

## Tuning the Geometric Structure by Doping Silicon Clusters

Philipp Gruene,<sup>[a]</sup> André Fielicke,<sup>\*[a]</sup> Gerard Meijer,<sup>[a]</sup> Ewald Janssens,<sup>[b]</sup> Vu Thi Ngan,<sup>[c]</sup> Minh Tho Nguyen,<sup>[c]</sup> and Peter Lievens<sup>\*[b]</sup>

Ever since the discovery of  $C_{60}$ , much effort has been expended in search of similar, finite-size stable clusters as building blocks for nanostructures.<sup>[1]</sup> Apart from carbon, silicon has attracted much attention due to its vicinity to carbon in the periodic table as well as its importance in the semiconductor industry. In contrast to carbon, however, silicon favours  $sp^3$  hybridization and thus tetrahedral coordination, which leads to rather asymmetric and reactive structures for small, bare silicon clusters.<sup>[2,3]</sup> It has been argued that this deficiency can be solved by suitable doping of silicon clusters with transition metal ions.<sup>[4]</sup> Following up on this idea, many theoretical studies have investigated  $Si_nM$  structures for various dopants and cluster sizes.<sup>[5,6]</sup> Experimental information on doped silicon clusters has been obtained from mass spectrometry,<sup>[7]</sup> photoelectron spectroscopy (PES),<sup>[8]</sup> chemical probe methods,<sup>[8,9]</sup> and photodissociation studies at fixed wavelengths.<sup>[10]</sup>

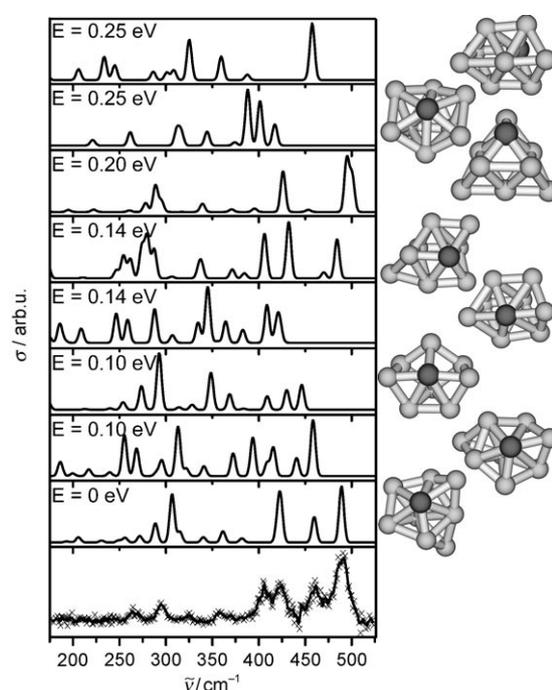
While there is no doubt that the structure of silicon clusters can be changed upon appropriate doping, detailed experimental studies on the growth mechanisms of doped silicon clusters are rather scarce, as it is difficult to investigate the structure of gas phase clusters experimentally. A deep knowledge about the influence of the dopant on the clusters' structure, however, is necessary for the design and production of tailor-made silicon materials.

It has recently been shown that infrared multiple photon dissociation (IR-MPD) of complexes of metal clusters with rare-gas atoms is a suitable experimental technique to obtain vibrational spectra for clusters in the gas phase.<sup>[11]</sup> Comparison of experimental IR-MPD spectra of clusters with those obtained in calculations for different geometries, for example by using density functional theory (DFT), allows for the deduction of the cluster-size-specific structures.<sup>[12]</sup>

Herein we present the vibrational spectra of the small cationic copper- and vanadium-doped silicon clusters  $Si_nCu^+$  and

$Si_nV^+$  ( $n=6-8$ ). Copper- and vanadium-doped silicon clusters show the same critical size for the transition from endohedral to exohedral structures, which has been rationalized by the similar atomic radii of the dopants.<sup>[9]</sup> It is thus interesting to investigate whether doping with these two atoms will generate clusters with the same geometric structure.

Figure 1 shows the vibrational spectra of  $Si_8V^+$ . The experimental spectrum (bottom panel) is obtained upon IR-MPD of its complex with one argon atom. In the case of resonant ab-



**Figure 1.** Vibrational spectra of  $Si_8V^+$ . The lower trace shows the experimental multiple photon dissociation spectrum of the corresponding complex with one argon atom. It is compared to the calculated stick spectra for low-lying isomers. The calculated stick spectra are folded with a Gaussian line width function of  $5\text{ cm}^{-1}$  full width at half-maximum for ease of comparison. The experimental data points are overlaid with a three-point running average to guide the eyes.

sorption of one or several far-infrared photons, delivered by the 'Free Electron Laser for Infrared eXperiments' (FELIX), the cluster heats up. This eventually leads to evaporation of the loosely bonded argon atom and depletion of the complex in the mass spectrum. The IR absorption cross section  $\sigma$  is constructed by recording the ion intensities of the cluster-argon complexes as a function of the FELIX frequency (see the Experimental Section). It is characterized by at least four strong ab-

[a] P. Gruene, Dr. A. Fielicke, Prof. Dr. G. Meijer  
Fritz-Haber-Institut der Max-Planck-Gesellschaft  
Faradayweg 4–6, 14195 Berlin (Germany)  
Fax: (+49) 30-8413-5603  
E-mail: fielicke@fhi-berlin.mpg.de

[b] Dr. E. Janssens, Prof. Dr. P. Lievens  
Department of Physics and Astronomy and INPAC-Institute for Nanoscale  
Physics and Chemistry, University of Leuven  
Celestijnenlaan 200D, 3001 Leuven (Belgium)  
E-mail: peter.lievens@fys.kuleuven.be

[c] V. T. Ngan, Prof. Dr. M. T. Nguyen  
Department of Chemistry and INPAC-Institute for Nanoscale Physics and  
Chemistry, University of Leuven  
Celestijnenlaan 200F, 3001 Leuven (Belgium)

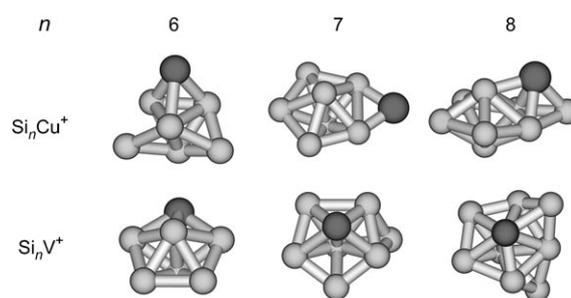
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sorption lines between 400 and 500  $\text{cm}^{-1}$  and additional, less intense features between 275 and 375  $\text{cm}^{-1}$ .

These features can be compared with calculated IR absorption spectra for low-lying isomers. The number of possible geometrical isomers increases rapidly for increasing cluster size and this holds especially true for binary systems. In fact, our extended search for structural isomers resulted in a large variety of local minimum structures—many of which are very close in energy. Figure 1 shows the calculated spectra for the eight lowest-lying isomers (see the Supporting Information for a more detailed description), which are all in a singlet electronic state and lie within 0.25 eV, relative to the lowest energy isomer. A structural assignment of the clusters, based only on quantum chemical calculations, is thus not straightforward.

For  $\text{Si}_6\text{V}^+$ , most of the experimental spectral features are reproduced in the simulated spectrum of isomer 1—the calculated minimum energy structure. Its structure is that of a bicapped pentagonal bipyramid with the dopant atom in an axial position. The peak positions are in good agreement, although the experimental doublet at  $\sim 420 \text{ cm}^{-1}$  and  $430 \text{ cm}^{-1}$  is split by three wavenumbers only in the calculation and appears as a single line in the simulation. The peak intensities deviate between theory and experiment. In particular, the low-energy absorptions around  $300 \text{ cm}^{-1}$  are less pronounced in the experiment, which could be due to the larger number of photons needed for photodissociation. Furthermore, one has to keep in mind that the IR–MPD spectra do not correspond directly to linear absorption spectra.<sup>[13]</sup> Upon comparison of experiment and theory, the coexistence of isomers, which is known for bare silicon clusters in certain size ranges,<sup>[2]</sup> cannot be excluded. However, the experimental spectrum can be explained almost completely by a single isomer and without radiation, the absorption at  $\sim 490 \text{ cm}^{-1}$  leads to depletion down to 25% of the initial ion intensity that is measured without IR irradiation. Thus, the major fraction of  $\text{Si}_6\text{V}^+$  can be assigned to the most stable isomer 1.

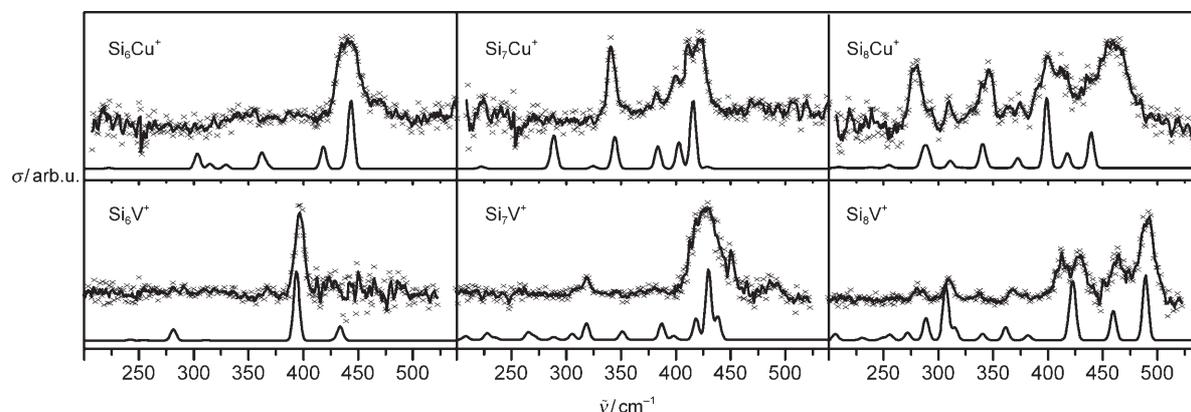
Figure 2 shows the experimental and theoretical vibrational spectra of  $\text{Si}_n\text{Cu}^+$  and  $\text{Si}_n\text{V}^+$  ( $n=6-8$ ). Only the theoretical spectrum of the particular isomer that best reproduces the experimental spectrum is shown (see the Supporting Information



**Figure 3.** Structures of  $\text{Si}_n\text{Cu}^+$  (top) and  $\text{Si}_n\text{V}^+$  (bottom) ( $n=6-8$ ) of which the calculated vibrational spectra fit best the experimental findings.

for a detailed comparison of experiment with various low-lying isomers). The corresponding structures are shown in Figure 3. The good agreement between experiment and theory justifies refraining from time-consuming global optimization algorithms for these smaller clusters. In almost all cases, the experimental spectrum is reproduced best by the calculated lowest-energy structure. With one exception, all of these are in a singlet electronic state. For  $\text{Si}_6\text{V}^+$ , theory finds a Si-capped octahedron as the lowest-energy structure, while the experiment is reproduced much better by the spectrum of a triplet state pentagonal bipyramid with vanadium in an equatorial position, which is calculated to be 0.03 eV higher in energy. Interestingly, the experiment does not show any features that would point to the coexistence of a second isomer, although the isomers are calculated to be extremely close in energy. However, due to the limited signal-to-noise ratio of the experimental spectra, the presence of trace amounts of other isomers cannot be completely excluded.

For  $\text{Si}_7\text{Cu}^+$ , theory finds two singlet isomers with similar geometries, which are separated by only 0.12 eV. Both consist of a pentagonal bipyramid of silicon atoms. For the isomer calculated to be lowest in energy, copper binds to the equatorial edge, whereas for the higher-lying isomer, the dopant atom is situated in a more facial position. Both isomers are characterized by similar IR spectra, which makes the structural assignment difficult. Additionally, the lowest-energy isomer shows



**Figure 2.** Vibrational spectra of  $\text{Si}_n\text{Cu}^+$  (top row) and  $\text{Si}_n\text{V}^+$  (bottom row) ( $n=6-8$ ). The upper traces in each panel show the experimental multiple photon dissociation spectra of the corresponding complex with one argon atom. They are compared to the calculated vibrational spectra of the best fitting isomer.

absorptions at around  $280\text{ cm}^{-1}$ , which are absent in the experimental spectrum. However, the spectral features between  $350$  and  $450\text{ cm}^{-1}$  agree well and the not-negligible energy difference between the two calculated structures points towards an edge-capped position of the copper atom.

The structures obtained for differently doped silicon clusters can now be compared among themselves as well as with the predicted structures of bare cationic silicon clusters in order to elucidate the influence of the dopant. There is general agreement about the structures of small cationic silicon clusters.<sup>[14]</sup> For  $\text{Si}_6^+$ , an edge-capped trigonal bipyramid is found to be the lowest-energy structure.  $\text{Si}_7^+$  is a distorted pentagonal bipyramid of  $C_{2v}$  symmetry, while  $\text{Si}_8^+$  is a bicapped distorted octahedron, also of  $C_{2v}$  symmetry. There is less consensus for  $\text{Si}_9^+$ , with various structures found in the literature. In principle, three types of doped silicon structures are possible. The dopant can 1) add to or 2) substitute a silicon atom in a bare silicon cluster structure or it can 3) induce a complete geometric reconstruction.  $\text{Si}_6\text{V}^+$  is an example of the second type, in which vanadium adopts the position of a silicon atom in the pentagonal bipyramid structure of  $\text{Si}_7^+$ . Copper doping leads instead to the third type, resulting in a new structure that can be described as a distorted bicapped trigonal bipyramid with copper sitting in an axial position. A very similar structure has been suggested previously.<sup>[5]</sup> The resulting  $\text{Si}_6\text{Cu}^+$  has been shown to be especially stable in photodissociation studies.<sup>[10]</sup> The situation changes for the clusters with one more silicon atom. Now copper leads to a structure that belongs to the first type. The copper dopant simply adds to the equatorial edge of a  $\text{Si}_7^+$  pentagonal bipyramid. This structure is supported by photodissociation experiments, in which  $\text{Si}_7^+ + \text{Cu}$  is the primary dissociation channel for  $\text{Si}_7\text{Cu}^+$ .<sup>[10]</sup> Vanadium prefers a higher coordination and occupies the axial position of a pentagonal bipyramid which is face-capped by a silicon atom, thus creating a whole new structure. In  $\text{Si}_8\text{V}^+$ , a silicon atom is added to the face of  $\text{Si}_7\text{V}^+$ , further increasing the coordination of the dopant. The pentagonal bipyramid backbone is also retained in the case of  $\text{Si}_8\text{Cu}^+$ , this time, however, entirely consisting of silicon atoms. The copper dopant occupies a face of the bipyramid and additionally coordinates to an edge-capping silicon atom. Again, the structure is not related to that of any bare silicon cluster.

In summary, we have obtained detailed insights into the structural properties of doped silicon clusters upon comparison of the IR-MPD vibrational spectra of their complexes with argon, and theoretical IR absorption spectra for various low-lying isomers. It is shown how three different types of doped clusters are formed; the dopant can simply add to a bare silicon cluster ( $\text{Si}_7\text{Cu}^+$ ), it can substitute a silicon atom of a bare cluster ( $\text{Si}_6\text{V}^+$ ), or it can lead to a complete structural reconstruction producing entirely new geometries ( $\text{Si}_6\text{Cu}^+$ ,  $\text{Si}_7\text{V}^+$ ,  $\text{Si}_8\text{Cu}^+$ ,  $\text{Si}_8\text{V}^+$ ). Especially the latter type opens the door for tailoring the properties of doped silicon clusters.

## Experimental Section

The IR-MPD experiments are carried out on a molecular beam setup described previously, coupled to the beamline of the 'Free Electron Laser for Infrared eXperiments' (FELIX).<sup>[15,16]</sup> Doped silicon clusters are prepared by pulsed-laser vaporization and condensation in a mixture of helium and argon using a dual target source.<sup>[9,17]</sup> In a cooled reaction channel doped silicon-argon complexes form and pass through a skimmer and an aperture of  $1\text{ mm}$  in diameter before entering the extraction region of a reflectron time-of-flight mass spectrometer. A counter-propagating pulsed far-IR beam delivered by FELIX is overlapped with the clusters in the beam. Resonant absorption of IR light by the cluster complex may lead to the evaporation of the argon ligand and depletion of the complex in the beam. Depletion spectra are constructed by recording the ion intensities of the argon complexes as a function of the FELIX frequency. From this, the far-infrared absorption spectra are obtained.<sup>[16]</sup>

## Computational Methods

All density functional theory calculations were carried out using the Gaussian03 package.<sup>[18]</sup> Geometries of clusters were optimized using the pure exchange-correlation BP86 functional in conjunction with the all-electron  $6-311+G(d)$  basis set. Harmonic vibrational frequencies calculated at the same level were uniformly scaled by a factor of  $1.03$ . IR intensities were plotted on an arbitrary scale relative to the largest peak. For each system, a large number of isomeric structures in different spin multiplicities were considered.

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- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162.
- [2] K.-M. Ho, A. A. Shvartsburg, B. Pan, Z.-Y. Lu, C.-Z. Wang, J. G. Wacker, J. L. Fye, M. F. Jarrold, *Nature* **1998**, *392*, 582.
- [3] a) A. A. Shvartsburg, R. R. Hudgins, P. Dugourd, M. F. Jarrold, *Chem. Soc. Rev.* **2001**, *30*, 26; b) S. Yoo, X. C. Zeng, *Angew. Chem.* **2005**, *117*, 1515; *Angew. Chem. Int. Ed.* **2005**, *44*, 1491.
- [4] H. Hiura, T. Miyazaki, T. Kanayama, *Phys. Rev. Lett.* **2001**, *86*, 1733.
- [5] C. Xiao, F. Hagelberg, W. A. Lester Jr., *Phys. Rev. B* **2002**, *66*, 075425.
- [6] a) J. Lu, S. Nagase, *Phys. Rev. Lett.* **2003**, *90*, 115506; b) P. Sen, L. Mitas, *Phys. Rev. B* **2003**, *68*, 155404; c) C. Majumder, S. K. Kulshreshtha, *Phys. Rev. B* **2004**, *70*, 245426; d) H. Kawamura, V. Kumar, Y. Kawazoe, *Phys.*

- Rev. B **2005**, *71*, 075423; e) J. Wang, J.-G. Han, *J. Chem. Phys.* **2005**, *123*, 064306; f) G. K. Gueorguiev, J. M. Pacheco, S. Stafstrom, L. Hultman, *Thin Solid Films* **2006**, *515*, 1192; g) N. Uchida, T. Miyazaki, T. Kanayama, *Phys. Rev. B* **2006**, *74*, 205427; h) L. Ma, J. Zhao, J. Wang, B. Wang, Q. Lu, G. Wang, *Phys. Rev. B* **2006**, *73*, 125439; i) E. N. Koukaras, C. S. Garoufalos, A. D. Zdetsis, *Phys. Rev. B* **2006**, *73*, 235417; j) L.-J. Guo, X. Liu, G.-F. Zhao, Y.-H. Luo, *J. Chem. Phys.* **2007**, *126*, 234704; k) M. B. Torres, E. M. Fernandez, L. C. Balbas, *Phys. Rev. B* **2007**, *75*, 205425.
- [7] a) S. M. Beck, *J. Chem. Phys.* **1989**, *90*, 6306; b) J. J. Scherer, J. B. Paul, C. P. Collier, R. J. Saykally, *J. Chem. Phys.* **1995**, *102*, 5190; c) S. Neukermans, X. Wang, N. Veldeman, E. Janssens, R. E. Silverans, P. Lievens, *Int. J. Mass Spectrom.* **2006**, *252*, 145; d) Z. Chen, S. Neukermans, X. Wang, E. Janssens, Z. Zhou, R. E. Silverans, R. B. King, P. v. R. Schleyer, P. Lievens, *J. Am. Chem. Soc.* **2006**, *128*, 12829.
- [8] K. Koyasu, J. Atobe, M. Akutsu, M. Mitsui, A. Nakajima, *J. Phys. Chem. A* **2007**, *111*, 42.
- [9] E. Janssens, P. Gruene, G. Meijer, L. Wöste, P. Lievens, A. Fielicke, *Phys. Rev. Lett.* **2007**, *99*, 063401.
- [10] J. B. Jaeger, T. D. Jaeger, M. A. Duncan, *J. Phys. Chem. A* **2006**, *110*, 9310.
- [11] A. Fielicke, A. Kirilyuk, C. Ratsch, J. Behler, M. Scheffler, G. von Helden, G. Meijer, *Phys. Rev. Lett.* **2004**, *93*, 023401.
- [12] K. R. Asmis, A. Fielicke, G. von Helden, G. Meijer, in *The Chemical Physics of Solid Surfaces., Vol. 12, Atomic Clusters: From Gas Phase to Deposited Atomic Clusters* (Ed.: D. P. Woodruff), Elsevier, **2007**, pp. 327.
- [13] J. Oomens, A. G. G. M. Tielens, B. G. Sartakov, G. von Helden, G. Meijer, *Astrophys. J.* **2003**, *591*, 968.
- [14] a) S. Wei, R. N. Barnett, U. Landman, *Phys. Rev. B* **1997**, *55*, 7935; b) R. Kishi, Y. Negishi, H. Kawamata, S. Iwata, A. Nakajima, K. Kaya, *J. Chem. Phys.* **1998**, *108*, 8039; c) A. A. Shvartsburg, B. Liu, M. F. Jarrold, K.-M. Ho, *J. Chem. Phys.* **2000**, *112*, 4517; d) S. Nigam, C. Majumder, S. K. Kulshreshtha, *J. Chem. Phys.* **2004**, *121*, 7756.
- [15] G. von Helden, D. van Heijnsbergen, G. Meijer, *J. Phys. Chem. A* **2003**, *107*, 1671.
- [16] A. Fielicke, G. von Helden, G. Meijer, *Eur. Phys. J. D* **2005**, *34*, 83.
- [17] W. Bouwen, P. Thoen, F. Vanhoutte, S. Bouckaert, F. Despa, H. Weidele, R. E. Silverans, P. Lievens, *Rev. Sci. Instrum.* **2000**, *71*, 54.
- [18] *Gaussian03, Revision C.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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