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Ab initio Study of Neutral and Charged $Si_nNa_p^{(+)}$ ($n \leq 6$, $p \leq 2$) Clusters

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Ab initio calculations in the framework of the density functional theory, with B3LYP functional, are performed to study the lowest-energy isomers of silicon sodium clusters $Si_nNa_p^{(+)}$ ($n \leq 6$, $p \leq 2$). The stability and the structural and electronic properties of neutral and positively charged systems are examined. The structure of Si_nNa_p keeps the frame of the corresponding Si_n cluster unchanged, and the electronic structure of Si_nNa_p is similar to that of the corresponding negative system Si_n^{p-}. Adsorption energies, vertical and adiabatic ionization potentials, electric dipole moments, and static dipolar polarizabilities are calculated for each considered isomer.

1. Introduction

Semiconductor clusters, especially silicon, have been intensively studied both experimentally and theoretically because of their intrinsic interest from the point of view of chemical structure and bonding as well as for their importance in the microelectronics industry.[1−7]

Binary clusters containing silicon atoms have been substantially studied. For example, the experimental investigation by mass spectrometry of small mixed transition metal−silicon clusters (Si_nM, M = Cr, Mo, W, $n < 19$) had been reported.[8] More recently, Kaya and co-workers[9] have studied geometric and electronic structures of Si_nM, M = Ti, Hf, Mo, and W, using photoelectron spectroscopy. On the theoretical point of view, the Si_nM_p clusters have been usually investigated in the framework of the density functional theory (DFT). This latter allows calculation of some properties, particularly the geometrical structures of large systems, for a reasonable computational effort. Very recently, Binning and Bacelo[10] have investigated structures and energetics of Si_nBe_n and Si_nBe_{2n} ($n = 1−4$) clusters, while Zhang and co-workers[11] have published an investigation of Si_nAg ($n = 1−5$) clusters. Majunder and Kulshreshtha[12] have investigated impurity-doped Si_{10} clusters showing that the location of the impurity atom on the host cluster depends on the atomic size and the nature of interaction between the host cluster and the impurity atoms. The principal question in studying metal-doped silicon clusters is the comprehension of the modifications of the properties compared to the case of bare silicon clusters.

Alkali metals adsorbed on semiconductor surfaces have been extensively studied[13−17] because they work as a promoter in catalysts. Dissociation adsorption of molecules such as O_2, N_2, CO, or NO at semiconductor surfaces may be promoted by alkali-metal adsorbates. Namiki and co-workers[15] have shown that the role of the latter is local in nature in the case of dissociative adsorption of NO on the silicon surface. Moreover, both the most favorable site of the adsorbed metal and the nature of chemical bonds between the alkali atoms and the dangling bonds of the surface Si atoms have been already studied, but different approaches have led to controversial results.[18,19] The study of alkali−silicon clusters could furnish a better understanding in the interaction between silicon and alkali atoms and could help to find the best sites of adsorption. The ionization potentials of sodium-doped silicon clusters Si_nNa_p, $3 \leq n \leq 11$, $1 \leq p \leq 4$, have been experimentally determined from the threshold energies of their ionization efficiency curves.[20] On the theoretical aspect, the structural and electronic properties of Si_nNa ($n \leq 10$) have been studied through calculations based on the Moller Plesset (MP2) method[20] or in the framework of DFT.[21] It has been found that the ionization potential for Si_nNa clusters presents local minima with $n = 4$, 7, and 10, correlating with the measured low values[22] of the electron affinity of bare silicon clusters Si_n. The ab initio calculations indicate that, on doping with a Na atom, the electron charge migrates from the sodium atom to the silicon cluster without disturbing seriously the original framework of the silicon cluster.

In the present work, we present a DFT study of the lowest-energy isomers of silicon sodium Si_nNa_p. Both neutral and singly ionized clusters are investigated. We have considered sizes up to $n = 6$ and $p = 2$. To our knowledge, present work is the first theoretical investigation of Si_nNa_2 clusters and of singly charged $Si_nNa_p^+$. Details of the calculations are introduced in section 2. In section 3, we present and discuss the calculated properties of the clusters including structures, absorption energies, adiabatic and vertical ionization potentials, electric dipole moment, and static dipolar polarizability.

2. Computational Details

Calculations were achieved in the linear combination of atomic orbitals scheme using a 6-31+G(d) Gaussian basis. This latter was (17s11p1d) contracted into [*5s4p1d*] on silicon atoms and (17s11p1d) contracted into [5*s*4*p*1*d*] on sodium atom. The electronic calculations performed in the framework of the density functional theory used the hybrid B3LYP functional which involves Becke's three-parameter exchange functional.[23] Calculations have been carried out by use of the computational chemistry program Gaussian98[24] and the graphical user interface Gabedit.[25]

For each size, a number of structures were tested. We have tried to start the geometry optimization of Si_nNa_p clusters with the frame of the corresponding Si_n cluster on which sodium

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atoms were located on Si atoms or bridged over two atoms or capped on several atoms. We have also tested structures for which the frame of the corresponding Si_n cluster used as initial geometry was deformed. All optimizations were carried on without symmetry constraints (C_1 symmetry group). The stability of Si_nNa_p was examined by evaluating the harmonic frequencies. For each of these clusters, all the computed frequencies were confirmed to be real. Therefore, the geometric structures of these clusters were indeed at the local minimum on the potential-energy surface. The calculated harmonic vibrational frequencies will be distributed on request through electronic mail.[26] In the discussion we only report the lowest energy isomers determined in our optimizations. For each stable structure, the charge on Na atoms have been estimated through a natural population analysis (NPA).[27] Furthermore, the dipole moment μ as well the averaged static dipolar polarizability $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ have been calculated.

3. Results and Discussions

A. Lowest-Energy Structures and Isomers.

To check the accuracy of our DFT/B3LYP calculations, we first consider the diatomics SiNa and $SiNa^+$. The ground state for SiNa is found to be a $^4\Sigma^-$, a $^2\Pi$ excited state that is located 0.25 eV above. The bond lengths are found to be 2.724 and 2.875 Å for $^4\Sigma^-$ and $^2\Pi$, respectively, in good agreement with previous calculated values of 2.70 and 2.90 Å (CI values[20]) and 2.697 and 2.858 Å (QCISD values[28]). The dissociation energy for the ground state is found to be 1.19 eV, in agreement with the CI value of 1.45 eV from Kaya and co-workers.[20] The ground state for the ion $SiNa^+$ is found to be a triplet ($^3\Pi$ state) with a bond length of 3.159 Å and a binding energy of 0.533 eV. A singlet state is found to lie 0.453 eV above the triplet. The adiabatic ionization potential of SiNa is found to be 6.06 eV in good agreement with the experimental value, which shows a value between 5.97 and 6.42 eV.[29]

The optimized geometries of the Si_nNa clusters, together with the energies of isomers relative to the lowest-energy one as well as the spin multiplicities, are shown in Figure 1. The ground state of all the Si_nNa ($n > 1$) clusters examined is a doublet. Our results concerning the structure and the electronic properties of the lowest isomer are similar to those of Kaya and co-workers[20] with MP2 calculations confirming the reliability of our DFT/B3LYP calculations. The structure of the most stable isomer keeps the frame of the corresponding Si_n unchanged. This means that the Si−Si bond predominates on the Si−Na one. The adsorbing site of a Na atom is a bridge-site type in which the Na atom is bridged over two Si atoms for $n = 2$, 3, and 5 or a bridge-site type in which the Na atom is capped over four Si atoms for $n = 4$ and 6. For Si_4Na, the lowest-energy structure 4a is only slightly more stable than 4b by 0.04 eV. For all the Si_nNa clusters, the valence electron of the Na atom is transferred to the LUMO (lowest-unoccupied molecular orbital) of Si_n and the electronic structure of Si_nNa clusters corresponds to that of $Si_n^- + Na^+$. As a matter of fact, the NPA[27] indicates a charge q_{NPA} of about +0.8 on the Na atom (Table 1).

The geometries of the Si_nNa_2 clusters, together with the relative energies of isomers and the spin multiplicities, are shown in Figure 2. The ground state is found to be a singlet for $n = 2-6$, while it is found to be a triplet for $SiNa_2$. The geometrical structure of the most stable isomers is similar to that of Si_nNa in which a second Na atom is located on a site far from the first Na atom. The adsorbing site of the second Na atom is a bridge-site type in which the Na atom is bridged over two Si atoms for $n = 2$, 3, and 6 or a bridge-site type in which the Na atom is capped over three Si atoms for $n = 4$ and 5. For Si_4Na_2, the structure 4a is slightly more stable than 4b by 0.033 eV. In these two structures, the Na atoms are located on both sides of the rhombus Si_4. For Si_5Na_2, the isomer 5a is below isomer 5b by 0.027 eV. For Si_6Na_2, the two first isomers (6a and 6b), which present a similar structure, are degenerated within 0.001 eV. For all the Si_nNa_2 clusters, the 3s electrons of the two Na atoms are transferred to the LUMO of Si_n and the electronic structure of Si_nNa_2 clusters correspond approximatively to that of $Si_n^{2-} + 2Na^+$. As a matter of fact, the NPA indicates a charge q_{NPA} within the 0.7−0.9 range on each Na atom (Table 1).

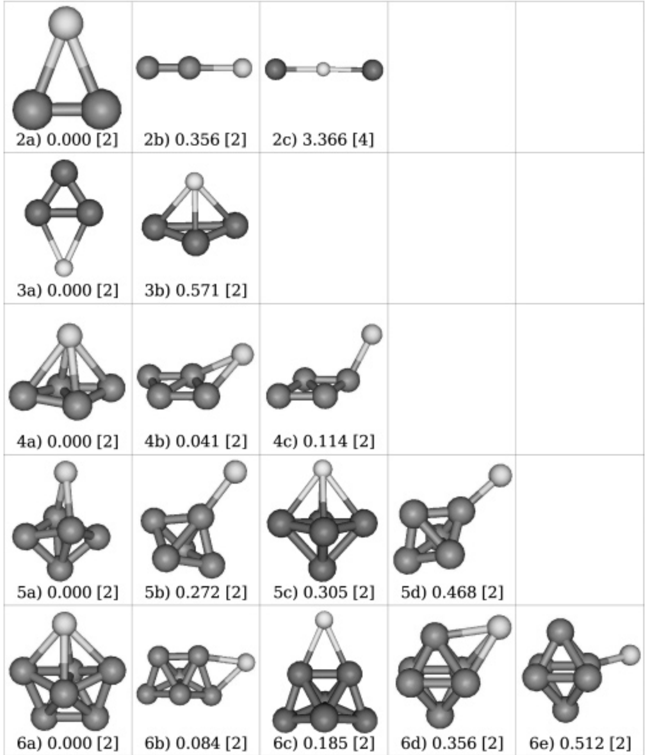

Figure 1. Optimal geometries of neutral Si_nNa clusters. Relative energies are given in eV. The spin multiplicity is indicated in square brackets.

We now discuss the singly charged Si_nNa^+ clusters for which relative energies and spin multiplicities are displayed in Figure 3. The ground state is found to be a singlet except for Si_2Na^+ for which the most stable isomer is found to be a triplet. The electronic structure of Si_nNa^+ can be described as $Si_n + Na^+$. The localization of the sodium ion is not the same one as that of the neutral atom in Si_nNa. The Na^+ ion is generally located on a Si atom, except for $n = 5$ for which it is capped over three Si atoms. The structures in which the Na atom bridges over two Si atoms are found to be not stable except for isomer b of Si_2Na^+ and of Si_6Na^+. The isomer 2a of Si_2Na^+ has a linear structure similar to that of $Si_2 + Na^+$, the Na^+ ion being at 2.94 Å from the nearby Si atom. Si_3Na^+ is of C_s symmetry and is made of an irregular triangle Si_3 and of Na^+ tail on a Si atom (at 2.93 Å). The C_{2v} symmetric structure with an isosceles triangle Si_3 is found to have two imaginary frequencies and so is not a true minimum. Si_4Na^+ presents a C_{2v} symmetry with a Na^+ tail on a Si at 2.89 Å. Si_5Na^+ is of C_s symmetry; its structure is distorted from the one of the corresponding Si_5. Finally, Si_6Na^+ keeps the frame of the corresponding Si_6 unchanged with the Na^+ located on a Si atom, while in the case of the neutral Si_6Na the Na atom was capped over four Si atoms.

TABLE 1: Calculated Relative Energies, Sodium Binding Energies (E_b), Dipole Moments (μ), Static Dipole Polarizabilities (α), and Charges on Sodium Atoms from Natural Population Analysis (q_{NPA})

cluster		energy (eV)	E_b (eV)	μ (Debye)	α (Å^3)	q_{NPA}
SiNa		0.000	1.194	7.036	14.930	0.425
Si_2Na	2a	0.000	2.099	6.762	20.237	0.760
	2b	0.356		9.712	20.015	
	2c	3.366		2.475	38.700	
Si_3Na	3a	0.000	1.780	7.964	20.837	0.842
	3b	0.571		6.340	22.601	
Si_4Na	4a	0.000	1.274	6.617	24.533	0.823
	4b	0.041		8.983	28.419	
	4c	0.114		10.189	31.485	
Si_5Na	5a	0.000	1.741	7.361	28.632	0.850
	5b	0.305		7.026	28.419	
	5c	0.272		11.131	31.485	
	5d	0.468		12.288	33.217	
Si_6Na	6a	0.000	1.399	7.154	31.179	0.895
	6b	0.084		9.596	34.046	
	6c	0.185		9.797	33.422	
	6d	0.356		8.624	31.980	
	6e	0.512		10.523	39.664	
$SiNa_2$	1a	0.000	2.410	0.000	36.197	0.737; 0.737
	1b	0.101		5.083	34.419	
	1c	2.152		7.867	41.028	
Si_2Na_2	2a	0.000	3.973	7.143	26.538	0.703; 0.703
	2b	0.356		8.533	31.211	
Si_3Na_2	3a	0.000	3.633	6.808	30.695	0.815; 0.815
	3b	0.441		2.540	36.558	
	3c	0.718		9.464	44.602	
	3d	1.176		3.977	28.606	
	3e	1.439		7.776	60.090	
	3f	1.459		4.723	71.346	
Si_4Na_2	4a	0.000	2.454	0.000	39.407	0.692; 0.692
	4b	0.033		4.952	38.868	
	4c	0.163		9.917	44.791	
	4d	0.321		5.419	0.000	
Si_5Na_2	5a	0.000	3.660	6.090	33.863	0.857; 0.857
	5b	0.027		8.285	33.893	
	5c	0.962		5.509	36.513	
Si_6Na_2	6a	0.000	2.784	2.221	37.589	0.890; 0.892
	6b	0.001		8.915	40.11	
	6c	0.055		4.798	36.932	
	6d	0.306		0.137	38.416	
	6e	0.359		0.000	42.538	
	6f	0.480		12.177	38.535	

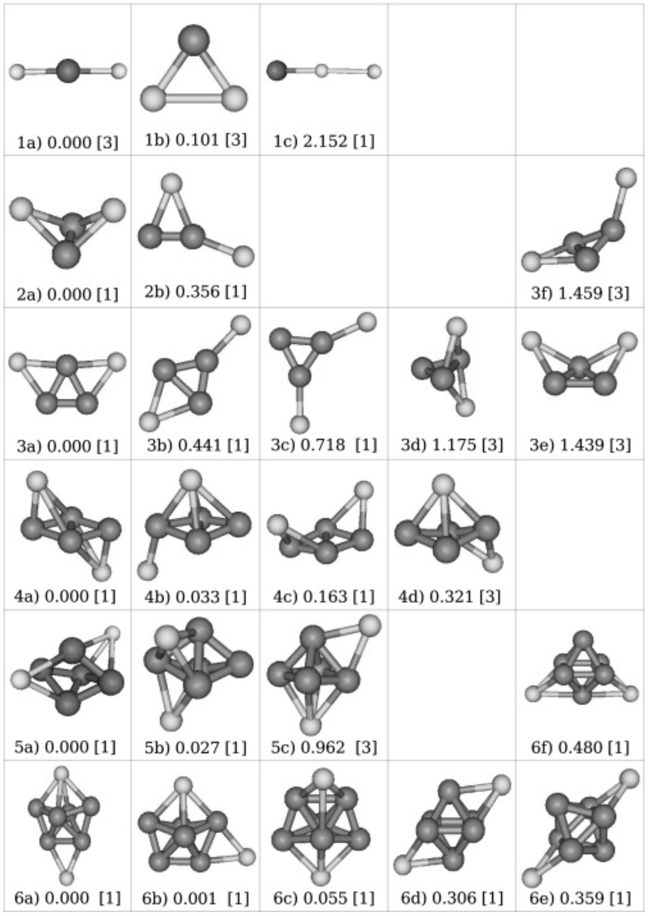

Figure 2. Optimal geometries of neutral Si_nNa_2 clusters. Relative energies are given in eV. The spin multiplicity is indicated in square brackets.

The geometries of the $Si_nNa_2^+$ clusters, together with the relative energies of isomers and spin multiplicities, are shown in Figure 4. The ground states of all the examined $Si_nNa_2^+$ clusters examined are doublets. The electronic structure is similar to that of $Si_n^- + 2Na^+$. The frame of Si_n is approximatively similar for both $Si_nNa_2^+$ and Si_nNa_2 clusters, except for $n = 6$. However, for $Si_nNa_2^+$ clusters, Na atoms are generally located on Si atoms, except for $n = 2$ and 5, while for Si_nNa_2 clusters, they are generally bridged over two or four Si atoms. For both $Si_nNa_2^+$ and Si_nNa_2 clusters, the second Na atom is located on a site far from the first Na atom. For $Si_3Na_2^+$, $Si_5Na_2^+$, and $Si_6Na_2^+$, isomers a and b are found to be quasidegenerated (within about 0.02 eV).

B. Sodium Binding Energies.

The binding energy of Na to Si_n cluster calculated as $E_b = -[E(Si_nNa_p) - E(Si_n) - pE(Na)]$ is listed in Table 1 for the most stable isomer. In all cases, Na atoms are stably adsorbed on the Si_n cluster. The evolution of E_b against the number of silicon atoms is shown in Figure 5. For Si_nNa clusters, our values are in correct agreement with the previous values by Kaya and co-workers[20] using MP2-type calculations and with values calculated by Landman and co-workers[21] with a local-spin-density functional method. E_b oscillates as a function of n, showing a local minimum for $n = 4$ and local maxima for $n = 2$ and 5. One can notice the parallelism between E_b and the electron affinity of Si_n (see Figure 5). This is due to the fact that the binding of a Na atom to Si_n cluster leads to a electronic charge transfer from Na to Si_n. The binding energy of two Na atoms is approximatively equal to twice the binding energy of one Na atom.

C. Ionization Potentials.

We now discuss the ionization potentials. We provide both the vertical (when the ion is at the geometry of the neutral) and the adiabatic (including the relaxation of the ion geometry) ionization potentials, hereafter labeled IP_v and IP_a, respectively, for the Si_nNa and Si_nNa_2 clusters (see Table 2 and Figures 6 and 7).

Table 2 displays the ionization potential calculated in the present study, together with previous calculations[20,21] available only for Si_nNa and experimental values.[20] For Si_nNa clusters, Kaya and co-workers[20] have calculated the IP_v with MP2-type calculations, while Landman and co-workers[21] have investigated both IP_v and IP_a using a post local-spin-density (PLSD) method. Our values for IP_v overestimate those obtained by Kaya et al. from 3 to 10%. Our IP_a values underestimate those obtained by Landman from 3 to 8%. The IP for the sodium-doped cluster are significantly lower (1−2 eV) than those for the parent Si_n cluster.[30] The decrease reflects the change in the orbital being ionized, which in Si_nNa is of similar character as the lowest-unoccupied molecular orbital (LUMO) of the parent Si_n. The evolution of the present calculated IPs against the number of silicon atoms are shown in Figure 6 for Si_nNa. The experimental data are represented with vertical dotted arrows to take into

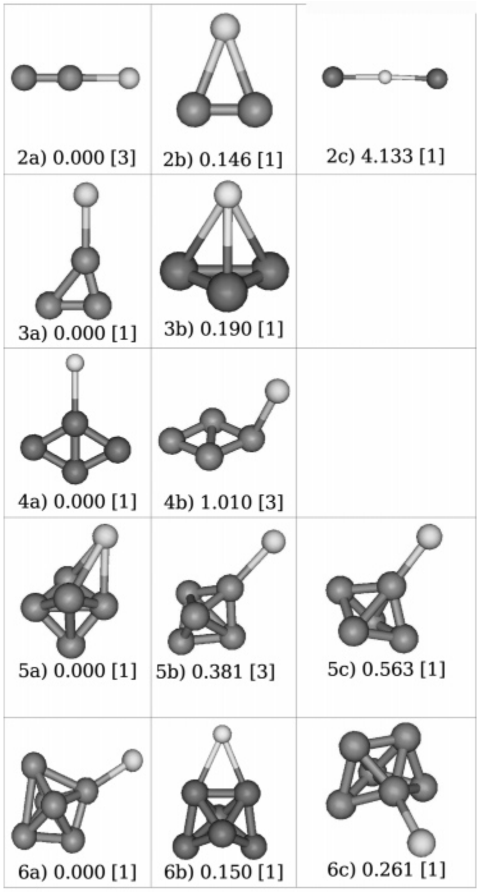

Figure 3. Optimal geometries of cationic Si_nNa^+ clusters. Relative energies are given in eV. The spin multiplicity is indicated in square brackets.

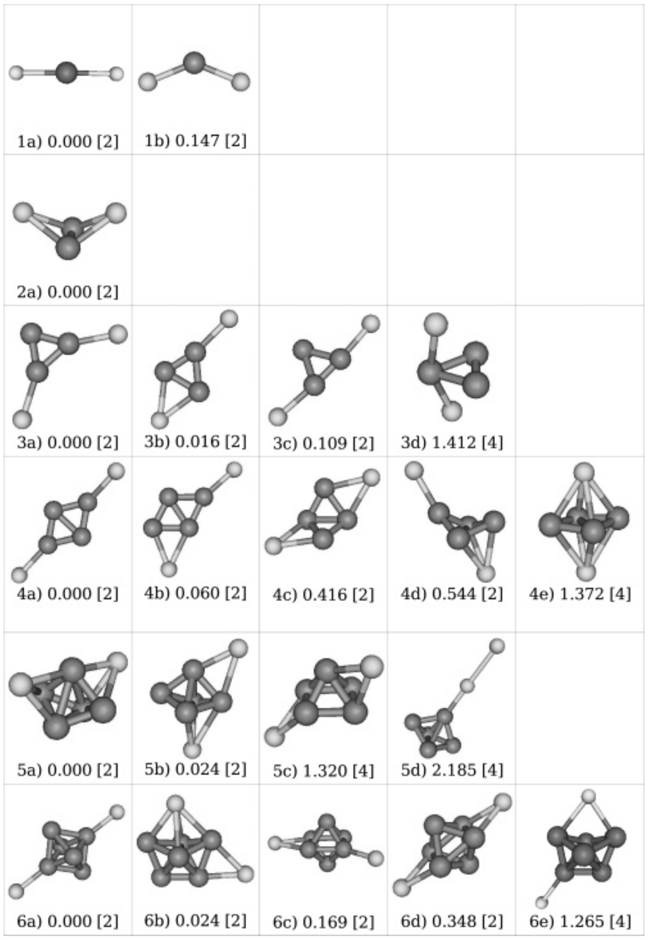

Figure 4. Optimal geometries of cationic $Si_nNa_2^+$ clusters. Relative energies are given in eV. The spin multiplicity is indicated in square brackets.

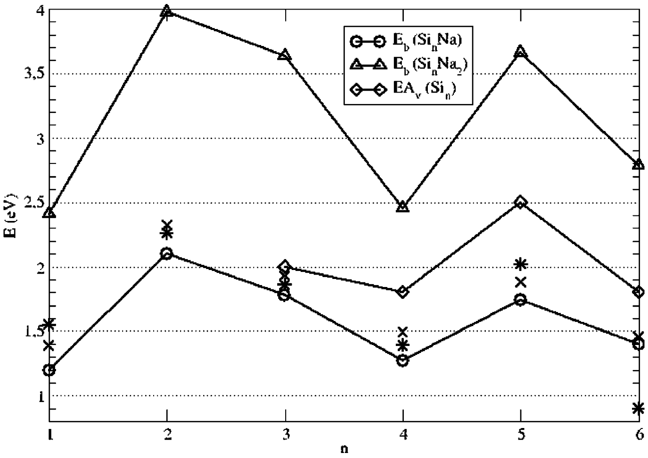

Figure 5. Calculated binding energy (E_b) of Na atoms to Si_n cluster for Si_nNa and Si_nNa_2, together with the experimental value of the vertical electron affinities (EA_v)of Si_n.[22] The previous calculated values of E_b from Kaya and co-workers[20] (star) and Landman and co-workers[21] (cross) are also displayed.

account experimental uncertainties. A good agreement is found since our calculated values are within the experimental inaccuracies. Our results confirm the parallelism between the ionization energy of Si_nNa and the electron affinity of Si_n, the latter giving a minimum for $n = 4$ and a maximum for $n = 5$ (see Figure 5). This parallelism had already been noticed by Kaya and co-workers[30] and can be easily understood as the HOMO (higher occupied molecular orbital) of Si_nNa is the LUMO of Si_n.

Results for Si_nNa_2 clusters are given in Figure 7. For Si_6Na_2, the two first isomers were found to be degenerated; the IP_v calculated for isomers 6a and 6b are 5.68 and 6.15 eV, respectively. The evolution of the IPs against n is similar as that found for Si_nNa. This is due to the fact that the HOMO of Si_nNa_2 is similar to that of Si_nNa. The IPs for Si_nNa_2 are lower by about 0.5 eV that those for Si_nNa. A good agreement with the experimental data is found. No previous theoretical values are known.

D. Dipole Moments and Polarizabilities.

The dipole moments are interesting observables since they probe the charge distribution. They could in principle make possible discrimination between different isomers. For Si_nNa clusters, the transfer of one electron from the Na atom to the silicon cluster leads to a dipole moment μ. It has a value within the 6.62−7.96 D range for the most stable isomer, and it is oriented from the center of mass of the silicon atoms toward to the sodium atom (Table 1). The value of the dipole moment is related to the geometric structure of the cluster. The Na-tail-type structures (isomers 2b, 4c, 5c, 5d, and 6e) have a significantly larger dipole than structures where the Na atom bridges four atoms (isomers 4a and 6a). For Si_nNa_2 clusters, the dipole moment depends on the relative position of the two Na atoms. The symmetric structures (isomers 1a, 4a, and 6c) have a zero dipole moment.

The calculated averaged static dipolar polarizabilities, $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ are also given in Table 1. For Si_nNa clusters, α increases monotonically with n. We have performed calculations of the polarizability of both neutral and negatively charged

TABLE 2: Calculated and Experimental Ionization Potentials (in eV) for Si_nNa and Si_nNa_2

cluster	IP_a(B3LYP)[a]	IP_v(B3LYP)[a]	IP_v(MP2)[b]	IP_a(PLSD)[c]	IP_v(PLSD)[c]	IP_{exptl}[b]
SiNa	6.07	6.21	6.01	6.28	6.36	5.97−6.42
Si_2Na	6.44	6.71	6.50	6.94	7.07	>6.42
Si_3Na	6.32	7.07	6.38	6.79	6.97	>6.42
Si_4Na	5.81	6.41	6.11	6.11	6.22	5.91−6.42
Si_5Na	6.41	7.07	6.68	6.61	7.38	>6.42
Si_6Na	5.82	6.49	6.00	6.06	6.22	5.99−6.42
$SiNa_2$	4.96	4.98				
Si_2Na_2	5.59	5.69				5.60 ± 0.02
Si_3Na_2	5.61	5.87				5.51 ± 0.07
Si_4Na_2	4.94	5.34				5.42 ± 0.02
Si_5Na_2	5.86	6.31				5.85 ± 0.06
Si_6Na_2	5.31	5.68				5.37 ± 0.02

[a] Present work. [b] Reference 20. [c] Reference 21.

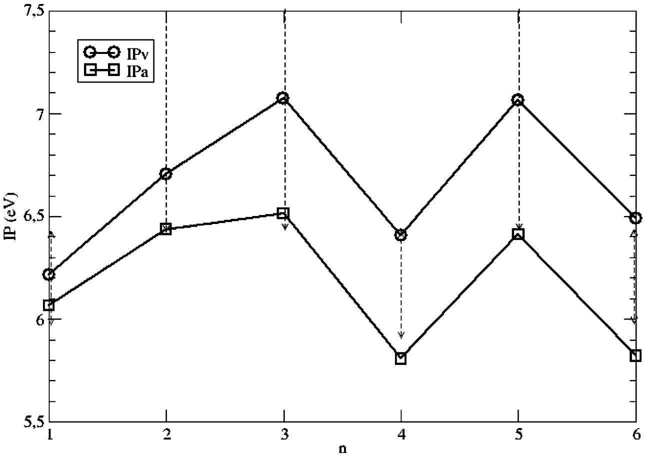

Figure 6. Calculated vertical (circle) and adiabatic (square) ionization potentials for Si_nNa. The experimental values[20] are displayed with vertical dotted arrows to account for experimental uncertainties (see also Table 2).

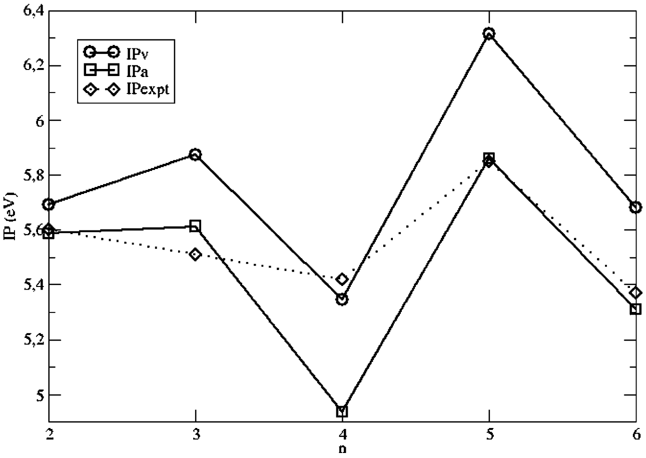

Figure 7. Calculated vertical (circle) and adiabatic (square) ionization potentials compared to experimental values[20] (diamond) for Si_nNa_2.

species for Si_4 and Si_5 clusters by keeping the Si coordinates identical to those in Si_nNa ($n = 4$ and 5). The polarizabilities were found to be 20.30 and 27.41 Å^3 for Si_4 and Si_4^-, respectively, and 24.23 and 30.48 Å^3 for Si_5 and Si_5^-, respectively. The latter can be compared to α values of Si_4Na and Si_5Na (respectively, 24.53 and 28.63 Å^3). It is shown that the polarizability for Na-doped Si_n cluster is between that of the neutral Si_n and that of the anion Si_n^-.

4. Conclusions

We have presented a DFT/B3LYP study of the lowest-energy isomers of silicon sodium clusters $Si_nNa_p^{(+)}$ ($n \leq 6$, $p \leq 2$). The structure of Si_nNa_p keeps the frame of the corresponding Si_n cluster unchanged, and the electronic structure of Si_nNa_p corresponds approximatively to that of $Si_n^{p-} + p$Na$^+$. Ionization potentials were found to be in good agreement with the experimental data. The size dependence of the IP of Si_nNa_p is consistent with that of the electron affinities of Si_n. The dipole moments and static dipolar polarizabilities were calculated. Values of dipole moments are tightly connected to geometrical structures. To the best of our knowledge, the present work is the first theoretical investigation of Si_nNa_2 clusters and of positively charged $Si_nNa_p^+$ clusters.

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