A THEORETICAL INVESTIGATION ON VIBRATIONAL INFRARED SPECTRA OF $\text{Si}_n\text{Mn}_2^+$ ATOMIC CLUSTERS ($n = 5-9$)

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Received: 15 August 2017; Accepted for publication: 5 February 2018

ABSTRACT

Comparison between measured vibrational infrared spectra and corresponding computed ones has been used as a powerful approach to assign the ground state geometry of isolated atomic clusters. Nevertheless, the coexistence of more than one stable isomers often makes the geometrical assignment practically more challenging especially for large-size and doped species. In this study, we report the vibrational infrared spectra of most stable $\text{SinMn}_2^+$ clusters ($n=5-9$) using density functional theory calculations. An attempt has been made to theoretically construct infrared spectra of the investigated clusters in case of more than one stable isomers coexisting. The finding results would serve as fingerprints for further structural identification of interested clusters.

Keywords: silicon cluster doped manganese, density functional theory, infrared spectroscopy.

1. INTRODUCTION

Silicon is an important element in industry for many years due to its precious electronic properties. During the last decades, the atomic clusters containing few of silicon atoms have been studied extensively by the desire to understand their novel aspects in the quantum scale [1-5]. Literature has shown 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. Therefore doping transition metal atoms into silicon clusters is expected to create clusters which have prolific magnetic properties [6-9]. The invention of gas-phase cluster sources using laser ablation technique has made experimental studies of cluster structures possible [10]. One of the most effective approaches to obtain the cluster geometrical information is to use the vibrational infrared spectroscopy, and structures of specific cluster-size could be assigned by comparing their calculated vibrational spectra and experimental ones [11-13]. In this context, the structures of cationic $\text{SiNb}^+$, $\text{SiV}^+$, $\text{SiCo}^+$, $\text{SiMn}^+$ etc. clusters have also been determined using the
above mentioned method [13-15]. Though it is suggested that for large doped silicon clusters, multiple isomers can coexist and contribute to measured infrared spectra, making the judgement on ground-state cluster structures no longer straightforward.

The cationic silicon clusters doped with Mn atoms have been of particular interest owing to the expected strong interaction from half-filled d-orbitals of the dopant. Geometrical and electronic structures of a silicon cluster doped with Mn atoms inside Mn@Si$_{14}^+$ have also been investigated by DFT and CASPT2/CASSCF computations [16]. Several theoretical calculations using B3P86/6-311+G(d) functional/basis set have also been performed in this work for the structures of cationic single Mn-doped silicon clusters Si$_n$Mn$^+$ and for the interaction of the clusters with Ar atoms [17]. Electronic and magnetic properties of Si$_n$Mn$^+$ clusters have been investigated by mass spectroscopy and infrared spectroscopy [6, 7]. Unlike singly-doped Si$_n$Mn clusters, doubly doped Si$_n$Mn$_2$ species have been far less understood. Neutral and anionic Si$_n$Mn$_2$ (n = 1–8) clusters have been theoretically computed [18], showing that the magnetic order of two dopants can be switched depending on the clusters size and charge state. Mn$_2$@Si$_{15}$ cluster has been reported as the smallest triple ring tubular silicon cluster [19]. The Mn$_2$ dimer doped in silicon tube Si$_{18}$ [20] was found to be nonmagnetic. Most recently, the geometries, electronic structures, relative stabilities, and magnetic properties of cationic Si$_n$Mn$_2^+$ and Si$_n$Mn$^{n+}$ (n=1-10) clusters have been systematically examined and compared by DFT calculations. For all studied clusters, the two Mn atoms prefer to apart from each other. Si$_3$Mn$_2^+$, Si$_3$Mn$_3^+$, and Si$_5$Mn$_3^+$ clusters are relatively stable as compared to the neighboring sizes. For all of the investigated ground-state structures, two Mn atoms have ferromagnetically coupled to each other and their unpaired 3d electrons govern the total magnetic moment of the clusters. The Si$_5$Mn$_2^+$ and Si$_5$Mn$_3^+$ have highest spin moments (11μB) while Si$_7$Mn$_2^+$ has lowest one (7μB) [21].

Unfortunately, there has been no direct link between simulations and future experiments provided at that moment to assign the ground state geometries of those species. This paper has been motivated by the purpose of bridging this gap. The vibrational infrared spectra of most stable isomers of Si$_n$Mn$_2^+$ (n=5-9) cation clusters are calculated and discussed. The coexistence of more than one stable isomers are taken into account when investigating infrared spectra to guide further confirmative measurements.

2. METHOD OF CALCULATIONS

We use the method of density functional theory (DFT) which is implemented in the Gaussian 09 software [22,23] to investigate the manganese doped silicon cationic cluster Si$_n$Mn$_2^+$ (n = 5-9). The B3P86/6-311+G(d) functional/basis set combination is used for our calculations [24-26] since this has been proved suitable for describing structures of the silicon clusters doped with manganese [7]. The optimization calculations followed by frequency calculations have been done for searching minima of the clusters. The optimization calculations have been performed as the following ways: we first optimized the smallest Si$_3$Mn$_2^+$ clusters with different spin multiplicities; then one more Si atom is added to the low-lying isomers of the previous cluster size in all plausible positions to create input structures. The other way to make input geometrical structures of the clusters is that into the most stable isomers of the pure Si$_n$ cluster the two Mn atoms were added in many possible positions. These input structures of the Si$_n$Mn$_2^+$ cluster were then optimized. Geometries, relative energies are deduced from these calculations.
3. RESULTS AND DISCUSSIONS

The low-lying isomers found for studied clusters have been reported in our previous study [21]. Herein the most stable structures of Si$_n$Mn$_2^+$ clusters with $n = 5$-9 are displayed in Fig. 1 before we discuss their infrared spectra. For convenience, only four lowest-energy isomers are considered for each species. We denote each structure as $n.x$, in which $n$ stands for number of Si atoms in cluster Si$_n$Mn$_2^+$ and $x$ is labeled as A, B, C, and D for isomers with increasing order of energy. It is known that by investigating the infrared vibrational spectra of each cluster, one can match the actual oscillating frequencies of cluster bonds with those corresponding to a specific isomeric geometry. The best match can be used to assign the ground-state structure for the cluster. Nevertheless, in some cases the assignment becomes ambiguous and inconclusive [27]. In the following, we will discuss the structural importance that can influence the structure-matching process.

Figure 1. Geometries, relative energies, and electronic states of the most stable isomers of Si$_n$Mn$_2^+$ clusters ($n = 5$-9).

First of all, it should be mentioned that silicon doped with manganese clusters could appear in many isomers with rather low relative energies. In fact our extended search for structural isomers resulted in a large variety of local minimum structures – many of which are close in energy. For example, 17 structural and spin isomers have been considered for Si$_5$Mn$_2^+$ and all of
them are 3-dimensional. The number of detected isomers for the clusters with larger sizes is even more. For n = 5, the ground-state isomer 5.A seems to be considerably more stable than the next isomers 5.B, 5.C, and 5.D with a relative energy of at least 0.39 eV. However, as can be seen in Fig. 1 the lowest-lying isomers of Si<sub>n</sub>Mn<sup>+</sup> clusters with n=6-9 are quite stable and almost degenerate in energy. It is suggested that they might practically co-exist in experiments and the obtained infrared vibrational spectra could contain the overlapped structural information from different isomers. A structural assignment of the clusters, based only on matching results of traditional DFT calculations and experimental infrared spectra, is thus not straightforward anymore. To this end, we introduce an approach to construct the infrared spectrum theoretically on the basis of convolutions of individual infrared spectra of different isomers for each clusters-size. The convolutions have been implemented by taking into account the Boltzmann distribution of each conformer [28]:

\[
\frac{N_i}{N_{total}} = \frac{e^{-E_{rel} RT}}{\sum_{k=1}^{N_{total}} e^{-E_k RT}}
\]

The left hand side is the equilibrium ratio of conformer i to the total. \(E_{rel}\) is the relative energy of the \(i\)-th conformer from the minimum energy conformer. \(E_k\) is the relative energy of the \(k\)-th conformer from the minimum energy conformer. \(R\) is the molar ideal gas constant equal to 8.31 J/(mol·K) and \(T\) is the temperature in Kelvin (K). The denominator of the right side is the partition function.

The population distributions of conformers which are calculated at room temperature are listed in Table 1. The convoluted infrared spectra of the Si<sub>n</sub>Mn<sup>+</sup> (n = 5-9) are illustrated in Fig. 2. The results show that the spectra have many small peaks, different with results of Si<sub>n</sub>C or SiB [29, 30]. The ground state structures of Si<sub>n</sub>Mn<sup>+</sup> clusters are represented in Fig.1 show that all studied clusters are found to be exohedral with two Mn atoms preferably apart from each other, less symmetrical than the pure Si<sub>n</sub>. In this research we would like to answer a question: which is the frequency of the Si-Mn vibrational mode for the investigated clusters? Following the optimization calculations the frequency calculations have been done, and on a close inspection of that result we could assign the frequency of the Si-Mn vibrational mode. For instance, the convoluted infrared spectrum of Si<sub>5</sub>Mn<sup>+</sup> appears with the major contribution from the 5.A isomer, of which the peaks centered at ~264 cm<sup>-1</sup> and 226 cm<sup>-1</sup>. These peaks are assigned for the asymmetrical vibrational mode of the Si-Mn bonds. Three other small peaks emerge at the higher frequency side, ~447 cm<sup>-1</sup>, 397 cm<sup>-1</sup> and 351 cm<sup>-1</sup>, corresponding to the symmetrical vibrational mode of the Si-Si bonds in the Si<sub>5</sub> frame. Similar argument can be made for Si<sub>6</sub>Mn<sup>+</sup> and Si<sub>7</sub>Mn<sup>+</sup> since their spectra are dominated by that of 7.A and 8.A isomers since others are unlikely produced at the room temperature. The spectrum of Si<sub>5</sub>Mn<sup>+</sup> cluster is contributed from all four most stable isomers but majorly from 6.A and 6.B. In which a peak centered at ~90 cm<sup>-1</sup> with highest absorption intensity is assigned for the asymmetrical vibrational mode of the Si-Mn bonds of the 6.A isomer. The peak at ~380 cm<sup>-1</sup> is assigned for the vibrational mode between Si-Si bonds in the Si<sub>6</sub> frame of the 6.A isomer while the peak at ~345 cm<sup>-1</sup> is resulted from the vibrational mode in the Si<sub>6</sub> frame of the isomer 6.B. The peak at 295 cm<sup>-1</sup> is the complex vibration of the Si<sub>6</sub> frame of both 6.A and 6.B isomers. The one at 183 cm<sup>-1</sup> is formed by the asymmetrical vibrational mode of the Si-Mn bonds of the 6.A isomer. The populations of isomers 6.C and 6.D are too small and can be ignored. The infrared spectra of Si<sub>n</sub>Mn<sup>+</sup> (n = 6-14) clusters have been systematically examined [6]. The spectrum of Si<sub>6</sub>Mn<sup>+</sup> cluster, the peaks centered at ~234 cm<sup>-1</sup> and ~300 cm<sup>-1</sup> are assigned for the vibrational mode of the Si-Mn bonds. Three other peaks emerge at the higher frequency side, ~338 cm<sup>-1</sup>, 389 cm<sup>-1</sup> and 420 cm<sup>-1</sup>, corresponding to the vibrational mode of the Si-Si bonds in the Si<sub>6</sub> frame. Unlike Si<sub>6</sub>Mn<sup>+</sup> cluster,
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The Si$_5$Mn$_2^+$ appear small peak at the lower frequency 125 cm$^{-1}$ corresponding to the vibrational mode of the Mn-Mn bonds. Similar behavior can be found in the convoluted infrared spectrum of Si$_5$Mn$_2^+$, Si$_7$Mn$_2^+$, Si$_8$Mn$_2^+$ and Si$_9$Mn$_2^+$.

Table 1. The population distributions of different conformers of the Si$_n$Mn$_2^+$ clusters ($n=5$–$9$) calculated at room temperature.

| Cluster | Isomer | Relative energy, eV | Relative energy, J/mol | $e^{-E_{rel}/RT}$ | \(N_i/N_{total}\) |
|---------|--------|---------------------|------------------------|--------------------|---------------------|
| Si$_5$Mn$_2^+$ | 1 | 0.00 | 0.00 | 1 | 1 |
|           | 2 | 0.39 | 37564.8 | 2.6.10$^{-7}$ | ~0 |
|           | 3 | 0.45 | 43344.0 | 2.525.10$^{-8}$ | ~0 |
|           | 4 | 0.45 | 43344.0 | 2.525.10$^{-8}$ | ~0 |
| Si$_6$Mn$_2^+$ | 1 | 0.00 | 0.00 | 1 | 0.5988 |
|           | 2 | 0.02 | 1926.4 | 0.459 | 0.275 |
|           | 3 | 0.05 | 4816.0 | 0.143 | 0.0858 |
|           | 4 | 0.07 | 6742.4 | 0.0658 | 0.0394 |
| Si$_7$Mn$_2^+$ | 1 | 0.00 | 0.00 | 1 | 0.9755 |
|           | 2 | 0.12 | 11558.4 | 9.417.10$^{-3}$ | 9.186.10$^{-3}$ |
|           | 3 | 0.12 | 11558.4 | 9.417.10$^{-3}$ | 9.186.10$^{-3}$ |
|           | 4 | 0.14 | 13484.8 | 4.327.10$^{-3}$ | 4.22.10$^{-3}$ |
| Si$_8$Mn$_2^+$ | 1 | 0.00 | 0.00 | 1 | 0.971 |
|           | 2 | 0.09 | 8668.8 | 0.03 | 0.029 |
|           | 3 | 0.30 | 28896.0 | 8.606.10$^{-6}$ | ~0 |
|           | 4 | 0.31 | 29859.2 | 5.834.10$^{-6}$ | ~0 |
| Si$_9$Mn$_2^+$ | 1 | 0.00 | 0.00 | 1 | 0.8222 |
|           | 2 | 0.04 | 3852.8 | 0.2112 | 0.173 |
|           | 3 | 0.14 | 13484.8 | 4.327.10$^{-3}$ | 3.56.10$^{-3}$ |
|           | 4 | 0.18 | 17337.6 | 9.138.10$^{-4}$ | 1.24.10$^{-3}$ |
Figure 2. Convoluted infrared vibrational spectra of Si$_n$Mn$_2^+$ clusters (n = 5-9).

4. CONCLUSION

A serie of calculations using density functional theory (DFT) employed rather high level of theory B3P86/6-311+G(d) has been performed for searching the possible infrared vibrational spectra of Si$_n$Mn$_2^+$ clusters (n = 5-9), which are not yet available in literature. We believe our finding results would be useful for theoretical understanding of doubly doped Si$_n$Mn$_2^+$ clusters and guiding future experiments to eventually determine the structures of Si$_n$Mn$_2^+$ species.
Acknowledgement: This research is funded by the Ministry of Education and Training of Vietnam under grant number B2015-17-68 and the Institute of Materials Science, Vietnam Academy of Science and Technology under grant number CSCL 05.17. The authors thank Center for Computational Science, Hanoi National University of Education for using its computational facility.

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