

Temperature-dependent vibrational spectra and melting behavior of small silicon clusters based on *ab initio* molecular dynamics simulations

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Vibrational spectra of Si_n ($n=4-7$) clusters are obtained by using Fourier transformation of the velocity autocorrelation function of the atoms calculated based on Car-Parrinello molecular dynamics. By comparing the calculated vibrational spectra with experimental results, the ground-state atomic structures of the clusters can be determined. Changes in the vibrational spectra and the bond-length root-mean-square fluctuation with temperature are obtained. It is shown that the characteristic structures of the vibrational spectra with ground-state configuration start to disappear before the melting start points indicated by sharp increase in the bond-length root-mean-square fluctuation with temperature. Therefore the vibrational spectra cannot be used to identify the existence of these clusters in gases before the temperature going down well below their actual formation temperatures. Melting of these small silicon clusters starts at a temperature lower than the bulk material and undergoes transition states over a finite temperature range. The trajectories of the atoms in configuration space are used to show that the structure changes during the melting process depend closely on the ground-state structures. The calculated electronic energy levels of Si_4 cluster, as an example, indicate that during melting process there are considerable energy-level broadenings caused by atomic thermal motions.

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I. INTRODUCTION

In recent years, a number of researches for small silicon clusters have been performed because of their importance roles in microelectronics industry [1]. Most researches have been done on the thermodynamic behavior of the clusters from the viewpoint of energy. The temperature-dependent vibrational properties of silicon clusters, particularly in the melting transition, are less revealed. Actually, the vibrational properties play an important role in understanding the peculiar structure and thermodynamic properties of these clusters. On one hand, the vibrational spectra can be used to identify the ground-state (GS) structures of small clusters. Directly observing small cluster structures by experiment is much difficult, thus a combination of theoretical calculation and experimental measurements is necessary to definitively establish cluster structures. One feasible way is comparing calculated vibrational spectra with experimental values [2,3]. Li *et al.* [4] reported the experimental infrared spectra of Si_n ($n=3-7$), which were in agreement with their calculated vibrational frequencies by using QCISD method. The structures of small silicon clusters containing only up to seven atoms were studied by using surface-plasmon-polarization (SPP) enhanced Raman spectroscopy [5], where the Raman-active vibrations were in good agreement with their predictions based on *ab initio* calculations. In the meantime, majority of the theoretical studies is devoted to investigating ground-state structures of small silicon clusters [6-9]. Unfortunately, there are inconsistencies between different theoretical results. Li *et al.* [6] indicated that the ground-state structure of Si_6 was the tetragonal bipyramid with D_{4h} symmetry, whereas the result obtained by Panda *et al.* [7] showed that Si_6 had C_{2v} symmetry. In this study, the ground-state struc-

ture of Si_6 was determined using vibrational spectra.

On the other hand, vibrational spectra are expected to reveal the vibrational dynamical motion of the atoms in the cluster during melting process, which gives a complement for experimental measurement. Vaporization and gas condensation are often used to produce clusters. In this kind of production processes, abundance and structure of the clusters change with temperature and pressure. Most recently, structures of small neutral gold clusters in the gas phase produced by laser vaporization were revealed by using vibrational spectroscopy [10]. Definite structural information from the measured vibrational spectra needs detailed knowledge of the vibrational dynamical motions of the atoms in the cluster and their temperature dependence. This kind of knowledge is also needed to understand the thermodynamical properties of the materials consisting of atoms and clusters. Generally, it is believed that the structural characteristics of the spectra exist for solid states only. However, details of the changes in the vibrational spectra with temperature far below, across, and well above the melting temperature are helpful for people to understand what are actually measured in a temperature changing process.

There is a common feature in many experiments [11,12] that the melting temperature of clusters are lower than those of the corresponding bulk materials. However, ion mobility measurement performed by Shvartsburg *et al.* [13] showed that tin clusters melt at least 50 K above the bulk melting point in the range of 16-30 atoms, which was confirmed by theoretical calculation [14] where it was further indicated that the melting point of tin cluster with less than 13 atoms is at least 800 K above the bulk melting point. Subsequently, other elemental clusters which melt at higher temperatures than the bulk materials are gradually observed by experiments and simulations [15-18]. Most of them are semiconductor clusters, therefore, the melting behavior of semiconductor clusters is the subject of intensive research recently.

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Up to now, there have been many investigations [18–21] on the melting behavior of semiconductor clusters. A number of experimental investigations revealed that the fragmentation occurs commonly within the clusters of semiconducting group IV elements [22]. Mitas *et al.* [23] reported that silicon clusters with 6–10 atoms are the most abundant fragments. *Ab initio* molecular dynamics study for small silicon clusters by Krishnamurty *et al.* [24] showed that the finite temperature behavior of Si₁₀ was dominated by isomerization and fragments around 2800 K without melting as well as Si₂₀, which fragments around 1200 K. Si₁₅ exhibits a liquidlike phase over a short temperature range before fragmenting around 1800 K. The investigations on the ground-state geometries of medium sized silicon clusters show that these clusters are built upon stable tricapped trigonal prism (TTP) units. The high stability of TTP units results in fragmentation of these clusters instead of solidlike to liquidlike transition [24] with increase in temperature.

However, the vibrational spectra in the region of melting transition of these clusters are not yet clear, regardless it could be expected to introduce an experimental guidance to reveal the melting details. The relation between the structural transition and atomic dynamics in the melting process of small silicon clusters is also needed to reveal. These lacks of knowledge have limited our understanding of the melting processes of clusters. Therefore, it is also necessary to investigate the melting process of small silicon clusters from the viewpoint of vibrational spectra.

II. THEORETICAL MODEL

In the present study, Car-Parrinello (CP) [25] molecular dynamics simulation within the local-density approximation (LDA), as implemented in the QUANTUM-ESPRESSO (QE) package [26], is adopted to investigate the vibrational spectra and the melting behavior of Si_{*n*} (*n*=4–7) clusters. The CP method which combines the density-functional theory (DFT) with the molecular dynamics method is a powerful technique to investigate electronic and atomic structures of semiconductor clusters. In the current case, we consider the silicon clusters as isolated systems, thus a supercell model [27] is proposed. The atoms that exhibit special geometry within clusters are put into the center of a large cubic cell. Periodic boundary conditions are imposed on the large supercell with edge of 30 a.u. to ensure that there is no appreciable interaction between periodic images. In the DFT framework, we use the Ceperley-Alder exchange-correlation potential functional with the parametrization of Perdew and Zunger [28] to treat the exchange-correlation interactions between electrons. The interaction between the ionic core and valence electrons is described by a norm-conserving pseudopotential. We choose 3s² and 3p² as valence electrons and use a plane-wave basis set with an energy cutoff of 15 Ry. Only the Γ point is used to sample the Brillouin zone.

In order to calculate the eigenvibrational spectra of the clusters with ground-state configurations, we simulated the motion of atoms in silicon clusters with microcanonical ensemble. Verlet algorithm is used to integrate the motion equation. The time step is taken to be 20 a.u. with the ficti-

tious electronic mass of 260 a.u., which provide conservation of the total energy within 10⁻⁴ Ry. The initial momenta of the atoms are set to be zero and the total angular momentum of the cluster is also hold to be zero to restrict cluster rotation. The forces generated by the initial deformation drive the atoms to move. The temperature within the whole simulation process is less than 5 K. The trajectory is propagated 35 000 steps, wherein the starting 5000 steps are used to make cluster reach stable state and the subsequent 30 000 steps (about 14.5 ps) are used for statistical calculation. The vibrational density of states (VDOS), which presents peaks at the phonon eigenfrequencies, is obtained by using the Fourier transformation of velocity autocorrelation function (VAF) $C(t)$ [29,30]

$$I(\omega) = 2 \int_0^{\infty} C(t) \cos \omega t dt \quad (1)$$

with

$$C(t) \equiv \frac{\langle \mathbf{v}(t_0 + t) \cdot \mathbf{v}(t_0) \rangle}{\langle \mathbf{v}^2(t_0) \rangle} = \frac{\sum_{j=1}^{n_t} \sum_{i=1}^N \mathbf{v}_i(t_{0j} + t) \cdot \mathbf{v}_i(t_{0j})}{\sum_{j=1}^{n_t} \sum_{i=1}^N \mathbf{v}_i^2(t_{0j})}, \quad (2)$$

where $\langle \rangle$ is the time averaged value calculated along the entire trajectory, N is the number of atoms in the cluster, and n_t is the number of time origins. In the present work, n_t is taken to be 200 with the interval of 20 time steps.

With the purpose of studying the vibrational spectra of the clusters cross melting transition process, canonical ensemble is used to simulate the motion of silicon clusters coupled to the Nosé-Hoover thermostats [31]. In order to keep the system on the Born-Oppenheimer surface at high temperatures, we use two Nosé-Hoover thermostats for the ionic and electronic subsystems, respectively, where the electronic Nosé frequency is set to 100 THz and the ionic Nosé frequency is chosen to be 20 THz. We split the temperature range 100–2000 K into many different temperatures by 100 or 200 K. The time step is taken to be 10 a.u. At each temperature the trajectory is propagated 80 000 steps (about 19.3 ps) for statistical calculations. In order to characterize the melting process of clusters, the bond-length root-mean-square (rms) fluctuation δ defined by [29]

$$\delta = \frac{2}{N(N-1)} \sum_{i < j} \frac{(\langle r_{ij}^2 \rangle_t - \langle r_{ij} \rangle_t^2)^{1/2}}{\langle r_{ij} \rangle_t} \quad (3)$$

is also calculated, where r_{ij} is the distance between atoms i and j . Since δ is sensitive to structure distortion, it is often used for studying the changes of small clusters structure with temperature [21].

Adiabatic changes in the electronic structures of clusters with atomic dynamic motion during melting are also very important issues to understand the melting process. Therefore, the electronic density of states (DOS) of Si₄ is calculated by using augmented plane wave plus local orbital (APW+lo) method. The DOS is integrated with the Gaussian smoothing of discrete atomic energy levels. The same super-

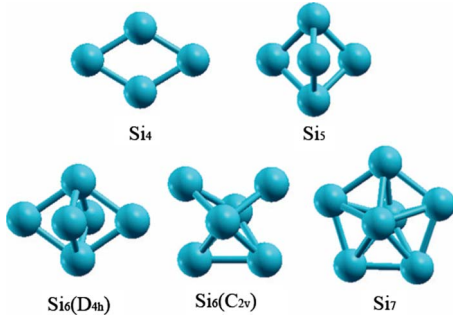


FIG. 1. (Color online) The ground-state structures of Si_4 - Si_7 .

cell model is used with periodic boundary conditions. The local-density approximation is used to take exchange-correlation interactions into account. Brillouin-zone integrations are performed using 10 \mathbf{k} points in the irreducible part of the BZ. RK_{max} is 5.0 Ry. The radii of muffin-tin (MT) spheres are determined to ensure that all MT spheres are tangent as much as possible.

III. RESULTS AND DISCUSSION

A. Vibrational spectra of small silicon clusters in ground state

The bond lengths quoted in Ref. [6] are used to generate starting geometries for Si_4 - Si_7 clusters, from which the structural relaxation of the clusters to their ground-state geometries are carried out using CP molecular dynamics simulation with damp algorithm. The energy of every stable structure is also calculated. For Si_6 , two structures with both D_{4h} [6] and C_{2v} [7] symmetries are considered. It is shown that in all cases the relaxation is small and the optimized bond lengths are consistent with values in literatures [6,7]. The relaxed cluster structures are shown in Fig. 1. The ground-state structure of the Si_4 shows rhombus configuration with D_{2h} symmetry. The trigonal bipyramid with D_{3h} symmetry is the most stable structure of Si_5 clusters. The most stable geometry for Si_7 is the pentagonal bipyramid with D_{5h} symmetry. For Si_6 , two structures with both D_{4h} and C_{2v} symmetries are stable structures. It is shown that the two structures are energy degenerate and the energy barrier between of them is 10^{-4} eV. Therefore, it can be concluded that the two structures with D_{4h} and C_{2v} symmetries coexist in the ground state of Si_6 cluster. The following calculated vibrational spectra give an evidence for such a conclusion too.

Based on the optimized structures, the eigenvibrational spectra of these clusters are calculated. The results for Si_4 - Si_7 clusters are shown in Fig. 2. For Si_6 , Fig. 2 shows only the result of D_{4h} structure because the frequencies of normal modes of the two structures are in good agreement and the vibrational spectra are almost the same. Therefore, the following calculations are only done for D_{4h} structure. Since there are $3n-6$ vibrational degrees of freedom for the cluster with n atoms, the number of vibrational frequencies of normal modes is $3n-6$. As shown in Fig. 2, there are several degenerate normal modes. In order to clarify the degenerate normal modes and check the correctness of molecular dy-

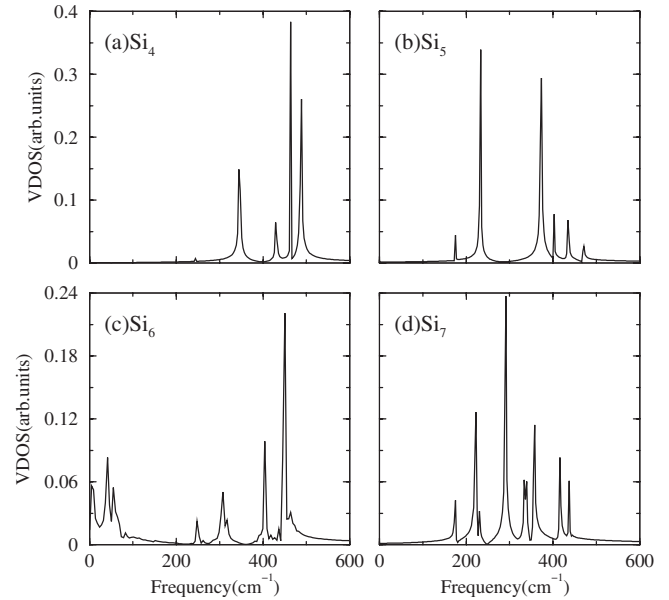


FIG. 2. The vibrational density of states for the ground-state Si_4 - Si_7 clusters. (c) is the result of Si_6 with D_{4h} symmetry.

namics simulation, the Hessian matrix obtained by differentiating the Hellmann-Feynman forces with respect to atomic coordinates is diagonalized to give the eigenvibrational frequencies of the ground-state configurations. The results for Si_n ($n=4-7$) are shown in Table I compared with both experimental values [4,32] and other theoretical values [2]. It shows very good agreement between the frequencies computed using the two theoretical models, with typical differences of approximately 10 cm^{-1} except the two lowest eigenfrequencies (8 cm^{-1}) of Si_6 of D_{4h} symmetry. A definite conclusion cannot be made for the two lowest eigenfrequencies (8 cm^{-1}) of Si_6 of D_{4h} symmetry because there is no corresponding experimental value to match. Our results are also in excellent agreement with experimental values. Therefore, comparing our simulation results with the experimental measurements, the ground-state structures of Si_n ($n=4-7$) optimized in our work can be obtained without doubt.

B. Changes in the vibrational spectra with temperature across the melting process of small silicon clusters

For small silicon cluster, its properties are strongly correlated with the cluster size [19]. Therefore, the melting behavior of small silicon clusters is expected to vary from each other. In the present work, the melting processes of small silicon clusters are investigated with two indicators. One is the temperature dependence of the bond-length rms fluctuation δ , indicative of mean amplitude of atoms within clusters, and the other is the temperature dependence of the vibrational spectra.

For Si_4 , it can be seen clearly from Fig. 3(a) that changes in the bond-length rms fluctuation δ is characterized by three stages. The first stage is below 1200 K, in which δ increases almost linearly from 0.02 to 0.07 with small slope. The cluster behaves very similar to a typical solid characterized by atomic vibrations around their equilibrium positions. The

TABLE I. Comparison of the calculated eigenvibrational frequencies of the ground-state silicon clusters using CP molecular dynamics simulation, diagonalization of the Hessian matrix, and LDA model [2], along with the experimental values [4,32]. For Si₆, frequencies are given for both structures with *D*_{4h} and *C*_{2v} (in parentheses) symmetries. Frequencies are given in units of cm⁻¹.

	CP	Hessian	LDA	Expt.
Si ₄		53	53	
	244	244	249	
	347	346	346	345
	429	430	436	
	464	463	470	470
	488	488	496	501
Si ₅	175	176	174	
	175	176		
	233	234	234	
	374	375	382	
	374	375		
	403	406	412	
	435	436	443	
	435	436	444	
	472	473	476	
	Si ₆	41(37)	8(36)	
56(45)		8(60)	51	
152(148)		153(146)		
248(252)		242(262)	270	252
308(308)		304(313)	315	300
317(308)		326(315)	319	
381(381)		392(379)	384	386
404(402)		412(399)	410	
418(417)		412(403)	412	404
450(451)		456(449)		
464(466)	456(454)	463	458	
464(466)	456(456)	463	461	
Si ₇	175	175		
	175	175		
	223	223		
	223	223		
	231	232	240	
	292	294	301	289
	292	294		
	334	339	347	340
	334	339	347	340
	339	341		
	339	341		
	358	359	362	358
	416	421	430	422
416	421			
438	442	448	435	

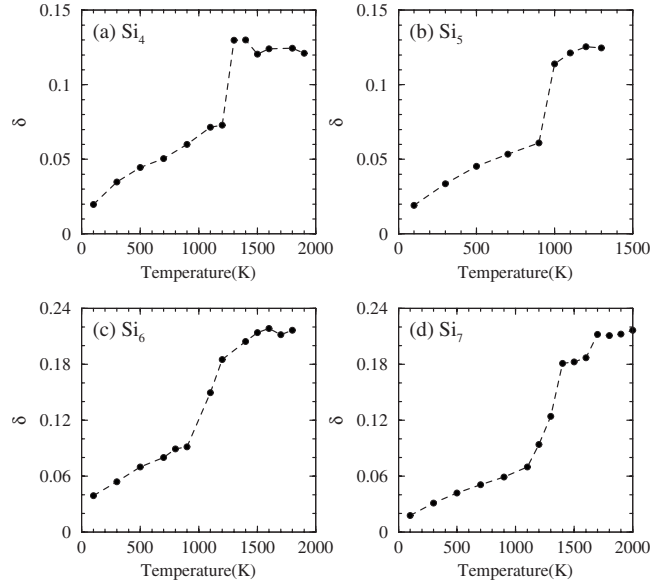


FIG. 3. Changes in the calculated bond-length root-mean-square fluctuation δ [Eq. (3)] with temperature for Si₄-Si₇ clusters.

cluster is in solidlike state. The second one is from 1200 to 1300 K, in which δ increases rapidly from 0.07 to 0.13. It indicates that the cluster must have undergone the structural or phase transformation. The analysis of ionic motion at various temperatures indicates that all atoms are bonded together and there is no fragmentation during all the simulation time. Hence, from 1200 to 1300 K the cluster is in transitions from solidlike to liquidlike states. Above 1300 K, δ is almost constant and the cluster remains in liquidlike state.

In Fig. 4, the VDOS of Si₄ at different temperatures are presented. It is noted that below 700 K the characteristic peaks become broader as temperature rises. However, the

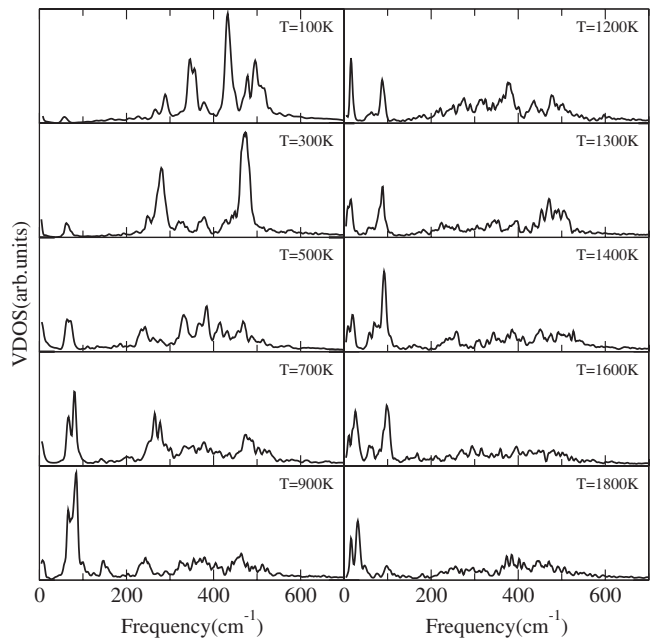


FIG. 4. The calculated VDOS of Si₄ at different temperatures.

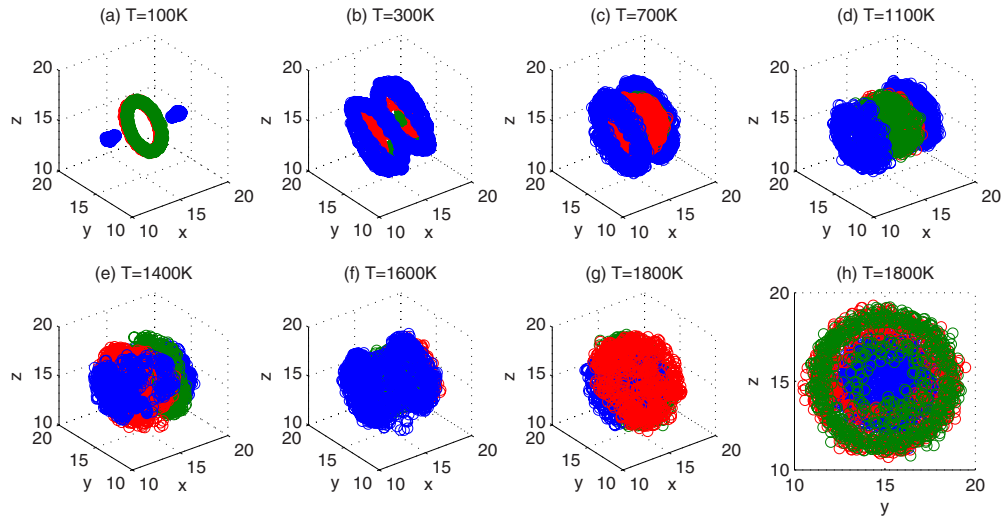


FIG. 5. (Color online) The atomic trajectories of Si_4 cluster in the configuration space at different temperatures. The atoms are distinguished with different colors (grayscale). (h) is the yz -plane projection of the atom trajectory at 1800 K. Coordinates (x , y , and z) are in units of a.u.

normal modes related to the typical cluster in rigid structure can be clearly identified. It indicates that the anharmonic vibration caused by thermal motion is weak below 700 K. As temperature rises continuously, the peaks begin to confuse and the characteristic peaks of high-frequency band disappear gradually, which indicates the anharmonicity has an increasing impact on the vibrations of atoms. Above 1400 K, the peaks in high-frequency band disappear completely, whereas several characteristic peaks in low-frequency band still exist. Actually, the peak having the smallest frequency in Fig. 4 is associated with the rotation of Si_4 according to the following analysis. We can clearly see that there is a peak which transforms from about 50 cm^{-1} in Fig. 4(a) to about 100 cm^{-1} in Fig. 4(h). This mode is the b_{1u} mode, the only out-plane mode for Si_4 . The reason why the b_{1u} mode exists all the time is that for planar structure cluster this mode is harder to destroy than the modes in plane as temperature rises. Comparing the changes in δ and vibrational spectra with temperature, one cannot see the corresponding dramatic changes in the vibrational spectra as one did for δ . The cause lies in that the effect of anharmonicity on vibration is gradually increased with temperature rising, thus the normal modes do not disappear sharply but gradually before the melting process indicated by the bond-length rms fluctuation.

In order to characterize visually the atomic dynamics of small silicon clusters, we show the atomic trajectories at different temperatures in the configuration space for Si_4 in Fig. 5. It must be noted that, in the current case, the X component of the total angular momentum of Si_4 is not zero but a very small value and other two components equal zero. Therefore, it can be seen that entire Si_4 rotates around on X axis with very small rotational velocity. Thus there is a corresponding rotational mode with quite low frequency in Fig. 4. In addition, we can see from Fig. 5 that the atoms keep staying in respective shells whatever the temperature is low or high, even at 1800 K. It is consistent with above analysis.

For Si_5 , similar analysis on the melting behavior is done as for Si_4 . Figure 3(b) shows the changes in δ of Si_5 with

temperature, which are similar to those of Si_4 . The temperature range of transition state is from 900 to 1000 K. The vibrational density of states at different temperatures is shown in Fig. 6. Below 900 K, the eigenvibrational peaks in vibrational spectra can be distinguished clearly, although there is small broadening as temperature rises. The frequency distribution of VDOS concentrates around 400 cm^{-1} gradually with the increase in temperature. In the melting transition state from 900 to 1200 K the peaks disappear gradually. Above 1300 K, the peaks related to the harmonic vibration disappear completely, and the cluster is thus in liquidlike state. According to the above analysis, the temperature-dependent vibrational spectra of Si_4 and Si_5 exhibit different behavior. The reason for this difference lies on the different bonding strength between silicon atoms in cluster and the different space configuration and symmetry of the cluster. The atoms in Si_5 cluster bonded more strongly with each other compared to the atoms in Si_4 . The three-dimensional configuration of Si_5 with stronger bonds is thus more difficult to destruct due to atomic thermal motions. Therefore, one can see that the vibrational spectra of Si_5 changes dramatically from 900 to 1200 K only.

The atom trajectories of Si_5 in configuration space are similar to those of Si_4 , except that the very low-frequency peak corresponding to rotational mode does not exist for Si_5 . From the atomic trajectories in at different temperatures, it is shown that the atoms of Si_5 are bonded together and Si_5 does not undergo fragmentation until the temperature is up to 1800 K, the same as for Si_4 . A number of researches have pointed out that liquid-gas transition simulation of cluster depends on the details of the method, including the range of the potential and the container size confining the clusters [33–35]. In this simulation, the cubic supercell can be considered as an enough large container for one small cluster to observe its fragmentation behavior. Therefore, only energy redistribution and fluctuation among the bonds in a single cluster are considered in this simulation, and the energy fluctuation of the cluster is strictly limited to low level. Actually,

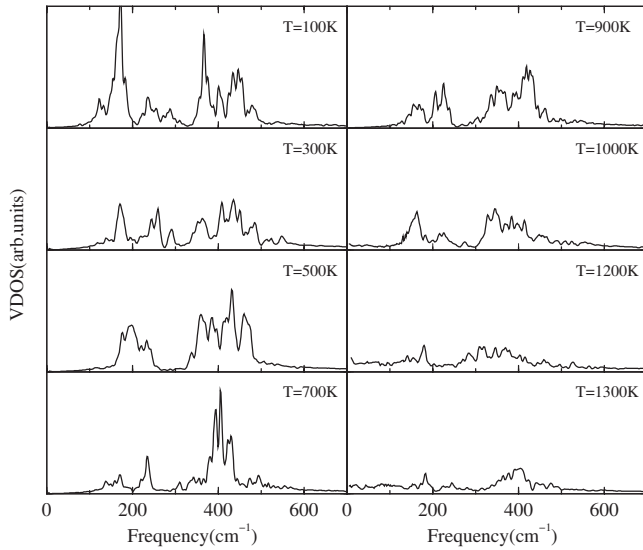


FIG. 6. The calculated VDOS of Si_5 at different temperatures.

thermal dissociation is a spontaneous process occurring for individual clusters as soon as the thermal energy exceeds the dissociation barrier. However, the typical time scales of thermal dissociation of the small cluster exceed that our simulations can afford with the present model so that the fragmentation can hardly be observed even if it could really occur at the temperatures our simulation had covered. It is also possible that thermal dissociation of the present systems does not occur at all at these temperatures. Nevertheless, a definite conclusion cannot be made for the fragmentation based on the present simulations. In addition, the collisions between clusters and the energy fluctuation among the clusters in an aggregate of clusters are not included in the present model either.

For Si_6 , the trend of the plotted curve of δ [shown in Fig. 3(c)] is similar to Si_4 and Si_5 , but there is a wider temperature range of solid to liquid transition state, from 900 to 1600 K. The VDOS at different temperatures are shown in Fig. 7. There are two distinct frequency bands, 0–200 cm^{-1} and 200–500 cm^{-1} . Both of them are clearly identified below 900 K. The peaks which characterize the harmonic vibration of rigid structure are also clear to see. However, there is coupling between different modes. The higher the temperature is, the stronger the coupling is. With temperature rising continuously, the two frequency bands begin to merge and the eigenvibrational peaks disappear gradually. When temperature is up to 1500 K, almost all of the modes structures disappear. The cluster is completely melted at that time. In Fig. 8, we show the process of structure evolution and atom trajectories at different temperatures in the configuration space for Si_6 . Unlike Si_4 , the total angular momentum of Si_6 is zero, namely, there is no rotational modes in Fig. 7.

One can see clearly the atomic trajectories of Si_6 during the heating process in Fig. 8. At low temperatures each atom in the cluster moves around the equilibrium positions and the cluster retains its rigid structure [see Fig. 8(a)]. As temperature rises, the vibrational amplitudes of atoms obviously increase and the structure become softer than the initial one.

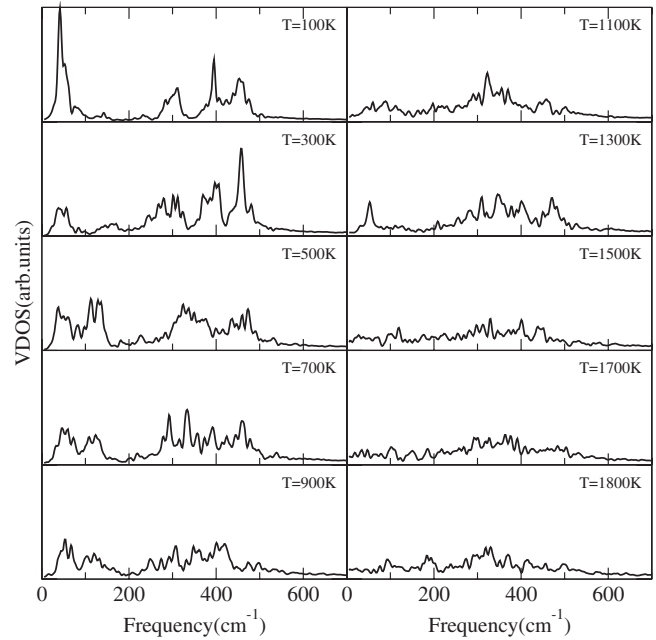


FIG. 7. The calculated VDOS of Si_6 at different temperatures.

When the temperature rises to certain value, the rigid structure disappears and the atoms can diffuse through the cluster. However, the atoms are still restricted within the region of cluster by the weak bonds between the atoms with no fragmentation in the whole simulation time. Another feature of the atomic thermal motions is that different atoms exchange positions frequently and shell structure in the cluster disappears at high temperature.

For Si_7 , the curve of δ [shown in Fig. 3(d)] is similar to that of Si_6 , and there is a wide range of transition state region from 1100 to 1700 K in temperature. We show the VDOS of Si_7 at different temperatures in Fig. 9. By analyzing the two indicators, it can be seen that the melting behavior of Si_7 is much similar to Si_6 because both of them have cage-like structure.

From above discussions, knowledge of atomic dynamics of small silicon clusters during the heating process can be obtained. At low temperature each atom in the cluster moves around the equilibrium positions and retain its equilibrium structure. As temperature rises, the mode coupling is stronger and the rigid structure begins to be distorted. When the temperature rises to certain value, which is usually lower than the melting start temperature determined by the bond-length rms fluctuation, the rigid structure becomes soft and the atoms can diffuse throughout the cluster. Although the covalent bonds between silicon atoms are weak when temperature is high enough, the atoms are still restricted within the region of cluster. The melting processes of Si_5 – Si_7 are similar as analyzed above, while Si_4 is an exception. The cause lies in that Si_4 has planar structure while other three clusters have cage-like structure. Therefore, we can conclude that the thermal properties of small silicon clusters are closely relative to their ground-state structures.

According to Lindemann's criterion, a bulk crystal material will melt when the bond-length rms fluctuation of the

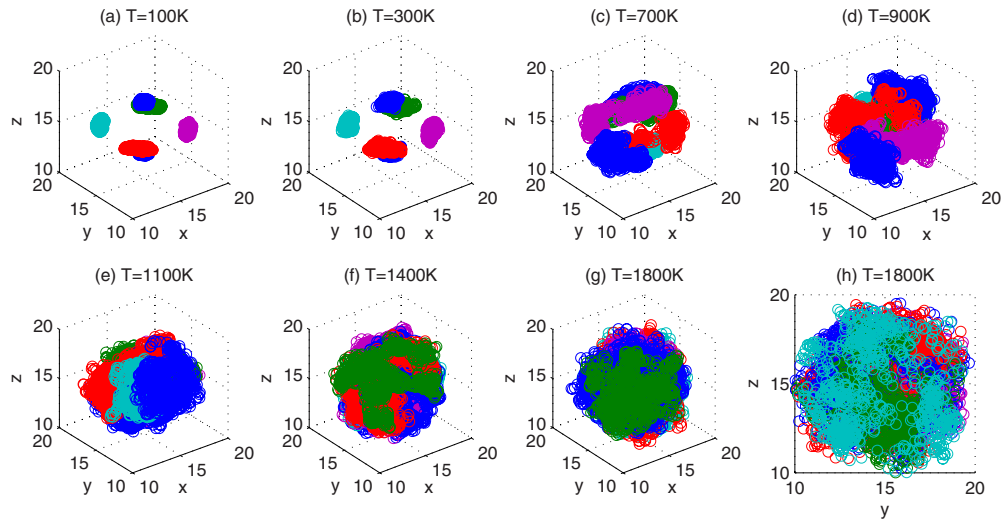


FIG. 8. (Color online) The atomic trajectories of Si_6 cluster in the configuration space at different temperatures. (h) is the yz -plane projection of the atom trajectory at 1800 K. Coordinates (x , y , and z) are in units of a.u.

atoms is more than 10% of the equilibrium bond distance in the crystal. In the present case, there are no definite critical values for Si_4 - Si_7 in the melting process. This is due to the fact that the structures of small clusters are very different from bulk. Most of the atoms in small cluster lie on the surface and the ratio of surface to volume for small clusters is much higher than bulk materials. As shown in Fig. 3, the transition state spans wide temperature range, thus it is difficult to define the melting temperature definitely. There have been several methods suggested to define the melting point [18]. One of them is the mean value of temperatures of the whole transition state stage. According to this definition, the melting points of Si_4 - Si_7 are approximately 1250, 950, 1250,

and 1400 K. The result for Si_6 and Si_7 is in good agreement with the result in Ref. [19]. From the above discussions, one can see that the melting points of all Si_n ($n=4-7$) clusters are lower than that of the bulk (about 1700 K [18]) material. The physical cause [36] lies in the fact that the surface atoms are more weakly bound and less constrained in their thermal motion than atoms in the body of a bulk material.

C. Adiabatic broadening of electronic energy levels with atomic thermal motions

The adiabatic changes in electronic structures of clusters with the atomic thermal motion are also important for us to understand the evolutionary process from electronic energy levels of atoms to energy bands of solid material. In the present study, we take Si_4 as an example for the sake of the effects of atomic thermal motions on electronic structures of small silicon clusters. In Fig. 10, we show the electronic DOS of the ground-state structure and four structures took out from molecular dynamics simulations every 20 000 steps at 1800 K. Si_4 cluster can be considered as an isolated molecule and thus there are no energy bands but discrete energy levels. Each atom in Si_4 cluster has four valence electrons, so there are 16 valence electrons in total for Si_4 cluster. Each molecular orbital can be occupied by two electrons at most, thus there are at least eight orbitals to contain these valence electrons. As shown in Fig. 10, there are eight energy levels below the Fermi energy level, which just contain the 16 valence electrons. From the right figures in Fig. 10 we can see that both s electron and p electron contribute the eight energy levels. It indicates that the $3s$ orbital and $3p$ orbital hybridize first, then the hybrid orbitals bond together. An obvious characteristic of the electronic DOS of different structures is that all energy levels have shifted and the extent of shift varies from each other as shown in Fig. 10. It indicates that there are energy-level shifts caused by atomic thermal motions. In fact, the distances between the atoms in Si_4 cluster change all the times because the structure of Si_4 transforms from one to another ceaselessly due to atomic thermal motions. The den-

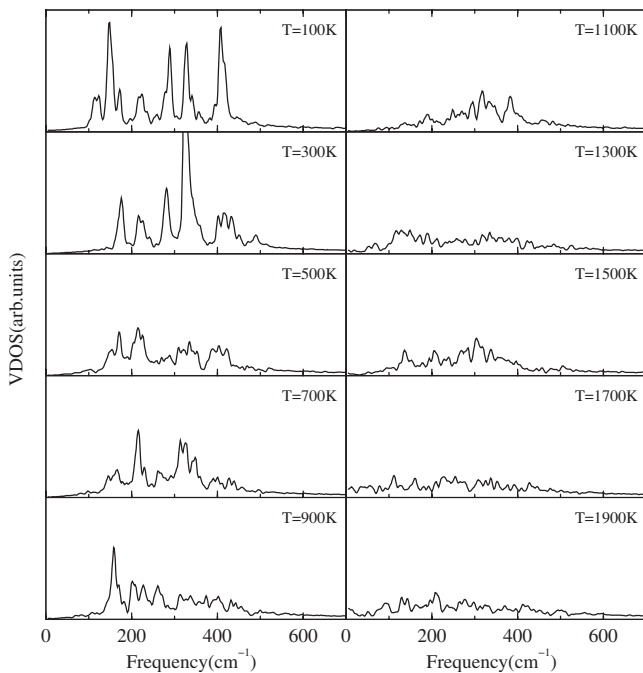


FIG. 9. The calculated VDOS of Si_7 at different temperatures.

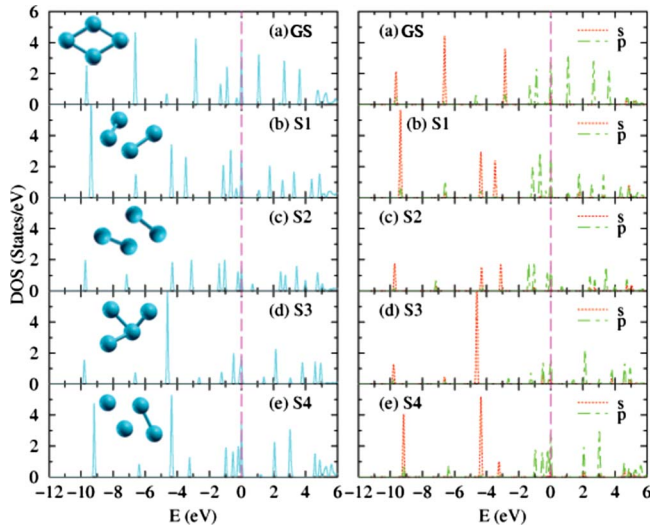


FIG. 10. (Color online) The electronic density of states of five configurations of Si_4 at 1800 K. (a) is the DOS of ground-state configuration of Si_4 , (b)–(e) are four configurations taken out from the molecular dynamics simulations every 20 000 steps at 1800 K. Left column shows the total DOS, and right one shows s and p partial DOS. The vertical long-dashed lines indicate the Fermi energies.

sity of electron in the cluster region changes accordingly. Therefore the electronic energy levels of Si_4 shift adiabatically from one structure to another. If calculating the time-average value of DOS from the entire trajectories, we can see that there are energy-level broadenings caused by atomic thermal motion. Experimental measurements can observe this average effect, which can be considered as a criterion to analyze the melting behavior of small clusters. Consequently, the energy-level broadening effect is important for us to understand the melting behavior of small clusters.

IV. CONCLUSIONS

In conclusion, we have performed *ab initio* molecular dynamics-simulation at different temperatures to study the temperature dependent vibrational spectra of small silicon clusters across the melting process, which is identified using the sharp increase in the bond-length rms fluctuation with temperature. Accuracy of the calculation is confirmed by reproducing the ground-state vibrational spectra and atomic structures of Si_n ($n=4-7$) clusters. By analyzing the vibrational spectra, the bond-length rms fluctuation, the atom trajectories in the configuration space, it is shown that these small silicon clusters exhibit dramatic changes in vibrational spectroscopy from far below the melting temperature, across the melting process, and to well above the melting temperature. These clusters undergo an transition state in the melting process with a wide temperature region. The characteristic features of the vibrational spectra start to disappear far below the melting temperature and identification of the cluster formation in the gas phase using the finger structure in spectra cannot be done before the temperature of the gas going down well below the actual formation temperature of the cluster. The thermal properties of small silicon clusters are closely related to their ground-state structures. It is also shown that there are considerable electronic energy-level broadenings caused by atomic thermal motions.

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