LASER ANNEALING OF SEMICONDUCTOR CLUSTERS: TRIMETHYLAMINE REACTIONS WITH POSITIVE AND NEGATIVE CLUSTERS

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ABSTRACT

Reaction studies with trimethylamine on positively charged laser-annealed silicon clusters of 39, 43, and 48 atoms magnetically levitated in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer reveal the same relative reaction pattern as previously observed for identical studies with ammonia and ethylene. The 39th cluster was found to be considerably less reactive than the other positive cluster sizes, and significantly, its negative ion is also relatively less reactive than the 43rd and 48th. The continued observation of this reactivity trend provides additional experimental evidence that the annealed clusters adopt well-organized structures, and that these crystal forms are similar for both charge states.

INTRODUCTION

Structure is the single most critical aspect of chemistry. The geometrical arrangement of atoms within molecules, and the detailed alignment between molecules as they react is what chemists spend most of their time thinking about. Yet, in spite of the major advances over the past few years in the study of surfaces, and the small clusters which are increasingly used to mimic them, structure is often the one parameter we know least about. In the case of small gas phase silicon clusters this problem is particularly difficult since there is currently no way of directly imaging these species. Unlike ordinary molecules, one cannot simply trap the species in a solvent and perform NMR, or in a single crystal and analyze the x-ray diffraction pattern. Clusters of elements like silicon are like the bare surfaces: they readily react with each other, and with most other materials. Their chemical valences are not satisfied, so they are not molecules in the rigorous sense of the word. As a result, we will always be limited to indirect evidence of the structure obtained from the free cluster traveling in empty space.

This does not mean, however, that one cannot learn about structure, or perform systematic experiments on clusters of known structure, even though they exist only as isolated species in the gas phase. In fact, the recent exciting activity in carbon cluster research is an example of how unique structures taken by a wide range of clusters can be worked out from indirect evidence. This evidence was accumulated from detailed gas phase experiments starting with exactly the same sort of supersonic beam laser vaporization

cluster experiments [1] as are now being performed with silicon, germanium, and a wide variety of metals and semiconductors. The key observations leading to the proposal of the soccerball structure of C_{60} [2] and the rugbyball structure of C_{70} [3], focussed on the fact that these clusters are remarkably unreactive toward chemical attack by small carbon radicals, under conditions where all other clusters reacted away [4,5].

The example of carbon clusters is instructive since C_{60} and C_{70} really are molecules which can be isolated and studied in condensed phase environments where ordinary structural probes are applicable. In this case the NMR spectral pattern observed for C_{60} and C_{70} provided definitive proof [6-9] of the structures which were originally proposed on the indirect evidence of their behavior in beams.

Studies of the gas phase silicon clusters have also produced some intriguing reactivity results. Here too, specially unreactive forms of some of the clusters have been identified [10-15]. Unlike carbon there was no evidence on the basis of the original silicon cluster distribution that there are any special clusters -- they all were found to add further Si atoms and small Si_x radicals as they grew to successively larger sizes [16,17]. A few years ago during experiments with positive silicon cluster ions levitated in the 6 Tesla magnetic field of the FT-ICR, it became clear that clusters with 21, 25, 33, 39, and 45 atoms are specially unreactive towards ammonia chemisorption. Since most clusters react readily with ammonia, these special sizes were termed the "magic number" clusters. Since then, this result with ammonia has been extensively verified [11,12], and the same pattern emerged with ethylene [13,14]. Again, as was the case with carbon, these specially unreactive clusters of silicon have been the focus of substantial activity within the theoretical community, and a number of structures for them have been proposed [18-24]. However, unlike carbon where the bonding rules were fairly well established and there was really only one compelling explanation, the mystery with silicon is deeper. There are many more possibilities, and the answer is likely to be far more subtle.

Not only do unreactive structures need to be deduced for the magic number clusters, but if this same trend continues to be detected in different chemical systems, an explanation that encompasses the entire trend must be found. This way the common factors that govern bonding in these special clusters may be discovered, if in fact there are any. Recently we have been engaged in trying to map out the extent of this trend, and this was the motivation for exploring the effect of changing not only the chemical reagent involved in the chemisorption, but also changing the charge state of the cluster, and switching the element itself from silicon to germanium.

Surprisingly, we have found that a simple annealing procedure affects the reactivity of these clusters more dramatically than any of the other parameters mentioned above. Annealing prior to reaction is critical to eliminate the confusion due to multiple structural isomers of each cluster size that react at different rates. Irradiation with the light of a XeCl excimer laser after the clusters are trapped in the ICR cell is quite effective [13-15]. We have also sought to resolve apparent differences between our results using the FT-ICR technique with those of Jarrold and co-workers using tandem quadrupole mass spectroscopy [25-28]. In their most recent work with silicon clusters reacting under at least partially annealed conditions at high temperatures [28] Jarrold's group has begun to observe some of the same magic numbers, but there are still discrepancies yet to be understood. They have proposed that part of the difference in results from the two methods may lie in the much lower pressure conditions of the FT-ICR

apparatus, and the consequent difficulty of observing direct molecular chemisorption of ammonia [28].

In order to further address such questions we present here an extension of our previous work on laser-annealed silicon clusters, in this case using trimethylamine (TMA) rather than ammonia, and probing both the negative as well as the positive clusters. Because of the large number of internal vibrational modes in TMA, and its greater basicity, we suspected this reagent would be much more effective at molecular chemisorption in the FT-ICR apparatus than ammonia. We find that the magic number pattern persists under these conditions, and appears to apply to the negative clusters as well.

EXPERIMENTAL

The silicon cluster ions were generated by laser vaporization in a supersonic cluster beam that was directly injected into the analysis cell of the FT-ICR apparatus. The apparatus and methods, including our new cluster source, have been described in detail elsewhere [13-15]. A slight modification to the ICR cell has been made. The i.d. is smaller by 20% to accommodate a liquid nitrogen dewar that surrounds the whole cell that was kept at room temperature in this study. Successive cluster pulses were roughly mass selected by pulsed deceleration of the flight tube as the clusters entered the cell, and injected at a rate of 10 Hz until the cell was full, here 120 pulses. The ions execute typical cyclotron orbits about the field lines of the 6 Tesla magnet, and are trapped along the magnetic axis by electrostatic potentials at either end of the cell. The trapped clusters are then thermalized for 3 seconds by collisions with argon at 1×10^{-6} Torr, or about 100 collisions.

Even though a rough mass selection is done during the injection process, many ions that we don't need may be subsequently ejected. Following a 1 second waiting period to pump out the thermalization gas, ions can be eliminated from the cell by increasing the radius of their cyclotron orbits so that impact with the cell walls occurs. This is accomplished by selective rf excitation of resonance cyclotron frequencies by the application of a SWIFT waveform (stored waveform inverse Fourier transform). SWIFTing involves the calculation of the inverse Fourier transform of the desired rf excitation and use of a fast digital to analog converter to place this computed voltage waveform on the excitation plates of the ICR cell [12]. This SWIFT excitation was followed by a second 100 collision thermalization period with argon to ensure the clusters were at room temperature. The mass distribution of selected clusters after the SWIFT procedure is shown in the top panel of Fig. 1.

Reaction was carried out on the selected cluster inventory by exposing the clusters to TMA. TMA is admitted to the vacuum system by a pulsed valve from the front of the cell. Because of the poor conductance of the ICR cell, and the relatively large sticking probability of TMA to the stainless steel walls of the vacuum system, the pressure readings on either side of the ICR cell failed to reach a constant value during the reaction time. As a result, the pressure values we have reported are uncertain by a factor of ten. The reactant gas was allowed to pump out of the cell for 5 seconds before exciting the ICR transient.

To compare the reaction of the annealed clusters, the injection, thermalization and SWIFT sequence is repeated, but after the second thermalization period, the clusters in the cell are radiated with XeCl excimer

laser light. This beam went through a 1-cm diameter light baffle down the axis of the magnet. A thermalization period follows the laser treatment before an identical exposure to TMA. Again a 5 second waiting time to pump the TMA out of the cell was allowed before exciting the ICR transient.

RESULTS AND DISCUSSION

Figure 1 displays the result of a typical reaction experiment with TMA on a few selected positive clusters of silicon. Since the purpose of this initial study was simply to check if roughly the same pattern of reactivities seen before would apply to TMA as well, we selected (using SWIFT) what had previously appeared to be one of the most inert, Si_{39}^+; one of the most reactive, Si_{43}^+; and one of intermediate reactivity, Si_{48}^+. The top panel (a) of Fig 1, shows the FT-ICR mass spectrum of this initial set of cluster ions. Note that the SWIFT selection was made so that somewhat different isotopic widths were left behind for each of these three cluster sizes. We have found this to provide a convenient tracer of the parentage of subsequent chemisorption products.
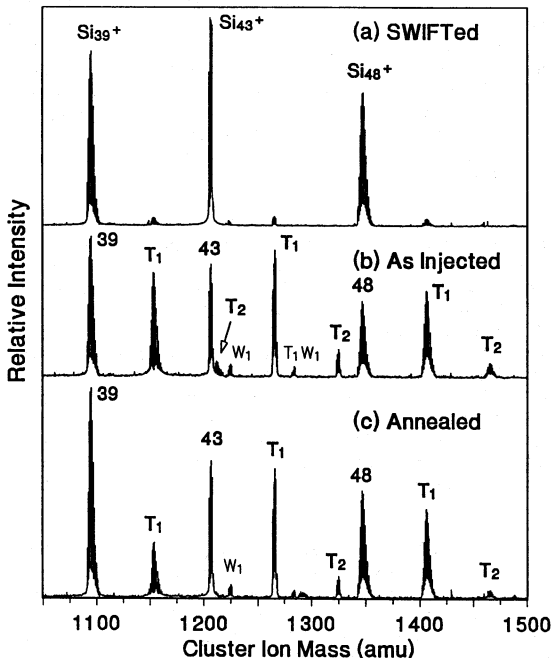

Figure 1. Positive silicon cluster ion reaction study using FT-ICR: (a) mass spectrum of cluster distribution prior to reaction, as selected by SWIFT ejection, (b) result of 9 second exposure to TMA at roughly 5×10^{-8} torr, (c) result of identical exposure to TMA, but with the clusters previously annealed by 30 pulses of a XeCl laser followed by a 3 second thermalization with argon at 1×10^{-6} torr.

The middle panel (b) of Fig. 1 shows the resultant mass spectrum after reaction with TMA at 5×10^{-8} Torr for 9 seconds. T_1 marks the addition of one TMA to each bare cluster, and further to the right of each bare cluster T_2 indicates the addition of a second TMA. Notice the thicker width of the $Si_{39}[TMA]_2^+$ peak that is riding on the shoulder of the thinner bare cluster Si_{43}^+ peak. The peak labeled W_1 is $Si_{43}H_2O^+$ due to reaction with the background water in the cell. The unannealed clusters all react readily, in fact, the addition of one and two TMA groups is evident on all three of the bare clusters. Notice that without the laser treatment, there is only minor variation in the reactivity of these three clusters to TMA.

The bottom panel of Fig. 1 is the result of an identical TMA exposure. after annealing the clusters. To study the annealed clusters, the injection, thermalization and SWIFT sequence was repeated, but after the second thermalization time, 30 pulses of XeCl light at 50 Hz and 1mJ/cm2-pulse radiated the clusters in the cell, followed by another 100 collisions with argon for cooling. To verify that the annealing was complete, we reproduced the results of the previous ammonia experiment [14] with these annealing conditions just before the TMA reaction. The relative reactivity of Si_{39}^+ and Si_{43}^+ is remarkably different from the unannealed clusters. Si_{39}^+ is less reactive to the single addition of TMA, and no addition of two TMA groups is observed. Particularly striking is the fact that the vertical scale on the lower two panels is the same. The bare cluster signal for Si_{39}^+ is actually enhanced, indicating that conversion of a reactive form of Si_{39}^+ to a less reactive form is occurring, not photofragmentation of the less energetically stable isomer.

The positive clusters show the same relative reactivity pattern toward TMA as NH_3 [14], except the contrast between Si_{39}^+ and Si_{43}^+ is less pronounced. We suggest this is due to TMA being a better base, therefore it has a better binding affinity even for the relatively unreactive clusters. We hoped that comparing the results of the TMA and NH_3 experiments might also give us a clue concerning the chemisorption mechanism of these reagents. We reasoned that if the chemisorption is dissociative, then we could expect the methyl groups to dissociate differently onto the cluster than the hydrogens would. Instead, the reactivity pattern is the same, at least for these three clusters. During the course of these experiments, we noticed that TMA could be removed from the silicon clusters with the XeCl light, and no other products were seen except the bare parent cluster. We see no suggestion in our data that a dissociative chemisorption mechanism, as proposed by Jarrold et.al. [28], is occurring here.

As shown in Fig. 2, results on the negative ions are very much like the positive ions. The negatives are generally less reactive than the positives, but all clusters in the middle panel show reaction products. Annealing the negative ions is trickier than the positives since the negative ion is likely to photodetatch its extra electron. Signal loss due to this mechanism hindered execution of this experiment that was completed with less laser light. Only 15 shots of XeCl light at 0.7 mJ/cm2-pulse were used as the annealing treatment for the clusters shown in the bottom panel of Fig. 2. As a result we are not confident that the negatives are completely annealed, and we plan to try the annealing with a longer wavelength laser to get below the photodetatchment threshold. All three clusters react with TMA and Si_{43}^- is specially reactive. Even fewer of the Si_{39}^- clusters react after annealing, enhancing the reactivity difference between Si_{39}^- and Si_{43}^-. Even though these negative clusters may not be annealed completely, the same contrast in reactivity between Si_{39}^- and Si_{43}^- is clear. Note that the vertical scale for panels (b) and (c) is the same, as in Fig. 1. This pattern is in agreement

with earlier results on the negative ion with ammonia [12], and we interpret this as additional evidence for dramatically different structures for silicon clusters of 39 and 43 atoms.

The persistence of the magic number pattern with different reagents and charge states for silicon continues to support the idea that these annealed silicon clusters arrange themselves into unique structures. Not only is this trend observed with the negative silicon ions, but initial results of reaction of germanium clusters with NO show that the same size clusters, Ge_{39}^+ and Ge_{45}^+ are relatively inert, and Ge_{43}^+ is the most reactive [15]. We plan to look for the same magic number trend on germanium with TMA.

As more and more evidence is collected that this reactivity pattern is real and easily repeatable on an annealed cluster sample the conclusion that unique structures exist is strengthened. The same behavior for the negative clusters, and possibly germanium, suggests that we are looking at a fundamental property, and that the structural packing is a robust consequence of the bonding in these tetravalent elements. As such, the magic number
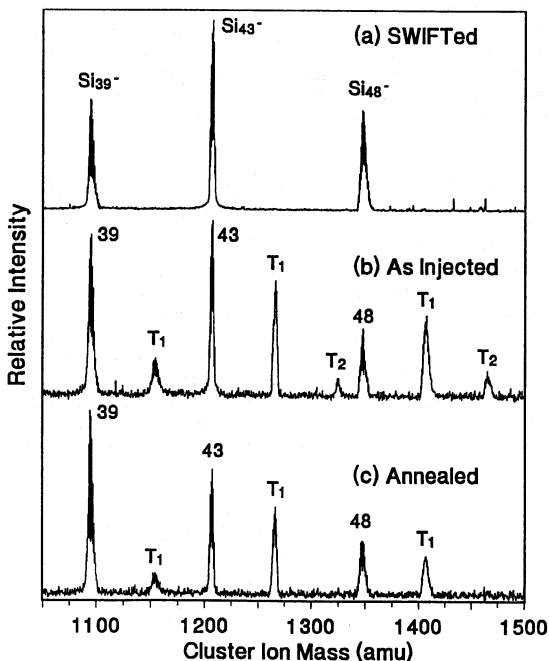

Figure 2. Negative silicon cluster ion reaction study using FT-ICR: (a) mass spectrum of cluster distribution prior to reaction, as selected by SWIFT ejection, (b) result of 10 second exposure to TMA at roughly 1×10^{-7} torr, (c) result of identical exposure to TMA, but with the clusters previously annealed by 15 pulses of a XeCl laser followed by a 3 second thermalization with argon at 1×10^{-6} torr.

clusters will continue to be useful targets for theoretical modeling to deduce what these nanocrystalline forms might be. If the magic number reactivity trend continues to be seen in such a wide range of experiments, the common factor, if it exists, that results in this set of clusters being specially unreactive may provide important insight into the rules that govern how these clusters like to come together, and how the bulk surfaces like to reconstruct.

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