A THEORETICAL STUDY ON CHEMICAL BONDING AND INFRARED SPECTRA OF Si\textsubscript{n}M (M = Sc, Y; \(n = 1\text{-}10\)) CLUSTERS

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ABSTRACT

In this paper, we applied the B3P86 method and DGDZVP basis set to investigate electronic properties and infrared (IR) spectra for Si\textsubscript{n}M (M = Sc, Y; \(n = 1\text{-}10\)) clusters. The NBO analyses show that electron transfers from the dopant atoms to silicon frame of the Si\textsubscript{n}M clusters. It is remarkable that the Si-M bond is mainly formed by the overlaps of the 3s-AOs and 3p-AOs of Si atoms, and 3d-AOs and 4s-AOs of Sc (or 4d-AOs and AO-5s of Y). The chemical bonds in the SiM and Si\textsubscript{2}M clusters are dominated by the covalent character including sigma and pi bonds. In addition, the analysis of the IR spectra suggests that the vibrational modes of Si\textsubscript{n}M clusters are delocalized over the whole cluster. Moreover, the high-frequency and strong-intensity modes usually involve the vibrations of the dopant atoms. The results of this work provide fundamental information for experimental studies on transition-metal doped silicon clusters.

Keywords: Sc-doped Si cluster, Y-doped Si cluster, B3P86, chemical bonding, infrared spectra.

1. INTRODUCTION

In recent years, physical and chemical properties of silicon clusters have been studied extensively both theoretically and experimentally because silicon plays an important role in processing semiconductors and synthesizing novel materials as well as its nanoscale applications such as solar cells, microelectronics, etc. Some classes of stable carbon clusters have been found such as the fullerences (C\textsubscript{60}) and bigger cages with special geometry of the sp\textsuperscript{2}-hybridized carbon atom. However, Si atom favors sp\textsuperscript{3} hybridization to form compact structure that is difficult to act as building blocks to assemble nanomaterials [1]. This deficiency of the pure Si clusters can be solved by doping with suitable transition metal to improve the stability and lead to outstanding properties [2].

In cluster science, there usually exist several isomers that are very close in energy for each cluster from the theoretical computations. There are many experimental techniques used to study structural and electronic structures of cluster. For example, the photoelectron spectroscopy reveals electronic structure of the cluster [3, 4]; the photodissociation experiments give
information about the enhanced stability clusters compared to its neighboring clusters [5]. Although infrared (IR) spectra provide valuable information about geometrical structure and are used extensively in determining structure of classical compounds, it is applied restrictively for nanocluster due to the low particle density which limits the light absorption directly.

Moreover, clusters of many different sizes are usually formed simultaneously in a molecular beam thus the size-selected process is necessary. To overcome this challenge, noble gas is used as a substrate to select clusters before leading them to infrared or Raman spectroscopy. Infrared spectra of some small-size clusters such as Si₃-Si₇ can be measured using this method [6]. Nevertheless, structure of cluster can not be determined based only on infrared spectra and thus leading to urgency in combination of theory and experiment. To the best of our knowledge, the most reasonable way to describe structure of cluster is combining infrared spectroscopy, mass spectrometry and the computational results [2]. The information about geometry, chemical bonding and electronic structure of cluster is fundamental data that is important in designing materials with preeminent properties.

The electronic properties and nature of chemical bond of the Si clusters doped with Sc and Y have not been explored particularly. Some recent reports on Sc/Y-doped silicon clusters [7, 8] predicted the contribution of valence atomic orbitals (AOs) in molecular orbitals (MOs) based only on the results from density of states (DOS) analysis. Mechanism of bond formation in these clusters has not been proposed yet.

Therefore, in the present work, we study the electronic properties, nature of chemical bonding and infrared spectra of the SiₙM clusters (M = Sc, Y; n = 1-10) whose structures and stabilities were investigated by using quantum chemical methods [9].

2. COMPUTATIONAL METHOD

The calculations are carried out by using Gaussian 03 package [10] and the hybrid B3P86 functional in combination with the Gaussian-type valence splitting double-zeta basis set added with polarization function, namely DGDZVP. All the optimization and frequency calculations are performed for the most stable isomers of each cluster to calculate infrared spectra of the SiₙM clusters. The Natural Bond Orbital analysis (NBO) is performed to determine charge and electronic configuration per atom and calculate Wiberg bond order in the SiₙM clusters (M = Sc, Y; n = 1-10) using NBO 5.0 program [11].

The structures of the lowest-lying isomers of the SiₙSc and SiₙY (n = 1-10) clusters at the B3P86/DGDZVP level of theory which were found in elsewhere [9] are shown in Figure 1. Their symmetry point groups, electronic states are presented in the parentheses.
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3. RESULTS AND DISCUSSION

3.1. Electronic Population Analysis of the Si$_n$Sc and Si$_n$Y ($n = 1-10$) clusters

To investigate the charge transfer in these doped clusters and the changes upon varying dopant, we calculate the atomic charges and magnetic moments on the Y and Sc dopants of the clusters by using the NBO 5.0 program. The obtained results are shown in Table 1.

Data in Table 1 show that positive atomic charges on the dopant atom is a consequence of the electron transfer occurring from the dopant Sc/Y atom into the Si$_n$ framework. This result is similar to the Co, Mn-doped silicon clusters in the recent studies [12, 13]. The isolated Sc, Y atoms have magnetic moment of 1.0 $\mu_B$. The magnetic moment on the Sc/Y dopant atom in the Si$_3$M and Si$_6$M clusters is approximate to ~1.0 $\mu_B$ which is similar to the total magnetic moment of the Si$_n$M clusters ($M = Sc, Y; n = 2-10$). This means that the Si$_3$ and Si$_6$ frameworks are able to retain the magnetism of the doped metals and therefore, they might be good candidates for building blocks of novel magnetic nanomaterials. In contrast, the magnetic moments in the other clusters seem not to localize on the dopant, which is evidenced by the small values of magnetic moment on the M atom (Table 1). Based on NBO analysis, the electronic configurations of the Sc and Y atoms in Si$_n$Sc and Si$_n$Y are listed in Table 2.
Table 1. The atomic charge (e) and magnetic moment ($\mu_B$) on M atom in the Si$_n$M (M = Sc, Y; $n$ = 1-10) clusters using NBO analysis.

| $n$ | Atomic charge on Sc (electron) | Magnetic moment on Sc ($\mu_B$) | Atomic charge on Y (electron) | Magnetic moment on Y ($\mu_B$) |
|-----|--------------------------------|------------------|------------------|------------------|
| 1   | 0.43                           | 1.41             | 0.49             | 1.41             |
| 2   | 0.86                           | 0.66             | 0.89             | 0.59             |
| 3   | 0.95                           | 1.00             | 0.95             | 0.87             |
| 4   | 1.18                           | 0.34             | 0.96             | 0.15             |
| 5   | 1.08                           | 0.42             | 1.09             | 0.36             |

Table 2. Electronic configuration of M atom in the Si$_n$M (M=Sc, Y; $n$ = 1-10) clusters.

| $n$ | Electronic configuration of Sc atom | $n$ | Electronic configuration of Y atom |
|-----|------------------------------------|-----|-----------------------------------|
|     | 3d 4s 4p 4d                        |     | 3d 4s 4p 4d                        |
| 1   | 1.27 1.24 0.06 -                    | 1   | 1.25 1.22 0.05 -                   |
| 2   | 1.52 0.59 0.04 0.01                 | 2   | 1.54 0.56 0.03 -                   |
| 3   | 1.68 0.36 0.02 0.01                 | 3   | 1.76 0.30 0.01 0.01                |
| 4   | 1.41 0.33 0.07 0.02                 | 4   | 1.81 0.24 0.02 0.01                |
| 5   | 1.50 0.37 0.05 0.02                 | 5   | 1.56 0.34 0.03 0.01                |
| 6   | 1.75 0.17 0.03 0.02                 | 6   | 1.40 0.73 0.04 0.01                |
| 7   | 1.41 0.34 0.07 0.06                 | 7   | 1.48 0.26 0.06 0.01                |
| 8   | 1.44 0.27 0.08 0.09                 | 8   | 1.58 0.29 0.05 0.01                |
| 9   | 1.44 0.24 0.07 0.09                 | 9   | 1.53 0.21 0.04 0.02                |
| 10  | 1.40 0.30 0.05 0.09                 | 10  | 1.43 0.31 0.03 0.02                |

The obtained results show that the electron populations in the AO-3d of Sc and AO-4d of Y are about 1.2 to 1.8 e which is higher than that of the isolated Sc and Y atom (1.0 e). In addition, the electron populations in the AO-4s of Sc and AO-5s of Y are smaller than 2.0 e in SiM clusters, and are smaller than 1.0 e in the other Si$_n$M clusters. More remarkably, there exist negligible population in AO-4p and AO-4d of Sc and AO-5p and AO-5d of Y. All of the evidences support to a conclusion that the Si-M bonding formation in the Si$_n$M clusters is mainly accounted for the overlap of the AO-3d and AO-4s of Sc, and AO-4d and AO-5s of Y and AO of Si atoms.

To further understand the nature of chemical bonds in the Si$_n$M clusters, we examined the combination of the valence AOs of Si and M atoms in the SiM and Si$_2$M clusters. The valence...
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αMOs and βMOs of the SiSc and SiY dimers at quartet spin state are presented in Figure 2 which includes the five highest occupied αMOs (from αHOMO-4 to αHOMO), the two highest occupied βMOs (βHOMO-1 and βHOMO), αLUMO and βLUMO. The valence orbitals of SiSc and SiY have similar shapes, and only slight difference in the energy order of αHOMO-3, αHOMO-2 and αHOMO-1. Accordingly, the formation of Si-Sc and Si-Y bonds in the SiM clusters is generally explored with the z axis selected as the bond axis of Si-M.

Considering the pair of αMO and βMO with similar shape and their contribution to the bond order of the Si-M bond in the SiM clusters, we found that:

| SiSc  | αHOMO-4 | αHOMO-3 | αHOMO-2 | αHOMO-1 | αHOMO | αLUMO | βHOMO-1 | βHOMO | βLUMO |
|-------|---------|---------|---------|---------|-------|-------|---------|-------|-------|
| SiY   | αHOMO-4 | αHOMO-1 | αHOMO-3 | αHOMO-2 | αHOMO | αLUMO | βHOMO-1 | βHOMO | βLUMO |

Figure 2. The shape of frontier MOs of SiM clusters (isovalue = 0.01 au).

αHOMO-4 and βHOMO-1 are formed by the out-of-phase combination of AO-4px of Sc (AO-5px of Y) and AO-3s of Si. Nevertheless, AO-4px of Sc and AO-5px of Y make a minor contribution compared with AO-3s of Si to these MOs. Consequently, these orbitals are considered as non-bonding MOs localized on the Si atom, and their electrons hardly contribute into the bond order. αHOMO-3 of SiSc and αHOMO-1 of SiY and βHOMOs are σ-bonding MOs that are formed by the in-phase contribution of AO-4s of Sc or AO-5s of Y and AO-3px of Si. This means that electrons in these MOs contribute +1 into the bond order.

For the αHOMO-2 and αHOMO-1 of SiSc and αHOMO-3 and αHOMO-2 of SiY and αHOMO orbitals: there is not any occupied βMO with the similar shape of these occupied αMOs, so these αMOs contain unpaired electron. The αHOMO is formed by the out-of-phase combination of AO-3px of Si and AO-4s of Sc or AO-5s of Y. Nevertheless, this MO is considered as nonbonding MO localized on Sc or Y with the shape of s-orbital because of the negligible contribution of AO-3px of Si. This leads to no contribution of electrons in this MO to the bond order. The αHOMO-2 and αHOMO-1 of SiSc and αHOMO-3 and αHOMO-2 of SiY have similar shapes and lie on two perpendicular planes. They are π-bonding MOs formed by the in-phase interaction of AO-3px of Si and AO-3dxy of Sc (AO-4dxy of Y); AO-3px of Si and AO-3dxy of Sc (AO-4dxy of Y), respectively. This indicates that the electrons in these MOs contribute +1 into the bond order.

In short, there are ca. 2 electrons in the σ-bonding MO, 2 electrons in the π-bonding MO and no electron in any anti-bonding MO. This leads to the bond order of 2.0 for the SiM clusters which is 1.34 calculated by the Wiberg approach. The AO-4s of Sc and AO-5s of Y of SiM contain unpaired electron and do not participate in bonding formation, resulting in the higher electron density in these AOs as compared to that in the other clusters (Table 2).

Figure 3 represents valence orbitals of Si2Sc and Si2Y with α and β spin at doublet state, which includes the six highest occupied αMOs (from αHOMO-5 to αHOMO), the five highest unoccupied βMOs (from βHOMO-4 to βHOMO) and αLUMO, βLUMO. The orbitals of both Si2Sc and Si2Y have similar shapes and similar orders of energy levels.
For the ease of the analysis we choose the coordinate system with the $z$ axis coinciding with the $C_2$ rotational axis of the Si$_2$M clusters. A thorough analysis of the formation of MOs taking from the valence orbitals of Si and M atoms in Si$_2$M is performed.

$\alpha$HOMO-5 and $\beta$HOMO-4 are formed by the in-phase combination of AO-3s of two Si atoms and the out-of-phase combination of AO-4p$_x$ of Sc or AO-5p$_x$ of Y. Nevertheless, the contribution of AO-4p$_x$ of Sc or AO-5p$_x$ of Y relative to the AO-3s orbitals of two Si atoms to these two MOs is insignificant. Accordingly, $\alpha$HOMO-5 and $\beta$HOMO-4 can be approximated as $\sigma$-bonding MOs and their electrons contribute +1 into the bond order of Si-Si bond.

$\alpha$HOMO-4 and $\beta$HOMO-3 are in turn the $\sigma^*$-antibonding MOs of Si-Si and $\sigma$-bonding MO of Si-M which are resulted from the out-of-phase combination of AO-3s of the two Si atoms, and the in-phase combination of AO-3s of the two Si atoms and AO-3d$_{xz}$ of Sc or AO-4d$_{xz}$ of Y. This implies that the electrons in these MOs contribute -1/3 and +1/3 into the bond order of Si-Si and Si-M bond, respectively.

$\alpha$HOMO-3 and $\beta$HOMO-2 are the $\pi$ and $\sigma$-bonding MOs of Si-Si and Si-M bonding, respectively. These MOs are formed by the in-phase combination of AO-3p$_z$ of Si and AO-4s of Sc or AO-5s of Y, and this gives rise to the consequence that the electrons in the two MOs contribute +1/3 into the bond order of each bond.

$\alpha$HOMO-2 and $\beta$HOMO-1 are the $\pi$-bonding MOs of all 3 bonds of clusters, which are contributed by the in-phase AO-3p$_y$ of Si and AO-3d$_{x^2-y^2}$ of Sc or AO-4d$_{x^2-y^2}$ of Y. As a result, the bond order of Si-Si and Si-M by +1/3 is contributed by the electrons in these two MOs. $\alpha$HOMO-1 and $\beta$HOMO are also the bonding MOs of all three bonds in the clusters Si$_2$M, which are formed by the in-phase combination of AO-3p$_x$ of Si and AO-3d$_{x^2}$ of Sc or AO-4d$_{x^2}$ of Y. Electrons in these MO contribute +1/3 into the bond order of each bond.

$\alpha$HOMO is the bonding MO of Si-M and $\pi^*$-antibonding of Si-Si. This orbital is resulted from the out-phase combination of AO-3p$_x$ of two Si atoms, and their in-phase combination and AO-3d$_{xz}$ of Sc or AO-4d$_{xz}$ of Y. Therefore, the electron in $\alpha$HOMO contributes +1/6 into the bond order of each Si-M and -1/6 that of Si-Si (because this MO has 1 electron only).

In summary, the manual calculated bond order of Si-Si bond is: $1-1/3+1/3+1/3+1/3-1/6 = 1.5$, in good agreement with the Wiberg calculation which is of 1.75 and 1.74 for Si$_2$Sc and Si$_2$Y, respectively. Otherwise, the bond order of Si-M is: $1/3+1/3+1/3+1/3+1/6 = 1.5$ which is comparable to 1.23 and 1.25 for Si-Sc and Si-Y, respectively, as calculated by the Wiberg
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The obtained results show that each method has its own advantages. Thus, the value of the bond order estimated by Wiberg calculation is more accurate than that manually calculated based on the valence MO shapes, nevertheless the latter provides insights into the nature of chemical bonding.

3.2. IR spectra of SiₙM clusters (M = Sc, Y; n = 1-10)

Nowadays, many research groups all over the world can measure IR spectra of cluster by using modern techniques. In this part, IR spectra are theoretically explored to provide useful information about vibrational frequencies and their intensities of the SiₙM clusters, and the calculated results are plotted in Figure 4.

*Figure 4. IR spectra of the lowest isomers of the SiₙM (M = Sc, Y; n = 1-10) clusters.*

Analysing the IR spectra of the SiₙM clusters we obtained some important conclusions as follows:

i) IR spectra of SiₙM clusters can be measured in the frequency range from 0 to 600 cm⁻¹.

ii) IR spectra of SiₙSc and SiₙY that have the same shape are similar (with n = 1, 2, 3, 5, 6 and 9). Nevertheless, the vibrational frequencies of SiₙSc are slightly higher than those of SiₙY owing to difference in reduced mass.

iii) IR spectra of SiₙSc and SiₙY that have different geometric structures (with n = 4, 7, 8 and 10) are different significantly.
iv) Most of the vibrations of clusters encompass movements of many atoms. In other words, they are delocalized over the whole cluster, which might be due to the fact that electrons in clusters are delocalized over the whole clusters instead of being localized on bonding as classical organic compounds.

v) The vibrations that have high frequency and strong intensity are usually related to strong movement of the dopant atoms.

4. CONCLUDING REMARKS

Some concluding remarks are summarized as follows:

1) The electron transfer in the SiₙM clusters examined occurs from the M dopant atom to the Siₙ framework. The Si-M bonds are formed by the main contribution of 3d-AOs and AO-4s of Sc (4d-AOs and AO-5s of Y) and AO-3s, 3p-AOs of Si atoms.

2) Analyzing the valence MOs of SiM and Si₂M shows that the chemical bonds Si-Si and Si-M are, in general, covalent bond. The mechanism of bonding formation is similar in both the SiₙSc and SiₙY clusters (n = 1-2). Formal bonding orders of Si-M bond in SiM and Si₂M is 2.0 and 1.5, respectively. These results are quite consistent with the values calculated by Wiberg method.

3) The vibrational frequencies of the modes in the examined clusters are in the range from 0 to 600 cm⁻¹. The vibrational modes of the SiₙM clusters delocalize over the whole cluster which is different from those of the classical organic molecules. The high-frequency and strong-intensity modes usually relate to strong movements of the dopants.

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