corresponding to the stretching of Si-H bond, the strong band at ~ 900 cm⁻¹ is associated with H-Si-H bending mode. As shown in the insert of Fig. 2, the H-H stretch mode in H₂ is also clearly identified at 3800 cm⁻¹, which is in agreement with recent experimental results[19]. When heating the molecule from 110 K to 800 K, the peaks in vibrational density of states are smeared out gradually, but the essential feature remains, and more details will be published elsewhere[21].

Analysis of Si-H bonds shows that the H atoms are always attached to Si atom even at 800 K. The H atoms in SiH₃⁺ group, which are close to Si atom, vibrate with an average bond length of 2.9 a.u. and a fluctuation amplitude of 0.2~0.3 a.u. at low temperature. At T=800 K, the changes of average bond length is small, but the amplitude of vibration increases significantly up to 0.6~0.7 a.u.. The H atoms in H₂ group vibrate with an average bond length of 3.6 a.u. and a fluctuation amplitude of 0.5~0.6 a.u. at low temperature and 0.7~0.8 a.u. at high temperature (800 K).

Since there are two bonded H atoms which are weakly interacted with SiH₃⁺(see Fig. 1d), we have carefully analyzed the motion of H₂ relative to the other three H atoms and Si atom. These two H atoms are found to rotate around the C₃ axis. In Fig. 3, we show

the distances, R1 (solid line) and R2 (dotted line), between one H atom in H_2 and other two H atoms in SiH_3^+ at $T=110$ K. To make the figure visible, only the results for the first two pico second are presented. We can see that, at the first ~ 0.7 ps, the dash line is always lower than solid line, i.e., R1 is larger than R2. From the structure of SiH_5^+ as shown in Fig. 1d, it indicates that there is no rotation around the C_3 axis in SiH_3^+ . After ~ 0.7 ps, R1 and R2 change their relative magnitude periodically, it suggests that the H_2 begin to rotate about the C_3 axis. From Fig. 3, this rotation frequency can be roughly estimated to be $5\sim 6$ THz, this is only about one tenth of frequency in Si-H stretch mode.

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. Since in C_{2v} structure, two atoms in H_2 move closely to Si and while the distances between themselves increased significantly. We have observed the distance changes for more than 6 ps, the average distance between Si and H remains unchanged with only some fluctuations. So our calculations up to 800 K show that scrambling motion involving a C_{2v} transition state structure would be very 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 was well identified. The dynamical simulation found that[6], the temporal H_2 can be formed in CH_5^+ and the time averaged structure for CH_5^+ can be recognized as a strongly interacted $CH_3^+ + H_2$. While in SiH_5^+ , H_2 is always there which interacts with SiH_3^+ weakly and it has also a specific rotation around the C_3 axis of SiH_3^+ . So, although the ground state structures for SiH_5^+ and CH_5^+ are different and H_2 does not exist at 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 $MH_3^+ + H_2$ ($M=Si, C$).

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 method[23,24], but the Si_2H_3 was studied only at SCF level. 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 with only 0.03 eV higher in energy. The H_2SiSiH -like structure is about 0.12 eV higher. The H_3SiSi -like structure, which was predicted to the ground state[23], is found to be 0.3 eV higher in energy. We have also studied the SiH_3Si -like structure, it is significantly higher in energy (~ 0.6 eV) than one bridged structure. For $Si_2H_3^+$, we find that the SiH_3Si -like structure has the lowest energy (see Fig. 1f), it is consistent with the result of CI calculation[24]. Moreover, we find that H_3SiSi -like structure has very high energy, 0.2 eV relative to the ground state.

Comparing to the results of CI calculation, two isomers, whose energies are close to energy of the ground state structure, HSiH_2Si (Fig. 1g) and H_2SiHSi (Fig. 1f), have correctly identified. Our calculations also show that the structure with C_2 symmetry for Si_2H_3^+ is not stable, although an isomer with HSiHSiH -like (with C_{2v}) was identified, but this isomer has 0.8 eV higher in energy than the SiH_3Si -like structure. Generally our obtained structures are in better agreement with the results of high precise CI method than the SCF method.

The dynamical simulation on Si_2H_3^+ , started with HSiH_2Si -like structure has 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 the equilibration. Fig. 5 shows the vibrational density of states obtained at the 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 Si-H stretch mode, the band at about 1000 cm^{-1} is associate to H-Si-H and Si-Si-H bend mode. The band at 500 cm^{-1} can be attributed to Si-Si stretch, and the band at 1500 cm^{-1} comes from Si-H stretch for those H atoms at the bridge site. The increasing of 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 the Si_2H_3^+ at finite temperature. At low temperature and room temperature, it seems that all 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. 6, we show the instantaneous atomic distances between one Si(1) and three H atoms, H1, H2, H3 respectively at high temperature. At the beginning, there are two H atoms at the bridge position ($R_{\text{Si-H}} \sim 3.5\text{ a.u.}$) and H3 atom which is only strongly attached to Si(2) atom. For $\sim 1.2\text{ ps}$, all H atoms are vibrating at the equilibrium positions with amplitude of 1.0 a.u. At 1.2 ps, H2 atom at the bridge position interchanges the position with H3 atom, then H2 becomes more strongly bonded to Si(2). At $\sim 2.1\text{ ps}$, H1 and H2 interchange the position, and about half pico second later, H1 and H2 move back. At $\sim 3.2\text{ ps}$, H2 interchanges the positions with H3. At $\sim 3.8\text{ ps}$, H3 atom moves back to bridge position, at the same time, the H1 moves away from the bridge position. Up to 4.1 ps, the H atoms only interchanges the positions and the structure remains the same. But at 4.2 ps, H3 atom moves away from the bridge position and H1 atom does not move back, consequently the structure changes from HSiH_2Si -like to H_2SiHSi -like. Afterwards, H3 atom comes back and the structure becomes HSiH_2Si -like again.

Comparing to CH_5^+ , in which the H atom at the bridge site was found to change the positions and also move to one C atom and another which is in agreement with experimental

observation. While in SiH_5^+ , it is also observed that H atoms can interchange the positions. Since the energy of HSiHSiH-like structure is very high, H atom can only jump from bridge site to one of the two silicon atoms and the HSiHSiH-like structure is not observed in our simulation up to 1050 K.

In summary, we have performed *ab-initio* molecular-dynamics on two selected SiH_5 and Si_2H_3 and their ions. The obtained equilibrium structures are in good agreement with the results of CI method. An interesting isomer for SiH_5 has been identified, that might be one of the possible transition states from SiH_5 to $\text{SiH}_3 + \text{H}_2$. Our dynamical studies have provided a direct information on the structural properties of these Si-H molecules, the internal rotation and structure changes have been clearly observed. The similarity and difference between the dynamical properties for Si-H and C-H molecules have been discussed.

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Figure Captions

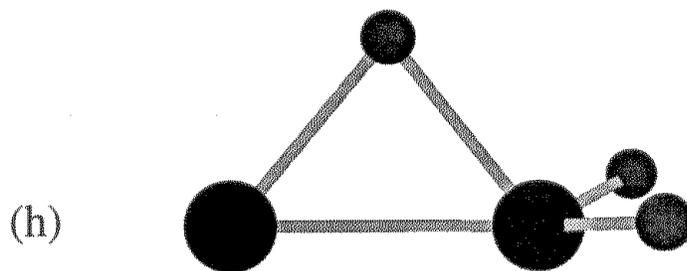
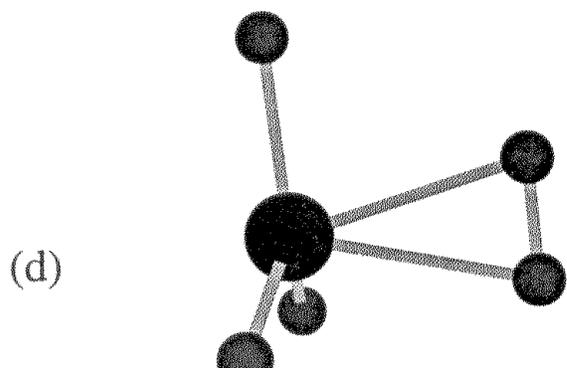
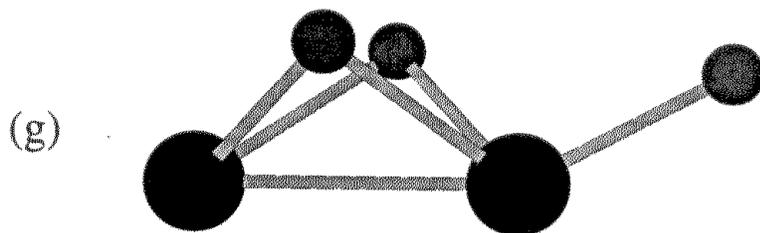
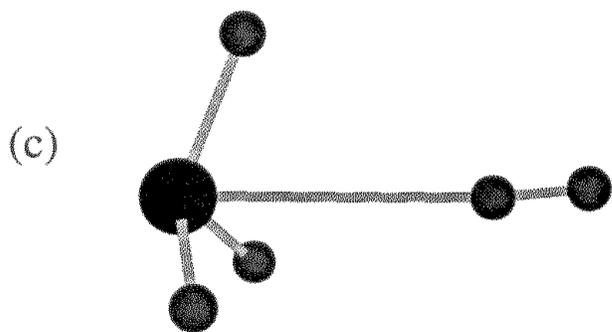
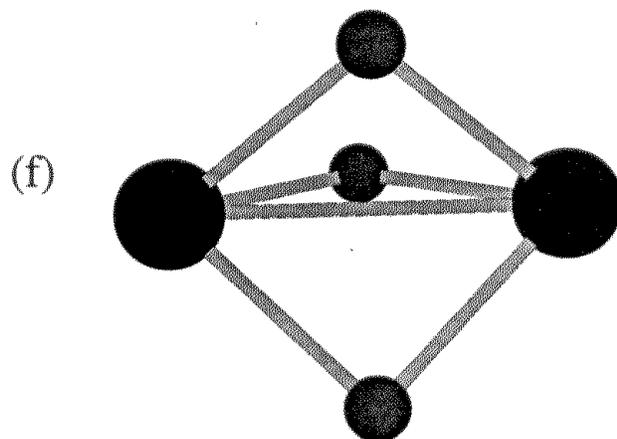
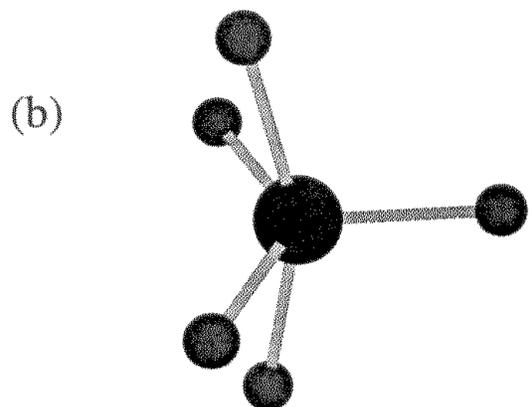
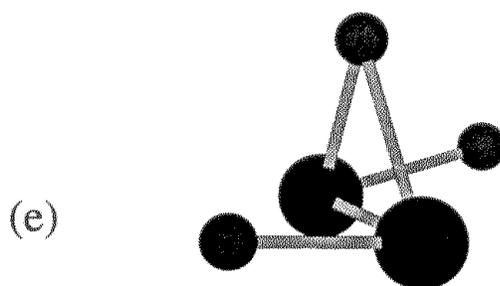
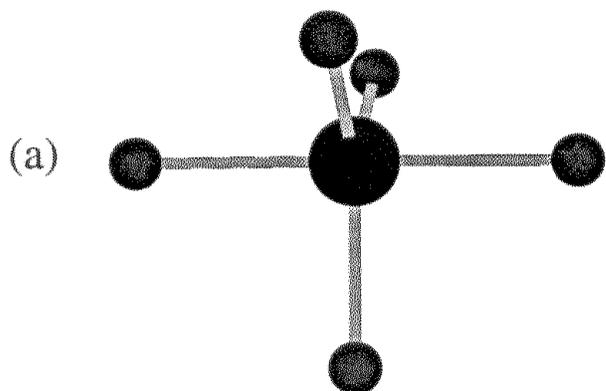
Fig.1 Structures for $\text{SiH}_5(\text{SiH}_5^+)$ and $\text{Si}_2\text{H}_3(\text{Si}_2\text{H}_3^+)$. Big balls for silicon atoms and small balls for hydrogen atoms.

Fig.2 Vibrational density of states for SiH_5^+ . The inset shows the spectrum of the scaled H-H mode.

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

Fig.4 Vibrational density of states for Si_2H_3^+ .

Fig.5 Temporal atomic distances between one Si atom and three H atoms in Si_2H_3^+ .



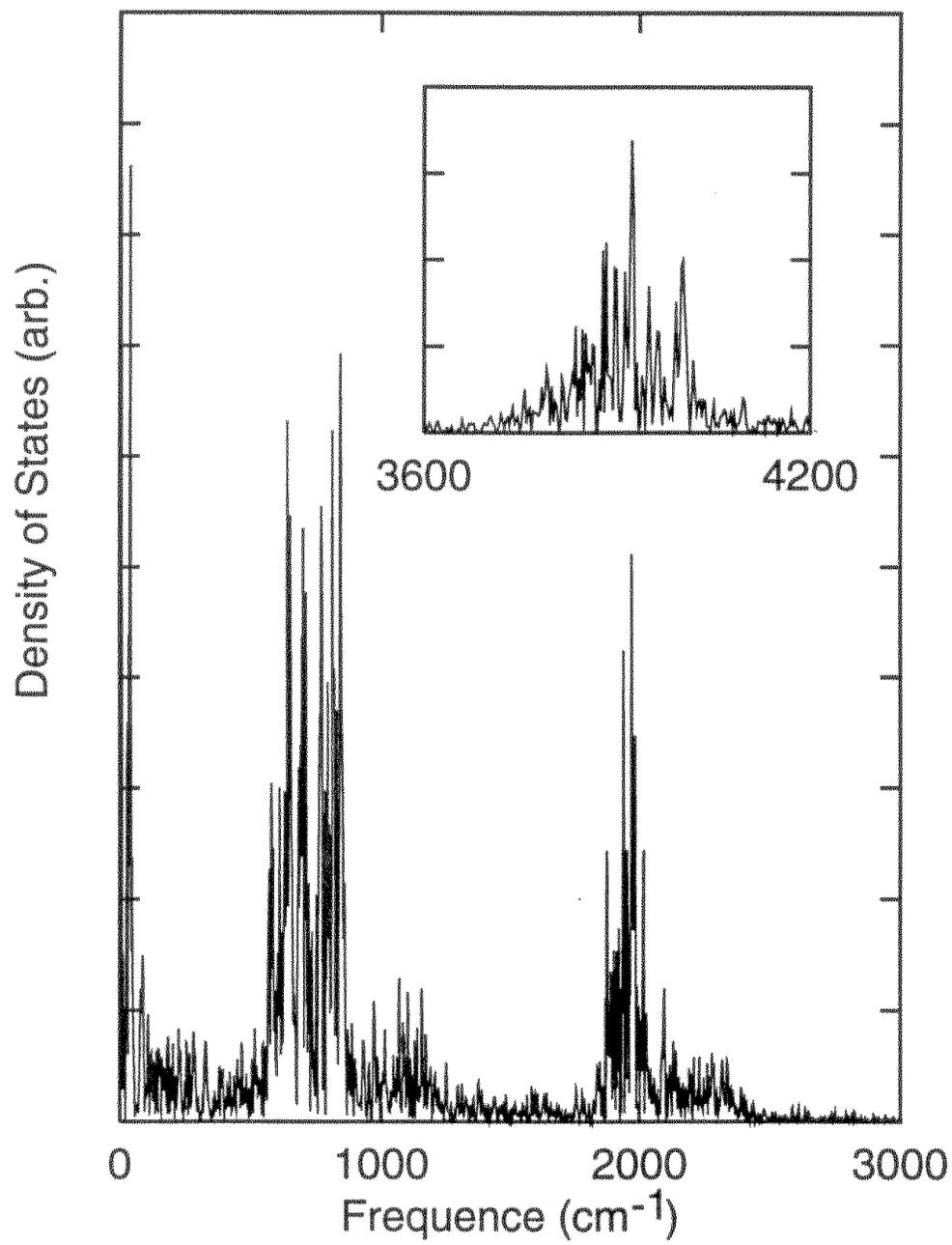


Fig. 2

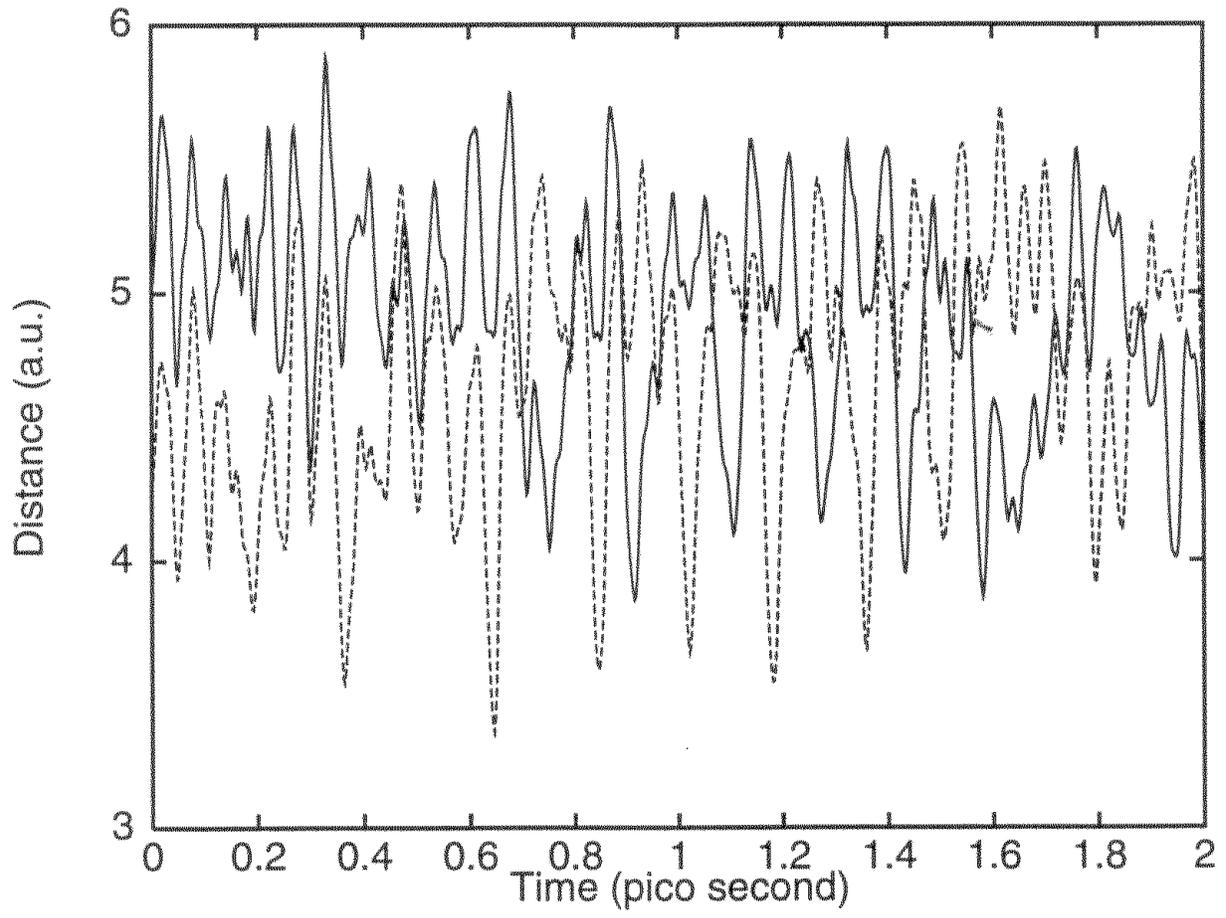


Fig. 3

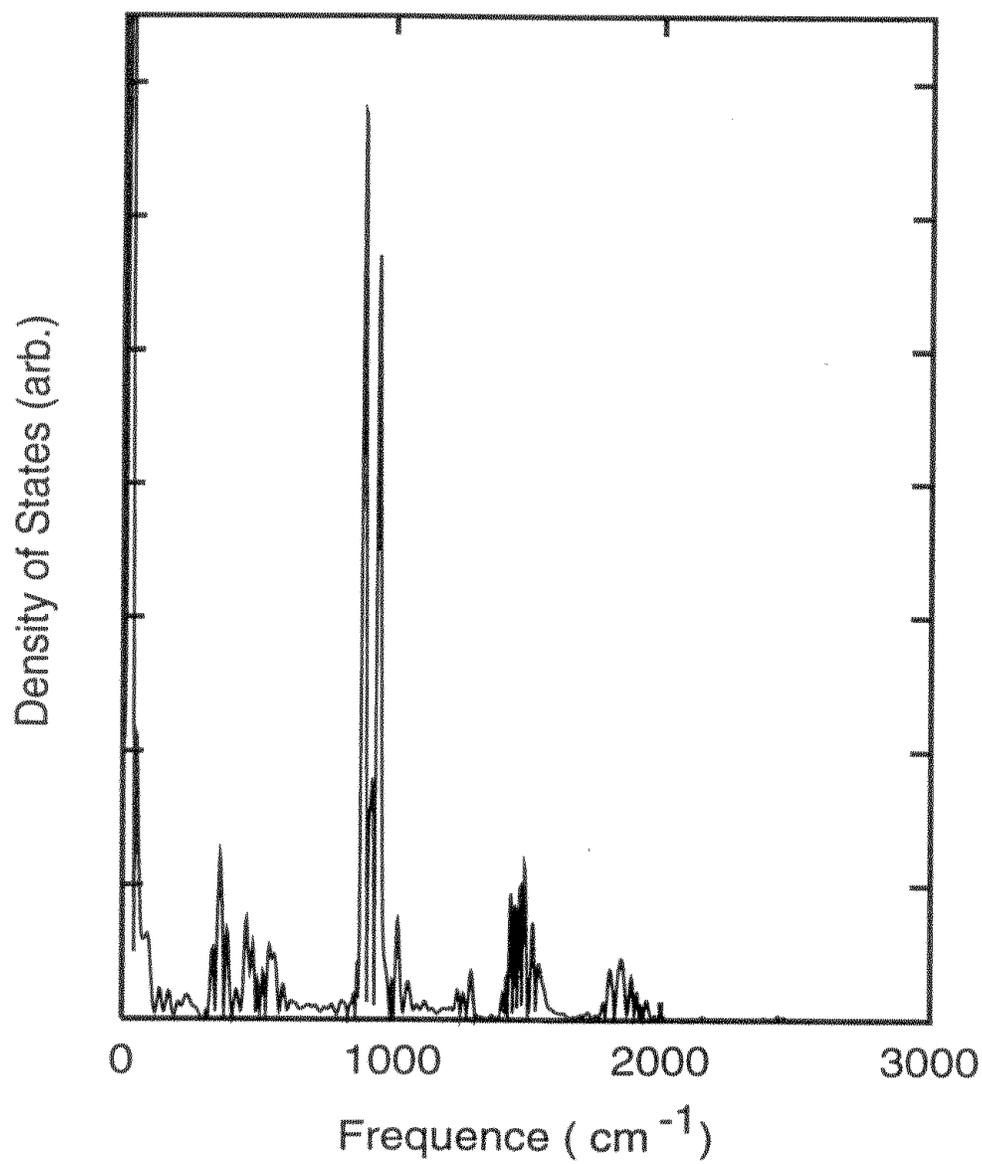


Fig. 4

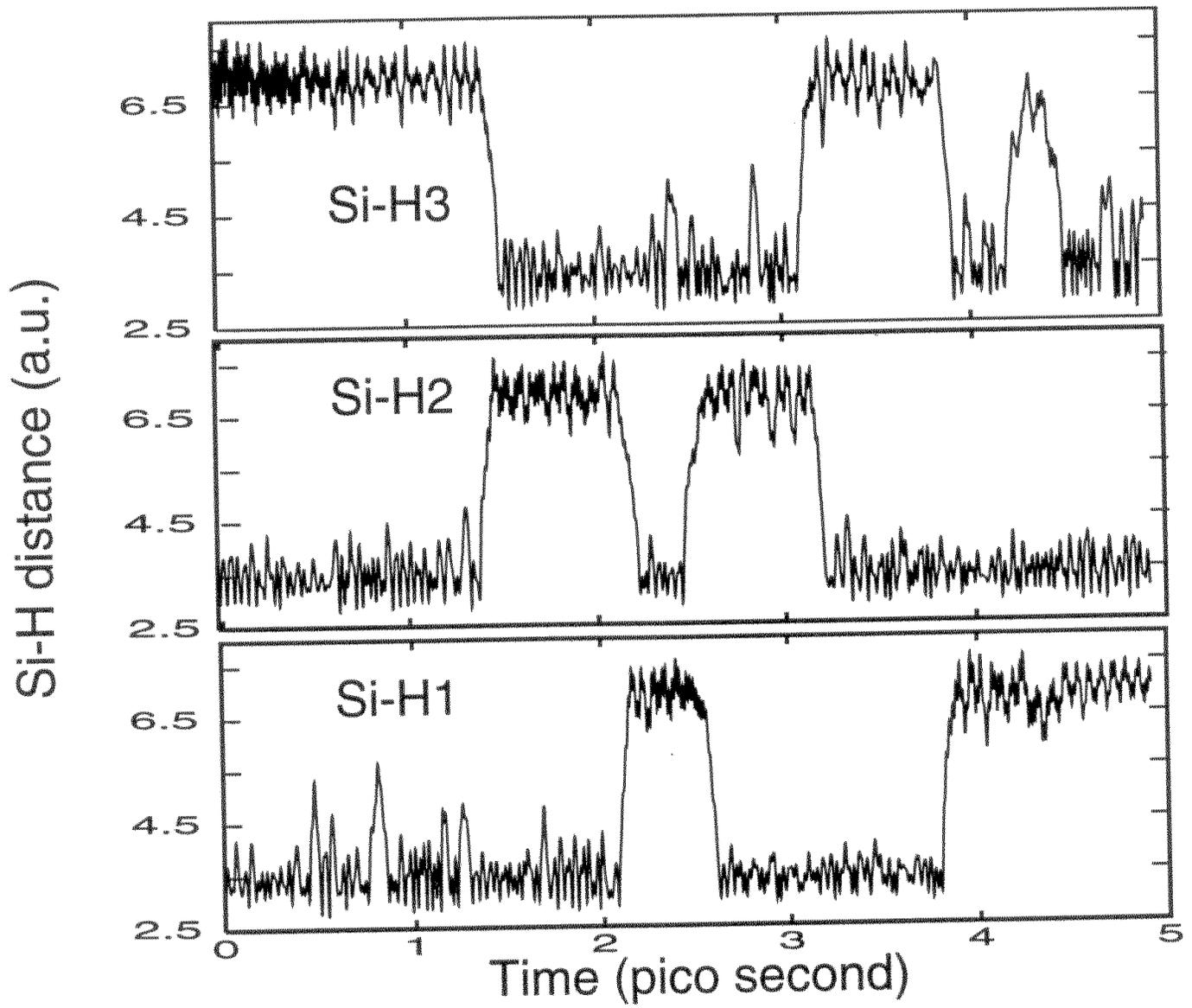


Fig. 5

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