

Structures of Silicon Cluster Cations in the Gas Phase

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Abstract: We present gas-phase infrared spectra for small silicon cluster cations possessing between 6 and 21 atoms. Infrared multiple photon dissociation (IR-MPD) of these clusters complexed with a xenon atom is employed to obtain their vibrational spectra. These vibrational spectra give for the first time experimental data capable of distinguishing the exact internal structures of the silicon cluster cations. By comparing the experimental spectra with theoretical predictions based on density functional theory (DFT), unambiguous structural assignments for most of the Si_n^+ clusters in this size range have been made. In particular, for Si_8^+ an edge-capped pentagonal bipyramid structure, hitherto not considered, was assigned. These structural assignments provide direct experimental evidence for a cluster growth motif starting with a pentagonal bipyramid building block and changing to a trigonal prism for larger clusters.

Introduction

Silicon clusters have received considerable attention over the past two decades due, in part, to the dominant role of silicon nanostructures in the semiconductor industry. With the current trends in miniaturization, components in electrical devices may eventually reach cluster size ranges. Recent efforts have also been made toward making silicon nanowires, which potentially have structures resembling assemblies of smaller silicon clusters.¹ A particular characteristic of small clusters is the size dependence of their chemical and physical properties. For example, the geometric structures of silicon clusters are believed to follow different structural motifs depending on size that are dissimilar from pieces of the bulk material.^{2,3} Hence, understanding the precise structure of silicon clusters could aid in implementing silicon nanostructures with tailor-made properties.

Theorists have made many predictions about the geometries and properties of neutral silicon clusters,^{4–9} demonstrating that different ab initio and density functional methods predict varied ground-state structures.^{9–11} Although the ground-state geometries are not precisely known for most silicon clusters, they

have nevertheless been used as test cases for global optimization techniques.^{5,12} There exist fewer theoretical studies of the geometries of charged silicon clusters,^{13–18} but different ground-state structures have also been proposed for many of these ionic clusters. For example, theoretical proposals were reported for the structure of Si_8^+ as both a bicapped octahedron^{13,14} and a face-capped pentagonal bipyramid.¹⁵ Thus, there exists a need for experimental data to validate theoretical predictions.

Until now, vibrational spectroscopy on Si_n in inert matrices^{19–21} and vibrationally resolved anion photoelectron experiments^{22,23} have led to sound structural assignments of a number of Si clusters, although so far restricted to small ($n \leq 7$) neutral and anionic clusters. For ionic clusters, mass spectrometry has shown that Si_6^+ and Si_{10}^+ are “magic” clusters with enhanced stability.²⁴ Ion mobility measurements^{2,3,25–27} and photodissociation ex-

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periments in the ultraviolet/visible spectral region²⁸ have provided information on the shapes of silicon cluster cations and anions. Photoelectron experiments have additionally aided the search for the structures of negatively charged silicon clusters.^{22,23,29,30} However, apart from the vibrational spectroscopy experiments on small neutral and anionic clusters, these experimental techniques cannot distinguish between isomers possessing similar geometries.² Hence, there is a gap in the knowledge of the detailed structures of silicon clusters. The aim of this work is to address this issue for cationic clusters containing between 6 and 21 atoms. Vibrational spectra of Si_n^+ are obtained by infrared multiple photon dissociation (IR-MPD) of their complexes with Xe atoms. IR-MPD spectroscopy is an effective technique that in many cases yields infrared spectra similar to linear IR absorption spectra.³¹ By comparing the observed spectra with those predicted by quantum chemical calculations, we assign cluster geometries unambiguously.

Experimental and Theoretical Methods

Details of our IR-MPD experiments have been reported previously.^{32–34} In brief, silicon atoms were produced by laser ablation of a continuously moving silicon plate using the second harmonic output of a Nd:YAG laser.^{35,36} Clustering of the atoms took place in a pulsed flow of helium gas with a dilute concentration (0.5%) of enriched xenon-129. Tagging of the xenon atoms to the clusters was promoted by cooling the thermalization channel of the cluster source to approximately 100 K. The molecular beam was overlapped with a pulsed infrared (IR) beam from the Free Electron Laser for Infrared Experiments (FELIX)³⁷ in the 166–600 cm^{-1} range, and the size distribution of cationic clusters was then analyzed in a reflectron time-of-flight (TOF) mass spectrometer. In these experiments, FELIX pulses typically had durations of 6–8 μs with an average energy in the 20–50 mJ range. When a vibrational resonance of a specific sized Si_n^+ -Xe cluster occurred, absorption of several photons could lead to the evaporation of the xenon atom and a depletion of the signal in the mass spectrum. Hence, recording mass spectra while scanning FELIX led to depletion spectra of all of the Si_n^+ -Xe complexes present in the molecular beam simultaneously. Absorption spectra were then reconstructed from the depletion spectra.³³ These spectra were recorded in three independent runs from different beam time periods. The three sets of data points were interpolated with 0.5

cm^{-1} intervals to obtain a common x -axis spacing and subsequently averaged. In the experimental spectra reported here, the dots are the resulting original data points, while the line corresponds to a 7-point binomial weighted average to account for the line width of FELIX.

Quantum chemical calculations were performed to make structural assignments by comparing the predicted IR spectra for multiple isomers with the IR-MPD spectrum for each cluster size. All calculations were performed using the Gaussian 03 program.³⁸ The BP86 functional^{39,40} was employed, and silicon atoms were given a SVP basis set⁴¹ to model the silicon cluster cations. Given the complexity of including a xenon atom in the calculations, for example, the possibility of multiple bonding sites on each cluster isomer, only bare silicon cluster cations were computed. This approach appears justified by the overall good agreement between our IR-MPD spectra with those predicted by theory. However, to evaluate the influence of Xe on the spectra, for selected species a single Xe atom was included in the calculations. The results prove that in these cases the Xe had only a minor effect on band positions and IR intensities (Figure S1), which reflects the weak interaction of the rare gas atom with the cluster. B3LYP and BPW91 density functionals^{39,42,43} were additionally used with the 6-311+G(d) basis set⁴⁴ to test the effects of different methods and basis sets for select cluster sizes. For the pure DFT methods, the density fitting approximation was utilized.⁴⁵ In most cases, we noted similar results for the different levels of theory, with the lone exception being for Si_{11}^+ where the different methods yielded dissimilar infrared spectra for practically the same structures. Geometries of several structural isomers were converged without symmetry constraints, and vibrational frequencies were computed analytically. All reported structures of the Si_n^+ clusters are true minima, and all relative energy values given include zero-point vibrational corrections. Initial cluster geometries were either provided by the authors of refs 2 and 14 or taken from the Cambridge Cluster Database.⁴⁶ If the predicted infrared spectra of these clusters did not match our experimental spectrum, additional geometries were created. For small cluster sizes (Si_6^+ – Si_{10}^+), different spin multiplicities were explored, and in all of these cases the doublet states were found to be the lowest in energy. Computed infrared frequencies were scaled by a multiplication factor of 1.03 and were plotted by broadening the predicted frequencies with a Gaussian line shape possessing a full width at half-maximum of 8 cm^{-1} . This frequency scaling factor was chosen as it has been previously used for doped silicon clusters.³⁴ Unless otherwise noted, all theoretical results refer to those obtained with the BP86/SVP method.

Results and Discussion

In what follows, we discuss the IR-MPD spectra and structural assignments in three size ranges, that is, Si_6^+ through Si_{11}^+ , Si_{12}^+ through Si_{15}^+ , and Si_{16}^+ through Si_{21}^+ . For simplicity, we show the IR-MPD spectra together with only the calculated IR spectrum corresponding to the structure we assign here. The exceptions are for Si_8^+ and Si_{14}^+ , where we also give the predicted IR spectra of the other structural isomers that we theoretically considered. For Si_8^+ , we assign the observed spectrum to a new isomer that has not been previously

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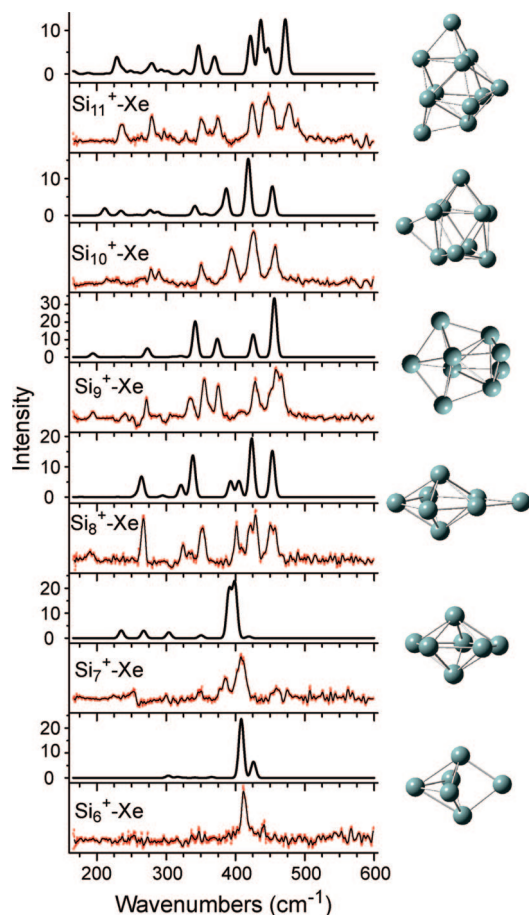


Figure 1. IR-MPD spectra of the Si_6^+ through Si_{11}^+ clusters tagged with a xenon atom as compared to the corresponding predicted infrared spectra for the bare clusters. In the experimental spectra reported here, the dots are the original data points, while the line corresponds to a 7-point binomial weighted average to account for the line width of FELIX. The y-axis is in km/mol for the theoretical infrared intensities (arbitrary units for experiment). The assigned structures are depicted to the right of the corresponding spectra.

considered, and for Si_{14}^+ we assign the second lowest energy structure to the isomer responsible for the major part of the IR-MPD spectrum. We also present the computed IR-MPD spectra of Si_{12}^+ for multiple isomers, as this is a cluster that we were unable to definitively assign to any individual isomer. The section is closed by discussing the geometric trends observed as a function of cluster size.

Si_n^+ ($n = 6-11$). The IR-MPD spectra in this size range, shown in Figure 1, have well-defined features in the 250–500 cm^{-1} spectral region. For Si_6^+ and Si_7^+ , the spectra are rather sparse, and both show primarily two absorptions between 380 and 450 cm^{-1} , although the strongest absorption for Si_7^+ is slightly broader as compared to that for Si_6^+ . For Si_8^+ , the spectrum becomes much richer with multiple intense absorptions. The spectrum for Si_9^+ is similar with strong absorptions at frequencies close to those for Si_8^+ , while the IR-MPD spectra of Si_{10}^+ and Si_{11}^+ are both dominated by a strong triplet of bands between 390 and 480 cm^{-1} .

There is considerable support in the literature that the structures of Si_6^+ and Si_7^+ have an edge-capped trigonal bipyramid (which can also be seen as a distorted octahedron)^{2,3,13,14} and a pentagonal bipyramid^{2,3,14,15,18,28} structure, respectively. The observed IR-MPD spectra of both sizes are rather simple with two features at 411 and 441 cm^{-1} for Si_6^+

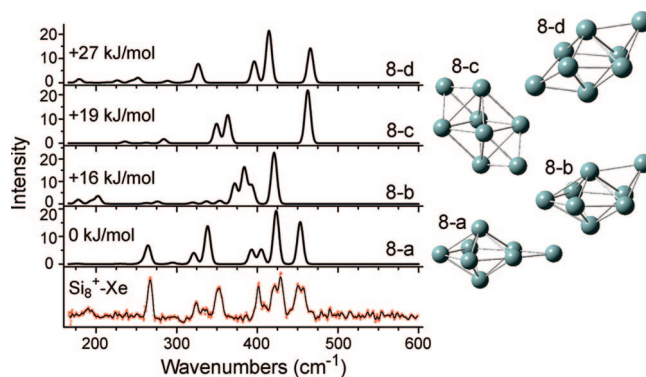


Figure 2. The IR-MPD spectrum for the Si_8^+ cluster tagged with a Xe atom is shown in the bottom panel. The predicted IR spectra of four Si_8^+ structural isomers are shown above the experimental spectrum with their relative energies in kJ/mol, and the structures are illustrated to the right of the spectra. The y-axis of the graph is in km/mol for the theoretical infrared intensities (arbitrary units for experiment).

and at 385 and 408 cm^{-1} for Si_7^+ . The computed IR spectra for the two generally accepted geometries fit these experimental peaks well. Although fluxional behavior of Si_6 along the distortion axis from D_{4h} symmetry has been previously predicted by high level calculations,⁴⁷ it is not evident in the observed IR-MPD spectrum.

The spectrum for Si_8^+ has considerably more features than Si_6^+ or Si_7^+ with several major absorption peaks between 260 and 460 cm^{-1} . Two geometries have been previously reported as the ground state of Si_8^+ , a distorted bicapped octahedron (structure 8-c in Figure 2)^{13,14} and a face-capped pentagonal bipyramid (8-b),¹⁵ but our calculated infrared spectra for these shapes do not fit the experimental spectrum. A third isomer we calculated, which is a more distorted version of the bicapped octahedron (8-d), is higher in energy. None of these three geometries predict an intense band below 300 cm^{-1} , whereas the experimental IR-MPD spectrum has a pronounced band at 267 cm^{-1} . In search of additional structural isomers, we optimized an edge-capped pentagonal bipyramid structure (8-a). This geometry is computed by all of our theoretical methods to be the lowest lying isomer (computed to be over 15 kJ/mol lower than any other isomer), and the predicted IR spectrum matches the experiment well, especially as this computed isomer has an intense absorption at 264 cm^{-1} . Hence, we assign this edge-capped pentagonal bipyramid geometry (8-a) to the Si_8^+ cluster. To our knowledge, no previous report has considered this isomer for cationic Si_8^+ . It has, however, been computed previously to be a higher energy isomer of neutral Si_8 .⁸

The Si_9^+ cluster is thought to have a bicapped pentagonal bipyramid structure.^{2,3,13-15} Although ref 13 does not name their C_s structure and ref 14 states that this structure possesses two parallel bent rhombuses that are capped, they appear to be similar to a bicapped pentagonal bipyramid. A tricapped prism has also been previously suggested.²⁸ Our calculations on the bicapped pentagonal bipyramid complex without symmetry constraints yielded an infrared spectrum very similar to the experimental result. The only disagreement is that the IR intensity is predicted to be considerably smaller than that observed for one of the triplets of bands at 335 cm^{-1} . Although the attachment of noble gas atoms to clusters typically has only little effect on the geometry of the cluster or on the position of IR absorptions, in some instances it may affect the intensities.

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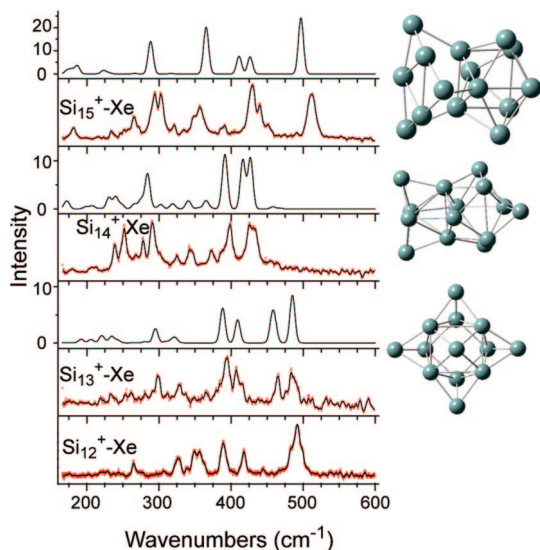


Figure 3. IR-MPD spectra of the Si_{12}^+ to Si_{15}^+ clusters tagged with a xenon atom as compared to the corresponding predicted infrared spectra for the bare cluster (except for Si_{12}^+ where a structural assignment could not be made). The y-axis is in km/mol for the theoretical infrared intensities (arbitrary units for experiment).

For this sized cluster, we performed additional calculations including the attached Xe atom. However, these calculations did not significantly change the predicted IR intensities. The presence of a minor amount of an unidentified isomer in the IR-MPD spectrum cannot be excluded. However, a possible tricapped trigonal prism distorts during geometry optimization and is 30 kJ/mol higher in energy.

A tetra-capped trigonal prism structure^{13,14} and a tricapped pentagonal bipyramid¹⁵ have been reported previously as the ground state of Si_{10}^+ . The comparison of our experimental and theoretical results identifies the tetra-capped trigonal prism structure as the correct geometry for this cluster. Likewise, comparing the observed Si_{11}^+ IR-MPD spectra with those predicted for different isomers assigns the C_s symmetry structure previously predicted.^{2,3,13} While the BP86/SVP method for the ground-state isomer resulted in an infrared spectrum similar to that observed experimentally, we note that the other theoretical methods we employed failed to produce a fitting spectrum for this cluster, although the structure remained nearly identical. This is the only sized cluster where the different theoretical methods predicted varied results.

Si_n^+ ($n = 12\text{--}15$). The IR-MPD spectra in this size range, shown in Figure 3, are, for the most part, well resolved. The spectrum of Si_{12}^+ is dominated by an intense peak at 492 cm^{-1} , with several weaker features between 260 and 450 cm^{-1} . Many strong absorptions are observed in the spectrum for Si_{13}^+ . For Si_{14}^+ , all of the observed absorptions are at lower frequencies in the $230\text{--}430\text{ cm}^{-1}$ region, while the spectrum of Si_{15}^+ has an intense high frequency band at 512 cm^{-1} .

Si_{12}^+ has previously been predicted to have a C_s structure containing a distorted tricapped trigonal prism building block.^{2,3,13,27} Figure 4 depicts the observed infrared spectrum with those predicted for multiple 12-atom isomers. From this, it is clear that certain isomers can be ruled out as major contributors in our experiment (e.g., isomer 12-h is predicted to have no intense infrared active features above 400 cm^{-1} , whereas the strongest experimental absorption is centered at 492 cm^{-1}). However, the Si_{12}^+ cluster is an example where no satisfactory agreement between theory and experiment has been

obtained so far for any of the computed isomers. There are several possible explanations for this. First, it is possible that we simply have missed the proper isomer in our calculations. Second, for Si_{11}^+ we noted that the different DFT functionals and basis sets produced differences in the predicted IR spectrum. It is possible that other theoretical approaches might predict an infrared spectrum similar to that observed for Si_{12}^+ . Third, as already mentioned, the attached noble gas atom can influence the intensities of the different absorption bands. Interestingly, it was also impossible to definitively assign a structure on the basis of a photodissociation spectrum of $\text{Si}_{12}\text{Xe}^+$ in the $290\text{--}700\text{ nm}$ range.²⁸

For the Si_{13}^+ cluster, we computed the infrared spectrum for the structure previously predicted in the literature as the ground state, that is, a trigonal prism with seven caps.^{2,3,27,28} This star-shaped cluster has a computed infrared spectrum in agreement with that observed in the experiment (Figure 3).

In optimizing different structural isomers of Si_{14}^+ , the lowest energy structure found contains a central trigonal prism building block with eight additional atoms, four on each of the two sides (14-a in Figure 5). However, the infrared spectrum computed for this isomer is dominated by a strong absorption at 398 cm^{-1} , whereas the experiment reveals a multitude of bands of comparable intensities between 230 and 430 cm^{-1} . A much better fit with the experiment is obtained for the geometry 14-b that has been found in ion mobility measurements,^{2,3,27} and this structure is predicted to be only 7 kJ/mol higher in energy. In principle, it is possible that both isomers were present in our molecular beam. If this was the case, the lower energy isomer 14-a, with only one intense peak, would probably be masked, as the major observed structure is predicted to have three intense peaks at 391 , 416 , and 427 cm^{-1} . However, the presence of multiple isomers for Si_{14}^+ was not evident in ion mobility studies,²⁶ and the total depletion on the experimental bands in regions of the spectrum where 14-a has no intense bands reveals that 14-b is the prevailing isomer with at least 70% abundance.

The experimental spectrum of Si_{15}^+ has many intense features present between 290 and 520 cm^{-1} . Ion mobility experiments in combination with computations have indicated that the structure has a trigonal prism base with a six atom triangle attached and that it has C_{3v} symmetry,^{3,27} although other structures have been predicted to be close or lower in energy.^{2,3} Our calculation on this cluster predicted an infrared spectrum very similar to that which is observed (Figure 3), although the intensities are not a perfect match. The most interesting observed band here is the absorption at 512 cm^{-1} , as the smaller clusters do not show absorptions at such high frequencies. This peak corresponds to a Si–Si stretching mode of the 6 atom triangle, where the middle atoms oscillate between the corner atoms.

Si_n^+ ($n = 16\text{--}21$). The IR-MPD spectra obtained in this size range are shown in Figure 6. The observed IR-MPD spectrum of Si_{16}^+ appears to resemble that of Si_{15}^+ . Hence, it would be logical to presume the two have similar structures. Specifically, with the presence of such a high frequency band, one could assume that the 6 atom silicon triangle is also present for Si_{16}^+ . None of the structures we computed fit the experimental spectrum well (see Figure S7), and the lowest energy isomer has no resemblance to the structure of Si_{15}^+ . This lowest energy isomer may indeed be present in the observed spectrum, but it surely does not account for all of the observed peaks. Again, ion mobility studies have not found multiple isomers for Si_{16}^+ .²⁶ For Si_{17}^+ , our IR-MPD spectrum contains rather broad and strongly overlapping bands in the $220\text{--}500\text{ cm}^{-1}$ range (Figure

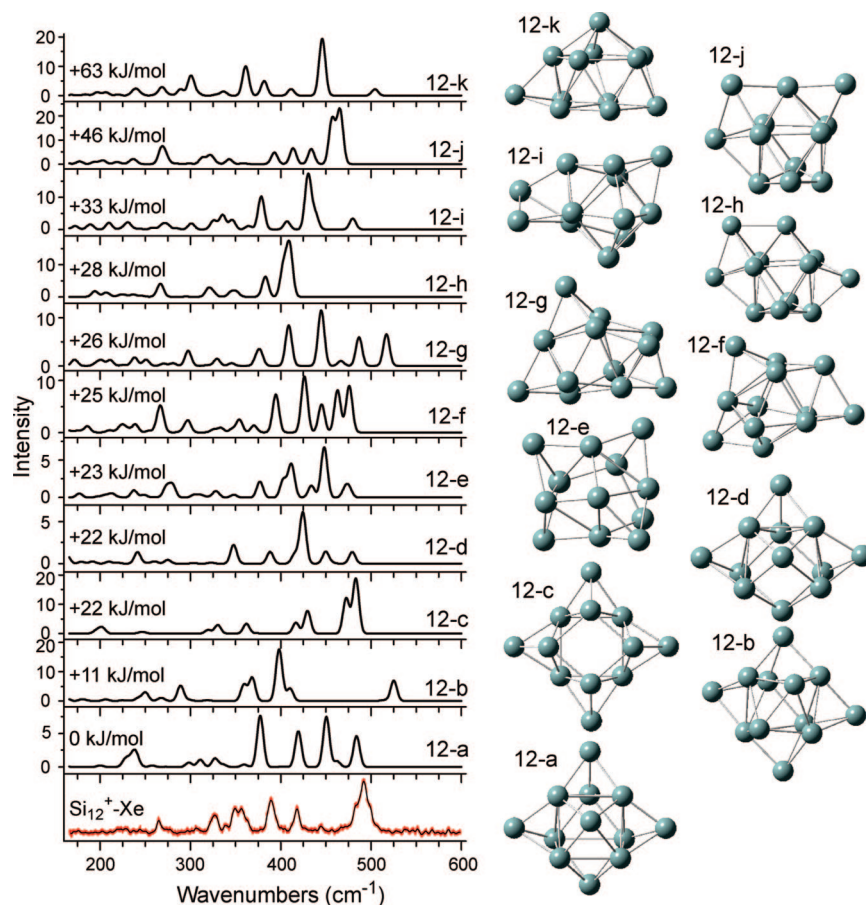


Figure 4. IR-MPD spectrum of the Si_{12}^+ cluster tagged with a xenon atom as compared to the predicted infrared spectra of multiple structural isomers. Their structures are illustrated to the right of the spectra, with the lowest energy isomer at the bottom. The y-axis is in km/mol for the theoretical infrared intensities (arbitrary units for experiment).

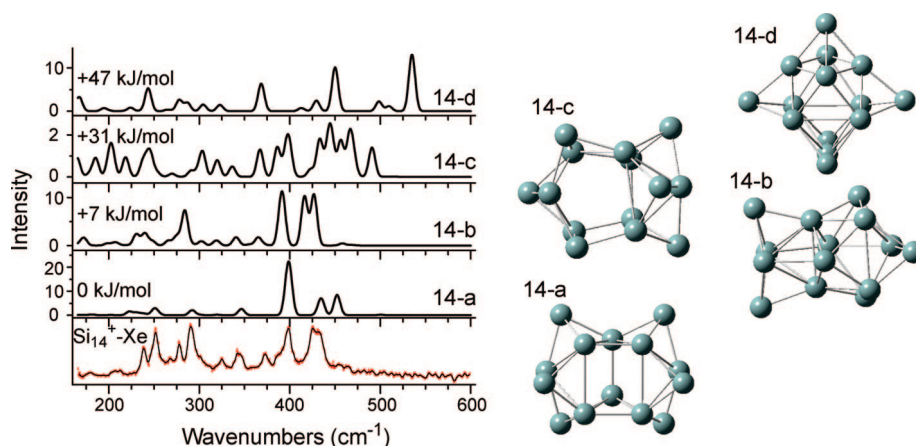


Figure 5. The IR-MPD spectrum of the Si_{14}^+ cluster tagged with a Xe atom is shown in the bottom panel. The predicted IR spectra of four Si_{14}^+ structural isomers are shown above the experimental spectrum with their relative energies in kJ/mol, and the actual structures are illustrated to the right of the spectra. The y-axis of the graph is in km/mol for the theoretical infrared intensities (arbitrary units for experiment).

6). This potentially indicates that multiple structural isomers are present, which have also been observed in ion mobility studies.^{3,26} The presence of the lowest energy isomer could only explain part of this IR-MPD spectrum (see Figure S8).

The Si_{18}^+ cluster is the only cluster in this size range for which we were able to find a structure whose predicted IR spectrum agrees with that observed in the experiments (Figure 7). It possesses a tricapped trigonal prism connected to a square bipyramid via pentagonal rings and resembles the lowest energy

isomer of Si_{17}^+ . This Si_{18}^+ structure is different from that previously suggested by ion mobility experiments.^{2,3,27} However, it has recently been predicted to be lower in energy.⁴⁸ Some minor features in the experimental spectrum remain unexplained by this structure, but ion mobility experiments have also seen a minor abundance of a second isomer.^{3,26} Neverthe-

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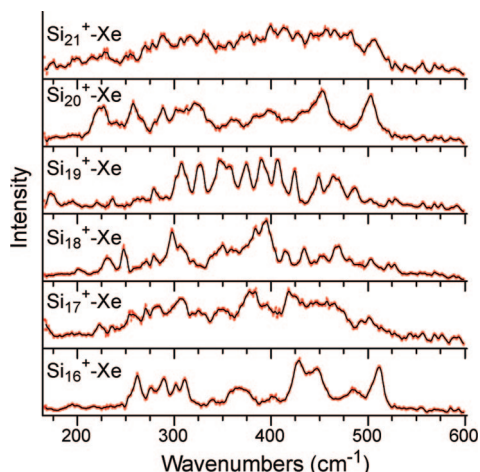


Figure 6. IR-MPD spectra of the Si_{16}^+ through Si_{21}^+ clusters tagged with a xenon atom. The y-axis is in arbitrary units.

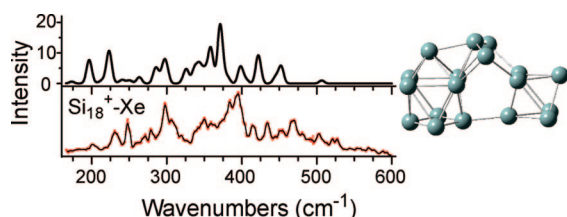


Figure 7. IR-MPD spectrum of the Si_{18}^+ cluster tagged with a xenon atom as compared to the corresponding predicted infrared spectrum. The y-axis is in km/mol for the theoretical infrared intensities (arbitrary units for experiment).

less, the most intense features in the spectrum can be explained by the present structure. Comparing the observed and computed spectra for this cluster, it is evident that the arbitrarily chosen frequency scaling factor (1.03) is too small to shift the computed bands to the positions observed in the IR-MPD spectrum. This tendency already becomes apparent for Si_{14}^+ and Si_{15}^+ . Obviously, our theoretical technique underestimates the vibrational frequencies of larger Si_n^+ clusters more than the predicted frequencies of the smaller clusters.

The IR-MPD spectra for the remaining Si_n^+ cluster sizes ($n = 19\text{--}21$) are given in Figure 6. Note that for Si_{18}^+ and Si_{19}^+ ,

there are no intense bands above 500 cm^{-1} . For Si_{20}^+ and Si_{21}^+ , intense bands can be seen at 503 and 506 cm^{-1} , respectively. This could indicate that for these sized clusters, part of the structure may include a planar substructure similar to the silicon triangle observed for Si_{15}^+ . Also, the IR-MPD spectrum of Si_{19}^+ shows very sharp features, whereas that for Si_{21}^+ is rather broad, indicating the possible presence of multiple isomers. We have computed infrared spectra for a few structural isomers in this size range, in particular, some of the geometries reported previously in ref 5 and by capping the structure we found for Si_{18}^+ , but none fit well with experiment. Nonetheless, the IR-MPD spectra reported here should aid to pinpoint precise structures. An extensive exploration of the configurational space will need to be performed to identify these structures. Application of global minimum search methodologies is beyond the scope of this Article, but will certainly allow assigning the structures of the larger clusters.

Growth Mechanism. Figure 8 gives an overview of the Si_n^+ cluster structures we have assigned in this Article. So far, no decisive conclusions could be made due to the lack of direct experimental information on their structure, although all of these structures have been suggested as potential ground-state structures in competition with other isomers. One exception is the structure identified for Si_8^+ , which has not been considered before. The present data provide solid ground for determining patterns in the cluster structure as the size increases. Indeed, some general trends in the growth can be noted. Si_7^+ is a pentagonal bipyramid. Si_8^+ and Si_9^+ retain this pentagonal bipyramid base with additional atoms capping an edge for the former or two faces for the latter. For Si_{10}^+ , a new base feature is present, that is, a trigonal prism. This tricapped trigonal prism building block has been previously predicted as a key feature in the growth mechanism of silicon clusters.^{26,27,30} It is interesting that Si_9^+ does not have a tricapped trigonal prism geometry; as mentioned previously, that structure is higher in energy. Si_{11}^+ , Si_{13}^+ , and potentially Si_{12}^+ build upon the trigonal prism base with additional capping of faces. Si_{14}^+ appears to be an “odd-ball” structure. Although one could argue this cluster may possess very distorted versions of either building block, we are reluctant to assign either. The tricapped trigonal prism reappears in the structure of Si_{15}^+ . The largest structure we were able to assign, Si_{18}^+ , has the tricapped trigonal prism base

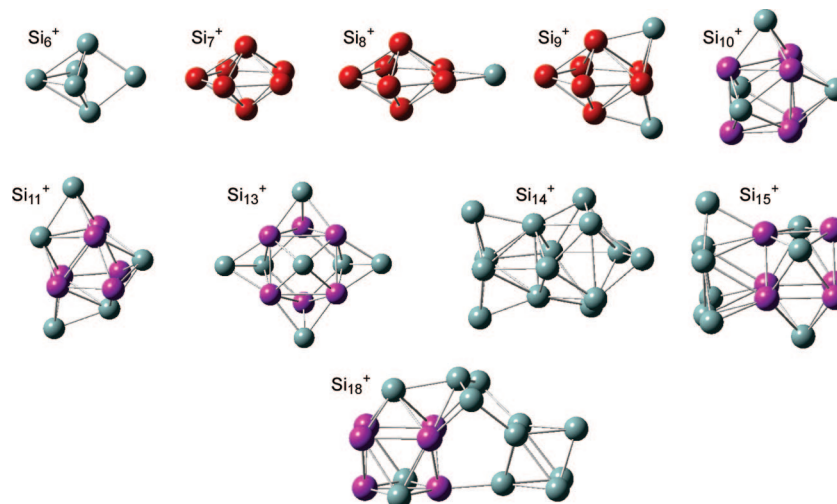


Figure 8. Structures of silicon cluster cations identified by vibrational spectroscopy. Pentagonal bipyramid and trigonal prism building blocks are colored red and purple, respectively.

connected to a tetragonal bipyramid by three pentagonal rings. Indeed, trigonal prisms and pentagons appear to be structural motifs for silicon cluster cations.

Conclusion

In this Article, we have presented well-resolved vibrational spectra of small silicon cluster cations possessing between 6 and 21 atoms. Comparison with theoretical predictions for multiple isomers has led to structural assignments for many of these sizes, for the first time based on direct experimental data on the internal cluster structure. We have assigned Si_8^+ to an edge-capped pentagonal bipyramid structure, which has not been previously considered for this cationic cluster size. Whereas the Si_7^+ , Si_8^+ , and Si_9^+ clusters prefer a pentagonal bipyramid building block, larger clusters build upon a trigonal prism base. From the experimental spectra, we find indications that for select cluster sizes multiple structural isomers are present. We expect that the presented IR-MPD spectra for all clusters will aid in the identification of the structures not assigned here. Hereto further elaborate computational efforts will be needed.

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Supporting Information Available: Complete citation for ref 38, Figures S1–S8 showing the effect the Xe atom has on the calculation for Si_9^+ , IR-MPD spectra and theoretical predictions for different isomers of Si_6^+ , Si_7^+ , Si_9^+ , Si_{10}^+ , Si_{11}^+ , Si_{16}^+ , and Si_{17}^+ , and the predicted coordinates and frequencies for all assigned clusters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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