

## A THEORETICAL STUDY ON CHEMICAL BONDING AND INFRARED SPECTRA OF $\text{Si}_n\text{M}$ ( $\text{M} = \text{Sc}, \text{Y}; n = 1-10$ ) 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  $\text{Si}_n\text{M}$  ( $\text{M} = \text{Sc}, \text{Y}; n = 1-10$ ) clusters. The NBO analyses show that electron transfers from the dopant atoms to silicon frame of the  $\text{Si}_n\text{M}$  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 5s of Y). The chemical bonds in the  $\text{SiM}$  and  $\text{Si}_2\text{M}$  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  $\text{Si}_n\text{M}$  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 fullerenes ( $\text{C}_{60}$ ) and bigger cages with special geometry of the  $\text{sp}^2$ -hybridized carbon atom. However, Si atom favors  $\text{sp}^3$  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  $\text{Si}_3$ - $\text{Si}_7$  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 preminent properties.

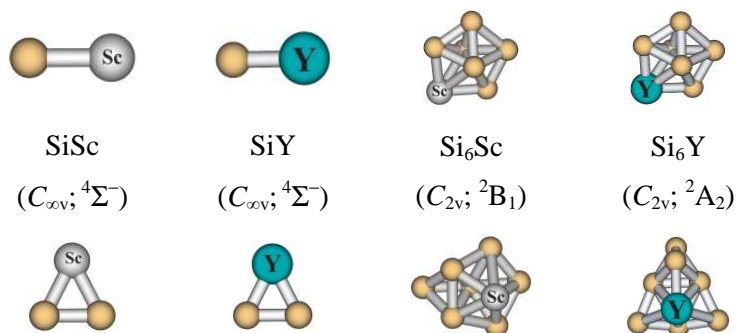
The electronic properties and nature of chemical bond of the Si clusters doped with Sc and Y have not been explored particularly. Some recent reports on Sc/Y-doped silicon clusters [7, 8] predicted the contribution of valence atomic orbitals (AOs) in molecular orbitals (MOs) based only on the results 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  $\text{Si}_n\text{M}$  clusters ( $\text{M} = \text{Sc}, \text{Y}; n = 1-10$ ) 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  $\text{Si}_n\text{M}$  clusters. The Natural Bond Orbital analysis (NBO) is performed to determine charge and electronic configuration per atom and calculate Wiberg bond order in the  $\text{Si}_n\text{M}$  clusters ( $\text{M} = \text{Sc}, \text{Y}; n = 1-10$ ) using NBO 5.G program [11].

The structures of the lowest-lying isomers of the  $\text{Si}_n\text{Sc}$  and  $\text{Si}_n\text{Y}$  ( $n = 1-10$ ) 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.



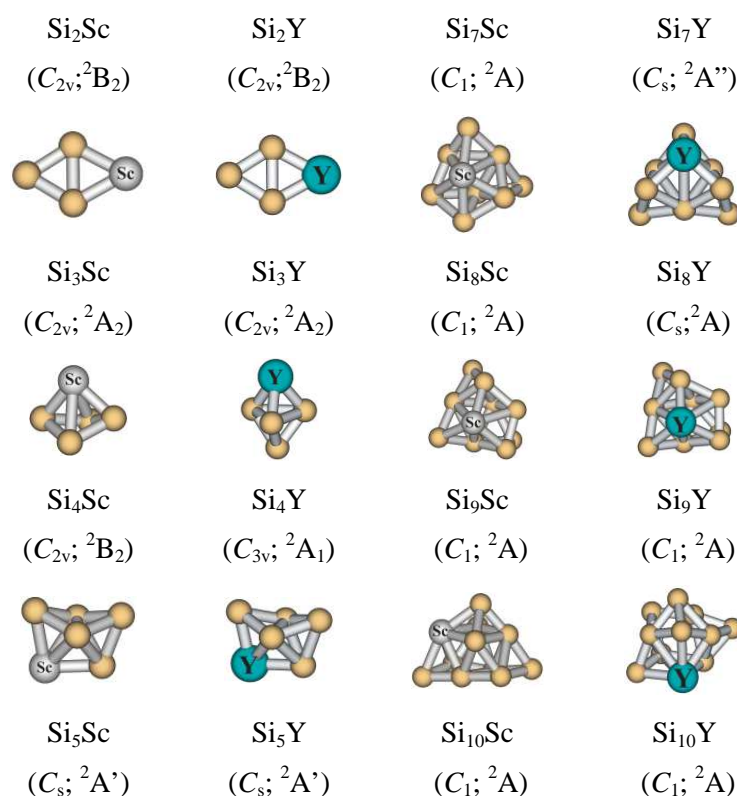


Figure 1. Shapes of the lowest-energy isomers of the  $Si_nSc$  and  $Si_nY$  ( $n = 1-10$ ) clusters.

### 3. RESULTS AND DISCUSSION

#### 3.1. Electronic Population Analysis of the $Si_nSc$ and $Si_nY$ ( $n = 1-10$ ) 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.G 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  $Si_3M$  and  $Si_6M$  clusters is approximate to  $\sim 1.0 \mu_B$  which is similar to the total magnetic moment of the  $Si_nM$  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  $Si_nSc$  and  $Si_nY$  are listed in Table 2.

*Table 1.* The atomic charge ( $e$ ) and magnetic moment ( $\mu_B$ ) on M atom in the  $Si_nM$  ( $M = Sc, Y; n = 1-10$ ) clusters using NBO analysis.

$n$	Atomic charge on Sc (electron)	Magnetic moment on Sc ( $\mu_B$ )	Atomic charge on Y (electron)	Magnetic moment on Sc ( $\mu_B$ )	$n$	Atomic charge on Sc (electron)	Magnetic moment on Sc ( $\mu_B$ )	Atomic charge on Y (electron)	Magnetic moment on Sc ( $\mu_B$ )
1	0.43	1.41	0.49	1.41	6	1.04	0.94	0.84	0.93
2	0.86	0.66	0.89	0.59	7	1.15	0.42	1.22	0.33
3	0.95	1.00	0.95	0.87	8	1.14	0.32	1.10	0.30
4	1.18	0.34	0.96	0.15	9	1.18	0.28	1.23	0.17
5	1.08	0.42	1.09	0.36	10	1.17	0.26	1.24	0.19

*Table 2.* Electronic configuration of M atom in the  $Si_nM$  ( $M=Sc, Y; n = 1-10$ ) 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  $Si_nM$  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  $Si_nM$  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  $Si_nM$  clusters, we examined the combination of the valence AOs of Si and M atoms in the  $SiM$  and  $Si_2M$  clusters. The valence

$\alpha$ MOs and  $\beta$ MOs of the SiSc and SiY dimers at quartet spin state are presented in Figure 2 which includes the five highest occupied  $\alpha$ MOs (from  $\alpha$ HOMO-4 to  $\alpha$ HOMO), the two highest occupied  $\beta$ MOs ( $\beta$ HOMO-1 and  $\beta$ HOMO),  $\alpha$ LUMO and  $\beta$ LUMO. The valence orbitals of SiSc and SiY have similar shapes, and only slight difference in the energy order of  $\alpha$ HOMO-3,  $\alpha$ HOMO-2 and  $\alpha$ HOMO-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  $\alpha$ MO and  $\beta$ MO with similar shape and their contribution to the bond order of the Si-M bond in the SiM clusters, we found that:

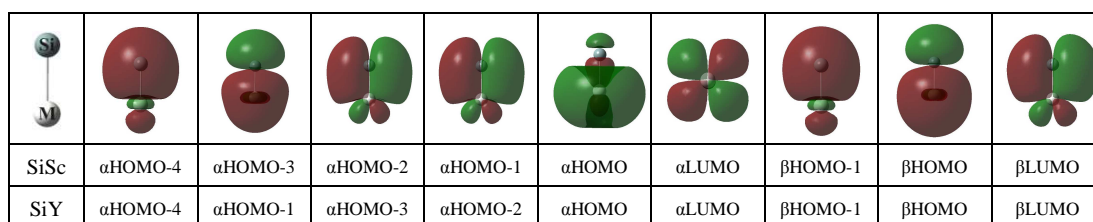


Figure 2. The shape of frontier MOs of SiM clusters (isovalue = 0.01 au).

$\alpha$ HOMO-4 and  $\beta$ HOMO-1 are formed by the out-of-phase combination of AO-4p<sub>z</sub> of Sc (AO-5p<sub>z</sub> of Y) and AO-3s of Si. Nevertheless, AO-4p<sub>z</sub> of Sc and AO-5p<sub>z</sub> 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.  $\alpha$ HOMO-3 of SiSc and  $\alpha$ HOMO-1 of SiY and  $\beta$ HOMOs are  $\sigma$ -bonding MOs that are formed by the in-phase contribution of AO-4s of Sc or AO-5s of Y and AO-3p<sub>z</sub> of Si. This means that electrons in these MOs contribute +1 into the bond order.

For the  $\alpha$ HOMO-2 and  $\alpha$ HOMO-1 of SiSc and  $\alpha$ HOMO-3 and  $\alpha$ HOMO-2 of SiY and  $\alpha$ HOMO orbitals: there is not any occupied  $\beta$ MO with the similar shape of these occupied  $\alpha$ MOs, so these  $\alpha$ MOs contain unpaired electron. The  $\alpha$ HOMO is formed by the out-of-phase combination of AO-3p<sub>z</sub> 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-3p<sub>z</sub> of Si. This leads to no contribution of electrons in this MO to the bond order. The  $\alpha$ HOMO-2 and  $\alpha$ HOMO-1 of SiSc and  $\alpha$ HOMO-3 and  $\alpha$ HOMO-2 of SiY have similar shapes and lie on two perpendicular planes. They are  $\pi$ -bonding MOs formed by the in-phase interaction of AO-3p<sub>x</sub> of Si and AO-3d<sub>xy</sub> of Sc (AO-4d<sub>xy</sub> of Y); AO-3p<sub>y</sub> of Si and AO-3d<sub>yz</sub> of Sc (AO-4d<sub>yz</sub> 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  $\sigma$ -bonding MO, 2 electrons in the  $\pi$ -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 Si<sub>2</sub>Sc and Si<sub>2</sub>Y with  $\alpha$  and  $\beta$  spin at doublet state, which includes the six highest occupied  $\alpha$ MOs (from  $\alpha$ HOMO-5 to  $\alpha$ HOMO), the five highest unoccupied  $\beta$ MOs (from  $\beta$ HOMO-4 to  $\beta$ HOMO) and  $\alpha$ LUMO,  $\beta$ LUMO. The orbitals of both Si<sub>2</sub>Sc and Si<sub>2</sub>Y have similar shapes and similar orders of energy levels.

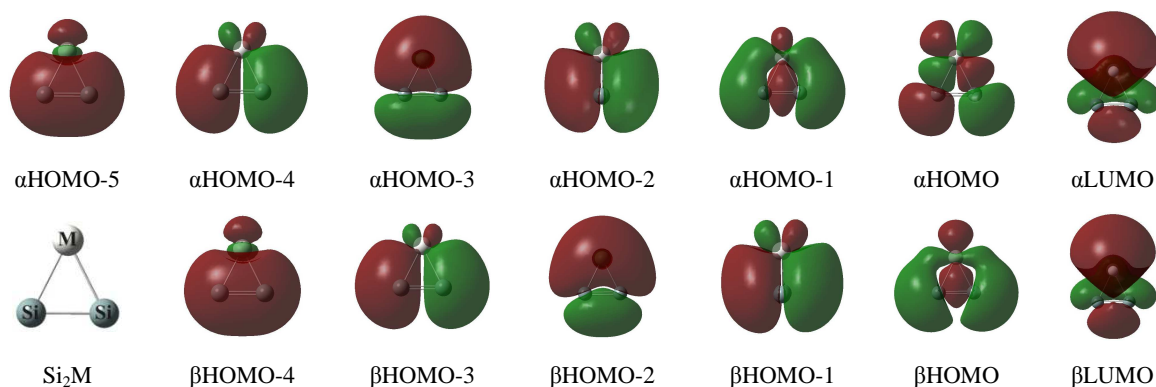


Figure 3. The shapes of some frontier MOs of the  $\text{Si}_2\text{M}$  clusters (isovalue = 0.01 au).

For the ease of the analysis we choose the coordinate system with the z axis coinciding with the  $C_2$  rotational axis of the  $\text{Si}_2\text{M}$  clusters. A thorough analysis of the formation of MOs taking from the valence orbitals of Si and M atoms in  $\text{Si}_2\text{M}$  is performed.

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

$\alpha\text{HOMO-4}$  and  $\beta\text{HOMO-3}$  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-3 $d_{xz}$  of Sc or AO-4 $d_{xz}$  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.

$\alpha\text{HOMO-3}$  and  $\beta\text{HOMO-2}$  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-3 $p_z$  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.

$\alpha\text{HOMO-2}$  and  $\beta\text{HOMO-1}$  are the  $\pi$ -bonding MOs of all 3 bonds of clusters, which are contributed by the in-phase AO-3 $p_y$  of Si and AO-3  $d_{x^2-y^2}$  of Sc or AO-4  $d_{x^2-y^2}$  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.  $\alpha\text{HOMO-1}$  and  $\beta\text{HOMO}$  are also the bonding MOs of all three bonds in the clusters  $\text{Si}_2\text{M}$ , which are formed by the in-phase combination of AO-3 $p_z$  of Si and AO-3  $d_{z^2}$  of Sc or AO-4  $d_{z^2}$  of Y. Electrons in these MO contribute +1/3 into the bond order of each bond.

$\alpha\text{HOMO}$  is the bonding MO of Si-M and  $\pi^*$ -antibonding of Si-Si. This orbital is resulted from the out-phase combination of AO-3 $p_z$  of two Si atoms, and their in-phase combination and AO-3 $d_{xz}$  of Sc or AO-4 $d_{xz}$  of Y. Therefore, the electron in  $\alpha\text{HOMO}$  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  $\text{Si}_2\text{Sc}$  and  $\text{Si}_2\text{Y}$ , 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

approach. 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 $\text{Si}_n\text{M}$ clusters ( $M = \text{Sc}, \text{Y}; n = 1-10$ )

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  $\text{Si}_n\text{M}$  clusters, and the calculated results are plotted in Figure 4.

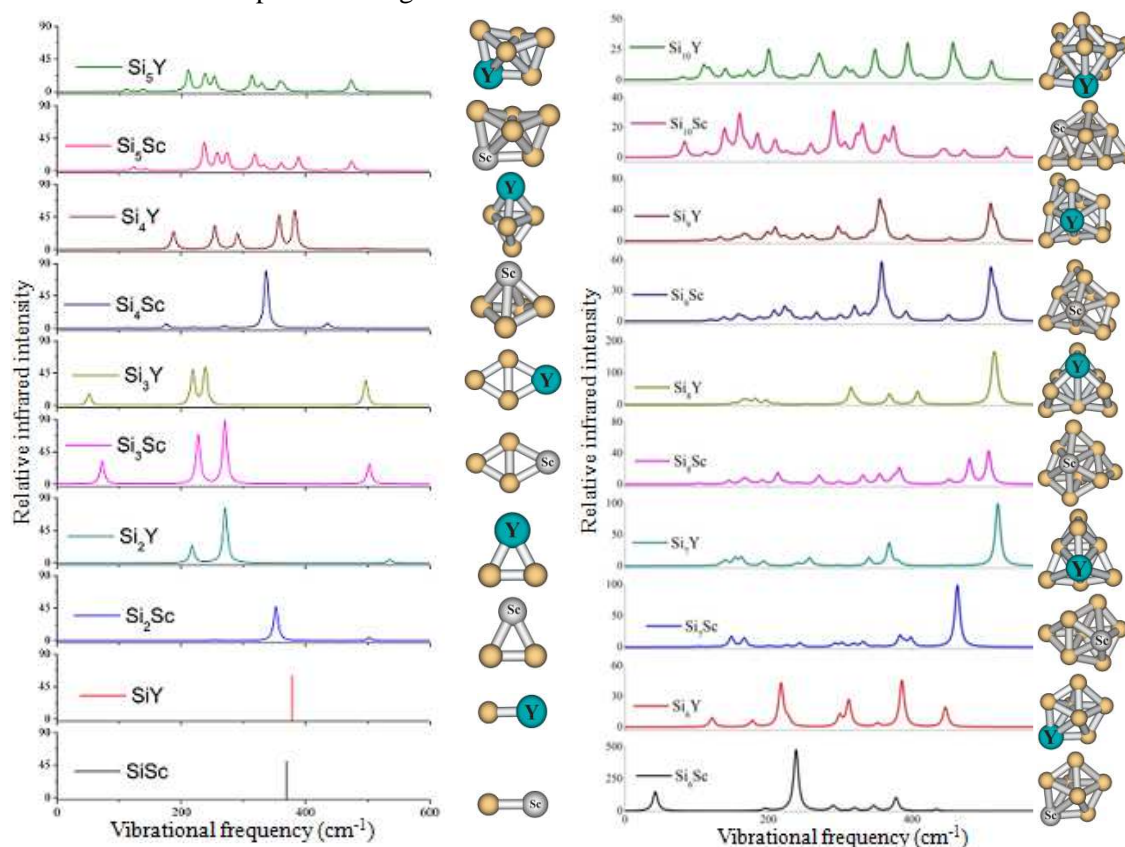


Figure 4. IR spectra of the lowest isomers of the  $\text{Si}_n\text{M}$  ( $M = \text{Sc}, \text{Y}; n = 1-10$ ) clusters.

Analysing the IR spectra of the  $\text{Si}_n\text{M}$  clusters we obtained some important conclusions as following:

- i) IR spectra of  $\text{Si}_n\text{M}$  clusters can be measured in the frequency range from 0 to 600  $\text{cm}^{-1}$ .
- ii) IR spectra of  $\text{Si}_n\text{Sc}$  and  $\text{Si}_n\text{Y}$  that have the same shape are similar (with  $n = 1, 2, 3, 5, 6$  and 9). Nevertheless, the vibrational frequencies of  $\text{Si}_n\text{Sc}$  are slightly higher than those of  $\text{Si}_n\text{Y}$  owing to difference in reduced mass.
- iii) IR spectra of  $\text{Si}_n\text{Sc}$  and  $\text{Si}_n\text{Y}$  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  $\text{Si}_n\text{M}$  clusters examined occurs from the M dopant atom to the  $\text{Si}_n$  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  $\text{SiM}$  and  $\text{Si}_2\text{M}$  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  $\text{Si}_n\text{Sc}$  and  $\text{Si}_n\text{Y}$  clusters ( $n = 1-2$ ). Formal bonding orders of Si-M bond in  $\text{SiM}$  and  $\text{Si}_2\text{M}$  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  $600\text{ cm}^{-1}$ . The vibrational modes of the  $\text{Si}_n\text{M}$  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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