Onset of Coulomb explosion in small silicon clusters exposed to strong-field laser pulses

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Abstract. It is now well established that, under intense laser illumination, clusters undergo enhanced ionization compared to their isolated atomic and molecular counterparts being subjected to the same pulses. This leads to extremely high charge states and concomitant Coulomb explosion. Until now, the cluster size necessary for ionization enhancement has not been quantified. Here, we demonstrate that through the comparison of ion signal from small covalently bound silicon clusters exposed to low intensity laser pulses with semi-classical theory, their ionization potentials (IPs) can be determined. At moderate laser intensities the clusters are not only atomized, but all valence electrons are removed from the cluster, thereby producing up to Si\textsuperscript{4+}. The effective IPs for the production of the high charge states are shown to be $\sim 40\%$ lower than the expected values for atomic silicon. Finally, the minimum cluster size responsible for the onset of the enhanced ionization is determined utilizing the magnitude of the kinetic energy released from the Coulomb explosion.

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1. Introduction

Silicon clusters have received considerable attention in recent years as a means of improving our electronics technology through a bottom-up approach. By combining specific clusters together as building blocks, new materials with tailored properties may be constructed. To make this a reality, clusters must first be characterized and subsequently stabilized to retain their unique properties. The most important property of silicon nanoscale material involves accessibility to various electronic states. The ionization potentials (IPs) of silicon clusters have previously been investigated through electron impact ionization [1], photoionization [2, 3], and most recently with high resolution synchrotron radiation [4]. Recently, the electron affinities of small silicon clusters were examined through photoelectron spectroscopy [5] and velocity map imaging [6]. Although a variety of techniques have investigated the properties of silicon clusters, they have not yet been examined with intense femtosecond lasers.

Calculations suggest that larger clusters can be assembled by connecting small-sized ‘magic’ (especially stable) clusters for the formation of new materials [7]. Silicon clusters are typically formed under plasma conditions, and therefore it is important to understand how they react under intense radiation. In the 1990s, the Castleman group first discovered that extreme ionization occurs in a variety of clusters subjected to intense femtosecond laser pulses leading to Coulomb explosion [8, 9]. Although our discovery of the influence of clustering on the enhancement of ionization has prompted extensive investigation, only recently have experiments explored the laser intensities required for this phenomenon. Döppner et al [10] utilized intensity resolved laser excitation to investigate ionization in xenon clusters embedded in helium droplets; showing that above saturation, there is a rapid onset of high charge states. Our recent results from ammonia clusters [11] and transition metal oxide clusters [12] have demonstrated that high charge states can arise from a narrow span of laser intensities for many types of clusters. The versatility of this technique is now applied to small covalently bound silicon clusters for comparison.

Although it is well established that the clustered phase exhibits an enhanced ionization, the intensity requirements for the production of high charge states in covalent clusters have not been previously quantified experimentally. Here, employing a femtosecond laser operated over...
a range of peak intensities from $\sim 5 \times 10^{12}$ to $\sim 6 \times 10^{14}$ W cm$^{-2}$, we examine the ionization rates and mechanisms of Si$_n$, up to $n = 10$, to determine their stability and electronic response under strong electromagnetic fields. Of particular interests are the accuracy of effective IPs as determined in the tunneling regime and the onset of enhanced ionization that induces the destruction of the material through Coulomb explosion. The term ‘enhanced ionization’ describes the appearance of an ion state at lower laser intensity than theoretical treatment prescribes for an atom based on the sequential ionization value.

Additionally, the minimum cluster size necessary for the onset of the ionization enhancement has not yet been explored in detail experimentally. Here, we find that kinetic energy release (KER) measurements for each charge state provide insight to the size of cluster undergoing Coulomb explosion and therefore suggests the role clustering plays on ionization enhancement. To utilize this information, expectation values for the KER are obtained from molecular dynamics (MD) simulations of the Coulomb explosion performed on small neutral silicon clusters upon ionization.

2. Experimental method

A detailed description of the experimental setup and methods have been previously described [13], and only a brief explanation including the changes made for this experimental investigation are given here. A translating and rotating Cu rod was used as an electron source upon ablation by the second harmonic of a Nd:YAG laser. Pulsed over the point of ablation was a jet of silane (SiH$_4$, $\sim 1\%$) seeded in high purity helium as a carrier gas. Clusters form through rapid collision and supersonic expansion of this gas jet as it expands into vacuum, and are collimated into a molecular beam as they pass through a skimmer. Neutral clusters enter the extraction region of Wiley–Mclaren time-of-flight mass spectrometer [14], where they are ionized with a linearly polarized, 100 fs laser pulse from a previously described [15] colliding-pulse mode-locked dye laser with wavelength centered at 624 nm. We utilize the intensity selective scanning (ISS) method [16], in which the laser intensity is attenuated by translation of a 60 cm focusing lens. A 2.00 mm ion slit replaces the last grid of the extraction region and is used to spatially limit the collection of ions to those produced from nearly constant laser intensity. This technique offers the advantage of increasing the collection volume at low laser intensities, where the ionization probability is smaller. This is beneficial in examining lower intensity processes, such as multiphoton ionization, single ionization and the onset of multiple ionization. To obtain insight into the neutral cluster distribution, the laser focus is translated away from the collection slit so that ions are detected from only the defocused part of the laser beam, where the cluster distribution is ionized, but fragmentation is limited. A typical cluster distribution, extending up to $n = 10$, obtained using a laser intensity of $3 \times 10^{13}$ W cm$^{-2}$ is displayed in figure 1(a). Higher laser intensities lead to the removal of all valence electrons from the silicon species as shown in the time-of-flight mass spectrum in figure 1(b) (laser intensities of $\sim 4 \times 10^{14}$ W cm$^{-2}$).

3. Theory

3.1. Ionization model

The method of extracting IPs from ionization signal has been previously described in great detail [11, 13]. Therefore only a brief description will be outlined here. At low laser intensities,
Figure 1. (a) Typical mass spectrum of Siₙ investigated through strong-field ionization taken at 3 × 10¹³ W cm⁻². (b) The mass spectrum of the high charge states taken at ∼4 × 10¹⁴ W cm⁻², demonstrating peak splitting arising from Coulomb explosion. The shaded peaks represent the forward and backward ejected ions for each charge state.

Multiphoton ionization is understood to be the dominant mechanism. Under this model, the number of photons absorbed by the sample is quickly determined by measuring the slope on a logarithmic plot of ion signal versus peak laser intensity. At higher intensities, tunneling takes over as the dominant mechanism [17] and is more difficult to quantify.

The well-known Ammosov–Delone–Krainov (ADK) model [18] is applied to ion signal obtained for both clusters and high charge states due to the ease of calculation and success with predicting the tunneling ionization rates of clusters and fragments. The ADK model assumes only sequential ionization, the process in which electrons are removed in a stepwise fashion. This utilizes the single active electron (SAE) approximation, with the remaining electrons assumed to be inert. Utilizing this model, a transformation is established between the IP and saturation intensity (Iₘ) [19]. The ion signal obtained for the high charge states are compared to literature values of sequential IPs for atomic silicon for quantification of the ionization enhancement. Error limits for the IP measurements are reported using the standard deviation of the fit parameters that determine Iₘ.
3.2. Coulomb explosion simulation

Theoretical calculations of pure silicon clusters were performed within a hybrid density functional theory (DFT) framework providing the ground state structures of the silicon clusters. *Ab initio* calculations were performed on small silicon clusters using Gaussian03 [20]. The geometry optimizations and energies were carried out using an unrestricted hybrid method that includes a mixture of Hartree–Fock exchange with density functional exchange correlation using 6–311++G(3df, 3pd) basis sets. The exchange and correlation integrals were treated with the generalized gradient approximation of Becke’s three parameters [21] and the dynamic Perdew and Wang’s 1991 [22] gradient-corrected correlation functional (B3PW91). Silicon clusters are covalently bonded systems. The structures of small silicon clusters determined here conform to recent literature geometries and energies [4]. The ground state of the dimer is found to be in a triplet state, but the rest are optimized with the lowest spin configurations. The structure of the neutral species remains planar up till the Si₃. The geometry of the Si₄ is determined to have a lowest energy structure of a planar rhombus shape; however, the tetrahedral geometry isomer is close in energy. The structure of the Si₅ is typically described as a distorted octahedron, and Si₇ as a pentagonal bipyramid. The ground state cluster geometries for the neutrals are presented in figure 1(a).

The Cartesian coordinates for the ground state structures are used as input for the MD simulation [23]⁴ used as an approximation to model the magnitude of the KER resulting from a Coulomb explosion. Each atom composing the cluster is set to a uniform charge state at the start of the simulation. The forces between the ions are computed under Coulomb’s law and then are allowed to act on the ions for a small step in time (typically 100 attoseconds), thereby accelerating them apart. After each step, the forces acting on the ions are recalculated using the new geometry and another time step is taken. This process is repeated until the ions are so distant that they contribute negligible forces on one another, thus no longer adding to the KER.

For a given cluster, each atom receives a unique value of KER determined by its position and charge. However, the experimental measurement represents an average over a distribution of clusters and therefore is not sensitive enough to detect small changes in geometry or determine structural information. Our MD simulations demonstrate that the average KER for a given cluster size is also insensitive to small changes in the ground state geometry. For instance, the tetrahedral structure for Si₄ with every atom at a +4 state obtains an average KER of 137 eV per atom, whereas 138 eV is obtained for the planar geometry. However, the magnitude of KER has a nearly linear growth with cluster size, assuming that the bond lengths do not significantly change and the cluster maintains a similar, in this case cage-like, structure. Thus, our MD simulation serves only to demonstrate the magnitude of KER possible for each cluster.

4. Results and discussion

4.1. Cluster size dependence on KER

The strong-field ionization of silicon clusters occurs faster than the nuclei have time to adequately respond, leading to highly charged ions in close proximity. These ions repel one another giving rise to large KER values, yielding a distinctive signature of Coulomb explosion with twin peaks for each *m/q* ratio. The peak shapes are brought about by initial kinetic energy

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⁴ This molecular dynamics simulation was written by Poth 1998 personal communication.
given to each ion inside the Wiley–Mclaren time-of-flight extraction grids. A single peak will be observed if the ions have no initial kinetic energy, as their flight times are governed only by the energy imparted by the electrostatic field. However, in the case that the ions obtain an initial kinetic energy (from Coulomb explosion), ions ejected toward the detector will arrive earlier (typically as a broader peak), and those sent in the opposite direction require additional time to turn around before being detected (typically as a more focused peak). For analysis, the magnitude of the KER is determined through the difference in time-of-flight arrival times between the forward and backward ejected ions as

\[
\text{KER (eV)} = \frac{0.1204q^2 \Delta t^2}{m} \left( \frac{\Delta U}{d} \right)^2,
\]

also known as the peak splitting method \[24\]. In equation (1), \( q \) is the integer of charge, \( \Delta t \) is the time between peak arrivals in \( \mu s \), \( m \) is the mass in amu, \( \Delta U \) is the voltage difference of the grids, \( d \) is the distance between grids in \( cm \) and the constant accounts for units.

The magnitude of the KER is expected to be dependent upon how quickly ionization occurs with respect to cluster expansion, both of which occur on the femtosecond time scale of the laser pulse. Any expansion during or prior to ionization will reduce the KER available. Therefore, the average KER from the MD simulations provides only a lower limit to the size of cluster responsible for producing the values measured for the high charge states. An upper limit to the cluster dimension cannot be determined, as any cluster larger than the size matching the MD simulation may also contribute to the ion signal. However, the intensity scans demonstrate that the peak splittings, and therefore KER, are not affected by changes in laser intensity suggesting that multiple ionization proceeds vertically as soon as the intensity is sufficient for electron removal. This justifies the simple approximation of instantaneous charging utilized in our MD simulation.

In figure 2, the experimentally measured KER values for each charge state are overlayed with the results of the MD simulations from each cluster size to reveal the influence that cluster size has on the charge state achieved. The simulations for singly charged ions match the experimental values for only the smallest of clusters, suggesting that \( \text{Si}^+ \) is produced from the Coulomb explosion of ions produced from \( \text{Si}_2 \) and \( \text{Si}_3 \). The results for the +2 state overlap at a cluster size around \( n = 5 \) or 6, suggesting that increases in cluster size encourage additional electron removal. Assuming negligible cluster expansion during ionization, the minimum cluster size able to produce the KER measured for \( \text{Si}^{3+} \) and \( \text{Si}^{4+} \) is shown to be \( \text{Si}_9 \). Smaller clusters cannot yield the magnitude of KER that is measured in the experiments and are therefore eliminated as possible routes for the creation of these ions. Thus, the results shown in figure 2 demonstrate a clear trend in that larger clusters undergo further ionization than smaller clusters.

### 4.2. Ionization enhancement

The experimental and theoretical ion yields for the intensity scan of the high charge states are overlapped in figure 3 and measurements are collected in table 1. The effective IP measured for the first charge state \( (8.17 \pm 0.02 \text{ eV}) \) shows good agreement with the ADK model, arising from a silicon atom with an IP of 8.15 eV. As the intensity increases beyond the \( I_{\text{sat}} \), the population of the \( \text{Si}^+ \) exhibits continued growth, arising from fragmentation of larger clusters. While the ion signal for the singly charged ion is in agreement with the ADK model, ionization enhancement begins at a laser intensity of only \( \sim 1.6 \times 10^{13} \text{ W cm}^{-2} \) with the appearance of \( \text{Si}^{2+} \). Applying the
sequential IP of atomic silicon to the ADK model, the Si$^{2+}$ is not expected until a laser intensity of $\sim 4 \times 10^{13}$ W cm$^{-2}$, which is more than double the experimental result. At an intensity of $7 \times 10^{13}$ W cm$^{-2}$, the ion signal for Si$^{2+}$ matches ADK theory for sequential ionization, and remains overlapped with the model’s prediction at higher intensities. Therefore, the measured $I_{\text{sat}}$ for Si$^{2+}$ is very close to the expectation value and a measurement for the effective IP of Si$^{2+}$ was obtained at $16.14 \pm 0.13$ eV, in close agreement to the literature value of 16.35 eV.
Table 1. The appearance intensities, saturation intensities and effective IPs for the high charge states of Si. The literature values are taken from the sequential IP for atomic silicon. All energies are given in eV, and intensities in W cm\(^{-2}\).

| Ion    | Appearance | \(I_{sat}\) | Effective IP (ADK) | Literature\(^a\) | KER |
|--------|------------|--------------|--------------------|-------------------|-----|
| Si\(^+\) | 6.0 \(\times\) 10\(^{12}\) | 1.57 \(\pm\) 0.02 \(\times\) 10\(^{13}\) | 8.17 \(\pm\) 0.02 | 8.15 | 4.2 |
| Si\(^{2+}\) | 1.6 \(\times\) 10\(^{13}\) | 5.61 \(\pm\) 0.12 \(\times\) 10\(^{13}\) | 16.14 \(\pm\) 0.13 | 16.35 | 54 |
| Si\(^{3+}\) | 3.0 \(\times\) 10\(^{13}\) | 6.50 \(\pm\) 0.09 \(\times\) 10\(^{13}\) | 20.61 \(\pm\) 0.10 | 33.49 | 160 |
| Si\(^{4+}\) | 7.0 \(\times\) 10\(^{13}\) | 8.74 \(\pm\) 0.08 \(\times\) 10\(^{13}\) | 25.33 \(\pm\) 0.08 | 45.14 | 296 |
| Si\(^{5+}\) | – | – | – | 166.77 | – |

\(^a\) Literature values taken from [29].

The effective IPs determined for both Si\(^+\) and Si\(^{2+}\) fit very closely to the sequential atomic literature value. However, the appearance of Si\(^{3+}\) is before the \(I_{sat}\) of Si\(^{2+}\), indicating the breakdown of the ADK model (SAE is no longer valid). The ion signal for Si\(^{3+}\) appears nearly an order of magnitude lower in laser intensity than predicted by the model, thereby demonstrating strong enhanced ionization. We extract effective IPs from the ion signal of the high charge states strictly to quantify the magnitude of enhancement observed based on deviation from literature values. An effective IP of only 20.61 \(\pm\) 0.10 eV is assigned for Si\(^{3+}\), which is \(\sim\)40% lower than the literature value of 33.49 eV. For the Si\(^{4+}\) ion, the \(I_{sat}\) is measured at only 8.74 \(\pm\) 0.08 \(\times\) 10\(^{13}\) W cm\(^{-2}\) giving an effective IP of 25.33 \(\pm\) 0.08 eV which is again \(\sim\)40% lower than the expectation value of 45.14 eV. Therefore, enhanced ionization is very prominent in both Si\(^{3+}\) and Si\(^{4+}\) signal. Combining this with the results from figure 2 suggests that enhanced ionization begins in very small clusters. Specifically, the measured KER suggests that a cluster size of only \(n \geq 9\) is necessary for the removal of all valence electrons at laser intensities \(\geq 1 \times 10^{14}\) W cm\(^{-2}\). The absence of Si\(^{5+}\) in the spectra is attributed to the valence shell closing at Si\(^{4+}\), leading to a much larger IP for its production.

We have previously reported on the ionization behavior of silane gas using an identical laser pulse with intensities up to \(\sim 1 \times 10^{15}\) W cm\(^{-2}\) and determined that, although complete atomization was achieved, multiply charged silicon ions were not observed [13]. The presence of multiply charged ions beginning at an intensity of only \(\sim 1 \times 10^{13}\) W cm\(^{-2}\) further demonstrates the role clustering has in effectively enhancing ionization. For the cluster distribution under investigation here, the laser intensity increases roughly an order of magnitude from the appearance of the singly charged species to the removal of all valence electrons. This is a very different result than observed in either xenon [10] or ammonia [11] clusters, where a sudden ionization avalanche occurs above the threshold for the first atomic ion. The spacing in laser intensity between ionization states (figure 3) is more pronounced than observed in metal oxide clusters [12], where a gradual increase in ionization was observed with increasing intensity. Thus, silicon clusters offer the ability to tune the extent of ionization by selecting the laser intensity. More specifically, for silicon clusters, each sequential increase in charge state requires approximately double the laser intensity of the previous charge state.

4.3. Ionization potentials of clusters

The IPs of the clusters are determined through the intensity scans in a similar method as was used for the high charge states. However, clusters exhibit a decline in signal at high intensities as...
a result of fragmentation and Coulomb explosion. The yield of Si\(_n\) formed in a laser vaporization source is quite low making it difficult to obtain reliable ion signal measurements discernible from the background noise. Therefore, only clusters up to Si\(_6\) could be determined accurately, although the presence of larger clusters is clearly marked in the mass spectra. The tunneling measurements are in excellent agreement with recent results [4] and also vertical IPs, with most values contained within the small error limits of the measurements. For example, we attribute an effective IP of 8.20 ± 0.07 to Si\(_4^+\), matching previous measurement of 8.2 ± 0.1 as well as the vertical IP calculated here to be 8.14 eV. The experimental data and the fit lines are shown in figure 4 and summarized in table 2. Additionally, the cluster signal was fit using the multiphoton ionization model. For all clusters investigated here, a photon order of 5 was determined from the initial slopes. This matches the expectation value for an IP between 7.96 and 9.95 eV, in agreement with literature values.

Signal for clusters larger than \(n = 6\) is small due to the exponential decrease in ion signal with cluster size. Although our defocused laser provides a representative cluster distribution, the exact abundance of the neutral clusters cannot be inferred from this ion signal. The KER splitting directly demonstrates that larger clusters (\(n \geq 8\)) must be present, but that we cannot observe them in large quantities as cations. Therefore, we estimate that the clusters are destroyed by the laser pulse rather than undergoing single ionization. This is further evidence of the extreme ionization occurring in Si\(_n\) clusters exposed to intense laser pulses.

For the cluster ion signal, a relatively good fit is obtained to the ADK model at high intensities except for Si\(_2^+\), which exhibits a growth at high laser intensities. This increase is

**Figure 4.** Ion signal arising from the clusters. The solid lines (black) represent the extrapolation used in the determination of the saturation intensity. The values reported are the corresponding effective IPs.
Table 2. The ionization signal of the clusters was measured, and fit using the ADK atomic model. Effective IPs are then determined and compared to both DFT calculations and recent literature results. All potentials are listed in eV. Error bars are reported from the standard deviation of the best fit line used in determining $I_{sat}$, which is then converted into the effective IP.

| Ion   | $I_{sat}$ (W cm$^{-2}$) | Effective IP | Vertical | Adiabatic | Literature$^a$ |
|-------|------------------------|--------------|----------|-----------|----------------|
| Si$^+$ | 1.57 ± 0.02 × 10$^{13}$ | 8.17 ± 0.02  | 8.11     | 8.11      | 8.13 ± 0.05    |
| Si$^+_2$ | 1.52 ± 0.03 × 10$^{13}$ | 8.09 ± 0.04  | 7.92     | 7.91      | 7.92 ± 0.05    |
| Si$^+_3$ | 1.62 ± 0.05 × 10$^{13}$ | 8.24 ± 0.07  | 8.16     | 8.00      | 8.12 ± 0.05    |
| Si$^+_4$ | 1.59 ± 0.04 × 10$^{13}$ | 8.20 ± 0.07  | 8.14     | 7.87      | 8.2 ± 0.1      |
| Si$^+_5$ | 1.58 ± 0.05 × 10$^{13}$ | 8.18 ± 0.08  | 8.19     | 8.00      | 7.96 ± 0.07    |
| Si$^+_6$ | 1.46 ± 0.03 × 10$^{13}$ | 8.00 ± 0.06  | 8.06     | 7.79      | 7.8 ± 0.1      |

$^a$ Experimental values taken from [4].

attributed to fragmentation of larger clusters augmenting its population. The experimental ion signal for the Si$^+_6$ species demonstrates magic behavior, being more intense in the cluster distribution than its closest neighbors (n ± 1) at all laser intensities. This is in agreement with photodissociation [25], collision-induced-dissociation [26] and oxygen etching [27, 28] experiments which have also identified Si$^+_6$ as having exceptional resistance to fragmentation.

5. Conclusion

In conclusion, we have shown that IPs can be accurately determined for small silicon clusters through the signal obtained from strong-field tunneling ionization and present a useful approach to identify magic clusters, resistant to fragmentation under intense electromagnetic fields. The onset of enhanced ionization and therefore efficient Coulomb explosion is shown to begin with Si$^{2+}$. The effective IPs for the higher ion states are measured at only ~60% of the expected value. Through comparison of the production of the high charge states with the KER measurements, we demonstrate that in the case of Si$_n$, ionization enhancement and efficient Coulomb explosion begins at a very small dimension. For clusters as small as only nine atoms, complete removal of all valence electrons may begin at a laser intensity of $1 \times 10^{14}$ W cm$^{-2}$.

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