Temperature effect on the structural stabilities and electronic properties of $X_{22}H_{28}$ ($X=C, Si$ and $Ge$) nanocrystals: A first-principles study

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Based on ab initio molecular dynamic simulations, we have theoretically investigated the structural stabilities and electronic properties of $X_{22}H_{28}$ ($X=C$, Si, and Ge) nanocrystals, as a function of temperature with consideration of vibrational entropy effects. To compare the relative stabilities of $X_{22}H_{28}$ isomers, the vibration free energies are obtained according to the calculated phonon spectrum, where the typical modes are shown to be dominant to the structural stabilities. In addition, there is a significant gap reduction as the temperature increases from 0 K to 300 K, where the decrements are 0.2 /0.5 /0.6 eV for C/Si/Ge nanocrystals, respectively. The dependence of energy gap on the variance of bond length is also analyzed according to the corresponding atomic attributions to the HOMO and LUMO levels. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Recently, there has been a great interest in hydrogenated diamond nanocrystals,1,2 where hydrogenated diamond nanocrystals were isolated and synthesized.3 Because of the biocompatibility and ultra-high hardness, hydrogenated diamond nanocrystals showed potential applications in the pharmaceutical industry.4-6 Hydrogenated diamond nanocrystals can also be used as fluorescent label and photoelectric devices7,8 owing to their high luminous efficiency. Characteristic optical properties9 evolution for the hydrogenated diamond nanocrystals as a function of size, shape, and symmetry in the subnanometer regime have been measured in the gas phase. Theoretically, the simulated optical adsorption by combining first-principles calculations and Important Sampling Monte Carlo methods in the basic diamond nanocrystals is in quantitative agreement with the experiment, demonstrating compelling evidence for the role of quantum nuclear dynamics in the photophysics.10

The indirect band gap of silicon (Si) limits its applications on optoelectronics, while Si nanostructures (such as porous silicon,11 Si nanoparticles,12 Si nanocrystals,13 and Si nanocrystals embedded in Si oxide14,15) have exhibited visible photoluminescence at room temperature14 due to the quantum confinement effect. Compared to bulk Si,16-19 there are few studies for the temperature effect on the Si nanocrystals. Franceschetti20 theoretically calculated temperature dependence of the gap of Si nanocrystals using constant temperature molecular dynamics (MD) methods. Hartel et al.21 investigated the temperature-dependent gap of the Si nanocrystals, which were embedded in Si substrates. Similarly, germanium (Ge) nanocrystals have also stimulated extensive researches about the preparative technique22,23 and the fundamental principles since the photoluminescence of Ge quantum dot.24

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Due to the fact of smaller gap, higher carrier mobility, and lighter effective mass, Ge nanocrystals can be used in charge storage, infrared optics, and optoelectronics. Especially, Ge is a candidate of green environment material, which is non-toxic compared with nanocrystals containing Pb, Cd, and Hg.

In our previous works, we have studied that the ground states of hydrogenated group IV nanocrystals $X_n H_m$ (X=C, Si, and Ge), as a function of the chemical potential of hydrogen. In this work, we use $X_{22} H_{28}$ as an example to investigate the structural stabilities and electronic properties as a function of temperature with consideration of vibrational entropy effect. $X_{22} H_{28}$ contains four face-fused cages, with three isomers that are one, two, and three dimension structures (1D, 2D, 3D) respectively. The vibration free energies according to the calculated phonon spectrum and total free energies obtained from the constant-temperature molecular dynamics methods were used to compare the relative stabilities of $X_{22} H_{28}$ isomers, where the typical modes are shown to be dominant to the structural stability. Furthermore, we obtained the gap variance of $X_{22} H_{28}$ from the constant-temperature molecular dynamics, where there is significant gap reduction as the temperature increases from 0 K to 300 K with the decrements are 0.2 /0.5 /0.6 eV for C/Si/Ge nanocrystals respectively. In addition, we not only consider the distribution of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) levels at zero temperature, but also the temperature effect on atomic attributions to HOMO and LUMO levels.

II. COMPUTATIONAL METHODS

The first-principle calculations of $X_{22} H_{28}$ nanocrystals were based on density functional theory (DFT) method implemented in the Vienna ab initio simulation package (VASP). The generalized gradient approximation (GGA) functional was employed for the exchange-correlation energy. With a mesh of $1 \times 1 \times 1$, all the structures are fully relaxed by the conjugate gradient minimization and the convergence of the forces on each atom is less than 0.01 eV/Å. The cutoff energy is 520 eV (360 eV) for carbon (silicon and germanium) nanocrystals and the vacuum distance is set to be 15 Å. Using Nosé-thermostat approach, we have performed the constant-temperature molecular dynamics simulations with the duration of 7 ps and the time step of 1 fs. We recorded the energy gaps and the total free energies of hydrogenated C/Si/Ge nanocrystals after 3 ps. At different temperature, the gaps and total free energies were obtained by averaging the corresponding values of every MD step. For the vibrational frequency calculations, the higher accuracy is needed, so the corresponding cutoff energy was set to 550 eV (400 eV) for C (Si, Ge) nanocrystals and the convergence of the forces on each atom is less than $10^{-7}$ eV/Å.

III. RESULTS AND DISCUSSIONS

In Sec. IIIA, we compare the relative stabilities for the three isomers of $X_{22} H_{28}$ according to the vibration free energies and the total energies, where the low frequency vibrational modes are also shown to be crucial to the structural stabilities. In Sec. IIIB, the gap reduction of $X_{22} H_{28}$ is discussed, and the relation between the gap and the variance of bond length is also analyzed. In Sec. IIIC, we show the distribution of HOMO and LUMO for $X_{22} H_{28}$, with analyzing the atomic attributions to HOMO and LUMO levels at various temperature.

A. Temperature effect on the stability

There are four isomers for $X_{22} H_{28}$, two of which are chirality. Thus we only consider three configurations ($X_{22} H_{28}(S1-2D)$, $X_{22} H_{28}(S2-1D)$, $X_{22} H_{28}(S3-3D)$), as shown in the top panels of Fig. 1. We find that the total energy of $X_{22} H_{28}(S3)$ is the lowest compared to those of $X_{22} H_{28}(S1)$ and $X_{22} H_{28}(S2)$ at 0K through the first-principles calculation. To study the thermodynamics properties of nanocrystals, we consider the vibration free energies under the quasi-harmonic approximation, which can be written as

$$F_{\text{vib}} = E_0 + \sum_i \hbar \omega_i / 2 + kT \sum_i \ln[1 - \exp(-\hbar \omega_i / kT)]$$  \hspace{1cm} (1)
FIG. 1. The structures of $\text{X}_{22}\text{H}_{28}$ and corresponding free energies as a function of temperature. (a, b, and c) Three isomers of $\text{X}_{22}\text{H}_{28}$. Blue and pink balls represent X and H atoms, respectively. (d, e, and f) Vibration free energies of $\text{X}_{22}\text{H}_{28}$ as a function of temperature. The blue dash dot, red dot, and olive solid line correspond to $\text{X}_{22}\text{H}_{28}(\text{S1})$, $\text{X}_{22}\text{H}_{28}(\text{S2})$, and $\text{X}_{22}\text{H}_{28}(\text{S3})$, respectively. (g, h, and i) Total free energies obtained from MD of $\text{X}_{22}\text{H}_{28}$ as a function of temperature. Blue half-filled circle, red hollow upper triangle, and olive full filled diamond correspond to $\text{X}_{22}\text{H}_{28}(\text{S1})$, $\text{X}_{22}\text{H}_{28}(\text{S2})$, and $\text{X}_{22}\text{H}_{28}(\text{S3})$, respectively.

Here $E_0$ is the total energy at 0 K and $\omega_i$ is the frequency of different vibrational mode, as both can be easily obtained from DFT calculations. The second term on the right side of Eq. (1) is zero point energy, which makes a positive contribution to the vibration free energies. $\hbar$ is the reduced Planck constant, and $k$ is the Boltzmann constant. We define the relative vibration free energies ($\Delta F_{\text{vib}} = F_{\text{vib}} - F_{\text{vib}}^0(\text{X}_{22}\text{H}_{28}(\text{S3}))$), where $F_{\text{vib}}^0(\text{X}_{22}\text{H}_{28}(\text{S3}))$ is the vibration free energy of $\text{X}_{22}\text{H}_{28}(\text{S3})$ at $T=0K$.

The $\Delta F_{\text{vib}}$ of $\text{X}_{22}\text{H}_{28}$ isomers as a function of temperature is shown in the panels of the middle row of Fig. 1. The vibrational free energy of $\text{X}_{22}\text{H}_{28}(\text{S3})$ is the lowest among three configurations, indicating that $\text{X}_{22}\text{H}_{28}(\text{S3})$ is the most stable one at $T=0 \sim 300K$. In order to further confirm this, we obtain the total free energies ($F_{\text{tot}}$) of these configurations at different temperature by averaging the energies of the last four thousand MD steps, where the relative total free energies ($\Delta F_{\text{tot}} = F_{\text{tot}} - F_{\text{tot}}^0(\text{X}_{22}\text{H}_{28}(\text{S3}))$) are also shown in the bottom panels of Fig.1. From the MD simulations and the vibration free energies, $\text{X}_{22}\text{H}_{28}(\text{S3})$ is the most stable structures among three configurations for X=C and Si at 0-300K. However, the differences in the free energies among these isomers are larger in the MD simulation as the temperature increases, compared to that from the vibration free energy of Eq.(1), which is under the quasi-harmonic approximation. For Ge$_{22}$H$_{28}$, the MD simulations show that there might be a transition from Ge$_{22}$H$_{28}$(S3) to Ge$_{22}$H$_{28}$(S1) when the temperature exceeds 60K, while Ge$_{22}$H$_{28}$(S3) is the most stable one among three configurations at 0-300K according to the vibration free energy.

In our calculations, we have found that the low frequency vibrational modes make a main contribution to the vibration free energies as the temperature increases according to Eq. (1). We have displayed the lowest frequency vibrational modes and corresponding vibrational frequency of $\text{X}_{22}\text{H}_{28}$ in Fig.2, which indicates that the lowest frequency vibrational modes are similar in the same configuration of $\text{C}_{22}\text{H}_{28}$, $\text{Si}_{22}\text{H}_{28}$, and $\text{Ge}_{22}\text{H}_{28}$. Besides, the vibrational frequency of $\text{C}_{22}\text{H}_{28}$ is the largest, and the one of $\text{Ge}_{22}\text{H}_{28}$ is the smallest in the same configuration. Besides, the atoms near the surface are more important to the low frequency vibrational modes compared to the atoms inside.
FIG. 2. The lowest frequency vibrational modes and corresponding vibrational frequencies of $X_{22}H_{28}$. (a, b, and c) The vibrational modes and corresponding vibrational frequency of three configurations of $C_{22}H_{28}$, cyan and pink balls represent C, H atoms, respectively. (d, e, and f) The vibrational modes and corresponding vibrational frequency of three configurations of $Si_{22}H_{28}$, yellow and pink balls represent Si, H atoms, respectively. (g, h, and i) The vibrational modes and corresponding vibrational frequency of three configurations of $Ge_{22}H_{28}$, green and pink balls represent Ge, H atoms. The dark blue arrows are the eigen-displacement vectors of corresponding atom.

B. Temperature dependence of the energy gap

The energy gap is one of the most important electronic properties of nanocrystals, while the materials are always measured experimentally at specific temperature (e.g. room temperature). We have obtained the gap of $X_{22}H_{28}$ nanocrystals at different temperature (T=100K, 200K and 300K) by averaging the values of the last four thousand MD steps (shown in Fig. 3), where the gap reduction depends on both the shape and the group-IV elements. The gap decrement of $C_{22}H_{28}$ is the smallest at the same temperature, while the one of $Ge_{22}H_{28}$ is the largest among these nanocrystals. For example, the gap reduction of $X_{22}H_{28}(S1)$ at $T= 300K$ is 0.190eV, 0.388eV, 0.592eV for C, Si, and Ge respectively, where there are similar phenomena for the $X_{22}H_{28}(S2)$ and $X_{22}H_{28}(S3)$. Meanwhile, the shape is also important to the gap reduction, where the decrement of $X_{22}H_{28}(S2)$ is smallest among these nanocrystals. For example, the gap reduction at $T= 300K$ is 0.388eV, 0.304eV, 0.509eV for $Si_{22}H_{28}(S1)$, $Si_{22}H_{28}(S2)$, and $Si_{22}H_{28}(S3)$, respectively. However, the difference between the gap reduction of $X_{22}H_{28}(S1)$ and $X_{22}H_{28}(S3)$ are not obvious for C and Ge.

We have also calculated the average variance of all the bond lengths of every MD step for the last 4000 MD steps compared with their corresponding bond lengths at zero temperature. The correlation between the variance of the bond length and temperature is also shown in Fig.3. We find that the variance of the bond length enlarges as the temperature increases, while the gap decreases. There are similar results for the three nanocrystals. Besides, $C_{22}H_{28}$ has the smallest gap reduction and variance of bond length, while $Ge_{22}H_{28}$ has the largest. Thus, the gap reduction might be mainly attributed to the variance of bond length.
C. Temperature effect on the charge distributions

In order to study the temperature effect on the electronic properties, we firstly analyzed the distribution of HOMO and LUMO levels at T= 0 K, as shown in the Fig. 4. The charge of HOMO levels of C$_{22}$H$_{28}$ is mainly distributed in the inner of nanocrystals, while the wavefunction square of the LUMO levels is primarily distributed near the C-H bond on the surface. For Si$_{22}$H$_{28}$ and Ge$_{22}$H$_{28}$, the wavefunction square of both HOMO and LUMO levels is mainly distributed in the inner of nanocrystals.

The variance of atomic attributions to HOMO and LUMO levels is the main reason to the gap change. In order to study the temperature effect on atomic attributions to HOMO and LUMO levels, we calculate the atomic attributions of one hundred structures that were selected in equal intervals of time from the MD simulations at 100K, 200K and 300K respectively, and then we average these values. Atomic attributions to HOMO and LUMO levels are similar for C$_{22}$H$_{28}$, Si$_{22}$H$_{28}$, and Ge$_{22}$H$_{28}$, and we take Si$_{22}$H$_{28}$ as an example since the gap reduction of its three isomers is obviously different at same temperature. The result of Si$_{22}$H$_{28}$ at 100K, 200K, and 300K are shown in Fig. 5. For Si$_{22}$H$_{28}$, there are H atoms and three types Si atoms: Si$_I$ is the one without bonding to H atoms, Si$_{II}$ and Si$_{III}$...
FIG. 4. Charge distribution of HOMO and LUMO levels of three configurations of X$_{22}$H$_{28}$. Charge density isosurfaces (blue and red) represent 50%, 30%, and 35% peak amplitude for C$_{22}$H$_{28}$, Si$_{22}$H$_{28}$, and Ge$_{22}$H$_{28}$, respectively.

are the ones with one and two bonding to H atoms (three types Si atoms of Si$_{22}$H$_{28}$ was shown in the top panels of Fig. 5). The atomic attributions of Si$_{22}$H$_{28}$ to HOMO and LUMO levels were shown in the second, third row panels, respectively. In Fig. 5, there are three columns corresponding to three isomers of Si$_{22}$H$_{28}$.

From Si$_{22}$H$_{28}$ isomers, we can find that the atomic contributions of Si$_{I}$ atoms are most important to both HOMO and LUMO levels, followed by that of Si$_{II}$, Si$_{III}$, and H atoms. For the structure of Si$_{22}$H$_{28}$(S2), the differences of atomic contributions to the HOMO and LUMO levels among the

FIG. 5. Si$_{22}$H$_{28}$ atomic attributions to the HOMO and LUMO levels at 100K, 200K and 300K. (a) Three types Si atoms of three configurations of Si$_{22}$H$_{28}$, and Si$_{I}$, Si$_{II}$, Si$_{III}$, and H atom marked with dark cyan, yellow, light blue, and pink color. (b, c) Atomic attributions of Si$_{I}$, Si$_{II}$, Si$_{III}$, and H atoms to HOMO and LUMO levels, which were labeled with dark cyan half-filled square, yellow half-filled circle, light blue full filled upper triangle, and dark pink full filled lower triangle, respectively.
three types of Si atoms are the smallest, while they are larger for Si$_{22}$H$_{28}$(S1) and Si$_{22}$H$_{28}$(S3). Note that the gap reduction is the smallest in Si$_{22}$H$_{28}$(S2) as the temperature increases, while it is larger for Si$_{22}$H$_{28}$(S1) and Si$_{22}$H$_{28}$(S3). There are similar phenomenon for C$_{22}$H$_{28}$ and Ge$_{22}$H$_{28}$, which would provide an understanding that the gap reduction is smaller in X$_{22}$H$_{28}$(S2) compared to that in X$_{22}$H$_{28}$(S1) and X$_{22}$H$_{28}$(S3).

IV. CONCLUSIONS

In summary, we have investigated the temperature effect on the structural stabilities and electronic properties of X$_{22}$H$_{28}$ by the first-principles calculations by considering vibrational entropy effect. The differences in the free energies among the isomers are larger in the MD simulation as the temperature increases, compared to that under the quasi-harmonic approximation. There is a significant gap reduction for the X$_{22}$H$_{28}$ as the temperature increases, where the decrement of C$_{22}$H$_{28}$’s gap is the smallest and that of Ge$_{22}$H$_{28}$ is the largest. The shape is also important to the gap reduction, since the decrement of one dimension structure (X$_{22}$H$_{28}$-1D) is smallest among these three kinds of isomers. In the one dimension structure, the contribution differences from the inner and surface atoms to the HOMO and LUMO levels among the three types of X atoms are the smallest, while they are larger for the two (X$_{22}$H$_{28}$-2D) and three dimension (X$_{22}$H$_{28}$-3D) structures. Our finding would provide a better understanding of the temperature effect on the properties of small nanocrystals.

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