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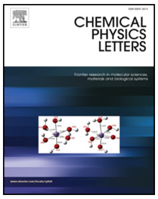

Research paper

Probing the geometric structures and bonding properties in $Nb_2Si_{20}{}^{-/0}$ clusters by density functional theory calculations

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HIGHLIGHTS

- Nb_2Si_{20} neutral adopts C_{2h} symmetric elongated dodecahedron cage structure.
- The Nb–Nb interactions in $Nb_2Si_{20}{}^{-/0}$ are strong.
- $Nb_2Si_{20}{}^{-/0}$ exhibit significant aromaticity.

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ABSTRACT

We present a theoretical investigation on the geometric structures and bonding properties of $Nb_2Si_{20}{}^{-/0}$ clusters using density functional theory calculations. The results showed that $Nb_2Si_{20}{}^{-}$ anion has an irregular Nb_2-doped endohedral structure, whereas Nb_2Si_{20} neutral adopts C_{2h} symmetric elongated dodecahedron cage structure, which is composed of twelve pentagonal faces. Bond length, Wiberg bond order, constant electronic charge density, and molecular orbital analyses suggest that the Nb–Nb interactions in $Nb_2Si_{20}{}^{-/0}$ are strong. Interestingly, $Nb_2Si_{20}{}^{-/0}$ exhibit significant 3D aromaticity.

1. Introduction

Transition-metals (TM) doped silicon clusters not only are useful for silicon-based catalysts, solar cells, and lithium-ion batteries [1,2], but also can be used as building blocks of cluster-assembled nanomaterials [3,4]. Different from single TM atom doped silicon clusters, silicon clusters doped with multiple-TM atoms may adopt very special geometric structures (tubular, pearl-chain style, wheel-like, stacked naphthalene-like, or dodecahedral structures) [5–9], and exhibit special magnetic properties (ferromagnetism or anti-ferromagnetism) [4,10,11].

Niobium doped silicon clusters have attracted great attention from both experimental and theoretical points of view because niobium is widely used in alloy industry and superconducting materials [12–14]. Geometric structures and electronic properties of silicon clusters doped with one or two Nb atoms have been studied previously by several theoretical calculations [15–22]. Diatomic $NbSi^-$ anion was investigated by photoelectron imaging experiments combined with theoretical calculations [23], and $Nb_{1-2}Si_n{}^-$ anions in the size range of n = 2–18 were investigated by anion photoelectron spectroscopy and theoretical calculations [24–26]. $NbSi_n{}^+$ (n = 6–20) and $Nb_2Si_n{}^+$ (n = 13–19) cations were studied by mass spectrometry and H_2O adsorption reactivity experiments [27], while $NbSi_n{}^+$ (n = 4–12) cations were investigated by argon-tagged infrared multi-photon dissociation (IR-MPD) experiments and density functional theory (DFT) calculations [28]. In order to get more detailed information regarding the geometric structures and bonding properties of Nb_2Si_n clusters, in this work, we investigated $Nb_2Si_{20}{}^{-/0}$ clusters with density functional theory calculations.

2. Theoretical methods

Full structural optimizations and frequency analyses of $Nb_2Si_{20}{}^-$ anions and their neutral counterparts were carried out employing density functional theory (DFT) with the Beck's three-parameter and Lee–Yang–Parr's gradient-corrected correlation hybrid functional (B3LYP) [29,30], as implemented in the Gaussian 09 program package [31]. The exchange–correlation potential and effective core pseudopotential LanL2DZ basis set [32] was used for the Nb atoms and the Pople's all-electron 6-311 + G(d) basis set [33] was used for the Si atoms. No symmetry constraint was imposed during the geometry optimizations for both anionic and neutral clusters. For anionic and

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neutral Nb_2Si_{20} clusters, numerous initial structures reported in the literature [7,34] were taken into accounts at all possible spin states. Additionally, the swarm-intelligence-based CALYPSO structure prediction software [35] was used to search the global minima for both anionic and neutral Nb_2Si_{20} clusters. The success of CALYPSO is due to the integration of several major techniques including structural evolution through PSO algorithm, symmetry constraint during structure generation, the Metropolis criterion, atom-centered symmetrical function, and bond characterization matrix (BCM), which can enhance the capability of CALYPSO in dealing with more complex systems and also reduce searching space, enhance the structural diversity, and eliminate similar structures on the potential energy surfaces to enhance searching efficiency. Here, structure predictions of anionic and neutral Nb_2Si_{20} are carried out. Cluster structures are ordered by generations in the particle swarm optimization method, in which each generation includes 50 structures, 60% of which are generated by the particle swarm optimization algorithm, while the others are generated randomly. Subsequently, we have picked out 30 generations to achieve convergence around the lowest minima of the potential energy surface. The searches can obtain a large database for low energy anionic and neutral Nb_2Si_{20} clusters. These low-energy structures within 1 eV of the global minimum structure were reoptimized with subsequent frequency calculations. Harmonic vibrational frequency analyses were performed to verify that the optimized structures are the true minima on the potential energy surfaces. To further evaluate the relative energies of the low-lying isomers, the single-point energies of $Nb_2Si_{20}^{-/0}$ clusters were also calculated by using the more accurate coupled-cluster methods including single, double, and perturbative contributions of connected triple excitations (CCSD(T)) [36,37] based on the geometries optimized at the B3LYP level of theory, in which the augmented correlation-consistent polarized valence double-zeta basis set (aug-cc-pVDZ) [38] and energy-consistent relativistic pseudopotentials and correlation consistent basis set (aug-cc-pVDZ-PP) [39] were used for the Si and Nb atoms, respectively. Zero-point energy (ZPE) corrections obtained from the B3LYP functional were included in all the calculated energies. The theoretical vertical detachment energies (VDEs) were calculated as the energy differences between the neutrals and anions both at the geometries of anionic species, whereas the theoretical adiabatic detachment energies (ADEs) were calculated as the energy differences between the neutrals and anions with the neutrals relaxed to the nearest local minima using the geometries of the corresponding anions as initial structures.

3. Theoretical results

The typical low-lying isomers of $Nb_2Si_{20}^-$ anion are presented in Fig. 1. The relative energies (ΔE) of low-lying isomers, the Nb–Nb bond lengths, and their theoretical VDEs and ADEs are also summarized in Fig. 1. In addition, the photoelectron spectrum of lowest-lying isomer is simulated based on the generalized Koopmans' theorem (GKT) [40,41] and is displayed in Fig. 2. In the DOS spectra, each transition is treated equally in the simulations. The typical low-lying isomers of Nb_2Si_{20} neutral are presented in Fig. 3, along with the relative energies (ΔE) of low-lying isomers and the Nb–Nb bond lengths.

3.1. $Nb_2Si_{20}^-$

As shown in Fig. 1, the global minimum of $Nb_2Si_{20}^-$, isomer 20A, is an irregular Nb_2-doped endohedral structure with a Nb–Nb elongated bond length of 2.75 Å. The calculated VDE and ADE of isomer 20A are 3.68 and 3.58 eV, respectively. As shown in Fig. 2, the simulated photoelectron spectrum of isomer 20A has a relatively weak peak at 3.68 eV and a high-intensity broad peak centered at 4.12 eV. The peaks at higher electron binding energies (EBE) region are more congested than those at lower EBE region, which may because the electron detachments of $Nb_2Si_{20}^-$ are easier and electronic transitions are more intensive at higher EBE region according to Frank-Condon overlapping. The other isomers of $Nb_2Si_{20}^-$, isomers 20B and 20C, are higher in energy than isomer 20A by 0.11 and 0.85 eV at the B3LYP level, respectively, and by 0.19 and 0.96 eV at the CCSD(T) level, respectively. Isomer 20B is a C_i symmetric elongated dodecahedron cage structure with a Nb_2 unit encapsulated inside the silicon cage and a bonding Nb–Nb distance of 2.50 Å, similar to the global minima of V_2Si_{20} [7] and W_2Si_{20} [42]. Isomer 20C is also an irregular Nb_2-doped endohedral structure with a Nb–Nb elongated bond length of 2.79 Å.

3.2. Nb_2Si_{20}

As shown in Fig. 3, the global minimum of Nb_2Si_{20} neutral (20A′) is a C_{2h} symmetric elongated dodecahedron cage structure with an Nb_2 unit encapsulated inside the silicon cage and a bonding Nb–Nb distance of 2.40 Å, similar to the second isomer of $Nb_2Si_{20}^-$. The Si_{20} cage is composed of twelve pentagonal faces. Isomers 20B′ and 20C′ are higher in energy than isomer 20A′ by 0.06 and 0.43 eV at the B3LYP level, respectively, and by 0.13 and 0.55 eV at the CCSD(T) level, respectively. Isomer 20B′ is a C_2 symmetric irregular Nb_2-doped endohedral structure with a Nb–Nb elongated bond length of 2.67 Å, which is similar with the lowest-lying isomer (20A) of $Nb_2Si_{20}^-$. Isomer 20C′ is a C_2 symmetric double hexagonal prisms stacked structure with an Nb_2 unit encapsulated inside the silicon cage and an elongated bonding Nb–Nb distance of 3.28 Å.

4. Discussion

The Nb–Nb bond lengths in $Nb_2Si_{20}^-$ anion and Nb_2Si_{20} neutral are 2.75 and 2.40 Å, respectively, indicating that the interactions between the two Nb atoms in Nb_2Si_{20} neutral are much stronger than those in $Nb_2Si_{20}^-$ anion, which can be confirmed by the calculated Wiberg bond orders. The calculations show that the Wiberg bond orders of the Nb–Nb bonds in $Nb_2Si_{20}^-$ anion and Nb_2Si_{20} neutral are 0.92 and 1.45, respectively. The high Nb–Nb bond orders suggest that the interactions between the two Nb atoms in $Nb_2Si_{20}^{-/0}$ are strong, consistent with the short Nb–Nb bond lengths in $Nb_2Si_{20}^{-/0}$. The strong interactions between the two Nb atoms are also revealed in the previous works of $Nb_2Si_{2-12}^{-/0}$ investigated by anion photoelectron spectroscopy and *ab initio* calculations [26].

It would be interesting to compare the geometric structures of $Nb_2Si_{20}^{-/0}$ clusters with those of $V_2Si_{20}^{-/0}$ clusters. The structures of $V_2Si_{20}^{-/0}$ have been reported by Xu et al. [7]. As for anionic clusters, the global minimum of $Nb_2Si_{20}^-$ is an irregular Nb_2-doped endohedral structure, while that of $V_2Si_{20}^-$ is an elongated dodecahedron cage structure with a V_2 unit encapsulated inside the silicon cage, which is similar with the second stable structure of $Nb_2Si_{20}^-$. For neutral clusters, the most lowest-lying isomers of Nb_2Si_{20} and V_2Si_{20} neutrals are both a elongated dodecahedron Si_{20} cage structure with an Nb_2 or V_2 unit encapsulated inside the silicon cage and with a strong metal-metal bond, but Nb_2Si_{20} neutral (C_{2h}) has a slightly higher symmetry than V_2Si_{20} neutral (C_1). In addition, the Si–Si distances of Nb_2Si_{20} dodecahedron cage structure are in the range of 2.31–2.49 Å, slightly longer than those (2.26–2.41 Å) of V_2Si_{20} neutral, most likely due to the atomic radius of Nb atom is larger than that of V atom, which is also revealed in the previous investigations of $NbSi_{3-12}^-$ and $Nb_2Si_{2-12}^-$ clusters, in which the structures of $Nb_{1-2}Si_n^-$ clusters are compared with those of $V_{1-2}Si_n^-$ clusters in detail [25,26]. These suggest that the structural evolution of vanadium and niobium doped silicon clusters is not always similar, even though they are in the same group.

To give insight into the effective atomic charge distributions of $Nb_2Si_{20}^{-/0}$, we carried out the natural population analysis (NPA) on the most stable isomers. The results show that the NPA charges on the two Nb atoms of $Nb_2Si_{20}^-$ anion and Nb_2Si_{20} neutral are −6.0 and −5.2 *e*, respectively, suggesting that the charges of Si_{20} frameworks are transferred to the two Nb atoms. That is more likely due to the existence of

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