

## Si<sub>11</sub>Mn<sup>0/+</sup> cluster is endohedral or exohedral: a proof by DFT calculation

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### Abstract

The geometries of Si<sub>11</sub>, Si<sub>11</sub>Mn<sup>+</sup> and Si<sub>11</sub>Mn<sup>0</sup> clusters have been determined by the method of density functional theory using B3P86/6-311+G(d) level of theory. The pure silicon clusters Si<sub>11</sub> have cage structure associating with a low spin state. Although the geometrical structure of the most stable isomer of Si<sub>11</sub>Mn<sup>+</sup> cationic cluster is exohedral, the endohedral isomers have their calculated IR spectra fitting well with the experimental IRMPD spectra. The Si<sub>11</sub>Mn<sup>0</sup> neutral cluster is found to be most stable in both exohedral and endohedral forms. The most stable isomers of manganese-doped silicon clusters Si<sub>11</sub>Mn<sup>0/+</sup> possess high spin states and local magnetic moment of the Mn atom is reduced or even completely quenched when it is encapsulated inside the Si<sub>11</sub> cage.

**Keywords.** Silicon cluster doped manganese, density functional theory (DFT).

### 1. INTRODUCTION

Silicon clusters doped with transition metal have been studied extensively in the last decade, owing to their prolific magnetic and optoelectronic properties that could lead to many application potentials [1-4]. Let us look a little more closely into the research work on this kind of cluster that has been done recently. It is shown in the literature that pure silicon clusters possess low spin states and are non magnetic type of materials. Transition metal atoms are magnetic owing to their non-fully filled *d* orbitals. Of the transition metals, manganese has a maximum number of unpaired electrons on its *3d* orbitals. Therefore doping manganese atoms into silicon clusters is very likely to create clusters which have prolific magnetic properties as well as improved band gaps [5-8]. Over the last few years, there has been much work on manganese doped silicon clusters. An interesting work on singly Mn-doped silicon clusters which combines experimental and theoretical investigation of small neutral vanadium and manganese doped silicon clusters Si<sub>n</sub>X (n = 6-9, X = V, Mn) was reported [7]. These species were studied by infrared multiple photon dissociation and mass spectrometry. Structural identification is achieved by comparison of the experimental data with computed infrared spectra of low-lying isomers using density functional theory at the B3P86/6-311+G(d) level. The assigned structures of the neutral manganese doped silicon clusters are compared with their cationic counterparts [9]. The structural, electronic and magnetic properties of

singly Mn-doped Si<sub>n</sub>Mn<sup>+</sup> clusters with n = 6-10, 12-14 and 16 have been investigated by using mass spectrometry and infrared spectroscopy in combination with density functional theory computations. This work has revealed that all the exohedral Si<sub>n</sub>Mn<sup>+</sup> (n = 6-10) clusters are found to be substitutive derivatives of the bare Si<sub>n+1</sub><sup>+</sup> cations, while the endohedral Si<sub>n</sub>Mn<sup>+</sup> (n = 12-14 and 16) clusters adopt fullerene-like structures. The clusters turn out to have high magnetic moments localized on Mn. In particular, the Mn atoms in the exohedral Si<sub>n</sub>Mn<sup>+</sup> (n = 6-10) clusters have local magnetic moments of 4 μB or 6 μB and can be considered as magnetic copies of the silicon atoms.[6] Recent theoretical work on manganese-doped silicon clusters has not yet confirmed the structures of Si<sub>11</sub>Mn<sup>+</sup> and Si<sub>11</sub>Mn<sup>0</sup> cluster. Whether the clusters are endohedral or exohedral, and whether or not the local magnetic moment of the Mn atom is completely quenched when doped in the silicon cluster.

### 2. METHODS OF CALCULATIONS

We use the method of density functional theory (DFT) which is implemented in the Gaussian 09 software [10, 11] to investigate the pure and manganese doped silicon clusters Si<sub>11</sub>, Si<sub>11</sub>Mn<sup>+</sup> and Si<sub>11</sub>Mn<sup>0</sup>.

The B3P86/6-311+G(d) functional/basis set has been used for our calculations [12-14], since this combination of functional and basis set are suitable for treating silicon clusters doped with manganese as

well as some other transition metals [6-8, 15-17]. The optimization calculations followed by frequency calculations have been done for searching minima of the clusters. Geometries, relative energies with zero point energy correction are deduced from these calculations.

### 3. RESULTS AND DISCUSSION

#### 3.1. Searching for the stable isomer of pure silicon cluster $\text{Si}_{11}$

Stable structures of the  $\text{Si}_{11}$  cluster have been determined as follows. Firstly, we have used the

Gauss View program for building as many structures of  $\text{Si}_{11}$  cluster as possible. These input structures have been optimized converging to 14 stable isomers which have been confirmed by frequency calculations. The stable isomers are shown in figure 1.

Of all the isomers found, the most stable isomer belongs to the  $C_s$  point group and has the structure that could be described as such: The structure has three layers. Both the first and the second layers contain five Si atoms, while in the third layer lies only one Si atom. This structure arises from the  $\text{Si}_8$  cluster with three other Si atoms adding to faces of the distorted cube of the  $\text{Si}_8$  cluster.

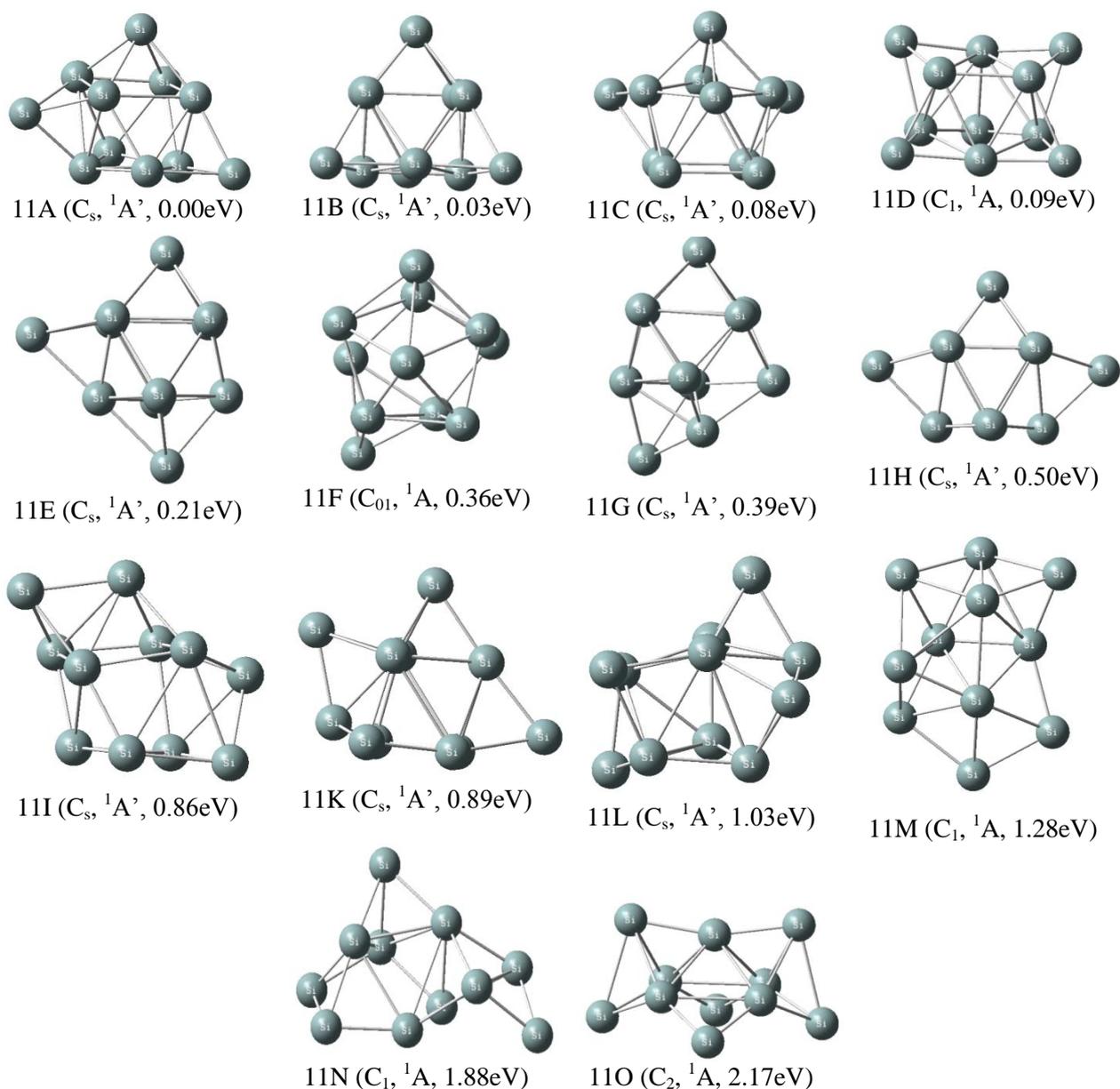


Figure 1: Stable isomers of the  $\text{Si}_{11}$  cluster, which have been optimized using DFT calculation with B3P86/6-311+G(d) functional/basis set. The grey balls represent Si atoms

Three other isomers 11B, 11C, 11D are found lying at 0.03 eV, 0.08 eV and 0.09 eV barely above the most stable isomer, respectively.

All the isomers are in their singlet spin states.

### 3.2. Searching for the most stable isomers of singly Mn-doped silicon cluster $Si_{11}Mn^+$

The searching for the stable isomers of the singly Mn-doped silicon cluster  $Si_{11}Mn^+$  has been performed as follows. After the optimization

calculations for stable isomers of the  $Si_{11}$  cluster, we added the Mn atom onto the low-lying energy isomers of the  $Si_{11}$  structures in as many positions as possible. The optimization calculations on the 54 input structures of the  $Si_{11}Mn^+$  clusters resulting in 21 stable isomers. All of them have 3-dimensional structure and 17 ones of them lying at below 1.50 eV are represented in figure 2 accompanying with their point groups, electronic states as well as relative energies (in parenthesis).

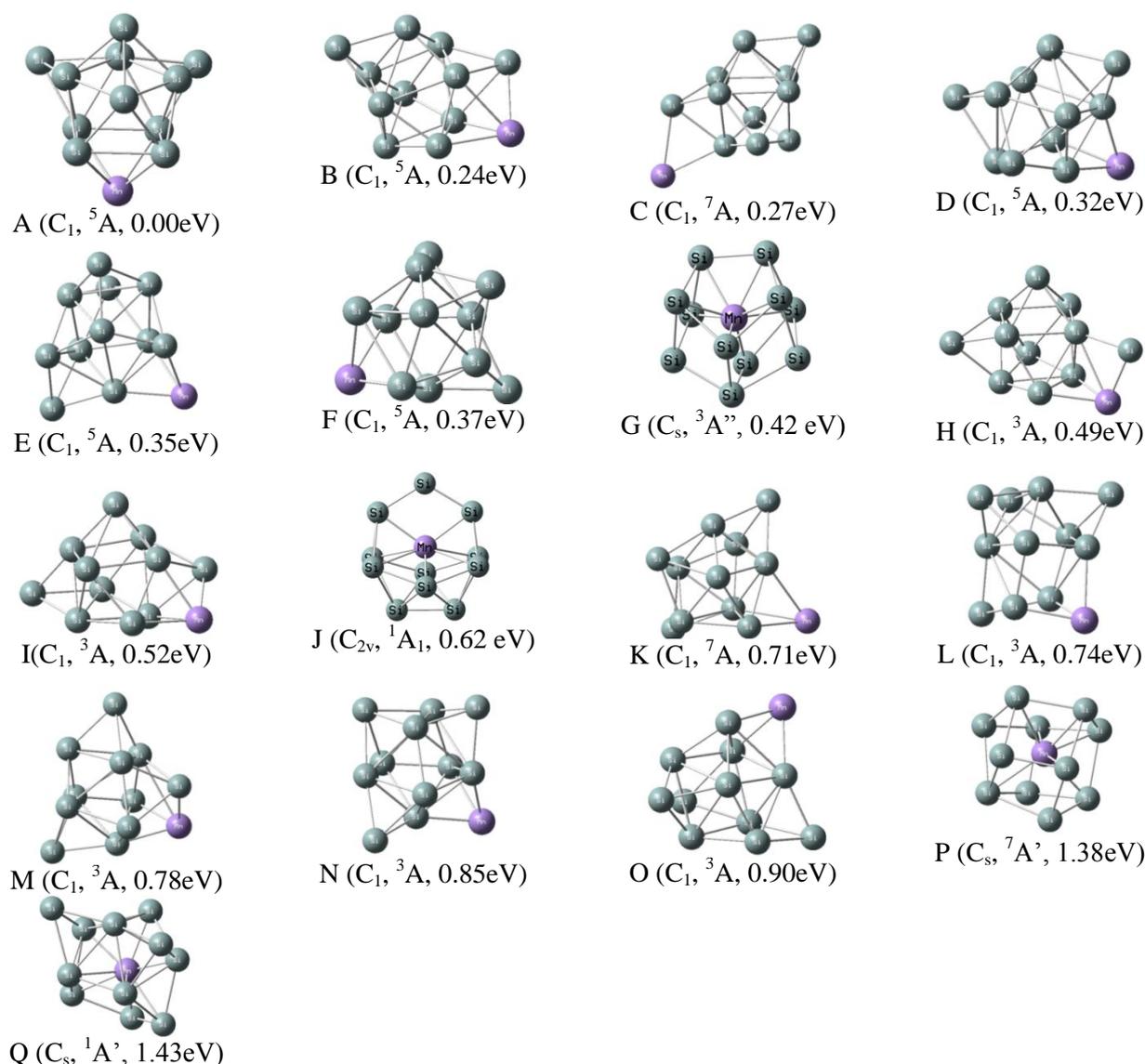


Figure 2: Stable isomers of the  $Si_{11}Mn^+$  cluster, which have been optimized using DFT calculation with B3P86/6-311+G(d) functional/basis set. The grey balls represent Si atoms, the pink ball represents the Mn atom

For the most stable isomer of the  $Si_{11}Mn^+$  cluster, isomer A ( $C_1$ ,  $^5A$ , 0.00 eV), the Mn atom capes onto the quadrilateral faces of the  $Si_{11}$ . This structural isomer associates with four unpaired

electrons locating in the Mn atom. This structure grows up from the  $Si_{11}$  pure silicon cluster-isomer3, which has the relative energy of 0.08eV, with the Mn atom added to the face of four Si atoms.

The most stable isomer of  $\text{Si}_{11}\text{Mn}^+$  cluster is exohedral. This means that the Mn atom attaches the outer sphere of the  $\text{Si}_{11}$  one. The spin density of the Mn atom, which is deduced from the calculation and listed in table 1, shows that the local magnetic moment of the Mn atom does not change significantly when doping outer of the  $\text{Si}_{11}$  cage.

Several low-energy lying isomers of the  $\text{Si}_{11}\text{Mn}^+$  cluster have been found, in which the Mn atom capes onto the outer faces of the  $\text{Si}_{11}$  cluster and they all have unpaired electrons.

Interestingly, we have found the two isomers G ( $C_s$ ,  $^3A''$ , 0.42 eV) and J ( $C_{2v}$ ,  $^1A_1$ , 0.62 eV) which are endohedral with the Mn atom locating inside the  $\text{Si}_{11}$  cage. They have relative energies of 0.42 eV and 0.62 eV as compared to the most stable isomer A.

We also found other endohedral isomers P, Q in which the Mn atom is encapsulated inside the cage of  $\text{Si}_{11}$  which are low spin with the spin multiplicity being equal to 1. They are much less stable with relative energies of 1.38 and 1.43 eV, respectively. The calculation results also show that isomers of  $\text{Si}_{11}\text{Mn}^+$  with quintet spin state are stable and those

with singlet spin state have very high relative energies, as compared to the ground state.

On a recent research work by Vu Thi Ngan et al. [6], the theoretical investigation has been performed on the geometrical structures of  $\text{Si}_n\text{Mn}^+$  on the basis of comparison the calculated vibrational spectra and the experimental ones. The structural identification is made by fitting the simulated spectra of stable isomers and the experimental Infrared Multi-photon Dissociation (IRMPD) spectra for each cluster stoichiometry. In that in tense work, although the structural assignments have been made for  $\text{Si}_n\text{Mn}^+$  ( $n = 6-10, 12-14, 16$ ) clusters, the  $\text{Si}_{11}\text{Mn}^+$  cluster was left unsolved. As a complementary to that research work, this one is done for searching the structural identification of the  $\text{Si}_{11}\text{Mn}^+$  cluster.

Table 1: Mulliken atomic spin density

Cluster	Mulliken atomic spin density on Mn
$\text{Si}_{11}\text{Mn}^+$ - isomer A	3.97
$\text{Si}_{11}\text{Mn}^+$ - isomer G	2.18
$\text{Si}_{11}\text{Mn}^0$ - isomer A	2.21
$\text{Si}_{11}\text{Mn}^0$ - isomer B	4.37

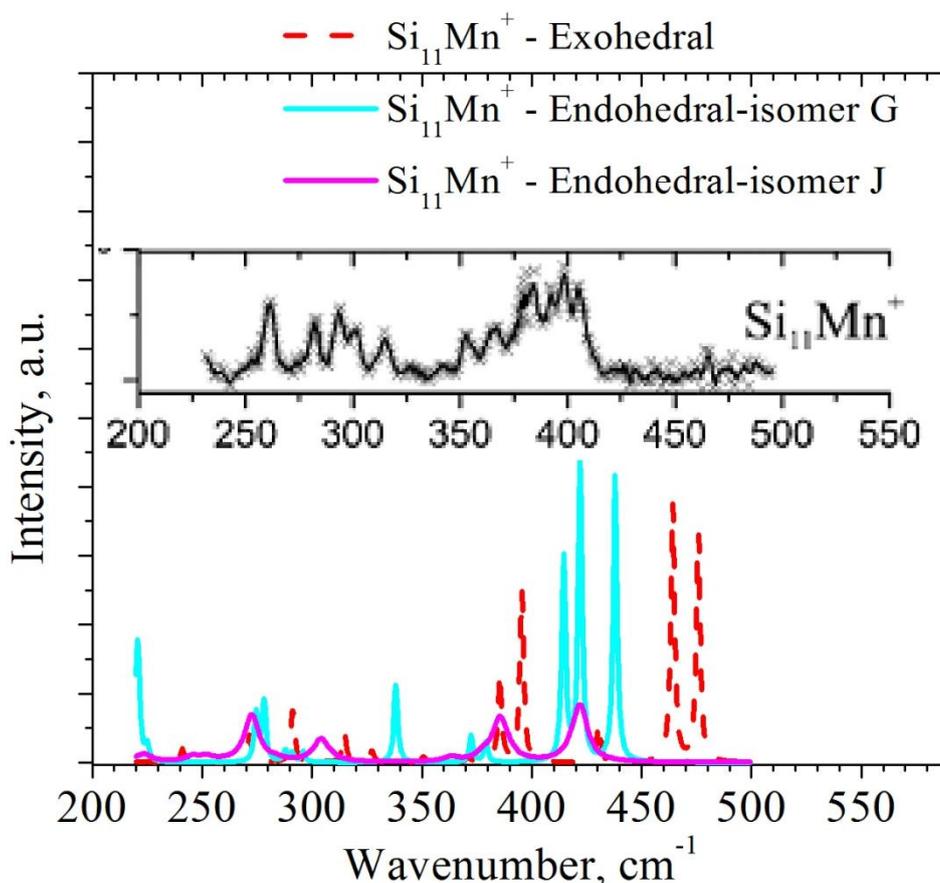


Figure 3: Calculated IR spectra of  $\text{Si}_{11}\text{Mn}^+$  exohedral cluster (red dashed curve), endohedral clusters isomer G (light blue curve) and isomer J (pink curve). The experimental IRMPD spectrum of the  $\text{Si}_{11}\text{Mn}^+$  cluster, which is taken from the reference [6], is presented in the insert

In order to assign the geometrical structure of the  $Si_{11}Mn^+$  cluster, we have plotted the IR spectra of all the low-energy isomers of the cluster, including the most stable isomer A-exohedral as well as the endohedral isomers G and J. The theoretical IR spectra are then compared with the experimental Infrared Multi-photon Dissociation (IRMPD) spectrum of the  $Si_{11}Mn^+$  cluster [6]. The calculated IR spectra of the endohedral isomers G and J turn out to fit better with the experimental one, as this could be seen in figure 3. Both of the two endohedral isomers have strong absorption bands at  $\sim 420\text{ cm}^{-1}$ , and less intense band at  $270\text{ cm}^{-1}$  which are found in the experimental one. The calculated spectrum of the exohedral isomer A - the lowest energy one - which is also plotted in figure 3 for inspection, has strong absorption peaks at  $\sim 470\text{ cm}^{-1}$  which are not observed in the experimental spectrum.

This analysis allows us to conclude that the  $Si_{11}Mn^+$  cluster appears in its endohedral forms, though they locate at 0.42 eV and 0.62 eV higher energies as compared to the exohedral isomer A.

The magnetic moment of the  $Si_{11}Mn^+$  cluster is decreased from quintet state as the Mn atom dopes outer of the  $Si_{11}$  cage, to triplet as well as completely quenched to singlet as the Mn atom is embedded inside the  $Si_{11}$  cage.

### 3.3. Searching for the most stable isomers of singly Mn-doped silicon cluster $Si_{11}Mn$

From stable isomers of the  $Si_{11}Mn^+$  cluster we construct the Gaussian input files for searching the geometrical structures of the  $Si_{11}Mn^0$  neutral cluster with spin multiplicities ranging from 2 to 8. The results of optimized geometries as well as their point groups, electronic states and relative energies are represented in figure 4.

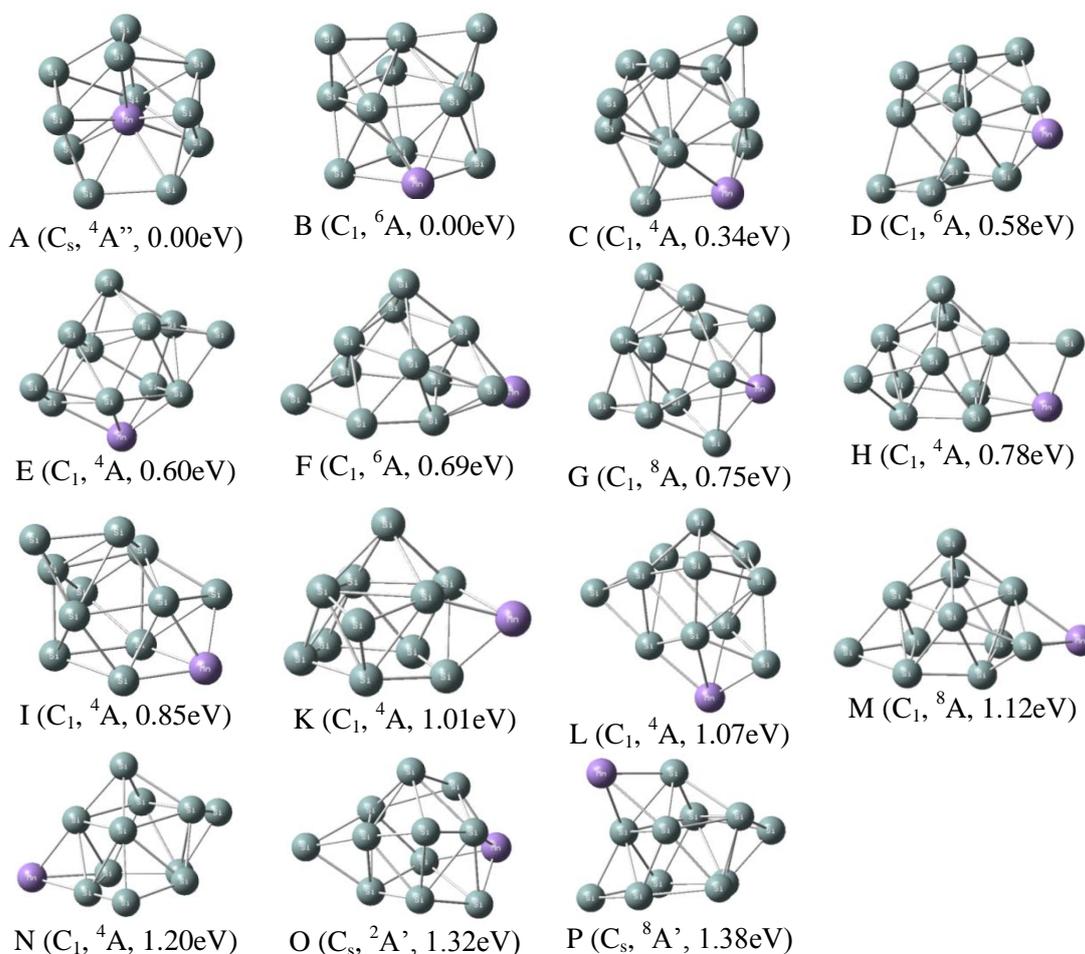


Figure 4: Stable isomers of the  $Si_{11}Mn$  neutral cluster, which have been optimized using DFT calculation with B3P86/6-311+G(d) functional/basis set. The grey balls represent Si atoms, the pink ball represents the Mn atom

The results show that for the  $Si_{11}Mn$  neutral cluster, there are two different geometrical structures

with the same electronic energy, isomer A( $C_s; 4A''$ ; 0.00 eV), and isomer B( $C_{01}; 6A$ ; 0.00eV). In isomer

A, the Mn atom is embedded inside the  $\text{Si}_{11}$  cluster binding with all the Si atoms. This structure associates with the quartet spin state and belongs to the  $C_s$  point group. In the second isomer, the Mn atom locates outer of the  $\text{Si}_{11}$  cage binding with 5 Si atoms. This isomer, which is similar to that of the lowest energy-lying isomer of the  $\text{Si}_{11}\text{Mn}^+$  cationic cluster, belongs to the  $C_1$  point group and has the spin multiplicity of 6.

On the optimization of structures, we have also found many other low energy-lying isomers of the  $\text{Si}_{11}\text{Mn}^0$  cluster. They all belong to low point groups ( $C_1$ ,  $C_s$ ) and almost all of them have spin multiplicities of 4, 6 and 8.

The spin density of the Mn atom, which is listed in table 1, shows that the local magnetic moment of the Mn atom does not change when doping outer of the  $\text{Si}_{11}$  cage and it is reduced to a triplet state rather

than it is quenched completely when embedded inside the  $\text{Si}_{11}$  cage.

We also found several isomers for this cluster, which are illustrated in figure 4.

In this section, for the sake of providing persuasive information on the  $\text{Si}_{11}\text{Mn}^0$  neutral cluster, the IR spectra of the  $\text{Si}_{11}\text{Mn}^0$  cluster in its exohedral as well as endohedral forms have been plotted and represented in figure 5. The result shows that for the  $\text{Si}_{11}\text{Mn}^0$  cluster of endohedral form – isomer A in figure 4, the IR spectrum has an intense absorption band at  $\sim 430\text{ cm}^{-1}$  wavenumber and bands at  $\sim 380\text{ cm}^{-1}$ ,  $\sim 300\text{ cm}^{-1}$  and  $\sim 250\text{ cm}^{-1}$  with lower intensities. The exohedral isomer B has absorption bands at  $\sim 465$ ,  $\sim 390$ ,  $\sim 350$  as well as  $\sim 250\text{ cm}^{-1}$  wavenumbers and all of them are less intense as compared with the endohedral one.

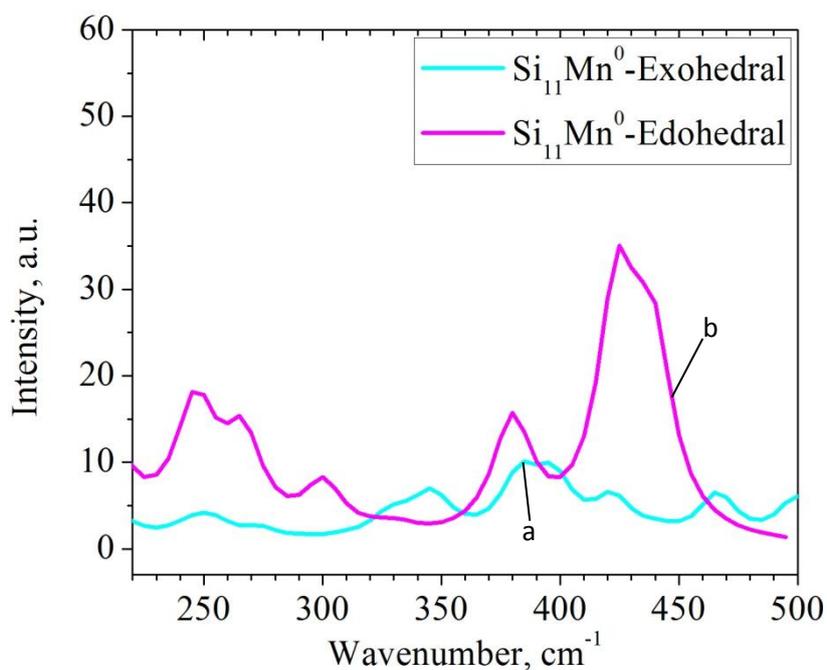


Figure 5: The calculated IR spectra of  $\text{Si}_{11}\text{Mn}^0$  exohedral cluster (a) And endohedral cluster (b)

#### 4. CONCLUSION

The B3P86/6-311+G(d) quantum chemical calculation method has been employed for searching the stable geometrical structures of  $\text{Si}_{11}$ ,  $\text{Si}_{11}\text{Mn}^+$ , and  $\text{Si}_{11}\text{Mn}^0$  clusters. While for the lowest energy structure of  $\text{Si}_{11}\text{Mn}^+$  cationic cluster, the Mn dopant locates outer the  $\text{Si}_{11}$  cage forming the exohedral isomer, the endohedral isomers which have relative energies of 0.42 and 0.62 eV possess the calculated IR spectra fitting well with the experimental IRMPD spectrum. The geometrical structures of the most

stable isomers of  $\text{Si}_{11}\text{Mn}^0$  neutral cluster are both endohedral and exohedral. The Mn-doped silicon clusters  $\text{Si}_{11}\text{Mn}^+$  and  $\text{Si}_{11}\text{Mn}^0$  prefer high spin states and they are reduced or even quenched completely as the Mn dopant moves into the cage of the silicon cluster.

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