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Photodissociation of Metal−Silicon Clusters: Encapsulated versus Surface-Bound Metal

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Metal−silicon cluster cations of the form MSi_n^+ (M = Cu, Ag, Cr) are produced in a molecular beam with pulsed laser vaporization. These species are mass-selected in a reflectron time-of-flight spectrometer and studied with laser photodissociation at 532 and 355 nm. For the noble metals copper and silver, photodissociation of the $n = 7$ and 10 clusters proceeds primarily by the loss of metal atoms, indicating that the metal is not located within the interior of silicon cages, and that metal−silicon bonding is weaker than silicon−silicon bonding. Chromium−silicon clusters for $n = 7$ also lose primarily the metal atom, but at $n = 15$ and 16 these dissociate via the loss of silicon, producing smaller metal−silicon species. This behavior is consistent with stronger metal−silicon bonding and encapsulated metal structures, as suggested previously by theory. MSi_6^+ cations are produced efficiently in all of these photodissociation processes, indicating that these species have enhanced stability compared to other small clusters. Improved values are obtained for the ionization potentials of Si_7 and Si_{10}.

Introduction

Gas-phase metal−silicon clusters produced by laser vaporization of different composite samples were first described by Beck.[1] This early work showed that these clusters exhibit surprising preferences for certain special stoichiometries that were different for different metals. The transition metals iron, chromium and tungsten were found to prefer MSi_{15} and MSi_{16} stoichiometries, whereas copper had enhanced abundance for the MSi_{10} species. This behavior was somewhat similar to that seen previously for metal carbide clusters of the early transition metals,[2−4] but the combining ratios for metal−silicon species were not the same as those for the carbides. On the basis of the unusual mass spectra, Beck suggested that the special stoichiometries represented metal−encapsulated silicon cages. More recent studies have reproduced the earlier cation mass spectrometry, finding similar stoichiometries for other transition metals, and have extended the work to anions.[5−7] Small MSi diatomics have been studied with electronic spectroscopy.[8] Various theoretical methods have investigated the geometries and electronic structures of these metal−silicon species.[9−19] These calculations agree that the early transition metals form strong bonds to silicon and that encapsulated metal structures are stable. However, copper−silicon species were predicted to adopt structures with surface-bound metal. Unfortunately, there have been no experiments that provide any direct confirmation of the structures of these clusters. In the present work, we apply mass-selected photodissociation to address this problem.

Photodissociation experiments have become a mainstay of gas-phase cluster science and have been applied to metal clusters,[20] carbon clusters,[21−23] pure silicon clusters,[24,25] silicon carbides,[26] metal carbides[3] and metal oxide species.[27] Other experiments have investigated metal−fullerenes.[28] Although kinetics and thermochemistry, as well as ionization dynamics, may all affect cluster growth and the apparent abundances of clusters in a distribution, dissociation channels tend to be governed by the intrinsic stability of the species under study. In particular, when clusters of many different sizes are investigated, it is often found that certain dissociation products are produced repeatedly, thus identifying stable cluster units. In other cases, dissociation patterns can reveal qualitative details of structure. For example, simple elimination of metal atoms from metallo-fullerenes indicates the presence of exohedral rather than endohedral metal.[28] In the present work, we apply these concepts to investigate metal silicon clusters. Dissociation channels probe suspected structural patterns involving encapsulated versus surface-bound metal.

Experimental Section

Clusters for these experiments are produced by laser vaporization of solid targets at 355 nm in a pulsed molecular beam machine.[3] In most experiments, vaporization of rotating metal rod samples is employed with an expansion gas containing 1−5% of silane. Plasma reactions with metal dissociate the silane and eliminate hydrogen, producing the desired metal−silicon species, in the same way that metal−carbide clusters are produced from metal−methane plasma chemistry.[3] For copper−silicon and silver−silicon clusters, additional experiments are conducted with vaporization of metal film-coated silicon rods.

Neutral clusters grown from the source are ionized with an excimer laser operating at 193 nm (Lumonics) and then detected with a reflectron time-of-flight mass spectrometer (RTOF). In some experiments on copper and silver systems, cation clusters grown from the source are sampled directly from the molecular beam. Specific cation clusters produced either way are mass selected via their flight time with pulsed deflection plates located

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in the first flight-tube section of the RTOF. Excitation of the selected cations at either 532 or 355 nm takes place in the turning region of the reflectron field, and then photodissociation products are mass analyzed by their flight time through the second flight tube section. The dissociation products are the same when the ions are produced by different methods. The details of this photodissociation experiment are described elsewhere.[3,26−28]

Results and Discussion

We explored various configurations of our cluster source with different expansion gases, sample holders and growth channels to optimize the formation of the desired metal−silicon clusters. The resulting mass spectra varied in understandable ways with the conditions and the configuration of the source. Depending on the relative concentration of the metal and silicon precursor materials, the masses corresponding to pure silicon or to mixed metal−silicon cluster masses were more prominent. Photoionization of neutrals produced larger signals than direct cation sampling for all of these systems. Copper−silicon and silver−silicon clusters could be produced in usable quantities by direct cation growth, but not chromium−silicon clusters. However, under every set of conditions, the most abundant metal−silicon masses were those that have been reported previously.[1,5−7] In the case of copper−silicon, the $CuSi_7^+$ and $CuSi_{10}^+$ species were prominent and no other mixed clusters were produced with enough concentration to study with photodissociation. Silver−silicon has not been studied previously, but its mass spectrum was very similar to that for copper−silicon. In the chromium−silicon system, the $CrSi_{15}^+$ and $CrSi_{16}^+$ species were prominent, as seen initially by Beck,[1] and in the smaller clusters $CrSi_7^+$ was most abundant. These were also the only mixed clusters produced with enough density to study.

In the photodissociation experiments, we studied each cluster ion with both 532 and 355 nm excitation and as a function of the laser pulse energy over the range of about 10−50 mJ/pulse (unfocused). At lower pulse energies, essentially no signal could be measured. The distribution of product ions varied with the laser power, producing smaller fragments more efficiently at higher laser powers. This is consistent with a multiphoton dissociation mechanism, in which a threshold of high laser fluence is required for dissociation, as we have discussed previously for other strongly bound clusters.[3,26−28] After this level is reached, continued absorption by fragment ions is then difficult to control, resulting in sequential dissociation processes. It is therefore difficult to distinguish such sequential processes from the nascent ones. However, to address this issue, we employ different dissociation laser colors and fluences as much as possible, and we compare the fragments seen here to those already well-known for the corresponding pure silicon cluster cations from photodissociation[24,25] or collision induced dissociation.[29]

Figure 1 shows the photodissociation of $CuSi_7^+$ and $CuSi_{10}^+$ at 355 nm. Because of the computerized difference method used, the depletion of the mass-selected parent ion is shown as a negative peak, and the positive mass peaks represent the fragment ions produced by photodissociation. As shown, the most intense fragments detected from $CuSi_7^+$ are the Si_7^+ and Si_6^+ species. A small amount of $CuSi_6^+$ is also found. The $CuSi_{10}^+$ parent ion produces the prominent fragment ions Si_{10}^+, $CuSi_6^+$ and Si_6^+ and less intense masses corresponding to Si_4^+, Si_5^+, $CuSi_4^+$ and $CuSi_5^+$. These fragmentation patterns are essentially the same when the photodissociation wavelength is 532 nm. At higher laser fluence for either wavelength, the smaller fragment ions gain in relative abundance, whereas at the lowest laser fluence, the larger fragments (Si_7^+ and Si_{10}^+, respectively) have the greatest intensity. As we have discussed previously, this behavior is consistent with a photodissociation mechanism that involves multiphoton excitation, rapid internal conversion, and dissociation in the ground electronic state. The fragment ions thus detected represent the initial photofragments from the lowest energy dissociation channels as well as their sequential dissociation products. These fragments are then the same ones expected if these ions were studied with collisional dissociation.

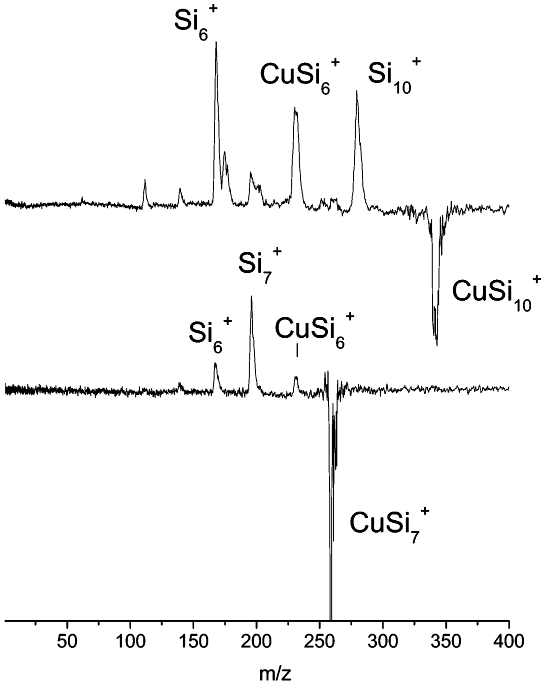

Figure 1. Photodissociation of mass-selected $CuSi_7^+$ and $CuSi_{10}^+$ at 355 nm.

From the results of power dependence and the previous work on pure silicon cluster cations,[24,25,29] we can establish the identity of the primary dissociation products in these two experiments. Si_6^+ is known to be a fragment ion produced from larger pure silicon clusters and its relative intensity is reduced at lower laser power. It is therefore likely to be formed via sequential dissociation of the larger fragment ions. The primary dissociation channel for $CuSi_7^+$ is therefore $Si_7^+ + Cu$, and the one for $CuSi_{10}^+$ is $Si_{10}^+ + Cu$. In both systems, $CuSi_6^+$ can only be produced by a separate parallel channel via the loss of neutral silicon atoms or clusters. In the $CuSi_7^+$ system this is a minor channel, but in the $CuSi_{10}^+$ system it is more important.

Considerations of mass and charge conservation allow us to comment on the ionization energies of the fragment ions detected. The wavelength independence of the signals seen indicates that dissociation takes place in the ground-state potential energy surface. If this is true, then the charge in the fragment ions produced will reside on the fragment species with the lower ionization potential. Si_7^+ must be produced via loss of neutral copper atom, and because the charge was retained on this silicon cluster, the ionization energy of Si_7 must be less than that of the copper atom (7.726 eV). In previous work, the ionization potential (IP) of Si_7 has been calculated to be higher than this (8.11,[30] 8.34[31] or 7.86[32] eV), and photoionization bracketing experiments had also estimated a higher value (about 7.9 eV).[33] In the same way, the $CuSi_6$ species must also have an IP less than that of the silicon atom (8.15 eV). This is consistent with calculations, which found that the IP of $CuSi_6$

is 6.88 eV.[10d] The observation of Si_{10}^+ indicates that the IP of Si_{10} is also less than that of the copper atom (7.726 eV). This cluster also has been studied with photoionization bracketing experiments and suggested to have a higher IP (about 7.9 eV),[33] but theory predicts lower values (7.66,[30] 7.49[31] or 7.95[32] eV), depending on the isomeric structure (C_{3v} or T_d).

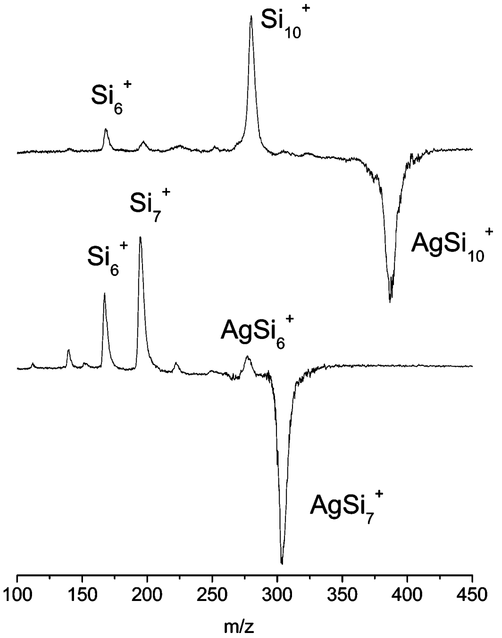

Figure 2. Photodissociation of mass-selected $AgSi_7^+$ and $AgSi_{10}^+$ at 532 nm.

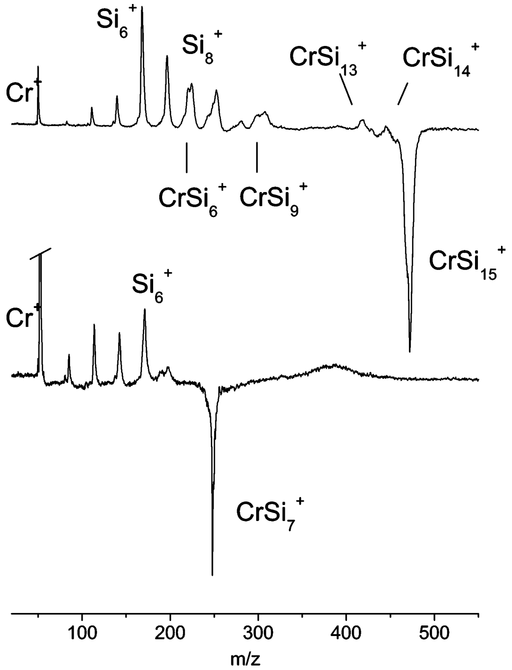

Figure 3. Photodissociation of mass-selected $CrSi_7^+$ and $CrSi_{15}^+$ at 355 nm.

These fragment ions also provide qualitative insight into the likely structures of these clusters and the relative strengths of metal−silicon versus silicon−silicon bonding. Some rearrangements in structure are certainly possible in the course of dissociation, but when clean production of one main fragment channel is observed, it is safe to make qualitative conclusions about structures. Because the elimination of copper atom and the formation of a pure silicon cluster cation is the most important primary photochemical process for both of these clusters, we can suggest that the copper atom lies in a position on the surface or in an exposed substitutional site in both of these clusters. Structures with exposed copper have been found by theory for $CuSi_7^+$,[10] and so this conclusion is consistent with theory. In the case of $CuSi_{10}^+$, early experiments suggested that the copper atom was encapsulated by silicon.[1] However, several isomeric structures have been proposed by theory, and the lowest energy isomer has surface-exposed copper.[10] An encapsulated-copper isomer is predicted at higher energy.[10] These results are actually not surprising, as the most prominent ions in the well-known pure silicon mass distribution are Si_7^+ and Si_{10}^+.[24,25,29] It is therefore likely that these stable and abundant silicon clusters are produced efficiently, and that $CuSi_7^+$ and $CuSi_{10}^+$ species result from addition of copper to these. In addition to these implications for structures, the efficient elimination of copper from both systems implies that copper−silicon bonding is weaker on average than silicon−silicon bonding. This conclusion is also supported by theory.[10] The surprise in these data is the prominence of the $CuSi_6^+$ fragment ion, especially as a fragment from the $CuSi_{10}^+$ parent, in both 355 and 532 nm dissociation experiments. This suggests that this cation is more stable than other small copper−silicon species, even though it is not prominent in the mass spectrum from the source. $CuSi_6^+$ was investigated previously by theory,[10] but there was never any suggestion that it has enhanced stability.

Figure 2 shows similar photodissociation data for $AgSi_7^+$ and $AgSi_{10}^+$ cations at 532 nm. As in the copper system, the most abundant fragment ions are Si_7^+ and Si_{10}^+, with smaller amounts of Si_6^+ that apparently comes from sequential dissociation of these primary fragments. The only evidence for metal-containing fragments is a small amount of $AgSi_6^+$ in the fragmentation of $AgSi_7^+$. Following the same logic discussed above, these data place an even lower upper limit on the IP's of Si_7 and Si_{10}, because both of these must now have values lower than that of the silver atom (7.576 eV). The efficient elimination of the metal atom in both of these systems again argues for structures with exposed or external metal, and again the metal−silicon bonding is apparently weaker on average than silicon−silicon bonding. Unfortunately, except for work on $AgSi_n$ ($n < 6$) species,[11] there are no other studies of the theoretical structures or bonding energetics for these silver−silicon clusters.

Figure 3 shows the photodissociation mass spectra of $CrSi_7^+$ and $CrSi_{15}^+$ at 355 nm. As in the copper and silver systems above, essentially the same dissociation channels are seen for excitation at either 532 or 355 nm. We also studied the photodissociation of $CrSi_{16}^+$, and its fragments are very similar to those of $CrSi_{15}^+$. These fragmentation patterns are quite different from those of the corresponding copper and silver systems. In particular, there is no evidence for the formation of the pure silicon cluster cation Si_n^+ as a product from either of the corresponding $CrSi_n^+$ parents.

In the case of $CrSi_7^+$, the most intense fragment ion is Cr^+, which is off scale in the figure. By mass conservation, this ion must be accompanied by the Si_7 neutral. This process is then analogous to that seen for $CuSi_7^+$ and $AgSi_7^+$, in the sense that the metal is eliminated. However, the IP of chromium is low (6.77 eV) and therefore the metal is charged and the silicon cluster is neutral. This places a lower limit on the ionization energy of Si_7. Combining this with the data from the silver system, the IP of Si_7 can be bracketed in the range of $6.77 < IP(Si_7) < 7.58$ eV. As in the discussion above, the clean elimination of metal here argues for structures with the metal exposed on the surface of the cluster. A second major channel in the fragmentation of $CrSi_7^+$ is the formation of Si_6^+. Because there is no primary fragment channel producing Si_7^+, this ion can only be formed with a corresponding neutral CrSi diatomic fragment. This indicates that the IP of CrSi is greater than that of Si_6. The observation of this mixed fragment suggests that the chromium–silicon bonding in this system is competitive with the silicon–silicon bonding.

The dissociation of $CrSi_{15}^+$ is significantly different from that of the other large metal–silicon clusters or the smaller $CrSi_7^+$ species. There is little, if any, evidence for the clean elimination of metal from an intact silicon cluster. No Si_{15}^+ fragment ion is detected, and the amount of Cr^+ is small, consistent with its production from sequential dissociation of other intermediate fragment ions. For the first time, we see large fragment ions that contain metal. For example, the largest fragments are $CrSi_{13}^+$ and $CrSi_{14}^+$, which can only result from the elimination of neutral silicon atoms or diatomics. In the only other photodissociation data on metal–silicon clusters, Beck reported a similar elimination of silicon atoms from $MoSi_{16}^+$.[1c] There are also noticeable amounts of $CrSi_6^+$, $CrSi_7^+$ and $CrSi_9^+$ present as overlapping mass peaks. Of these, $CrSi_6^+$ is most abundant, consistent with the MSi_6^+ ion seen for copper and silver. At lower mass, we have small pure silicon ions that could come from sequential fragmentation of the intermediate metal–silicon ions. For example, the lower mass range looks much like the fragments of $CrSi_7^+$ in the lower frame of the figure. However, there is no evidence for any strong signal from larger pure silicon clusters, such as Si_{10}^+, which is known to be especially stable. Likewise, there is no stable production of $CrSi_{10}^+$ in the mass spectrum analogous to the MSi_{10}^+ species seen for copper and silver. Apparently, the binding to chromium disrupts the tendency of silicon to form a stable $n = 10$ species. Therefore, the fragmentation of $CrSi_{15}^+$ (and $CrSi_{16}^+$, which is similar, but not shown) is significantly different from the smaller chromium–silicon cluster or from the copper– or silver–silicon systems. Stronger metal–silicon bonding is implied here, and this has in fact been suggested by previous theoretical calculations.[9–13] Encapsulated metal structures have been proposed previously for $CrSi_{15}^+$ and $CrSi_{16}^+$ clusters, and these fragmentation patterns are consistent with such structures.[9–13] However, other structures that have exposed metal might also be consistent with these data, as long as they give rise to particularly strong metal–silicon bonding.

Conclusion

Photodissociation processes are described for the first time for prominent copper–, silver– and chromium–silicon cluster cations. MSi_7^+ clusters of all three metals eliminate metal atoms, leaving an intact silicon cluster behind. For copper and silver, the higher metal atom ionization potentials lead to elimination of neutral metal and charged Si_7^+, whereas for $CrSi_7^+$ the metal is eliminated as an ion. In all three systems, additional fragmentation processes produce MSi_6^+ species, whose special stability has not been recognized before. This ion is prominent in fragmentation, but not in the nascent cluster distributions that grow from the source. Intense MSi_{10}^+ clusters are seen for both copper and silver systems, and these species also dissociate via the elimination of metal atoms. These fragmentation channels provide new data on the ionization potentials of Si_7 and Si_{10}. Chromium–silicon clusters in the higher mass range have more intense peaks at the $CrSi_{15}^+$ and $CrSi_{16}^+$ masses, as seen previously in other labs. These species dissociate by elimination of silicon atoms, producing a range of intermediate sized metal–silicon ions. These larger silicon clusters have significantly different dissociation patterns from the copper and silver systems, with stronger metal–silicon bonding.

Structures with encapsulated metal have been proposed in the past for many metal–silicon clusters. In the small cluster sizes, it is not possible to fully enclose metal atoms in a silicon framework. All the MSi_7^+ species studied here eliminate neutral or charged metal atoms, consistent with exposed-metal structures. In the case of $CuSi_{10}^+$, experiments originally proposed encapsulated structures, but more recent theory indicates that exposed-metal isomers lie lower in energy. We find that both $CuSi_{10}^+$ and $AgSi_{10}^+$ eliminate metal atoms with high efficiency, consistent with the exposed metal isomers. All recent theoretical calculations find that encapsulated structures are favored for transition metal–silicon systems when a large enough silicon network is present to enclose the metal. This is predicted for a number of MSi_{15}^+ and MSi_{16}^+ clusters, which exhibit high abundances in mass spectra. The dissociation of $CrSi_{15}^+$ and $CrSi_{16}^+$ is definitely different from those of the smaller clusters, with elimination of silicon rather than metal. This behavior could conceivably come from structures with a strongly bound surface metal. However, an interpretation that is consistent with theory and all of this photodissociation data, and is of course highly appealing, is that these systems represent encapsulated metal structures.

Overall, the fragmentation processes for these clusters point to stability patterns very different from those inferred from mass spectra alone. Apparently, kinetic effects are especially important in the growth of these metal–silicon systems, but photodissociation provides better insight into their stability patterns.

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