The structures of neutral transition metal doped silicon clusters, Si\textsubscript{n} X (n = 6–9; X = V, Mn)

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Citation: The Journal of Chemical Physics 138, 194301 (2013); doi: 10.1063/1.4803871
View online: http://dx.doi.org/10.1063/1.4803871
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/138/19?ver=pdfcov
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The structural properties of neutral transition metal doped silicon clusters, \( \text{Si}_n \text{X} \) \((n = 6–9; \ X = \text{V}, \text{Mn})\)

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(Received 5 February 2013; accepted 22 April 2013; published online 15 May 2013)

We present a combined experimental and theoretical investigation of small neutral vanadium and manganese doped silicon clusters \( \text{Si}_n \text{X} \) \((n = 6–9, \ X = \text{V, Mn})\). These species are 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 vanadium and manganese doped silicon clusters are compared with their cationic counterparts. In general, the neutral and cationic \( \text{Si}_{n \text{V}} \text{V}^{0,+} \) and \( \text{Si}_{n \text{Mn}} \text{Mn}^{0,+} \) clusters have similar structures, although the position of the capping atoms depends for certain sizes on the charge state. The influence of the charge state on the electronic properties of the clusters is also investigated by analysis of the density of states, the shapes of the molecular orbitals, and NBO charge analysis of the dopant atom. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4803871]

I. INTRODUCTION

The properties of silicon-based clusters attract a great deal of attention because of their importance in both applied and fundamental sciences. In current semiconductor industry, nano-electronic devices are constructed with the use of lithographic techniques. As a result of ongoing miniaturization, this top-down approach reaches fundamental limits and alternative bottom-up approaches using nanometer sized building blocks are considered. Clusters can play a key role in this quest. Thorough knowledge of their size, composition, and charge state dependent properties is essential to create opportunities to construct materials with application-specific features.

The incorporation of a dopant atom is a way to tailor the electronic, magnetic, and optical properties of silicon clusters. Doping with transition metal atoms with unfilled \( d \)-shells is a promising approach to create clusters with new properties. In particular, one might be able to construct silicon clusters with size-dependent magnetism.

Recently, charged doped silicon clusters have been studied in great detail via numerous different experimental techniques in combination with theoretical investigations. Structural insight was obtained in photoelectron spectroscopy studies on anionic clusters that monitor the electronic structure\(^{2-5} \) and photodissociation experiments that identify sizes or subunits with enhanced stability.\(^{6} \) Soft X-ray absorption spectroscopy has been used to investigate the local electronic structure of the dopant atom and to measure the HOMO-LUMO gaps of doped silicon clusters.\(^{7,8} \) More direct structural information about cationic doped silicon clusters has been obtained via infrared spectroscopy.\(^{9-12} \)

From an experimental point-of-view, neutral clusters are more difficult to investigate because common mass spectrometric techniques, such as mass selection or trapping, cannot be applied directly. Experiments on neutral clusters in the gas phase are usually done in a molecular beam and post-ionization is a prerequisite to detect the clusters. Therefore, the amount of experimental data on neutral (doped) clusters is limited. On the other hand, several theoretical studies have been conducted on bare\(^{13-16} \) and transition metal doped\(^{17-19} \) neutral silicon clusters, particularly focusing on the geometry of those species. Few experimental data are available to confirm the predicted structures. Structural determination of neutral \( \text{Si}_n \) \((n \leq 7)\) clusters in cryogenic matrices has been obtained via infrared spectroscopy of clusters produced by co-condensation of silicon atoms with rare gases\(^{20} \) as well as via Raman spectroscopy\(^ {21,22} \) after mass selection and low-energy deposition. Recently, we identified the geometrical structure of selected small neutral silicon clusters in the gas phase using two different approaches.\(^ {23,24} \) The first one uses a two color ionization scheme, consisting of infrared (IR) photo-absorption and ultraviolet (UV) photo-ionization. If the
energy of the UV photon is close to the threshold ionization energy of the clusters, prior IR photo-absorption enhances the ionization efficiency after absorption of the UV photon. Scanning the IR photon energy then allows to record the IR absorption spectrum, which was used to identify the geometry of Si$_n$ (n = 6, 7, 9, and 10).\textsuperscript{23,24}

The second approach, which is followed in the present work, uses infrared multiple photon dissociation (IR-MPD) of cluster-rare gas complexes in combination with post-ionization. The technique is described in Sec. II and was used before to identify the structures of neutral bare Si$_n$ (n = 8, 9, and 15),\textsuperscript{24} cationic bare Si$_n^+$ (n = 6−21),\textsuperscript{7} and cationic metal doped Si clusters.\textsuperscript{10,11}

In this paper we discuss the geometry of small neutral vanadium and manganese doped silicon clusters, Si$_n$V (n = 6−9) and Si$_n$Mn (n = 6, 8, and 9), using infrared multiple photon dissociation of the cluster−rare gas complexes combined with DFT calculations at the B3P86/6-311+G(d) level. Vanadium ([Ar] 3d$^{4}$4s$^{2}$) and manganese ([Ar] 3d$^{5}$4s$^{2}$) are chosen as dopant atoms because they both have an unﬁlled 3d-shell, but nonetheless show very distinct magnetic properties. We investigate the inﬂuence of these dopant atoms on the structure of the silicon clusters. The identiﬁed structures of the neutral doped silicon clusters are compared with their cationic counterparts\textsuperscript{10,11} and the inﬂuence of the charge state on the geometric and electronic structures of the clusters is analyzed.

II. EXPERIMENTAL AND THEORETICAL METHODS

The far-infrared spectroscopy experiments are performed at the Free Electron Laser for Infrared eXperiments (FELIX) facility of the FOM Institute for Plasma Physics “Rijnhuizen” in Nieuwegein, the Netherlands.\textsuperscript{25} The doped silicon clusters are produced in a two-stage molecular beam setup, containing a dual-target dual-laser vaporization source\textsuperscript{26} and a time-of-flight mass spectrometer, which is connected to a beamline of FELIX.\textsuperscript{27}

Transition metal doped clusters are formed by ablation of the two target materials using two independent Nd:YAG lasers and subsequent condensation of the ablated atoms in a He atmosphere containing a small fraction (0.6% for Si$_n$V and 2% for Si$_n$Mn) of isotopically enriched $^{129}$Xe. This small portion of xenon atoms in the carrier gas is needed to form the cluster−rare gas complexes, which are used to monitor the light absorption. Isotopically enriched $^{129}$Xe is used in order to reduce the number of isotopeomers present in the mass spectra. Given the natural isotope distribution of silicon and xenon, mass spectral overlap of the different species present in the molecular beam, Si$_n$X$_m$ · Xe$_p$ (n = 6−17, m = 0−2, p = 0, 1, X = V, Mn), would otherwise hamper unique identiﬁcation of a given mass peak. Thermalization of the clusters and formation of the cluster−rare gas complexes occur in a cooled extension channel of the source held at a constant temperature of 90 K. The cluster formation stops by expansion into vacuum, which creates a molecular beam. The central part of the molecular beam is skimmed using a 2 mm diameter skimmer. The beam thereafter passes through a second aperture (1 mm diameter), which ensures a good spatial overlap between the molecular beam and the FELIX laser light. The aperture is placed at a potential to deﬂect charged particles out of the molecular beam. The remaining neutral clusters are then ionized by a weakly focused beam of vacuum-ultraviolet (VUV) photons of 7.87 eV energy from an F$_2$ gas laser. For the considered size range of clusters, Si$_n$ (n = 6−9), Fuke \textit{et al.} reported ionization energies in the range of 7.46−7.90 eV.\textsuperscript{28} The ionization energy of V and Mn doped clusters is expected not to be signiﬁcantly higher than that of pure silicon clusters, since the ionization energies of the V atom (6.75 eV) and the Mn atom (7.43 eV) are below that of the Si atom (8.16 eV). The photon ﬂuence of the F$_2$ gas laser is kept low to avoid photofragmentation and to ensure single photon ionization.\textsuperscript{29}

Typical mass spectra of neutral vanadium and manganese doped silicon clusters are presented in Figure 1. It should be noted that due to diﬀerent ionization eﬃciencies, relative intensities of diﬀerent cluster sizes in the mass spectra (after postionization) may diﬀer from relative intensities in the cluster beam.\textsuperscript{28,30} Since relative intensities are not compared with one another, this has no inﬂuence on the resulting IR-MPD spectra. Only speciﬁc cluster sizes attach a xenon atom and could be postionized under the current experimental conditions, i.e., Si$_6$V (n = 6−9) and Si$_6$Mn (n = 6, 8, 9). For larger sizes Xe attachment might be hampered by the formation of endohedral clusters, where the dopant atom moves inside a silicon cage.\textsuperscript{31} For selected sizes the ionization eﬃciency of the cluster−Xe complex can be low at 7.87 eV. For instance, the abundance of postionized Si$_7$Mn and Si$_7$Mn · Xe is low under the current experimental conditions. The calculated adiabatic ionization energy of Si$_7$Mn is close to 7.87 eV, while we calculated lower values for Si$_6$Mn (7.23 eV), Si$_8$Mn (7.52 eV), and Si$_9$Mn (7.38 eV). Alternatively, the cluster−Xe bond in Si$_7$Mn · Xe may be particularly weak and the complex does not survive on the timescale of the experiment. The mass of
Si₈Mn differs only 1 u from that of Si₉⁺. Therefore, the IR-MPD spectra of the Si₈Mn clusters are recorded on the first isotope of the Si₈Mn·Xe complexes solely, to exclude mass coincidence with Si₉⁺·Xe.

Resonant absorption of IR photons and internal vibrational energy redistribution heat the clusters and may result in evaporation of the weakly bound Xe messenger atom. IR-MPD spectra are obtained in an alternating “light on—light off” manner, by recording the ion intensities of the cluster—xenon complexes as a function of FELIX photon energy (230–550 cm⁻¹), macropulses of 5–8 µs, linewidth 3–4 cm⁻¹. The intensities of the signal of a specific cluster with and without IR laser light are compared, resulting in depletion spectra from which the final IR absorption spectra can be calculated. These spectra are normalized according to the laser fluence.

To assign the structures of the investigated clusters, the measured IR-MPD spectra of the cluster—xenon complexes are compared with simulated infrared absorption spectra for different low-energetic isomers using density functional theory (DFT). The calculations are performed using the B3P86 hybrid functional and the 6-311+G(d) basis set. The B3P86 functional is composed of Becke’s hybrid 3-parameter exchange and the P86 non-local correlation, and has the same percentage of exact Hartree-Fock exchange (20%) as B3LYP. The B3P86 functional was selected, because it was shown to predict the infrared spectra of cationic Si₉⁺Mn⁺ (n = 6–16) clusters best, without the need for a scaling factor.¹¹ The initial geometries for the structural optimization are selected on the basis of the known isomers of cationic Si₉⁺ and Si₈⁺Mn⁺,¹⁰,¹¹ and structures derived from bare Si₉ cluster,²³,²⁴ where the dopant atom is added to the surface or substitutes an atom of the silicon framework. All the calculations are performed using the GAUSSIAN 03 package.³⁴ Atomic charges and local magnetic moments are evaluated based on natural population analysis which is performed at the same level of theory using the NBO 5.3 program.³⁵ Simulated infrared absorption spectra are folded with a Gaussian lineshape of 3 cm⁻¹ full width at half maximum (FWHM) corresponding to the linewidth of the infrared light source.

III. RESULTS AND DISCUSSION

The following discussion is organized in three parts. First, the IR-MPD spectra of neutral Si₉⁺V and Si₈⁺Mn are presented and compared with the infrared absorption spectra of the computed lowest energy isomers. Second, the structures and growth mechanisms of the neutral clusters are compared with their cationic counterparts. Finally, the influence of the added electron (from cation to neutral) on the electronic structure of Si₉⁺V⁺ and Si₈⁺Mn⁺ is discussed.

To assign the structures of the clusters using the IR-MPD spectra of the cluster—xenon complexes, the influence of the xenon messenger atom is explicitly taken into account in the computed harmonic vibrational spectra of the predicted lowest-energy isomers. The computed harmonic vibrational spectra of the lowest-energy isomer without Xe messenger atom are shown in the supplementary material.³⁶ Comparing the harmonic absorption spectrum of the lowest-energy isomer with and without xenon attached shows that the xenon might induce small shifts in the energy of some vibrational modes (typically less than 15 cm⁻¹). On the other hand, the xenon attachment can have a significant effect on the intensity of the infrared absorption bands. The calculations show for all investigated clusters that the Xe messenger atom binds to the transition metal dopant atom. The strengths of Xe—V and Xe—Mn bonds calculated by comparison of the total energies of the Si₈⁺V clusters and the Si₈⁺·Xe complexes are in the range of 0.2–0.3 eV. Earlier studies have shown that Xe binding energies on pure Si₈ clusters are weaker (of the order of 0.1 eV),²⁶,²⁴ with the exception of Si₉⁺ for which a Xe binding energy of 0.30 eV was found.³⁷ The addition of Xe has a marginal effect on the relative ordering of the isomers (taking into account a typical uncertainty of the computational method). It should, however, be noted that the used B3P86 level of theory does not explicitly describe long range van der Waals interactions.

Before making a detailed comparison of the IR-MPD spectra with the infrared absorption spectra we remark that a perfect agreement between theory and experiment cannot be expected for several reasons. The calculations use a harmonic single photon approach, whereas the IR-MPD experiment is a multiphoton experiment and potentials are anharmonic. Anharmonicities and multiphoton effects result in shifts between the harmonic absorption and the fragmentation spectra and can have a significant effect on the intensities of the bands.³⁸ Moreover, DFT approaches have difficulties to properly describe the influence of the cluster—Xe bond on the infrared spectrum. A good match between theory and experiment usually implies that the number of infrared active bands is correctly reproduced (although near degeneracy might make it difficult to count), and that vibrational frequencies are predicted with an accuracy better than about 5%. Relative intensities of bands can be, however, difficult to reproduce using a harmonic single photon approximation.

A. Infrared absorption spectra of Si₉⁺V (n = 6–9)

A comparison of the IR-MPD spectra of the Si₉⁺V·Xe complexes (n = 6–9) and the corresponding computed harmonic vibrational spectra of the predicted lowest-energy isomers at the B3P86/6-311+G(d) level of theory is presented in Figure 2. The geometric structures of other low-energetic isomers and their corresponding infrared spectra are shown in the supplementary material.³⁶ Notably, the overall shapes of the experimental spectra for the different sizes are quite different. In particular, the observed bandwidths can be rather different, e.g., compare Si₇⁺V and Si₈⁺V. Since the depletion spectra of all cluster sizes for a given dopant atom are measured simultaneously, the different bandwidths cannot be related to changes in the spectral bandwidth of the IR source. One possibility for the broader bands might be the presence of isomers with overlapping bands that could lead to a blurring of the experimental spectrum. We have, however, no clear indication for this from the theoretical studies. Another reason might be a fluxional behavior as previously observed for certain systems, e.g., for Si₈⁺V.¹²
The IR-MPD spectrum of neutral Si$_6$V, measured on the Si$_6$V$\cdot$Xe complex, is characterized by one intense absorption band centered at 390 cm$^{-1}$. Less intense features at lower and higher wavenumbers are also visible. The calculated ground state is a quartet and the spectrum of its xenon complex fits the experimental infrared absorption spectrum. The lowest-energy isomer of Si$_6$V is located on a V–Si–Si face.

2. Si$_7$V

The calculated IR spectrum of the lowest-energy isomer of Si$_7$V$\cdot$Xe and the corresponding IR-MPD spectrum are shown in Figure 2. Several broad absorption features are measured between 250 and 410 cm$^{-1}$. The calculated absorption spectrum of the xenon complex of the lowest-energy structure, a face-capped pentagonal bipyramid with $C_s$ symmetry in a doublet state, shows infrared active bands within the range of the experimentally observed bands, except for the band at the highest frequency (447 cm$^{-1}$). The lowest frequency bands do not show a conclusive match and the overall intensity pattern fits less well. However, also higher energy isomers do not give a better match (see supplementary material). The cationic counterpart, Si$_7$V$^+$, was also found to be a face-capped pentagonal bipyramid, although the position of the capping silicon atom differs. In the cationic Si$_7$V$^+$ this atom caps an “all silicon” face, while the capping atom for the neutral Si$_7$V is located on a V–Si–Si face.

3. Si$_8$V

This size shows, different to Si$_7$V$\cdot$Xe, a distinct experimental spectrum with good signal-to-noise ratio and relatively sharp bands with a FWHM of around 10 cm$^{-1}$. A very good agreement between the experiment and the computations is found for a double face-capped pentagonal bipyramidal structure ($C_{2v}$) in a doublet state, which is also calculated to be the lowest-energy isomer. Here, the vanadium atom occupies an eightfold coordinated position and the cluster has only triangular faces. The calculated band positions and their relative intensities correspond nicely with the experimental spectrum. The minor deviation around 300 cm$^{-1}$, where the experimental spectrum has two low intensity bands and the calculated spectrum only one, most likely is related to an underestimate of the frequency differences between the close lying peaks at 295, 298, and 302 cm$^{-1}$ in the calculated spectrum. Higher-energy isomers, built up by capping the pentagonal bipyramid structure of Si$_8$V, do not show good correspondence with the experiment (see supplementary material), assuring that the double face-capped pentagonal bipyramidal structure is indeed the isomer that is present in the molecular beam.

4. Si$_9$V

The experimental IR-MPD spectrum of Si$_9$V$\cdot$Xe shows broader and less pronounced bands than that of Si$_8$V$\cdot$Xe. The lowest-energy structure found, electronically a doublet, fits the experiment best in many details. This structure is obtained by capping one of the “all silicon” faces of Si$_9$V, and is similar to the tricapped pentagonal bipyramid structure of Si$_9$V$^+$, however, with a small distortion along the pentagonal ring. The vanadium atom remains 8-fold coordinated while the extra silicon atom gives the onset for cage formation at larger sizes, towards an endohedral structure with the dopant atom inside the cage. The experimental spectrum is well reproduced by this isomer, though the presence of multiple isomers cannot be excluded. Between 410 and 450 cm$^{-1}$ experimentally two peaks are seen but only a single peak is predicted for the lowest-energy isomer. Two slightly higher lying isomers iso 2 [+0.09 eV] and iso 3 [+0.11 eV] have bands in these ranges (see supplementary material) and their additional presence (one or both) could explain the remaining experimental bands.

Summarizing, we find a good agreement between theory and experiment for Si$_9$V and Si$_8$V. The agreement for Si$_9$V is reasonable, though the presence of additional isomers cannot be excluded. The structural assignment of Si$_7$V is not conclusive.
B. Infrared absorption spectra of Si$_n$Mn ($n = 6, 8, \text{and} 9$)

The IR-MPD spectra of the Si$_n$Mn·Xe complexes ($n = 6, 8, \text{and} 9$) are compared with the computed harmonic vibrational spectra of the lowest-energy isomers in Figure 3. For Si$_8$Mn, no definite structural assignment could be made based on a single isomer (see below); therefore, the second lowest-energy isomer, which is only 0.16 eV higher in energy, is presented in addition. No experimental IR-MPD spectrum for Si$_7$Mn·Xe could be recorded, as it is not abundant in the mass spectrum.

1. Si$_6$Mn

A good agreement is found between the IR-MPD spectrum of Si$_6$Mn·Xe and the calculated spectrum of the lowest-energy isomer, a sextet state with a $C_{2v}$ pentagonal bipyramid structure where the Mn atom takes one of the equatorial positions of the pentagon. The low energy part of the experimental spectrum (below 380 cm$^{-1}$) is well reproduced by the calculations. The higher energy part of the spectrum is dominated by a strong narrow band at 431 cm$^{-1}$ and can be related to a calculated double peak of similar frequency. Additional features in the IR-MPD spectrum at 388 cm$^{-1}$ and around 455 cm$^{-1}$ are not explained by this structure and point to the possible presence of an additional (still unidentified) isomer.

![IR-MPD spectra of Si$_6$Mn·Xe complexes](image)

**FIG. 3.** IR-MPD spectra (upper traces) of Si$_6$Mn·Xe complexes ($n = 6, 8, \text{and} 9$) and the corresponding calculated vibrational spectra of the xenon complexes of the lowest-energy isomers (lower traces). For Si$_6$Mn, the second lowest-lying isomer is also presented. The geometries are shown as insets next to their corresponding computed vibrational spectra. The experimental data points (red crosses) are overlaid with a three-point running average. The computed infrared spectra are calculated at the B3P86/6-311+G(d) level.

2. Si$_8$Mn

The IR-MPD spectrum of Si$_8$Mn·Xe has two main absorption regions: the low-energy region consisting of three clear peaks at 292, 303, and 314 cm$^{-1}$, and a high-energy region between 375 and 465 cm$^{-1}$. Many structural isomers are located (see supplementary material), but none shows a one-to-one agreement with the experiment. A combination of the two calculated lowest-lying isomers (iso 1—sextet [C$_8$, 0 eV] and iso 2—quartet [C$_7$, +0.16 eV], both bicapped pentagonal bipyramids) might explain the absorption spectrum in the low-energy region, although the infrared active modes of iso 2 have much lower intensities. The high-energy region cannot be explained by a coexistence of these two isomers. Therefore, no conclusive assignment can be made for Si$_8$Mn, which might imply that the correct isomer has not been found yet. In the following discussion, both lowest-lying isomers will be considered.

3. Si$_9$Mn

The IR-MPD spectrum of Si$_9$Mn·Xe is characterized by several distinct bands that are well reproduced by the infrared spectrum of the computed lowest-energy isomer. The assigned isomer is a sextet having a symmetry broken tetrahedron structure, similar to the structure found for the bare Si$_{10}^+$ with the Mn atom substituting a Si atom of the trigonal prism.

Summarizing, the structural assignment of Si$_6$Mn and Si$_8$Mn is conclusive, though for Si$_9$Mn the presence of a second isomer cannot be excluded. For Si$_9$Mn we cannot be sure that the correct isomer has been identified.

C. Influence of the charge state on the electronic structure of Si$_n$V$^{+,0}$ and Si$_n$Mn$^{+,0}$

A population analysis is performed on the basis of the density of states (DOS) of both charge states. Atomic charges, local magnetic moments on the dopant atom, and the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are calculated. The HOMO-LUMO gap, in the case of open electronic shell systems, is computed between the highest of the HOMOs and the lowest of the LUMOs, regardless of the spin type. For all studied clusters, except Si$_7$Mn (related to the particular magnetic structure of Si$_7$Mn$^+$), the electron added when going from the cation to the neutral occupies an orbital corresponding to the majority (alpha) spins. This follows from the singlet-doublet, triplet-quartet, and quintet-sextet transitions upon electron addition. Therefore, in the following, the DOS is discussed by considering the majority spin orbitals solely.

For Si$_8$V$^{+,0}$ (and also for Si$_9$V$^{+,0}$) the HOMO and LUMO levels are majority spin orbitals and the neutral and cationic clusters have a similar structure. As a result their electronic structure is very similar with exception of the occupation of the frontier orbitals. It is found that the LUMO of the cation is similar to the HOMO of the neutral cluster, as is...
FIG. 4. An overview of the frontier molecular α-orbitals of Si₆V⁺,0 and Si₉V⁺,0. The geometry of the clusters is shown in Figure 5.

visualized by the molecular majority spin orbitals in Figure 4. Such a behavior can only happen when the structures of both the cation and neutral are similar and when the HOMO and LUMO of the cation have the same spin. The LUMO of Si₆V⁺ consists of 63% V-d, 17.5% Si-5,6-p, 9.6% Si-2,3-p, which is very alike to the HOMO of Si₆V₀ (62% V-d, 18.5% Si-5,6-p, 7.2% Si-5,6-s, 8.2% Si-2,3-p). The atom numbering is represented in Figure 5. Similarly, the LUMO of Si₉V⁺ (8.3% V-d, 30% Si-1,5-s, 26.4% Si-2,4-s, 12% Si-8,9-s, 8.2% Si-1,5-p, 6.8% Si-2,4-p) resembles the highest SOMO of Si₉V₀ (8.8% V-d, 30.4% Si-1,5-s, 23.6% Si-2,4-s, 12% Si-8,9-s, 7.4% Si-2,4-p).

NBO local charge analysis demonstrates that for most studied sizes the charge on the transition metal dopant atom does not change significantly upon electron addition (see Table I). Si₈V is an exception in this respect as the vanadium atom receives a large fraction of the added electron, in comparison with the other clusters.

It was recently demonstrated that the manganese dopant atoms in cationic SiₙMn⁺ (n = 6–10) clusters carry large local magnetic moments of 4 μₜ to 6 μₜ. It was also found that the structures of SiₙMn⁺ (n = 6–10) can markedly be described as substitution derivatives of the bare Siₙ⁺ cations in spite of the very different electronic nature of Si and Mn. The comparison of neutral and cationic SiₙMₙ⁺,0 in Figure 5 and the results of the natural population analysis in Table I demonstrate that, with the exception of Si₇Mn, also the neutral SiₙMₙ clusters are substitution derivatives of Siₙ⁺ with a large local magnetic moment on the manganese dopant atom.

FIG. 5. Overview of the assigned structures of neutral and cationic clusters SiₙX⁺,0 (n = 6–9; X = V, Mn). The structure presented for Si₇Mn⁺ corresponds to the calculated lowest-energy isomer. The structures of the cationic SiₙV⁺ and SiₙMₙ⁺ are taken from Refs. 10 and 11, respectively. The Si atoms numbering is used in the discussion on the influence of the charge state.

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<th>HOMO − LUMO gap (eV)</th>
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IV. CONCLUSION

The structures of $\text{Si}_n\text{V} \ (n = 6\text{−}9)$ and $\text{Si}_n\text{Mn} \ (n = 6, 8, 9)$ are identified by comparing measured IR-MPD spectra of the cluster-Xe complexes with simulated infrared absorption spectra for different structural isomers found at the B3P86/6-311+G(d) level of theory. For all clusters, the best agreement was obtained with the located lowest energy isomers. Although no definite assignment could be made for $\text{Si}_8\text{Mn}$, the structures of the neutral clusters are compared with their cationic counterparts from earlier studies. The geometric structures of the neutral exohedrally doped silicon clusters do not differ much from their cationic counterparts, but, slight differences in positions of capping atoms are found. This similarity is also reflected in the electronic structure where the added electron will occupy the majority spin LUMO orbital of the cationic species. The analysis of the NBO charge on the transition metal atom shows that most of the extra electron, when changing charge state, is distributed over the entire silicon framework.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) for providing beam time on FELIX. The authors thank the FELIX staff for their skillful assistance, in particular Dr. B. Redlich and Dr. A. F. G. van der Meer. P.C. thanks D. Aguilar FELIX staff for their skillful assistance, in particular Dr. B. Oepts and C.02, Gaussian, Inc., Wallingford, CT, 2004.


40E. D. Glendening et al., NBO 5.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2004.
41See supplementary material at http://dx.doi.org/10.1063/1.4803871 for a more detailed comparison between the infrared absorption spectra of several low-energetic $\text{Si}_X\text{V} \ (n = 6\text{−}9; X = \text{V, Mn})$ isomers, calculated at the B3P86/6-311+G(d) level of theory, and the experimental IR-MPD spectra recorded on the corresponding $\text{Si}_X\text{V}$-Xe complexes. Also, low-lying isomers of $\text{Si}_X\text{Mn}$ calculated at the same level of theory are presented.