



Probing the structural and electronic properties of lanthanide-metal-doped silicon clusters: $M@Si_6$ ($M = Pr, Gd, Ho$)

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ABSTRACT

Density functional calculations are performed to investigate the electronic and structural properties of $M@Si_6$ ($M = Pr, Gd, Ho$). Generalized Koopmans' theorem is applied to predict the vertical detachment energies and simulate the photoelectron spectra (PES). Subsequently, a detailed comparison between previously published experimental PES spectra and the present theoretical simulations helps to identify the ground state structures. The most stable $M@Si_6^-$ ($M = Pr, Gd, Ho$) is a three-dimensional structure with the lanthanide-metal atom sitting on top (or bottom) of the regular pentagonal bipyramid. Instead, the neutral species show the impurity as a four-coordinate atom in the equatorial plane of pentagonal bipyramid. Moreover, the nucleus independent chemical shift (NICS) is discussed at various points at and over or under the center of the Si_5 ring plane, and the negative NICS values support the aromatic character of the $M@Si_6^-$ ($M = Pr, Gd, Ho$) clusters.

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1. Introduction

Since silicon is a semiconductor element of great importance in the microelectronics industry, it attracts great attention as building blocks for silicon-based nanomaterials. The continued miniaturization of electronic devices is pushing towards the nano- and molecular scales. Hence, it is important to understand the physical and chemical properties of silicon clusters with a few to hundred of atoms. Indeed, silicon clusters have been the subject of extensive experimental and theoretical studies in the past two decades [1–11]. It was observed that these clusters tend to form compact, diamond-like structures rather than the fullerene-like cages that are characteristic of their congener, carbon [12]. These results are ascribed to the fact that silicon atoms much prefer sp^3 hybridization to sp^2 . In contrast, carbon atoms can appear with sp , sp^2 , or sp^3 hybridization in compounds. The dangling bond makes Si clusters unstable, especially when they aggregate themselves, it is very important to quench that bond to make cluster-assembled materials [13–22]. One of the strategies for doing so is the doping of a suitable metal atom into a pure Si cluster; a highly stabilized cluster will open up a new avenue to cluster-assembled materials made from Si atoms. With metal atom doping, closed-shell electronic structures might lead to species that are remarkably stable, such as a new class of clusters with tran-

sition metal encapsulated by silicon. As we know, the first hints that silicon cages may be stabilized by the introduction of a doping atom emerged from the early, pioneering experimental work of Beck who observed enhanced ion intensities of metal–silicon clusters, MSi_n^+ ($M = Mo, Cr, and W$), around $n = 16$ when a transition metal atom was added to the cluster [17]. Since then, many stable MSi_n (at $n = 12, 14, and 16, etc.$) species have been reported in which various factors accounting for their formation have been examined experimentally [13–17] and theoretically [18–22]. For example, Nakajima and co-workers [13] reported the selective formation of highly stable MSi_{16} ($M = Sc, Ti, V$) clusters by fine tuning the laser vaporization source conditions, similar to the initial finding of C_{60} . A “magic” cluster in which metal is encapsulated in a Si cage can be viewed as a super-atom, and it is therefore of much interest to verify this “super-atom” behavior in metal atom-encapsulated silicon clusters experimentally. The existence of super-atoms suggests that, it should be possible to develop silicon-based devices for various optoelectronic applications, with proper assembly [18].

Up to now, only a few reports exist on lanthanide-metal-doped silicon clusters. However, interest in their potential applications spurred considerable activity over the past couple of years. Experimentally, the validity of the concept can be proved by using photoelectron spectroscopy (PES), which is shown to be a powerful experimental technique for probing electronic structures of size-selected clusters [23–26]. Especially, Bowen and co-workers have recently published the results of experimental photoelectron spectroscopic studies of lanthanide–silicon cluster anions $LnSi_n^-$ ($3 \leq n \leq 13$; $Ln = Ho, Gd, Pr, Sm, Eu, Yb$) [27] and $EuSi_n^-$ ($3 \leq n \leq 17$)

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[28]. In addition, Nakajima and co-workers have previously reported experimental photoelectron spectra and water reactivity of TbSi_n^- ($6 \leq n \leq 16$) [29]. Here, we report the generation of a series of lanthanide-metal-doped silicon cluster anions M@Si_6^- ($\text{M} = \text{Pr, Gd, Ho}$) using relativistic density functional theory (DFT) calculations with the aid of anion photoelectron spectroscopy (PES) [27] to derive the electronic properties and the geometric structures. Subsequently, a theory interpretation for already published experimental work by Bowen [27,28] and Nakajima [29] groups is also provided. It is found that all the most stable isomers have regular decahedral structures and resemble each other. We hope that our work would be useful to understand the influence of material structure on its properties and could offer relevant information for further experimental and theoretical studies. This Letter is organized as follows: Section 2 gives a brief description of the theoretical methods and computational details; then comparison of computed spectra with the experimental PES results are given in Section 3; the results and discussion are given in Sections 4 and 5, respectively; finally, the conclusions are summarized in Section 6.

2. Computational methods

Theoretical calculations of lanthanide-metal-doped silicon clusters M@Si_6^- ($\text{M} = \text{Pr, Gd, Ho}$) were determined using analytical gradients with the Stuttgart relativistic small effective core potentials (ECP) and the valence basis sets [30–32] that includes the 4f electrons in the core for M ($\text{M} = \text{Pr, Gd, Ho}$) and the 6-311+G(d) basis [33,34] for Si coupled with DFT geometric optimization. Generalized gradient approximation in the Perdew–Burke–Ernzerhof [35] (GGA-PBE) exchange-correlation functional form was chosen, implemented in the Gaussian03 package [36]. Scalar relativistic effects, or rather, the mass velocity and Darwin effects, were taken into account via the quasi-relativistic pseudopotentials. To search for low-lying structures of M@Si_6^- , the equilibrium geometries of bare host Si_6^- (Si_7^-) clusters were optimized first based on the previous calculation results. For the low-lying isomers of M@Si_6^- ($\text{M} = \text{Pr, Gd, Ho}$), we searched them extensively by two ways: (1) by considering the possible structures reported in the previous papers and (2) by placing an M atom at various adsorption or substitutional sites on the basis of optimized Si_6^- (Si_7^-) geometries, i.e., M-capped, M-substituted, and M-concaved patterns, as well as Si-capped pattern. For the low-lying isomers of neutral species, we also searched them extensively by the same method used for the anion cluster. Spin-restricted DFT calculations were employed for the singlet states, while spin-unrestricted DFT calculations were employed for all other electronic states. Alternative optimized structures are shown in Figs. 1–3. A selected set of anionic optimized structures were tested with several exchange-correlation functionals for accuracy and consistency. The calculated results using the PBE, BPW91 [37,38] and B3LYP [39–41] functionals are presented in Table 1. Vibrational frequency calculations were performed at the same level of theory to verify the nature of the stationary points. The vibrational frequency is provided in supplementary material to ensure the local minimum structure. Moreover, reliability of the present computational method was validated by performing calculations on the first vertical detachment energies (VDEs) and the adiabatic detachment energies (ADEs), for which experimental results are available (Table 2). The configuration are regarded as optimized when the maximum force, the root-mean-square (RMS) force, the maximum displacement of atoms, and the RMS displacement of atoms have magnitudes less than 0.00045, 0.0003, 0.0018, and 0.0012 a.u., respectively.

Vertical electron detachment energies (VDEs) were calculated using the generalized Koopmans' theorem by adding a correction term to the eigenvalues of the anion [42]. The correction term

Table 1

Relative energies in eV for selected low-lying isomers of M@Si_6^- ($\text{M} = \text{Pr, Gd, Ho}$) with different density functional methods.

Isomer	Sym	PBE- ΔE	B3LYP- ΔE	BPW91- ΔE
PrSi_6^-	(a) C_{5v}	0.000	0.000	0.000
	(b) C_s	0.276	0.225	0.264
	(c) C_s	0.332	0.274	0.309
	(d) C_2	0.490	0.430	0.445
	(e) C_s	0.701	0.618	0.718
	(f) C_s	0.761	0.627	0.713
	(g) C_s	0.846	0.905	0.804
	(h) C_s	1.128	0.888	1.129
GdSi_6^-	(a) C_{5v}	0.000	0.000	0.000
	(b) C_s	0.407	0.342	0.395
	(c) C_s	0.489	0.425	0.466
	(d) C_2	0.665	0.597	0.622
	(e) C_{2v}	0.583	0.490	0.593
	(f) C_{3v}	0.800	0.698	0.793
	(g) C_s	0.992	0.908	0.957
	(h) C_s	1.079	0.796	1.069
HoSi_6^-	(a) C_{5v}	0.000	0.000	0.000
	(b) C_s	0.438	0.371	0.428
	(c) C_s	0.561	0.493	0.538
	(d) C_2	0.724	0.656	0.683
	(e) C_{2v}	0.425	0.325	0.433
	(f) C_s	0.765	0.646	0.758
	(g) C_s	1.047	0.865	1.013
	(h) C_s	0.936	0.642	0.923

Table 2

Experimental adiabatic (ADE) and vertical (VDE) detachment energies of M@Si_6^- ($\text{M} = \text{Ho, Gd, Pr}$) compared to those calculated for the lowest energy isomers. All energies are in eV.

Isomer	Experimental [27]		Theoretical	
	ADE	VDE	ADE	VDE
PrSi_6^-	2.1 ± 0.1	3.05 ± 0.05	2.08	2.92
GdSi_6^-	2.1 ± 0.1	3.08 ± 0.05	2.19	3.03
HoSi_6^-	2.0 ± 0.2	3.11 ± 0.05	2.20	3.05

was calculated as $\delta E = E_1 - E_2 - \varepsilon_{\text{HOMO}}$, where E_1 and E_2 are the total energies of the anion and neutral, respectively, in their ground states at the anion equilibrium geometry and $\varepsilon_{\text{HOMO}}$ corresponds to the eigenvalue of the highest occupied molecular orbital (HOMO) of the anion. Each VDE was fitted with a full width at half-maximum (FWHM) of 0.3 eV to yield the simulated PES spectra. The methods have been used successfully in a number of previous studies and have been shown to yield VDEs in good agreement with PES data [23–26].

3. Comparison of computed spectra with the experimental PES results

We used three criteria in comparing the theoretical results with the experimental data to select our most likely candidate structures: (1) the relative energies, (2) the first vertical detachment energies (VDEs) and the adiabatic detachment energies (ADEs) (which also represent the electron affinities (EAs) of the corresponding neutral clusters), and (3) the number of distinct peaks of simulated photoelectron spectra in the low-binding-energy range of ≤ 3.49 eV and their relative positions. The first criterion addresses typical errors in DFT calculations, which is about more than ten of an electronvolt in relative energies for M@Si_6^- clusters. The calculated relative energies (within 1.0 eV) were tested with several exchange-correlation functionals (PBE, BPW91 and B3LYP) for accuracy and consistency. These results underline that the geometries of all the clusters obtained within three functionals are essentially identical. The calculated results using different

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