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Germanium clusters: More magic numbers

Anderson, Lila Rose, Ph.D.

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ABSTRACT

Germanium Clusters: More Magic Numbers

by

Lila R. Anderson

Clusters of silicon and germanium exhibit multiple isomers that can be annealed to single unique structural forms. The "magic number" reactivity trend observed for positive silicon clusters in the size range from 10 to 45 has also been observed in reactions with ammonia, and has also been observed with ethylene, water and trimethylamine (TMA). It was observed that Si_{21}^+ anneals to a reactive form, so is no longer a "magic number". Negative silicon ions also display the same pattern. Additionally, mass-selected germanium clusters were levitated in the FT-ICR, and probed in chemisorption reactions with nitric oxide, TMA, and water. Clusters in the 10 - 51 atom size range were effectively annealed to unique structural forms by collisional excitation and cooling through infrared radiation and collisions with argon. For clusters over 33 atoms in size the reactivity pattern for the two elements is the same, suggesting the structures of these clusters is identical and common to tetravalently bonded clusters. Fragmentation studies were also performed to elucidate the difference in relative stability of the clusters and a correlation between stability and reactivity was found.
Acknowledgment

Thanks to the entire ICR group who contributed to getting these experiments going: Ting Guo, Changming Jin, and Mike Alford. Many productive discussions with Mike were particularly appreciated. Special thanks to Peter Nordlander and Rick Smalley.

Question To Wolfgang Pauli:

If the surface was invented by the devil, who invented clusters?
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I. INTRODUCTION AND BACKGROUND

Microclusters as Molecular Models of Interfaces

It is hoped that the study of the physical and chemical properties of clusters, such as reactivity, photofragmentation, photodetachment, structure, ground state energy, and bonding will provide insight for surface scientists in understanding similar properties of bulk surfaces. In particular, clusters have the advantage of being discrete and finite molecular units. This makes them significantly simpler systems to model mathematically than the bulk surface, and in some cases their physical properties can be calculated from first principles. In anticipation of advances in parallel computing over the next ten years, it is likely that the calculation of the ground state energy of a silicon or germanium cluster of 100 atoms will be routine. Given this eventuality, we are accumulating experimental data that will guide future calculations. Instead of using semiconductor single crystals to idealize the surface, clusters can be used as molecular models to study electronic and geometric structure, and possibly also the effect of steps, defects, and dangling bonds. The high surface to volume ratio of these molecules makes them excellent for the study of catalysis, nucleation and growth of crystals, and thin film preparation of electronic materials. The novel structures of clusters provide a fertile testing ground for fundamental ideas and concepts about underlying principles that govern physical properties such as bonding, structure and reactivity that can be applied particularly at surfaces.

The idea that clusters will be useful as molecular models hinges on the premise that they actually adopt unique structural forms. In our work on silicon clusters, not only did we conclude that clusters annealed to single forms, but we
observed the same patterned reactivity trend with several different reagents, and also on both positive and negative ions. Initially it appeared that the pattern of germanium reactivity might be the same as silicon, and we see a strikingly similar pattern in germanium clusters with three reagents, nitric oxide and trimethylamine (TMA) and water. Fragmentation patterns from clusters of these two elements also bear a striking resemblance to one another. These patterns are clues to fundamental intrinsic rules about how these atoms bind together to form molecules. Since a cluster is more surface than internal volume these observations, and the conclusions we draw from them, may provide us with valuable insight about the surfaces and interfaces of their parent semiconductors.

**Cluster Structures**

Structure is the most critical aspect of the physics and chemistry of any molecular system. 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 and germanium clusters this problem is particularly difficult since there is currently no way of directly imaging these species. Clusters are formed in vacuum by way of a kinetic trick; unlike ordinary molecules one cannot simply trap them in a solvent and perform traditional analytical tests. Clusters of elements like silicon and germanium are like their parent bare surfaces: silicon clusters react readily react with each other, and with most other materials; germanium clusters, like germanium surfaces, are not very reactive at room temperature. However, the chemical valences of these
clusters 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 unusual behavior of $C_{60}$ in cluster beams led to the dramatic discovery of a new form of carbon: fullerenes. The recent exciting activity in carbon cluster research is an example of how unique geometries 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 single-line NMR spectral pattern of $C_{60}$ confirmed what had already been deduced from natural abundance data, photofragmentation data, photoelectron spectra, and the shrink wrapping experiments- the hollow closed cage structure of $C_{60}$, the third form of carbon.
**Semiconductor Clusters**

Since the advent of cluster research there has been a debate as to whether clusters adopt compact geometries of their own, or if they are more simply like pieces of their corresponding parent material that has been lifted off of a surface. This has been particularly heated about silicon. For the present, minimum energy structures have been calculated for silicon clusters up to 10 atoms in size\(^7\), but beyond this the problem quickly becomes numerically intractable owing to the many degrees of freedom involved. Searching for a lowest-energy configuration for a given size cluster by locating and comparing all the local energy minima is extremely difficult computationally for larger clusters.

But for the experimentalist, the immediate question is this: Can this lowest energy configuration be observed? If clusters obey their own set of bonding rules, are there single favored lowest energy structures for each size, or as the number of atoms in a cluster increases will there be many geometrical forms that a cluster may populate at room temperature?

For clusters in the size range 10-100 atoms, it is easy to imagine many different bonding patterns that the atoms could adopt. In many cases there could be several alternative structures that are isoenergetic, or nearly so\(^8\). In the worst case scenario the clusters continually change shape as they interconvert from structure to structure. Since these isomers have different physical properties, reaction rates and fragmentation patterns will be confused by the ambiguity of which structural isomer, or group of isomers, was studied in any particular experiment. Clearly for experimental results on cluster reactivity and fragmentation to be any reflection on structure, this problem of isoenergetic isomers must be thoroughly addressed and resolved.
Cluster growth in supersonic beams that are the result of laser vaporization occurs first by single atom addition, followed by aggregation of small clusters to form larger ones. This sequential growth sequence does not ensure that when cluster growth ceases, the resultant clusters will be in their thermodynamically favored forms. Cluster generation is, after all, achieved by a kinetic trick that allows us to trap and study bits of matter that are not stable by themselves in the condensed phase. If the clusters are cooled too rapidly, bond rearrangement will stop before the molecule has settled into its minimum energy geometry. It will be "frozen in" to a thermodynamically less favored configuration. In this case the cluster inventory will be a mixture of isomers. Therefore the rate of cooling must be considered an experimental parameter, and it must correspond to the clusters' intrinsic annealing time. It is with this problem in mind that work on cluster reactivity trends has keyed in on evidence for multiple isomers and the ability to alter the abundances of the isomers by annealing. In the limit of complete annealing all clusters will be in their favored configuration. This procedure insures that experiments can be done on the same cluster inventory from day-to-day and on differing experimental apparatuses.

Where semiconductor clusters are concerned, these questions began to arise concerning some astounding results compiled by Elkind et.al. in what consisted of straightforward chemisorption experiments. They reported a reactivity difference between silicon clusters that spanned two orders of magnitude. $\text{Si}_{33}^+$, $\text{Si}_{39}^+$, and $\text{Si}_{45}^+$ were found to be unreactive to chemisorption with ammonia and methanol, while $\text{Si}_{36}^+$ and $\text{Si}_{42}^+$ were found to react easily. This was the first data generated by the Smalley group that has
proven to be crucial information in the process of establishing the idea that molecular clusters do form particular geometrical structures which may be largely *unrelated* to the bonding pattern in the bulk element. It was also in this work that it was suggested that these clusters have well defined structures that may be driven by the minimization of surface energy. Unlike metallic clusters that consist essentially of a core of closely packed atoms, clusters of silicon and other covalently bonded materials consist of a core and a surface. Both compete in forming the best structure. The surfaces may tend to restructure to minimize dangling bonds, and is doing so dictate the presence or absence of reactive sites. So by observing differences in reactivity we are observing differences in structures.

**Magic Numbers**

Although less reactive than any silicon surface, single crystal or amorphous, most clusters react readily, however, there are these certain unreactive one, termed the "magic number" clusters that are the exception. In the case of medium-sized (20-60 atom) clusters of silicon the magic number behavior first seen by Elkind *et al.* was confirmed and expanded by Alford *et al.*\(^{10,11}\) (see figure 1). Sharp variations were seen in reaction rates as a function of cluster size in reaction with ammonia. Those clusters with 11, 21, 25, 33, 39, and 45 atoms appeared to be relatively inert while clusters *with only one atom more or less* reacted rapidly, \( \text{Si}_{43}^+ \) being the most reactive. Presumably, the magic-numbered clusters have surfaces that are constructed so as to avoid a reactive site and the more reactive clusters have a higher dangling bond density. Here again was more evidence that clusters are not amorphous chunks
Figure 1. Rate constants for chemisorption of one NH$_3$ onto silicon clusters of different sizes. Magic Numbers are unreactive compared to their neighbors.
of bulk material, but that each size has a favorite configuration. These clusters had "crystallized" to particular forms, some of which had few if any active sites for ammonia chemisorption on their surfaces.

Since then this result with silicon and ammonia has been extensively verified\textsuperscript{10,11}, and the same patterned reactivity emerged with ethylene\textsuperscript{12,13}, and water. Again, as was the case with the unusual carbon cluster results, these specially unreactive clusters are the focus of substantial activity within the theoretical community, and a number of configurations for them have been proposed\textsuperscript{8,13-18}. However, unlike carbon where the bonding rules were fairly well established and there was really only one compelling explanation, the cage of five- and six- membered rings, the mystery with silicon and germanium is deeper. There are many more possibilities, and the answer is likely to be far more subtle.

In spite of the intimidating computational intricacies, theorists have attempted some calculations on some of the larger silicon clusters. Restrictions on what the most likely structures might be are deduced from physical insight, empirically developed models, or geometrical and symmetry arguments. By considering the experimental data that we provide, theorists are able to impose limitations on the reasonable choices for structures of the clusters, thereby simplifying their job.

One particularly appealing example is a structure suggested by Kaxiras\textsuperscript{16} for Si\textsubscript{45}$^+$. The unusual low reactivity of these molecules motivated him to seek an explanation on physical grounds for the relative inertness of these molecules. It is based on the idea that the magic number clusters are relatively unreactive
Figure 2. The proposed Kaxiras structure for $\text{Si}_{45}$.
because the surface resembles a stable reconstruction of the bulk crystal around a core of tetrahedrally bonded atoms. This was a natural hypothesis to explore since we know that reconstructions passivate the bulk surfaces, and can diminish the number of dangling bonds by 60%. Figure 2 shows the proposed $\text{Si}_{45}^+$ structure. The surface of this cluster is similar to the 2x1 reconstruction of the Si(111) surface. The pi-bonding between the dangling bonds that stabilizes the bulk surface would seem to account for the passivation of the surface of this cluster. Additionally it has natural "cleavage planes" that would allow it to split off a six- or ten- membered fragment making it consistent with the fragmentation data. He has also proposed a structure for $\text{Si}_{33}^+$ that is similar to the 7x7 reconstruction.

The Importance of Annealing

After the implementation of a new cluster source$^{13}$ on the Fourier transform ion cyclotron resonance (FT-ICR) apparatus, we confirmed the magic number behavior with ammonia in substantially more detail, and also completed an extensive chemisorption study with ethylene.$^{12,19}$ that reveals the same oscillatory reactivity trend. All clusters exhibited more than one chemisorption reaction rate, which indicated multiple isomers were present. In fact it is expected that all silicon and germanium clusters larger than eight atoms will exhibit more than one isomeric form. Confronted with the clear existence of multiple isomers, it became imperative to find a reliable way either to sort them out quickly, or to anneal them. Otherwise experimental results would be hopelessly ambiguous and misleading.
Surprisingly we found that a simple annealing procedure affects the reactivity of these clusters more dramatically than any other experimental parameter - even what reagent is used, or even the charge state of the cluster. Annealing prior to reaction eliminates the confusion due to multiple isomers of each cluster size that react at different rates. Annealing clusters alters the abundances of the isomers, and in the limit of complete annealing, we have observed these cluster inventories of single structures. Irradiation with the light of a XeCl excimer laser after the clusters are trapped in the ICR cell is quite effective\textsuperscript{12,13,20}. The details of the experimental apparatus are given before an example of the annealing procedure (see section III), so that the procedure itself is more easily understood.

In fact, in the work of Alford et. al.\textsuperscript{10,11} partial annealing accidentally occurred due to the use of an ArF ionization laser for the production of ions of the large clusters. In irradiating the clusters to promote ionization, annealing also occurred. As a result the magic number clusters Si\textsubscript{39}\textsuperscript{+}, and Si\textsubscript{45}\textsuperscript{+} were seen in their unreactive forms. Without such a fortunate accident, the magic number reactivity pattern may have not been observed. In our later work on clusters injected into the FT-ICR cell without any photoexcitation, the low reactivity of these clusters is masked by higher apparent reaction rates due to the faster reacting isomer component that has been left in the cluster inventory. See the discussion of fig. 8 in section III.

We have also sought to resolve differences between our results using the FT-ICR technique with those of Jarrold and co-workers using tandem quadrupole mass spectroscopy at AT&T Bell Labs\textsuperscript{19,21-27}. In their most recent
work with silicon clusters reacting under at least partially annealed conditions at high temperatures\textsuperscript{25} 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, and the consequent difficulty of observing direct molecular chemisorption of ammonia\textsuperscript{28}. We think a more likely explanation is found in the differing time scales and pressure regimes for the two experiments. Reactions in the FT-ICR can be monitored for as long as 15 to 30 seconds. In the flow tube reactor, on the other hand, reactions are followed on the millisecond time scale. In his most recent chemisorption studies of annealed silicon clusters and ethylene he is beginning to observe the same magic numbers that we do. However, with ammonia as a reagent, he sees no annealing effect. Although he suggests that the difference with ammonia may be due to the two laboratories observing different processes: dissociative chemisorption versus molecular chemisorption, studies we have made on the dissociation energy of TMA chemisorbed onto silicon clearly indicate that a single TMA group is only loosely bound to the $\text{Si}_{45}^+$ cluster for instance. It may be that Jarrold is recording reactivity that is actually only a loosely bound physisorption of ammonia on the clusters, and if he could extend the observation time, he might see the ammonia desorb off of the clusters.

Jarrold has stated that his annealing procedure does not result in the conversion of his cluster inventory to single isomers. We suggest a simpler explanation. If an annealing procedure does not affect the reactivity of the resultant "annealed" clusters, and since he still observes multiple isomers, then he most probably simply isn't annealing the cluster inventory very well. The
effect of multiple isomers in this system is to wash out the oscillations in reactivity because the less stable isomers tend to react closer to the collision rate. The simplest explanation for the confusion evident in Jarrold's result is probably the same problem he has had all along: multiple isomers and incomplete annealing.

In an effort to establish a correlation between cluster stability and reactivity we have done a survey of germanium and silicon cluster fragmentation. One must be careful not to confuse relative stability of geometrical isomers, which may correlate with reactivity, with relative stability of different cluster sizes. We find an interesting correlation between stability and low reactivity, which is what is generally expected.

We Need a Theory That Explains the Existence of the Entire Trend.

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, and also the fragmentation data must be found. 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.

In order to further explore how general this reactivity trend is we present here an extension of our previous work on laser-annealed silicon clusters, in this
case using TMA rather than ammonia or ethylene, and probing both the negative as well as the positive clusters. Because of the large number of 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 same magic numbers pattern persists under these conditions for positive and negative silicon clusters. This patterned reactivity trend has now been observed for ammonia, methanol, ethylene, TMA, and for the negative ions as well.

Germanium Clusters: Further Evidence

In our previous work with germanium and nitric oxide part of the same pattern, Ge$_{39}^+$ and Ge$_{45}^+$ are unreactive and Ge$_{43}^+$ is the most reactive, was discovered (see section III). We also see this result in the study of germanium positive ions reacting with TMA presented here. *It is striking and unusual to see this similarity in chemisorption characteristics between clusters of two different elements in any size range.* We may be tracking the result of the similarity of bonding in four-coordinated covalently bonded solids. Our working hypothesis became this: If in fact lowest-energy configurations are driven by minimization of surface energy, perhaps the arrangements that most efficiently tie up dangling bonds for any particular cluster size are basically the same for all the semiconductors which are four-coordinated, and adopt the diamond lattice in the bulk phase - at least for some cluster sizes.
So our germanium work was initially motivated by the dramatic results we found that suggested the packing of silicon and germanium clusters may be identically the same. In expanding the search to germanium, we found the overall reactivity of germanium clusters to be at least an order of magnitude lower than silicon clusters. Even though the absolute reaction barrier is higher, the variation with cluster size and reactivity has some remarkable similarities.

In fact the reactivity patterns for silicon and germanium differ until up to cluster size approximately 33 atoms. It may be that for these cluster that the packing for these two elements is similar, with the added complication of different surface reconstructions which dominate due to their small size. For the medium size and larger clusters, however, the reactivity patterns begin to match up. This is a striking result that suggests the packing for well-annealed clusters in this size range is identically the same for both elements.
II. EXPERIMENTAL

FT-ICR is one of the most powerful techniques for studying ion-molecule reactions. Over the past decade a number of methods were pioneered for the extension of this technique to the use of external cluster ion sources\textsuperscript{29-32}. Alford \textit{et. al.}\textsuperscript{33,34} and Kofel \textit{et. al.}\textsuperscript{34,35} independently demonstrated that a simple einzel lens system would guide the clusters into the ICR cell as long as the ion beam was restricted to a narrow conical region centered around the central axis of the magnetic field of the ICR trap. For metal and semiconductor clusters this technique has opened up a vast array of new experiments\textsuperscript{9,10,35-37}. To extend the mass range of clusters we could routinely generate, and also to improve the reliability of its operation, we devised a new external cluster beam source, that we named the "Minisource" in recognition of its relatively diminished size.

\textbf{Minisource Design Philosophy}

The supersonic cluster ion beam source pioneered by this group was based on laser vaporization of a rotating, translating target surface mounted on the front of a pulsed supersonic valve\textsuperscript{38}. The pulsed valve at the heart of this design was a double solenoid nozzle (600 microseconds long gas pulse) that required a large chamber and a 30,000 \( \text{ls}^{-1} \) pumping station (total volume of 219 liters). Although a major innovation at the time, this source still had fundamental operating flaws. The necessity of extracting heavy ions from the cluster beam into the ICR cell limited the cluster mass range that could be studied, since extraction was increasingly inefficient as cluster size increased. Two other
problems that impeded progress of work were shot-to-shot variation in signal intensity and a high maintenance target disk movement system.

Experience with this source taught us much about what criteria would be important in its redesign. It worked well only under two conditions. When the carrier gas pressure above the target was too small to generate a good supersonic expansion, a cluster beam was generated but the clusters were hot. If a lot of gas was used the flow conditions were dominated by turbulence. We now know that when we got signal, a turbulent flow swept off the top portion of the plasma plume where some free atoms and small clusters were still present. But the signal intensity was chaotic and jumpy. Changes to the nozzle block itself and the positioning of the carrier gas valve with respect to the sample improved performance somewhat, and we learned that the timing of the vaporization laser relative to the helium carrier gas pulse is the most important parameter that governs clustering. If firing is too late in the pulse, a well-defined shock wave forms in the high density carrier gas above the target as the laser-vaporized plume begins to expand. Since this shock wave cannot travel much faster than the speed of sound in the carrier gas at the initial temperature of the nozzle, the vapor plume is confined for several microseconds resulting in most of the material emerging as macroscopic aerosol particles, with little if any net yield of clusters in the 1-1000 atom size range.

The operation of this source was not sufficiently flexible to address this plasma confinement problem, and this was the fundamental flaw in the system. The standard laser-vaporization nozzle source\textsuperscript{38} incorporated a straight-through flow of helium over the target disk, and the solenoid valve action was too slow
and sluggish for the gas pulse delivery to be a well-timed event compared to the laser shot (microsecond time scale).

Ideally the hot vaporized plume would expand unhampered by the presence of helium above the target, but only a few microseconds later the carrier gas must be available for cooling in the supersonic expansion. By firing the vaporization laser on the leading edge of an extremely fast-rising carrier gas pulse, the vapor plume expands unimpeded for a while before it is entrained in the rising density of the carrier gas pulse. By integrating such a valve into the design, we are able to adjust the clustering kinetics by dictating the confinement pressure felt by the hot rising plasma, and also ensure that a sufficient pressure of carrier gas follows to get a good supersonic expansion. The Minisource is compact, highly reliable, and clean. We routinely generate more intense, well-cooled supersonic metal and semiconductor cluster beams than were ever dependably available from the old source.

The Minisource is the smallest external ion source yet used with an FT-ICR apparatus. Because of its small size, it is readily pumped with a single 170 l s⁻¹ turbo pump. The resultant high quality vacuum properties of the source allow it to be mounted directly on the magnetic axis of the superconducting magnet of the FT-ICR without the use of an extraction step or focussing lenses. The Minisource has proved itself to be a workhorse that is compact, reliable, and easy to maintain, which makes for dramatically reduced spectrometer down time compared to the old source. Although primarily designed for the production of metal and semiconductor clusters, it may prove to be highly valuable for the
production and FT-ICR study of a wide variety of molecular ions and complexes, including peptides, nucleic acids, and other large biopolymers.

**Key Innovation: Magnetic Leaf Pulsed Valve**

The Minisource is shown in Fig. 3. Since the guiding concept for this design was that it is best to fire the vaporization laser on the leading edge of the rising carrier gas pulse, the fast valve is the most important component in the Minisource. The pulsed nozzle used is of the magnetic "current loop" variety first proposed by Dimov\(^39\), and used to provide short pulses for beam-beam scattering experiments by Gentry and Giese\(^40\). An early version was first implemented by Liverman, Beck, Monts, and Smalley\(^41\) for laser spectroscopy of cold molecules and radicals, and was used in the very first experiments in laser vaporization production of cluster beams\(^42\). Ironically, it was abandoned in favor of the double solenoid designs that delivered a higher gas flow\(^43\).

Although the current loop design delivers less total gas flow per pulse than the old double solenoid design, with a suitably miniaturized nozzle design the same high peak pressures may be obtained in the nozzle.

The pulsed valve used in this new cluster nozzle is derived from our original design, but is adapted from a much improved version now available commercially\(^44\) (labelled "fast pulsed valve"). The smaller gas load involved allows the source to be pumped by a single turbo pump, and the timing of the open/close mechanism is highly reproducible. This valve uses a gold-plated beryllium-copper leaf spring clamped to seal over the top of a 0.07 cm i.d. viton O-ring. As installed, the fundamental up-down flexing vibrational mode of this spring has a frequency of roughly 4 kHz. When a 20 microsecond current pulse
Figure 3. Minisource Schematic
is applied along the length of the spring the associated magnetic field repels a corresponding field generated from a return conductor mounted underneath, generating an impulse to excite the spring vibration. At some point in the upward travel of the center of the spring, the seal with the O-ring is broken and gas begins to flow through the valve, the flow continuing until near the end of the first half-cycle of the harmonic spring vibration when the seal with O-ring is re-established.

The exact opening and closing time of the valve is a function of magnitude of the current pulse that drives the valve, the gas pressure in the valve, the valve temperature, and the mechanical adjustment of the O-ring compression. Once these parameters are set, however, the timing of the valve is quite reproducible since it relies on what is effectively an impulse excitation of a simple mechanical resonance. The driving circuitry is controlled so that the spring is never driven past its elastic limit.

This mechanical resonance aspect of the magnetic current loop pulsed valve design is vital to the successful operation of the entire cluster beam apparatus. As long as the spring is neither overheated nor over-driven, its fundamental flexing frequency is constant. This provides the timing accuracy that is so critical in synchronizing the vaporization with the rising edge of the gas pulse within an error of a few microseconds.

The Supersonic Nozzle and its “Waiting Room”

The addition of the "waiting room" to the nozzle block was a significant design improvement over the original geometry that had a simple straight tube in
this position (see blow up Fig. 3). It is actually an integrating volume that permits
the hot plasma to expand unimpeded above the target disk before it is swept
away by the pulse of helium gas. This improvement, coupled with the unique
timing aspects of the pulsed valve has given us control over the kinetics of the
clustering and has allowed us the flexibility we need to optimize signal intensity
for each element.

Once the valve is open, the carrier gas passes through the main sealing O-
ring and flows down a conical tube machined in the O-ring mount. This gas
pulse then passes into the entrance tube of the nozzle block shown bolted to the
front of the fast pulsed valve in Fig. 3. After a 0.6 cm straight length of this
entrance tube, the gas expands into a cylindrical waiting room which is the zone
in the nozzle where the clusters are formed and thermalized. The main flow of
the carrier gas then passes through the entrance of a 2.0 cm long conical
expansion cone, $10^\circ$ total internal angle. The gas then undergoes a free
supersonic expansion, the central 0.2 cm diameter section of the jet being
skimmed at a distance of 8.4 cm downstream by an electroformed nickel
skimmer$^{45}$ with 25$^\circ$ total internal angle at the orifice.

The vaporization laser beam is the second harmonic of a Nd:YAG, 25 mJ
pulse$^{-1}$, five nsec pulse length, focussed to a 0.07 cm diameter spot. It is
directed through a 0.1 cm diameter entrance hole drilled in the 304 stainless
steel nozzle block. The vaporization laser beam passes through the waiting
room, and hits the target disk. The cross-hatched insert piece on the entrance to
the vaporization laser access hole is machined of Teflon. Its outer surface is
canted so that coarse mis-alignment of the laser beam is easily visible on the white Teflon surface, which remains unaffected by this wavelength.

**Target Disk Mounting and Motion Control**

The most unreliable components of the old source were the disk rotation and translation mechanism, and the nozzle block itself, that often became clogged with vaporized material. Since target disk positioning was the single most troublesome aspect, it received detailed attention in this design. The Minisource is so much smaller in absolute size than previous sources that we anticipated this target motion problem would be aggravated by the miniaturization.

In order to achieve the necessary control the new source has relegated this responsibility entirely to computer control via stepping motors. The mechanical assembly shown in Fig. 3 allows for careful utilization of the disk surface, having an overall repositioning accuracy under computer control of better than 0.01 cm. Not only do these "Minidiscs" wear evenly, but the ability to dial up a specific radius and angular position on the disk has some hidden benefits. Since silicon and germanium have a native oxide overlayers we were able to cycle the disks through five to ten surface ablations to remove the oxide and expose the pure electronics grade surface of our samples. This turned out to be an easy way to overcome a persistent contamination problem. This is important because even though we can eject oxygen or water contaminated clusters from the ICR cell, it will only hold a finite number of ions. So if we inject ten percent contaminated clusters, our bare cluster signal will be decreased by that amount. Also, when we did wear a hole or groove in the disk, we could map its radial and angular
extent and avoid that position while recording spectra. This allowed us to run
daily with the same disk in the source for over four weeks with no break-vacuum
maintenance.

The Minidiscs are cut roughly to size on a diamond saw, sanded to 1.2 cm
o.d., then torr sealed to the small aluminum mount shown in the Fig. 3. The seal
to the nozzle block is made by a Teflon ring 0.1 cm thick which slides over the
outside of the target disk and seats further back on the aluminum mount. After
assembly, this Teflon ring is sanded down so that the clearance between the
surface of the target disk and the nozzle block is 0.003 to 0.010 cm. The Teflon
ring can easily be removed later, after the disk has been worn down by extensive
laser vaporization, permitting the disk surface to be ground smooth for reuse.
The same Teflon ring then may be reused as well, with only a slight sanding to
readjust the gap.

The aluminum disk mount is manipulated by a "ball driver" which fits into the
head of a socket head screw epoxied into the rear of the mount. As shown in
Fig. 3, this ball driver shaft is held in a mount that is forced forward by a spring
on the rotation shaft, thereby pressing the disk mount against the nozzle block.
The central rotation axle itself is held in a block which is bolted on either side to
two linear slides which permit the axle block to travel up or down (note: the view
of this figure is from the top looking down; up/down motion is therefore
perpendicular to the page). The position of the rotation axle block on this linear
slide is determined by a second rotatory vacuum feedthrough operating via a
rack-and-pinion linkage.
Precise alignment of the laser through the nozzle block onto the target is easily achieved with this design. Fig. 3 shows that there is an alignment window mounted on the vacuum wall immediately behind the central rotation axis. For initial alignment after the target disk has been changed, or to check the alignment during operation, the computer is directed to move the disk out of the way, clearing the central laser axis so that the vaporization laser beam passes through the entrance and exit windows of the six-way cross. By monitoring the shape of the transmitted laser beam proper alignment is easily done or verified by one person in a few minutes.

While operating the cluster source the target disk is moved to a fresh spot prior to each vaporization laser pulse. Concentric circles are traced out on the disk and the distance moved is calculated so that the laser ablation of the disk is uniform, regardless of the radius. The ability to do this so precisely under computer control is a primary reason why this cluster source produces such reproducible beam pulses with little shot-to-shot variation over many days operation on a single target disk.

**Turbo Pumps and Direct Connection to the FT-ICR Apparatus**

As is evident in Fig. 3, one of the principle advantages of this new source is that it is small enough to fit entirely within a standard 15 cm o.d. conflat flange six-way UHV cross. Since the volume of this UHV cross is small (3 liters), a 170 $l/s^{−1}$ turbo pump is adequate to pump it out in between beam pulses at 10 Hz. Operating with helium at an inlet pressure of 10 atm, the pulsed valve used in this source is capable of putting out 0.05 Torr-liter in a 125 microsecond pulse. In
this 3 liter chamber such a fast pulse will temporarily raise the pressure to $2 \times 10^{-2}$ Torr, which would have been be completely unacceptable in the old source, that operated with three 10" diffusion pumps. However, for short periods of time this is not a problem for the small turbo pump.

The fast rise time of the pulsed valve and precise timing with the vaporization laser allow the entire process of generating a cluster beam pulse to occur in less than 100 microseconds. Even using helium as a carrier gas, this is such a short time that the shock waves coming back off the interior walls of this small vacuum chamber cannot interfere with the beam pulse reaching the skimmer. The result is that the cluster source is well balanced: it has about the right size for the pulse duration of the beams that will be produced. The longer pulses of previous solenoid nozzle designs required a considerably larger chamber, which in turn was not easily handled by turbo pumps.

In operation with a helium carrier at 10 Hz with a 0.05 Torr-liter per pulse gas output, the average pressure in this source is roughly $4 \times 10^{-3}$ Torr; but with the pulsed valve turned off the background pressure drops into the low $10^{-7}$ Torr range within a few seconds, and below $5 \times 10^{-8}$ Torr after 15 seconds. Given the high reliability of the pulsed valve, and the translation/rotation vacuum feedthroughs, the vacuum aspects of this cluster source are sufficiently safe that it may be attached directly to any UHV-sensitive machine. Figure 4 shows it attached directly to the bore tube of the FT-ICR apparatus featuring a 6.0 Tesla superconducting magnet with a 7.5 cm i.d. room temperature bore.
The remainder of this FT-ICR apparatus were much the same as described in earlier publications from this group\textsuperscript{10, 35}. The ICR trap was centered in the homogeneous region of the magnetic field where the radial ion motion was confined by the magnetic Lorentz force which determines the cyclotron motion. Along the magnetic central axis the confinement of the cluster ions in the trap was accomplished by two conical-shaped electrodes -- the "front" and "back" doors labelled in Fig. 4. Note that the doors had large (2.5 cm i.d.) holes in the center to permit the clusters to pass through whenever permitted by their axially-directed energy. These holes also allowed free passage of laser radiation without scattering. The side plates of the ICR trap were composed of four sectors of a 4.8 cm i.d. cylinder, 15.0 cm in length. Two opposing 120° sectors were used for rf excitation of the trapped cluster ions, while the other two 60° sectors were used for detection of the image current induced by the cyclotron motion. All electrodes of the ICR cell were made of copper electroplated with silver, with a thin layer of rhodium.

In front of the front door was a "screen" door which was mounted close to a 2-part tubular structure labelled the "deceleration tube". Unlike previous versions of this cluster FT-ICR apparatus, this "screen" door actually has no screen. Instead, it simply has a 2.5 cm i.d. internal aperture in order to eliminate any problem with scattered laser light in experiments requiring intense excitation of the trapped clusters. This absence of real screens does have the effect that the deceleration field formed between this door and the end of the deceleration tube has a slight curvature. These two parts of the deceleration tube were connected together by a flexible wire in the center, and to an external voltage pulser through a feedthrough at the front (source) side. During the cluster
Figure 4. FT-ICR Schematic
injection period of a typical experiment the side plates of the ICR cells were held at 0 volts, the front door at 2 volts and the rear door at 10 volts. Positively charged clusters travelling through the middle of this tube were effectively decelerated as they passed to the "screen" door because the decelerator tube was pulsed to a negative potential while they were still inside, and experienced no field in this nearly-closed conductor before they attempted to "climb out" of the decelerator tube to get back to ground potential at the screen door.

Cluster ions with energies less than 10 eV will be reflected when they reach the rear door, but by the time they bounce back to the screen door it has been pulsed back to 10 V and these 2-8 eV clusters are trapped. After each injection shot a pulse of argon gas was injected into the region of the ICR cell, bringing the pressure up to 1x10-5 Torr. Collisions of the trapped cluster ions with this argon gas starts the process of thermalizing the clusters, rapidly removing most of the axially-directed translational energy. This entire sequence of events continues at a rate of 10 Hz until the ICR cell was "full" - usually on the order of 100 shots for the experiments reported here.

Since the cluster ions are all accelerated to nearly the same 1.9x10^5 cm s^-1 velocity by the supersonic expansion, each cluster has a translational energy which is linearly dependent on its mass (For Si_{45}^+ this is about 24 eV). This fact permits a coarse selection of the range of clusters to be trapped in the ICR cell simply by controlling the deceleration voltage. In the example of shown in Fig. 5 the deceleration tube was pulsed to -11 V after a 400 microsecond delay from the vaporization laser pulse to allow the clusters sufficient time to pass deep into the tube while it was still at ground potential. As the cluster ion packet neared
the end of the deceleration tube 110 microseconds later, the screen door was pulsed from 10 V down to 0 V and held there for 50 microseconds, allowing the cluster ion packet to pass through as it decelerated. During the injection cycle the front door of the ICR cell was held at 4 V and the rear door at 10 V. This injection process therefore leaves the silicon clusters bouncing back and forth in the ICR cell with up to 10 eV translational energy. Collisions with the helium background gas scattered out of the supersonic beam begin the process of randomizing this axially-directed translational energy into motion along the other two spatial directions.

If the ion velocity had been exactly $1.9 \times 10^5$ cm sec$^{-1}$ for all clusters in the beam, these injection conditions should have trapped only those clusters in the size range from $\text{Si}_{28}^+$ to $\text{Si}_{40}^+$. As seen in the Figure, the actual trapped cluster distribution is a bit wider, and shifted to trap $\text{Si}_{36}^+$, $\text{Si}_{53}^+$ - heavier clusters than predicted. Much of this is a consequence of the partial conversion of translational energy to cyclotron motion.

The 0.2 cm i.d. skimmer reduces the expanded cluster beam so that the injected ions lie within a divergence of 10 milliradians. Since the mechanical alignment of the skimmer to the magnetic axis is accurate to within the tolerance of the six-way cross, we have ensured that this small diameter, well-collimated supersonic beam is very close to the central axis of the magnetic field where the magnetic mirror effect is minimal. Full numerical simulations from SIMION$^{46}$ of the injection of these ions through the divergent magnetic field show the maximum conversion of axially-directed translational energy into cyclotron motion upon injection to be only 10%. This loss alone would trap clusters of
Figure 5. Clusters "As Injected" and trapped in the FT-ICR cell.
silicon in the 31 - 50 atom size range. The additional few percent loss we attribute to inhomogeneity of the fringing field the clusters pass through at the entrance to the magnet and to velocity slippage of these clusters from the full terminal velocity of the supersonic beam.

After the injection cycle was complete the clusters were further thermalized by exposure to $2 \times 10^{-6}$ Torr argon for 10 s, which corresponds to roughly 350 collisions at the Langevin rate. After a 2-3 second delay to allow the ICR cell pressure to drop below $5 \times 10^{-8}$ Torr, the clusters were then selectively ejected from the cell so that only the particular isotopic forms of interest were left. These were then rethermalized by a second exposure to argon (roughly 50 collisions), and then exposed to the reactant gas of the annealing procedure.

As shown in Fig. 4, entrance and exit to the bore tube of the FT-ICR magnet was connected to two 15.0 cm flange diameter six-way crosses, each of which was pumped by a separate 170 l/s$^{-1}$ turbo pump. In addition, the last cross was fitted with a 20.0 cm i.d. CTI cryo-pump which was valved off under computer control by a single-vane butterfly valve during the injection cycle to avoid saturating it with helium. Base pressure for the experiments reported here near these six-way crosses on either side of the FT-ICR bore tube when the cluster beam source was off were in the low $10^{-9}$ Torr range. The experiments reported in this work were performed with the ICR cell at 300 K.

**Selective Excitation and Ejection of Ions: "SWIFT"**

As described in other recent publications from this group, excitation and manipulation of the cluster ions in the ICR trap involved extensive use of...
computer-generated RF waveforms. This manipulation is possible because the cyclotron frequency of a charged particle in a magnetic field varies inversely with mass and most importantly is independent of the energy of the ion. By exciting a wide band of frequencies, the image current induced on the detection plates by the circular motion of the ions yields a mass spectrum with high resolution and sensitivity. Several masses can be selectively excited for detection by sending only their corresponding frequencies to the ICR cell. The same technique of selective excitation can also be used to excite a cyclotron resonance to such high amplitude that the ions collide with the side plates of the ICR cell. This way unwanted cluster ions can be easily ejected.

In the silicon annealing experiments described below, a clear baseline between bare silicon clusters had to be established so that chemisorption products could be identified. One simple approach would be to scan the frequency of the rf excitation over the range of cyclotron resonances that need to be ejected. The problem with this is that any finite duration rf sweep will contain frequency components outside the range intended, so even though this would seem to be an obvious solution, it can not be effectively implemented in practice. Typically there will be substantial oscillations in rf power as a function of frequency within the sweep range, and a significant tail of excitation outside of this range.

An alternative method was first discussed by Marshall and is called SWIFT (stored waveform inverse Fourier transform). The range of cyclotron resonance frequencies we wish to scan are specified as blocks in frequency space. Then a time domain voltage waveform that has uniform rf power in this
frequency range and, ideally, zero rf power elsewhere, is calculated by taking the inverse Fourier transform of the specified power spectrum. This inverse Fourier transform is stored in the memory of a waveform generator. A voltage waveform is generated from the resulting time domain data set using a fast digital to analog converter (DAC). Typically we use a 30 millisecond SWIFT waveform generated by a 14 bit DAC from a 128 kword inverse Fourier transform.

The swift excitation waveform generator is designed around a high speed (ten megahertz) fourteen bit DAC fed from a commercially available four megabyte 32 bit VME bus dynamic random access memory (dram). Communication with our IBM computer was performed through a standard CAMAC interface. The SWIFT signal is filtered to remove any spurious high frequency noise produced by the digital switching. It is then applied to the two excitation plates of the ICR cell.

A phase splitter provides two versions of the swift waveform 180 degrees out of phase for the two excitation plates of the ICR cell. The output voltage of each side is amplified to a maximum of 24 volts peak to peak. A pair of analogue switches grounds the power amplifier inputs and isolates them from the swift output signal in order to minimize noise pickup on the ICR transient is being recorded. Although calculation of the waveform has been accomplished, in generating the actual voltage proportional to these numbers, another problem is encountered. All component frequencies of the waveform start out in phase. This expresses itself in the time domain waveform becoming very large and narrow at t=0, particularly when the frequency block is wide. To use this waveform we would have to generate a huge voltage spike at zero time, and
would also need a large dynamic range to pick up the smaller features in the waveform.

To avoid this, Marshall suggested including a phase factor trick in the calculation. Since the power of any particular frequency component is independent of its phase, we are free to choose phase factors any way that is convenient. Marshall chose a phase factor that depends quadratically on the frequency offset from the center frequency of the power spectrum block. Guan has argued that this quadratic phase factor is optimum for reducing the dynamic range of the SWIFT time domain waveform. The SWIFT technique was used extensively in the following annealing studies to confirm the existence of structural isomers. The swift technique allows us to cleanly inject unwanted clusters from either side of a particular cluster isotopic variant or group of isotopes.

The ICR transients were detected by a Stanford Research Systems model SR560 preamplifier, followed by 12 bit digitization and relatively straightforward FFT data processing to produce the mass spectra shown below. Other details of the electronics can be found elsewhere.
III. ANNEALING PROCEDURE

Figure 6 is a particularly illustrative example of the critical data for this procedure. The top panel is the FT-ICR mass spectrum of silicon clusters as injected from the Minisource. The injection process was repeated for 100 successive cluster beam pulses at a rate of 10 Hz in order to fill the ICR trap. The trapped clusters were then thermalized for 3 seconds by collisions with argon at $2 \times 10^{-5}$ Torr (about 2000 collisions) followed by an additional 10 second waiting period while the system was pumped down to less than $10^{-7}$ Torr prior to exciting the ICR transient.

The second panel of Fig. 6 shows the silicon cluster distribution in the ICR trap after SWIFTing away intermediate clusters. The SWIFT excitation was followed by a second 2000 collision thermalization period with argon to ensure the clusters were at the 300 K temperature of the ICR trap walls. The SWIFT excitation was chosen such that $\text{Si}_{39}^+$ and $\text{Si}_{45}^+$ have wider isotopic distributions than the other bare clusters left for each cluster size remaining in the ICR trap.

The third panel of Fig. 6 shows the result of exposure of these selected clusters to ethylene at $1 \times 10^{-6}$ Torr for 20 seconds -- about 500 collisions. The isotopic width does serve as a nice signature of the parentage of each reaction product since some fall in the same mass range. The chemisorption products are marked with the symbol $E_y$.

The bottom panel of Fig. 6, however, demonstrates a more significant point: these reactive isomers of the special clusters 39, 45, and 48 also turn out to be
Figure 6. (a) Clusters as injected. (b) After SWIFTing to clear the baseline for chemisorption. (c) Reaction of ethylene with unannelaed clusters. (d) Reaction of ethylene after annealing.
less stable energetically, since they can be annealed into the unreactive form by laser excitation. This panel shows the result of reaction with ethylene just as in panel (c), except now the clusters had been radiated with 30 pulses of light from a XeCl excimer laser (photon energy 4.0 eV) at a fluence of 1 mJ cm\(^{-2}\) per pulse, and then allowed to cool with an additional three second, 2000 collision thermalization period with argon. The reactivity of the clusters with 39, 45, and 48 atoms has been sharply reduced, while the clusters with 36, 42, and 51 silicon atoms appear to be even more reactive.

In fact, careful examination of the isotopic widths of the reaction products near \(\text{Si}_{39}^+\) and \(\text{Si}_{45}^+\) reveals that the majority of these reaction products are actually the result of multiple chemisorptions on smaller clusters. In panel (c) the adducts to the right of \(\text{Si}_{39}^+\) and \(\text{Si}_{45}^+\) bear the wider isotopic width signature indicating chemisorption of one, and two ethylene groups onto each cluster. For \(\text{Si}_{39}^+\) there is even chemisorption of three ethylene groups that appears as an isotopically wide peak that is overlying the narrow peak of \(\text{Si}_{42}^+\) bare cluster (compare to the \(\text{Si}_{42}^+\) bare cluster in panel (b)). In the bottom panel, however, the peaks corresponding to \(\text{Si}_{39}^+\text{E}_1\) and \(\text{Si}_{39}^+\text{E}_2\) in panel (c) are clearly not adducts of \(\text{Si}_{39}^+\) since these peak widths are thin. These have been assigned as the chemisorption of four and five ethylenes onto \(\text{Si}_{36}^+\), whose bare cluster peak has vanished completely. Similarly the peaks that match up to \(\text{Si}_{45}^+\text{E}_1\) and \(\text{Si}_{45}^+\text{E}_2\) in panel (c) are clearly the result of chemisorption of four and five ethylenes onto \(\text{Si}_{42}^+\) in panel (d). The annealed forms of the \(\text{Si}_{39}^+\) and \(\text{Si}_{45}^+\) atom clusters are effectively inert. The relative heights of \(\text{Si}_{36}^+\) and \(\text{Si}_{51}^+\) compared to their adduct peak heights indicate the chemisorption is occurring more quickly than before the laser treatment.
Annealing Not Photofragmentation

An alternative explanation for the disappearance of the reactive forms of Si\textsubscript{39}\textsuperscript{+} and Si\textsubscript{45}\textsuperscript{+} is that these less energetically stable structures, which also happen to be more reactive, are fragmented by the laser treatment. We explored this possibility by scanning a range of laser fluences and looking for signal loss from the bare cluster peaks in the mass spectrum. Compelling data that speaks to this point is shown in Fig. 7. In this case all injected ions except Si\textsubscript{39}\textsuperscript{+} and Si\textsubscript{42}\textsuperscript{+} were ejected from the cell. The top panel shows the reaction with ethylene after 500 collisions. Again it is evident that as injected Si\textsubscript{39}\textsuperscript{+} has a considerable fractional population of one or more reactive structural forms. However the lower panel reveals that there is in fact a tremendous difference in the annealed form, there being no adduct at all. While the annealed Si\textsubscript{39}\textsuperscript{+} displays no evidence of any reaction the annealed Si\textsubscript{42}\textsuperscript{+} remains highly reactive. A particularly significant aspect to the top and bottom panels of Fig. 7 is that they have the same vertical scale factor. The markedly higher intensity of the bare Si\textsubscript{39}\textsuperscript{+} cluster signal in the bottom panel therefore is real: the reactive forms initially present for this cluster size have been efficiently converted into the unreactive form by the laser treatment. If we were simply seeing the photofragmentation of the less energetically stable forms, there would be no enhancement of the Si\textsubscript{39}\textsuperscript{+} signal. It is therefore certain that the dominant effect of the laser treatment is, in fact, annealing.

Experiments such as these have been carried out over a range of XeCl excimer laser fluences from 0.03 to 1.6 mJ cm\textsuperscript{-2} per pulse, and over a broad range of laser pulse rates (2.5-50 Hz). In all cases the effect on the apparent
Figure 7. Annealing not Photofragmentation. Enhanced bare cluster signal on Si$_{39}^+$ after annealing. Note vertical scale on both spectra is identical.
cluster reactivities was found to be linear in the total fluence, suggesting the process requires absorption of a single 4.0 eV photon per cluster. Assuming the clusters had an internal temperature of 300 K to begin with, and further assuming that radiationless transitions and randomization of the initial laser excitation was fast, the annealing temperature for clusters in this size range appears to have been less than about 600 K. Only at the highest fluences with ArF some loss of clusters due to photofragmentation was observed, this fragmentation only slightly favored clusters 39 and 45, (which therefore do appear to be slightly more stable energetically). However, experiments performed at the rather moderate fluence and repetition rate as the data reported here indicated less than 5% loss due to fragmentation for any cluster.

These striking changes in reactivity persist even when the reaction cycle is initiated directly after the excimer laser annealing pulses, without an intervening thermalization process through collisions with argon. The clusters must therefore be able to anneal while cooling radiatively and perhaps also through the first few collisions with the reactant gas over the roughly 1-2 second interval necessary for this reactant gas pressure to build to a steady value.

NH$_3$ Chemisorption on Annealed Clusters

Figure 8 presents similar results for these clusters with ammonia as a reactant. Again the initial cluster distribution in the ICR trap was selectively ejected, leaving clusters 36, 39, 42, 45, 48, and 51 in the trap with the isotopic distribution as shown in Fig. 6, panel (b). The top panel of Fig. 8 shows the result of exposure of these cluster ions to 1000 collisions with ammonia. Note that these nozzle conditions produce clusters which initially display only a slight
Figure 8. Ammonia reaction. Magic numbers are evident after annealing, but not before.
variation in apparent reactivity toward ammonia. Yet the bottom panel shows again clear evidence of laser-induced annealing: Si$_{39}^+$ and Si$_{45}^+$ have been rendered far less reactive than any of the other clusters in this region. A detailed experiment to get quantitative data on the chemisorption of ammonia on the annealed silicon clusters is planned. From this data set we will be able to derive reaction rates and make a plot equivalent to Fig. 2 which is the original reaction rate data from the accidentally partially annealed clusters. We anticipate the variation in reactivity of the annealed clusters to be about five orders of magnitude, not the three orders displayed in Fig. 2.

In general, for all silicon clusters ammonia is simply more reactive than ethylene, although both react selectively. In the initial work from this group$^9$ it appeared that water was not selective in its reactions with the silicon clusters, but more careful experiments with the new apparatus now show that water actually is selective at low collision rates, with Si$_{39}^+$ and Si$_{45}^+$ clusters again being the least reactive. However, H$_2$O is sufficiently aggressive that all clusters ultimately do react. Similar magic number behavior with these three reagents shows that the reactivity pattern observed is due to an effect that is robust to changes in experimental parameters -- even to what reagent is used. Since surface structure plays a dominant role in chemical reactivity, we seem to be detecting the existence of different reactive sites on different clusters.

The Same Magic Number Trend is Seen With Germanium

So far in the work with silicon clusters, the magic number behavior persisted with three different reactants: ammonia, ethylene, and water. If this trend in
reactivity was due to a structural effect, it was reasoned that the same magic numbers might be observed with germanium clusters also. In fact the suggestion that the structures of germanium clusters in this size range are similar to those of silicon was proposed earlier by this group, based on photofragmentation data\textsuperscript{51}. When radiated with ArF light, clusters of both elements in this mass range shattered into fragments dominated by clusters ranging in size from 6 to 11.

In quick survey experiments with positive germanium clusters\textsuperscript{52}, nitric oxide reacted selectively, although water and ethylene did not react at all. It was not unexpected that we needed to use a more aggressive reagent since germanium is generally less reactive than silicon. It was most interesting that, like silicon, the least reactive germanium clusters were Ge\textsubscript{39}\textsuperscript{+} and Ge\textsubscript{45}\textsuperscript{+}, and the most reactive is Ge\textsubscript{43}\textsuperscript{+}.

Figure 9 shows the "as injected" spectra of germanium clusters in the 39-46 atom size range. Due to the five isotopes of germanium, all with substantial natural abundance there is quite an extensive range of masses present in the ICR cell as injected from the supersonic beam. These isotopomers leave very little baseline between peaks for adjacent clusters on which to look for reaction products. As seen in the top panel of Fig. 10, this initial distribution may be dramatically simplified by selectively sweeping some of the clusters from the cell with the SWIFT. This SWIFT waveform was chosen so as to clear a clean baseline between the dominant isotopic components of the germanium clusters.

The bottom panel of Figure 10 shows the result of exposure of the selected clusters to nitric oxide gas at a pressure of 1 x 10\textsuperscript{-5} Torr for 10 seconds, about
Figure 9. Germanium clusters as injected in the ICR cell. Notice 1 amu resolution on the Ge$_{45}^+$ detailed picture.
Figure 10. Reaction of germanium clusters with NO reveals similar magic number behavior.
3,000 collisions. Prior to the reaction the clusters had been thermalized to 300 K by roughly 2000 collisions with argon. For some clusters such as Ge$_{43}^+$ reaction products of the form Ge$_{43}$NO$^+$ and Ge$_{43}$(NO)$_2^+$ are clearly seen, whereas other clusters such as Ge$_{39}^+$ and Ge$_{45}^+$ show no evidence of reaction at all. These results are similar to the above data for ammonia and ethylene reactions on positive silicon clusters$^9$, $^{10}$, $^{20}$ where again the 43rd cluster appears to be the most reactive and the 39th and 45th are inert. That a similar cluster reactivity pattern exists for germanium supports the earlier photofragmentation evidence that germanium may adopt the same structures as silicon in these small clusters. There are, however, also differences in the reactivity of these clusters. Notably, 40 also shows no reaction and 41, 44 and 46 are almost inert.

To discover the rules that govern how these structures go together will require additional careful experimentation on both elements, and results need to be extended to larger cluster sizes. A change in reactivity due to annealing will be harder to follow with germanium because they are so much less reactive than silicon. For comparison approximately 500 collisions with ethylene were required to produce the reaction in fig. 6. Germanium clusters do not react at room temperature with ethylene at all, and in fig. 10, where the exposure was approximately 3,000 collisions, the reaction has not proceeded as far. There is easily a factor of ten difference in the reactivity of these two elements, which is in itself a basic finding. Since there is a difference in reaction barrier there may be a fundamental difference in the reaction mechanism. It was clear that to
discover the rules that govern how these structures go together will require additional careful experimentation on both elements.

We have uncovered a trend for silicon that is real and robust to changes in experimental parameters, and there already is some similarity for germanium cluster reactivity. With this data as a starting point, we have begun to map out the extent of this trend in further experiments on silicon and a survey of germanium reactivity and stability.
IV. RESULTS AND DISCUSSION

Reactivity of Silicon Ions With TMA

Figure 11 displays the result of a typical reaction experiment with TMA on a few selected positive clusters of silicon. The annealing procedure described in the previous section was used in this study. The purpose of this initial study was simply to determine whether the same pattern of reactivity that we saw before would apply with TMA as well. We selected what had previously been 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. 11, 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.

The middle panel (b) of Fig. 11 shows the resultant mass spectrum after reaction with TMA at 5 x 10^{-8} Torr for 9 seconds. T1 marks the addition of one TMA group to each bare cluster, and further to the right of each bare cluster T2 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 W1 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.
Figure 11. Chemisorption of TMA on positive silicon clusters. (a) SWIFTed keeping 39, 43, and 48. (b) Reaction with TMA for 9 seconds at $5 \times 10^{-8}$ Torr. (c) The same reaction with TMA after annealing with 30 shots XeCl excimer laser light at 50 Hz and 1 mJ/cm$^2$-pulse followed by 3 second thermalization with Ar at $1.2 \times 10^{-6}$ Torr. Note (b) and (c) have the same scale.
Figure 12. Chemisorption of TMA on negative silicon clusters. (a) SWIFTed keeping 39, 43, and 48. (b) Reaction with TMA for 10 seconds at 5 x 10^{-7} Torr. (c) The same reaction with TMA after annealing with 15 shots XeCl excimer laser light at 50 Hz and 0.7 mJ/cm^2-pulse followed by 3 second thermalization with Ar at 1.2 x 10^{-6} Torr. Note (b) and (c) have the same scale.
The bottom panel of Fig. 11 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/cm^2-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 with these annealing conditions just before the TMA reaction. 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 energetically less stable isomer.

The positive clusters show the same relative reactivity pattern toward TMA as ammonia, 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 ammonia 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 off the ammonia molecule would. Instead the reactivity pattern is the same, at least for these three cluster. 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 nothing in our data
to suggest that a dissociative chemisorption mechanism, as proposed by Jarrold
et al.\textsuperscript{25} to explain the discrepancy with his ammonia chemisorption work, is
occurring here. Molecular chemisorption of an adduct onto these clusters would
involve only one dangling bond on the cluster, which could be located anywhere
around its surface. Dissociative chemisorption, however, requires a much more
specific reactive site: there must be two dangling bonds and they must be the
right distance apart to accommodate the incoming molecule, otherwise the
dissociation will not occur.

As shown in Fig. 12, 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 photodetach it
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/cm\textsuperscript{2}-pulse were used as the annealing treatment for the clusters
shown in the bottom panel of Fig. 12. As a result we are not confident that the
negatives are completely annealed, and better results might be obtained if the
annealing is accomplished with a longer wavelength laser to get below the
photodetachment threshold. For Si\textsubscript{12}\textsuperscript{+} the threshold is 2.6 eV\textsuperscript{53}, and this value
increases with increasing cluster size so this number is a safe lower limit. By
getting under the threshold, the signal loss problem should be minimized, and
complete annealing should be more easily achieved. This could be done with
the dye laser in the lab.
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 11. This pattern is in agreement with earlier results on the negative ion with ammonia^{10,12} and ethylene^{20}, and we interpret this as additional evidence for dramatically different structures for silicon clusters of Si_{39}^- and Si_{43}^- atoms.

**Germanium Clusters: Similarities With Silicon**

Germanium surfaces are generally less reactive than silicon surfaces, and this is true for their clusters also. Although it is difficult to find reagents to use with reaction studies on germanium, it is not impossible. Water reacts only with Ge_{42}^+, and Ge_{43}^+, the most reactive cluster sizes in the trend^{52}. In the hope of observing a trend with different chemical systems, we tried the following reagents and found that they did not react with germanium clusters at room temperature: ethylene, ammonia, monomethylamine, and pyridine. We have found no conditions in the FT-ICR where the negative ions react with anything. As is true for silicon, negative ions are considerably less reactive than the positive ions.

Figure 13 shows the result that Ge_{39}^+ is inert in reaction with TMA. Panel (a) is Ge_{39}^+ and Ge_{41}^+ injected into the FT-ICR after Ge_{40}^+, and clusters larger than Ge_{41}^+ have been SWIFTed away. Reaction for 0.8 s with TMA at a pressure of 1 x 10^{-6} Torr. Notice there is no addition of TMA onto Ge_{39}^+, but Ge_{41}^+ has reacted easily to add one TMA group, and further to add
Figure 13. There is no addition of TMA onto Ge$_{39}^+$ during the same time that Ge$_{41}^+$ has added one and two TMA groups.
Figure 14. Annealing affect on reactivity of Ge$_{43}^+$ and Ge$_{45}^+$. Ge$_{45}^+$ is inert to chemisorption of TMA after the laser annealing, but chemisorption onto Ge$_{43}^+$ is enhanced.
two TMA groups. Reaction for 2 seconds with TMA at the same pressure shows chemisorption has proceeded facilely on Ge$_{41}^+$, with the product peaks now slightly larger than the parent ion, and a small peak that represents the addition of three TMA groups onto Ge$_{41}^+$. Even at this stage in the chemisorption onto Ge$_{41}^+$ there is no indication of any addition at all onto Ge$_{39}^+$.

In addition to the inertness of Ge$_{39}^+$, we also observe an annealing effect on Ge$_{43}^+$ and Ge$_{45}^+$. Figure 14 shows Ge$_{45}^+$ is inert to chemisorption of TMA after the laser annealing treatment. The top panel is ions Ge$_{43}^+$ and Ge$_{45}^+$ as injected into the FT-ICR cell after other clusters have been SWIFTed away. Panel (b) is chemisorption of TMA onto Ge$_{43}^+$ and Ge$_{45}^+$ after reaction for 2 seconds at a TMA pressure of 1 x 10-6 Torr. The addition of one TMA group onto Ge$_{43}^+$ is clear on the baseline between Ge$_{43}^+$ and Ge$_{45}^+$, and the addition of two TMA groups onto Ge$_{43}^+$ is indicated by the shoulder on the left side of the Ge$_{45}^+$ peak. The addition of one and two TMA groups onto Ge$_{45}^+$ is visible to the right of the Ge$_{45}^+$ parent peak, but it is clear that the addition onto Ge$_{45}^+$ proceeds much more slowly than the reaction onto Ge$_{43}^+$. The significant result is in the bottom panel, that shows chemisorption of TMA onto Ge$_{43}^+$ and Ge$_{45}^+$ after annealing the clusters with XeCl light. The addition onto Ge$_{43}^+$ has occurred faster after the laser annealing than before, as evidenced by the almost equal peak heights of Ge$_{43}^+$ and Ge$_{43}$TMA$. Reaction on Ge$_{45}^+$, however has been inhibited completely. This spectrum is noisier than panel (b) because of signal loss due to fragmentation during the laser annealing.

This is probably not the optimal wavelength for annealing germanium, as it fragments considerably more easily than do silicon clusters. We observe the
existence of multiple isomers here for Ge\textsubscript{43}\textsuperscript{+} and Ge\textsubscript{45}\textsuperscript{+} like silicon, and likewise Ge\textsubscript{43}\textsuperscript{+} is more reactive after annealing, and Ge\textsubscript{45}\textsuperscript{+} is more inert.

**Relative Reactivity of Unannealed "As Injected" Germanium Clusters**

Because we saw these initial common features between silicon and germanium in clusters of 39 and 45 atoms, we quickly turned our attention to broadening the mass range of clusters we observed. We completed a survey experiment on germanium cluster reactivity "as injected" into the ICR cell without any annealing procedure. It should be stressed that these are qualitative results yielding only information about a cluster reactivity relative to its nearest neighbors. This survey was completed by simple chemisorption reactions on groups of germanium clusters that were selected for reaction only by adjusting the magnitude of the deceleration voltage for entry of ions into the ICR cell. There has been no SWIFT waveform applied to these clusters. Although we cannot follow additions onto single clusters as we did above for Ge\textsubscript{39}\textsuperscript{+}, Ge\textsubscript{41}\textsuperscript{+}, Ge\textsubscript{43}\textsuperscript{+}, and Ge\textsubscript{45}\textsuperscript{+}, because we did not SWIFT a clear baseline between clusters, we can readily spot relative reactivity between neighboring germanium clusters by monitoring the diminution of the parent peaks.

Panel (a) in fig. 15 shows an example of this data. A range of clusters centered around the size of 12 germanium atoms, starting with the decel voltage at -10 volts that was admitted to the cell. After thermalization of the clusters with argon reaction proceeded at a pressure of 1 x 10\textsuperscript{-6} Torr TMA for 5 seconds. The spectra showing reaction results is in panel (b). It is clear that 11 and 13 atoms are less reactive than 12, which decreased in intensity to about one third of its original height. Fourteen and 15 have reacted relatively more than 16. By
Figure 15. An example of data from the germanium reactivity survey on unannealed clusters.
observing the reaction this way, we do not get quantitative data since we cannot follow the appearance of the adduct peak. It does indicate the relative reactivity of neighboring clusters. Panels (a) and (b) form a pair of spectra showing the progress of the TMA reaction. By a stepwise increase in the decel voltage we looked at chemisorption reactions for clusters up to $\text{Ge}_{45}^+$. We can see that oscillations in reactivity on unannealed germanium clusters, like we saw with silicon, are persistent, but not in a one-to-one mapping agreement with previous silicon results. Analysis of the survey reveals cluster sizes that react comparatively more easily than their neighbors are ions of clusters with these numbers of atoms: 12, 15, 17, 18, 21, 22, 24, 27, 28, 30, 33, 34, 38, 41, 42, and 43. Ions that are relatively unreactive are: 11, 14, 15, 16, 20, 23, 25, 26, 29, 31, 32, 36, 37, 39, and 45. Ions of intermediate reactivity are not listed. Results are tabulated in figure 20.

**Special Problems With Germanium Clusters**

This is the first survey data ever done on germanium clusters. This is due largely to the difficulty in achieving sufficient germanium signal in the ICR cell to maintain a coherent cluster ion signal throughout the number of collisions required to follow the addition reaction, and because germanium is unusually unreactive compared to other clusters, one must use the most aggressive reagent available. TMA, because of its many internal degrees of freedom is highly reactive, and also very effective in cooling the clusters because collisions with TMA are so sticky. TMA may react with germanium better than ammonia because of its ability to absorb energy evolved in bond formation. Along with these advantages, TMA also sticks to the walls of the FT-ICR and the time
required for TMA pressure to reach $1 \times 10^{-6}$ T in the cell after the valve was open was 2 to 3 seconds. It also requires a longer pumpout time to clear from the cell. As a result, the number of collisions of TMA with the clusters is uncertain, so deriving reaction rate numbers from this data is unwise until the pressure response of the system for TMA has been determined, and therefore the number of collisions will be known. Even so we can make good observations now about the relative reactivity of these clusters.

There were other problems that make germanium experiments challenging. For instance the mass of Ge$_{50}$ is 3630 amu. These are heavy ions that are hard to handle in the ICR cell. These compare in mass to the carbon's "giant fullerenes". Ge$_{50}$ corresponds to C$_{302}$. The five isotopes of germanium make the peaks broad, and in the higher masses, they actually begin to overlap each other. So in SWIFTing a clean baseline between clusters on which to allow the adduct products to appear on, many germanium cluster ions must be pushed from the cell. These ions are wasted as far as the experiment goes. Unfortunately they contribute to space charge in the cell, so when we fill the cell with ions, we are injecting many that must later be ejected. This leaves us with smaller Ge$_n$ cluster peaks to do chemisorptions or fragmentation on. We tried to improve on this situation by injecting several shots into the cell, thermalizing and SWIFTing some of them away, then following up with another injection series. Theoretically this should have allowed us to load the cell with more of the ions we wanted, but we saw no difference in the resulting ion signal. So we are left with smaller parent cluster signal intensity and a chemical system that is not very reactive. These experiments pushed up against the limit of how many collisions an ions can have in the ICR cell without being lost.
It is interesting that there are many more unreactive clusters for germanium than we see for silicon, in this unannealed inventory for the smaller cluster sizes (below 32). This is attributed to the fact that germanium is a larger atom and therefore can support a larger bond angle with less strain, so it will have more choices for tying up dangling bonds than silicon. Also it is well known that the germanium surface has more stable reconstructions available to it, so if these clusters are inert because they have managed to mimic a germanium surface reconstruction, we should expect there to be more inert clusters than there are for silicon. There are some interesting similarities and differences to the silicon reactivity pattern. Six magic numbers that we previously saw for silicon are represented in this data: 11, 25, 39 and 45. The two we do not see are 21 and 33. Strangely instead of 21, 19 and 20 are inert; and instead of 33, 32 is inert. This suggests that if Kaxiras's thinking is correct and clusters are chemically inert because they can reconstruct to tie up dangling bonds, then this shift for these two magic numbers has a simple explanation. For these two sizes the germanium clusters, because there are more reconstructions available to them, can configure to an inert geometry one size sooner than silicon can. Not only are a subset of these clusters unreactive, but clusters with just one or two atoms added or subtracted are very reactive. For example, 19 and 20 are unreactive, but 18 is reactive. Likewise 32 is unreactive, but 30, 33, and 34 are very reactive. Similarly for the other four magic numbers: 11, 25, 39 and 45 are unreactive, but 12; 24; 30, 33, 34; 37, 38; and 41, 42, 43 are very reactive.

Some of the reactive clusters of germanium correspond in their relative reactivities to their silicon counterparts. These are: 12, 15, 17, 18, 22, 24, 27, 28, 30, 41, 42, 43. Whereas there are few germanium clusters that are more
relatively reactive than their silicon counterparts (21, 33, 34, 38, 40), there are, however, more germanium clusters that are relatively inert, and whose silicon counterparts are not relatively inert: 16, 19, 20, 23, 26, 29, 31, 32, 36, and 37.

**Translational Activation of Ge\text{43}$^+$**

In looking at this germanium survey, it was natural to presume that if we annealed the germanium clusters we might recover a closer match with the silicon magic number pattern. Fortuitously, we had observed an effect in Ge\text{43}$^+$ in which the clusters' reactivity was enhanced by inadvertent translational excitation of the cluster. A divit in the adduct of the Ge\text{43}$^+$ TMA cluster was found to correspond to SWIFT block "leakage" into the frequency space occupied by the Ge\text{43}$^+$ parent cluster. The clusters that had been excited by the errant SWIFT waveform were more reactive than were the molecules in the middle of the mass packet that remained unaffected.

We were able to reproduce this affect by purposely exciting the frequencies that correspond to this mass range by a SWIFT block to it at a low power setting. This achieves a gentle translational activation of the chemisorption. By lightly exciting the ions in their cyclotron orbits we have induced collisions between them that heat the clusters slowly. We estimate we have added about 1 eV of energy to the clusters this way.

Figure 16 shows the increased reactivity of Ge\text{43}$^+$ after one second of such translational activation. This was the only cluster that displayed this kind of energy barrier behavior to reaction. The other clusters exhibited either no change in reactivity, or inhibited reactivity when subjected to the same
Figure 16. Increased reactivity of Ge$_{43}^+$ after one second of translational activation. The first indication that germanium cluster reactivity could be affected by inducing collisions in the ICR cell.
Figure 17. induced dissociation (CID) of Ge$_{42}^+$ accomplished by increasing the voltage applied to the SWIFT block. Loss of 10 is the favored channel.
translational activation procedure. This indicates that there is no reaction barrier for other clusters, making Ge$_{43}^{+}$ unique in this respect, in addition to it being the most reactive cluster. This was also the first clue that we could alter reactivity of the cluster inventory in the cell by inducing collisions. In the hope of annealing these clusters through slowly heating by collisions we began experimenting with using the SWIFT technique in this new way.

**Collisionally Induced Dissociation (CID) and Collisional Annealing**

Figure 17 shows the result of induced dissociation (CID) of Ge$_{42}^{+}$ accomplished by increasing the voltage to an applied SWIFT block. The top panel is the parent cluster after the neighboring clusters have been cleared from the cell. Notice the peaks at masses 32, 33, 34, and 35. These are probably due to clusters that fragmented during ejection, or due to fragmentation resulting form the first energetic collisions with the argon thermalization gas. The middle panel shows the result of applying the SWIFT excitation to Ge$_{42}^{+}$. The favored channel is loss of 10, as previously observed$^{53}$, with accompanying loss of 1, 2, and 3. In the bottom panel it is clear that fragmentation continues as the energy in the waveform is increased.

Since it is evident that these germanium clusters are significantly more fragile than their silicon counterparts, we looked at fragmentation under conditions we needed to complete collisional annealing of the clusters. Figure 18 is an example of a typical annealing procedure with this new method. The decel voltage was adjusted so that the clusters in the range 38 to 46 are admitted to the cell. In panel (b), conditions that we found were typical for annealing the clusters, there is significant signal loss due to fragmentation. Note
that the most prominent parent peaks left, and therefore the most stable relative
to other clusters, are 43, 44, and 45. Here we are considering stability of Ge_{n}^{+}
clusters compared to each other, and not the relative stability of multiple
structural isomers of the same cluster mass. This signal loss during annealing
was perhaps the most frustrating hurdle to overcome in doing these
experiments. It was typical to loose half, or more, of the signal intensity during
the collisional annealing. Signal loss using the laser for annealing was even
worse.

This was not the case for silicon. In those laser annealing experiments,
even with XeCl light we did not observe the pattern of differential signal loss
correlated with mass. In fact, a loss of less than 5% of signal intensity was
observed, each cluster mass loosing the same amount to fragmentation, as its
neighbors. Here, however is a significant difference with germanium. These
clusters are more brittle, and show a pattern of oscillating stability as cluster
mass increases. This lead us to do a fragmentation survey of unannealed
germanium clusters to explore this interesting and unexpected point of relative
stability.

**Stability Survey of Unannealed Germanium Clusters**

We were interested in finding a correlation between reactivity and stability,
so we did a CID survey. CID was accomplished by applying a low power SWIFT
waveform over the mass range of clusters we wanted to fragment. Germanium
clusters were surprisingly easy to fragment, and we observed the same three
fragmentation channels as had been discovered previously by this group\textsuperscript{51}. It
was found that fragmentation occurs by loss of 10, a patterned loss of 6-11, or
Figure 18. Germanium clusters are more fragile than their silicon counterparts. Under typical collisional annealing conditions there is significant loss due to fragmentation, see panel (b). Panel (c) indicates that the most stable clusters are 43, 44, and 45.
Figure 19. CID survey of unannealed germanium clusters - an example spectrum.
single atom loss. This prior study was one on unannealed clusters, as is this stability survey. Annealed clusters may show a preference for one of these channels. From this kind of fragmentation study we can make deductions about relative stability of the parent ions and perhaps about their structure, and also about the relative stability of the daughter ions they fragment into.

The amplitude of the SWIFT excitations used here are about one third the amplitude of the waveforms used to eject clusters from the cell. The CID SWIFT block waveform was 33 microseconds long and 0.21V in intensity. These experiments were facilitated by the new software that runs the FT-ICR, and now allows us to vary the experimental sequence any way we choose. Therefore we were able to insert a SWIFT step where previously it would have been prevented owing to a lack of flexibility of the software.

Like the reactivity survey, this survey was done by stepwise increase of the deceleration voltage to allow larger and larger ions into the ICR cell. After injection a SWIFT waveform was applied to excite the cyclotron resonance orbits corresponding to the mass range injected. Results are in Figure 19. Criteria for classifying a cluster as stable was its persistence as a daughter fragment, which presumes the daughters have no memory of their parent. Immediately apparent is the dominance of daughter fragments 9, 10, and 11, in the second panel, presumably from loss of 10 atoms from 19, 20 and 21. As the progression if followed through the mass range up to Ge$_{45}^+$, several other daughter fragments are favored. In addition to the prominence of 9, 10 and 11, in all of the CID spectra 14, 15, 16, 20, 22, 23, 26, 29, and 31 are present and seem to be
favored products. In the last panel three parent ions remain: 43, 44, and 45. These three clusters appear to be somewhat more resilient to fragmentation.

If we correlate this fragmentation data with the earlier reactivity information, it is discovered that of the fifteen more stable clusters listed above, eleven are listed as relatively nonreactive (relative to their nearest neighbors), two lie outside the range of the reactivity survey (Ge$_9^+$), and the remaining three are classified as relatively reactive. Of the magic number clusters 11, 25, and 45 are relatively stable to fragmentation, but interestingly enough 39 fragments particularly easily. If the nonreactivity is explained by surface reconstruction to tie up dangling bonds, could Ge$_{39}^+$ be especially brittle due to its reconstruction? If clusters of covalently bonded solids reconstruct their surfaces to minimize surface energy to the detriment of bonding to the core atom, we might expect them to be more brittle due to strain. The other significant exception to this trend is Ge$_{43}^+$. Although the most reactive cluster studied, it is also relatively stable. Apparently there is no reconstruction that will render Ge$_{43}^+$ nonreactive. This correlation between reactivity and stability of unannealed clusters was not seen with silicon, and has not been observed in any other lab. It was unexpected and intriguing. These results are tabulated in Fig. 20.

Fragmentation of Unannealed Silicon Clusters

For comparison we also did a cursory CID survey of unannealed silicon clusters as depicted in Figure 25, across the range 10-34. Criteria for stability was also the persistence of the daughter fragments. Silicon is harder to fragment than germanium and much higher voltages (factor of three) on the
Figure 20. Summary of reactivity and CID survey.

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* There is no data for Silicon after n=34.
SWIFT waveform were used to put more energy into each collision. The series
of spectra in Figure 25 shows progressive fragmentation as the voltage is
increased.

Surprisingly many of the same clusters survive. Common to both
elements are 10, 11, 14, 15, 22, 23, and 26. As tabulated in figure 20
unannealed germanium clusters are stable and nonreactive except for 15, 22,
39, and 43. Many more clusters of both elements anneal to less reactive forms:
It is unusual for a cluster to anneal to a more reactive form, examples being Si_{21}
and Si_{43} and Ge_{43}.

It will be interesting to see how these patterns change for fragmentation of
annealed clusters. It would be most useful to examine just one cluster at a time
to view exactly what fragments each one flies into.

Use of SWIFT for Collisional Annealing

After gaining some experience using a SWIFT block to excite the cluster
inventory, we turned our attention to using the SWIFT to observe an annealing
affect. Figure 21 shows the gradual annealing of Ge_{45}^+ by increasing the power
to the SWIFT block, applied in the experimental sequence before the ejection
cycle. In all four panels of fig. 21 all clusters except Ge_{39}^+ and Ge_{45}^+ have
been SWIFTed out of the cell. After thermalization with argon the clusters have
been allowed to react with TMA for 5 seconds at a pressure of 7 x 10^{-7} Torr. As
the energy supplied by the SWIFT annealing step is increased from zero in (a) to
typical annealing conditions in (d), the reactivity of Ge_{45}^+ decreases.
Figure 21. Gradual annealing of Ge$_{45}^+$. Reaction for five seconds at $7 \times 10^{-7}$ Torr TMA, while varying the voltage on the SWIFT annealing block.
Figure 22. Measurement of reaction rates for germanium clusters in n=50's size range.

(a) As injected

(b) Reaction with TMA

(c) Same reaction after annealing
Finally, we were ready to complete a more careful reactivity survey on germanium (see fig 23). An example of this data is in figure 22. Germanium clusters in the n=50's region reacting with TMA before and after annealing is shown. In this case all clusters have annealed to less reactive forms. Data was tabulated over the range 19 to 57. The peak heights of parent and adsorbate peaks were measured, and the uncertainty in these values was consistently about 10% due to the shape of the top of the peak. The natural log of the ratio of remaining parent to the sum of remaining parent plus the adsorption of one TMA was calculated. For deriving reaction rates quantitatively we would then plot the line formed by these ratios taken at increasing reaction times. Points on the graph tagged with an asterisk denote slopes derived from a linear fit that had a correlation coefficient less than 0.97. Upon annealing some clusters became more reactive, such as 43, 36, 37; and others became less reactive, such as 21, 28, 35, 40, 41, 44, 45, 48, 50-57. Clearly, most of the clusters, when annealed to their most thermodynamically favored forms become less reactive. This is a definite correlation between reactivity and stability as is generally expected.

Reaction rates plotted on annealed clusters are in fig. 23. These reaction rates were derived from chemisorption of TMA onto annealed germanium clusters. These rates can be compared to those for silicon in figure 1.

\( \text{Si}_{24}^+ \) Anneals to a Reactive Form; \( \text{Si}_{25}^+ \) to its Unreactive Form.

To compare this reactivity data to silicon reactivity data, we did a survey of silicon positive clusters from mass 15 to 33, since this is the range where multiple isomers were seen in previous work, and these have not been examined after annealing. This is again presented as qualitative information. We
Figure 23. Germanium cluster reaction rates.
discovered that for Si_{20}^{+}, and Si_{21}^{+}, and Si_{25}^{+}, all having two isomers (see figure 1), the first two anneal to more reactive form, but Si_{25}^{+} anneals to its unreactive form. As a result 21 is no longer considered a magic number, but 25 is. These were the only significant differences found by annealing the clusters. When the annealed reactivity patterns for silicon and germanium are compared we see that there are three regions to the data. From about cluster mass 15 to 33 the trends are completely different. From 34 to larger sizes the overall curve of reactivity is similar, then above 48 clusters of silicon becomes more reactive, but germanium becomes less reactive.

In the first mass range, clusters with masses 15 to 33 both elements have large amplitude oscillations in their reactivity, but the oscillations do not occur at the same masses. The patterns are completely different. For example silicon has minima at 11, 21, 25 and 33, but germanium minima are at 11, 14, 19, 26, and 32. If the structures are driven by minimizing surface energy, then these small clusters may have different structures since germanium surface reconstructions are different and more numerous than silicon surface reconstructions.

In the second region, the two trends track each other. 34 - 38 are relatively reactive in both trends, 39 is a minimum. A second deep minimum is at 45. Forty-two and 43 are both the most reactive clusters in both trends. Forty-six and 47 are relatively reactive in both trends, 48 is a dip in reactivity also (refer to figures 11 and 12 for reactivity of 48). In summary the relative reactivities of the two elements’ clusters track with the exceptions that there are more unreactive clusters in the germanium trend: More magic numbers. These
additional unreactive clusters all anneal to less reactive structures. Perhaps the packing in this region for these clusters is similar. It may be that in this size range there are structures with a core atom that is happily tetravalent, and the surface atoms are able to reconstruct around it in similar ways.

**Filled Fullerenes?**

In the high mass region, 49 - 57, reactivity for both elements levels off. The germanium clusters all anneal to low reactivity forms. 51 shows no reaction at all. Since 51 is an odd number it cannot be a filled fullerene. Filled fullerenes are a core atom with a shell of five and six membered rings surrounding them as has been suggested for larger silicon clusters. The silicon clusters in this mass range display multiple isomers (see fig. 1), and there is an indication that Si$_{54}^+$ anneals to an unreactive form. Could this cluster be a filled fullerene? It is possible that in the limit of good annealing some other unreactive forms would show up for silicon in this higher mass range. It appears clearly that the bonding in these tetravalent semiconductors drives their cluster structures to be identically the same.

**Different Results from AT&T: A Different Cluster Inventory**

There are several other research groups active in semiconductor cluster research. One of them is Martin Jarrold and coworkers at AT&T Bell Labs. This group has continued to produce data that is contradictory to data and conclusions from this work on the annealing of silicon and germanium clusters from the Smalley group. In of his most recent publications he raises the following points:
1. The effect of collisional annealing did not influence reactivity of silicon clusters towards ammonia. All clusters reacted at the collision rate.

2. Annealing does not dramatically alter the structure of silicon cluster ions up to 50 atoms large, but changes the relative abundances of the structural isomers that are present.

3. For some clusters the more reactive isomer is the more thermodynamically stable, therefore the chemical reactivity of the silicon clusters is not related to their thermodynamic stability.

4. Some suppression or reactivity is seen for ethylene adsorbed on silicon.

All four of these points depend critically on the completeness of annealing of his cluster inventory. He has argued in the past that he sees some fragmentation of clusters, so he must be putting in enough energy to anneal them. This alone is not sufficient evidence that the cluster inventory is annealed, as we have seen in our own work. In fact his statement that annealing does not dramatically alter the structure of these clusters is a direct comment on the degree of annealing that he has achieved. Given that this cluster inventory is incompletely annealed, his following results logically follow. In fact in our own work on the silicon and ammonia system, figure 8, unreactive clusters are present only after annealing, not before, and any correlation between stability and reactivity will be obscured by the presence of multiple isomers. We have found a correlation of reactivity and stability in the germanium clusters we studied in the 39 to 57 atom range, and we may also find this in our annealed silicon clusters.

It is interesting that he has begun to see some unreactive clusters emerging in experiments with ethylene. The simplest explanation for this is that
his cluster inventory was better annealed when he did his ethylene experiments. This will probably remain an unknown since he does not have a good criteria for determining when the clusters are annealed. Alternatively, he may be observing a different reaction mechanism than is followed in the FT-ICR cell, owing to the difference in time scales afforded by the two experiments. Jarrold’s drift tube experiments occur on the millisecond time scale and at higher pressure than the work done by our group. It is possible that Jarrold is observing a loosely bound physisorbed state that falls apart and is not observed on the time scale of the FT-ICR experiments, which is seconds. Most critically, Jarrold must provide evidence that his cluster inventory is comprised of single structures for each cluster mass, otherwise his results will continue to be confused by the existence of multiple isomers.

An Independent Criteria for Annealing: Fragmentation Pattern?

Lastly, the question of fragmentation pattern of the clusters remains. We could determine, in the ICR what the primary channel for fragmentation of each silicon cluster is. Jarrold has observed loss of Si$_6$ in his annealing experiments. The indication from germanium is that the loss of Ge$_{10}$ is the primary channel, and clusters that fragment through the other channels are not well annealed. The previous fragmentation study was completed on unannealed clusters, and we have an indication that annealed clusters may fragment only into the 10 loss channel. If this is true, it will give us a second way to evaluate the degree of annealing.

The discussion surrounding this contradictory data has motivated several theorists to continue their search for low energy structures. The confusion created by Jarrold’s results has made the job of the theorist difficult since it is
impossible to construct a model that can explain all the data. Swift et. al.\textsuperscript{54} have proposed two Si\textsubscript{45}\textsuperscript{+} structures, distinct from the Kaxiras structure, both of which have complete tetrahedral symmetry. Their proposed structures both have a tetrahedrally located central atom surrounded by what is described as a "reconstructed surface". There are two possible problems with this work. One is their choice of a modified tight binding model.

The tight binding model depends on making LCAO from atomic orbitals that are spatially compact and that go into narrow bands in a solid. It is recommended for transition metals with compact partially-filled d-orbitals. These calculations also depend on the periodicity of the lattice potential to make some integrals functions of relative position only (position of the atoms where the orbital is localized). The structure of the band depends on details of the orbitals outside the atomic cores and the lattice spacing. The question is whether these parameters are knowable enough to make these calculations good for clusters, or are the additional terms Swift puts in good enough to make up for the problem.

Plain vanilla TB theory depends on localized atomic orbitals and lattice periodicity. It is for calculation of electronic energy bands in a solid. It ignores the edge or surface - which is exactly problem of clusters. It is troublesome that Swift et. al. state that some of the potentials used were not designed for clusters, and further he supposes that silicon clusters will form graphitic plates like carbon does.

It is tempting to think that all tetrahedrally bonded solids will have the same cluster structures, but it is more realistic to hope that the factors that govern structural energy minimumization will be similar. The the interaction
between core and surface energy as well as coordination number, for example, will play a role in carbon, silicon and germanium cluster formation. Fullerene structures are driven by tying up dangling bonds. But structures may not be identical over a range of masses for clusters of these elements. For instance silicon does not form closed cages like carbon's fullerenes. It is questionable whether we should expect silicon to form graphitic sheets either.

Swift et al. also points out that there is no assurance that their modified TB model will apply to clusters and says the calculation will be more accurate the more the cluster is similar to the bulk. The problem of clusters is the unusually prominent role played by surface effects in determining their structures. Because the surface-to-volume ratio in clusters is large, surface effects are likely to dominate, especially for small clusters. The effect of atomic rearrangements which enhance the stability of the surface can potentially be of great importance. For all the clusters in the size range we have studied, the majority of the atoms are surface atoms, so we expect these clusters to adopt compact, low surface energy structures, even at the expense of slightly less favorable bonding for the core atom. We may be able to construct a bigger picture for carbon, silicon and germanium that takes into account the commonality that all of these will want to form clusters that are four-fold coordinated, but the effect of different surface reconstructions will cause structures to differ (for example in the 10-32 size range) in a way we may be able to predict. None of this reasoning supports the assumptions of the tight binding model.

The other main point in the work of Swift et al. is the emphasis of the role of the coordination number maximum and cohesion energy as calculated from the modified TB model. Coordination number and cohesion energy per atom are
properties of a bulk solid. By focussing on these parameters, the tradeoff between maximizing average coordination number (core energy) and an energy advantage of a surface reconstruction has no place to be considered. The consequence of this premise that cohesion energy and coordination number are the important parameters is that the oscillations in reactivity that we see in silicon and germanium cannot be predicted from this model. On the contrary, if surface atoms are all highly coordinated, the addition or subtraction of one atom should not affect the cluster reactivity - or cluster stability at all. As a consequence, as clusters get larger, they also become more stable. It would seem that Swift et al. has ignored not only the patterned reactivity that has been repeatedly established by the FT-ICR measurements, but also the fragmentation work on silicon and germanium. On the other hand, this is the behavior observed for the larger germanium clusters. Perhaps in this range, coordination number and cohesion energy are beginning to dominate over surface affects.

Reactivity is a direct indication of what the surface structure is, described in the language of reactive sites. Until the search for lowest energy structures through first principle molecular dynamics calculations can be attempted, it is a wiser choice to be guided in the limitation of the subset of possible candidates by physical insight and empirical fact. It is possible to construct a network containing a core of fourfold-coordinated atoms, similar to bulk silicon, which are surrounded by surface atoms of 3 or 4 coordination. Structures of unusually low reactivity, and high stability may be obtained when exactly all surface atoms participate in the surface reconstruction. A dangling bond is a high energy feature on a cluster, so tying them up should contribute not only to suppressing reactivity, but to increasing thermodynamic stability. Any change in size caused
by the addition or removal of an atom introduces "defects" on the surface which become reactive sites.

Furthermore this method of reasoning may explain the whole set of magic numbers for silicon. Along with the proposed structure for Si$_{45}^+$ Kaxiras proposed a structure for Si$_{33}^+$ that was similar to the 7x7 reconstruction of the silicon (111) surface$^{16}$. 
V. OUTLOOK

There are many additional experiments that could be done from this point. Certainly a quantitative study of reaction rates for positive annealed silicon clusters to clear up any questions about multiple isomers is a next step. Up to 49 all the magic numbers are odd, if oscillations in reactivity persist, and change over to even numbers, the filled fullerene theory for silicon structures may be accurate. Preliminary work indicates that there is a small dip in reactivity at Si$_{54}^+$, the first expected filled fullerene, but not a large difference in reactivity. This experiment was also done on unannealed clusters. Annealing in this range has not been tried, and differences in reactivity may be enhanced. Silicon and germanium negative clusters may be annealed with the dye laser below the photodetachment threshold. This may lead to more dramatic chemisorption results for negative ions.

Study of the primary channel for fragmentation of annealed silicon and germanium clusters may prove to be interesting. Since primary channels for annealed and unannealed clusters are clearly different, the fragmentation pattern may become a criteria for establishing the degree of annealing of a cluster inventory. In the course of this work relative cluster stability and correlation with reactivity can be established. It is interesting that Ge$_{39}^+$, although an unreactive cluster is also one of the most brittle. It is one of the exceptions to the correlation between stability and reactivity. It is possible that if surface strain drives the structure of these structures then the surface bonds that participate in the reconstruction are weak due to bond angle strain. It would be interesting to see if there is a silicon cluster that behaves similarly. Another exception to the stable and unreactive rule is Ge$_{43}^+$; it is stable but reactive. It
should be possible to determine the annealing energy for each cluster by tuning the SWIFT voltage in the induced annealing procedure. This would be critical information for a theorist working on cluster structures. In fact this study should yield optimal annealing conditions of germanium clusters.

Another area to explore is to try and understand more specifically and in some detail exactly what these different reactive sites might be. This might be done by looking at possible dissociative chemisorption on clusters, which requires a more complicated site than molecular chemisorption. Typically there must be two dangling bonds available on a cluster and they must be the right distance apart to accommodate the adduct. Some of these reactive clusters added two to five adduct molecules quickly, while other seem to add only one. Further investigation of this point would be interesting.
VI. CONCLUSION

Germanium and Silicon Cluster Structures - Identical?

These types of studies of semiconductor clusters are real challenges in chemical physics, and understanding what the results mean will take time, further experiments, continued discussion in the open literature and conversation with theorists. Clusters of silicon and germanium, as injected into the FT-ICR exhibit nonunique reaction rates in chemisorption experiments that indicate the clear existence of multiple isomers. These isomers can be annealed, or sorted out to unique structural forms. We have established annealing procedures for these cluster inventories involving laser light excitation and collisional annealing using the SWIFT technology. Silicon is more robust to fragmentation than germanium. We did not see evidence in the germanium annealing procedure that clusters had actually been converted to a different configuration, although we did observe this behavior clearly for silicon (see fig. 7). We may have been simply fragmenting less stable clusters, leaving the thermodynamically favored form in the FT-ICR cell inventory (see fig. 19). The importance of annealing clusters before pursuing chemisorption experiments is crucial to avoiding confusing ambiguous and misleading results due to the effect of multiple isomers. An example of this is the discovery that Si$_{21}^+$ anneals to its reactive isomer, so is not actually a "magic number".

The magic number trend first observed by Elkind et al. has proven to extend from the silicon and ammonia chemisorption system to include ethylene, water and TMA - and also the negative ion. The exception to this is Si$_{21}^+$, that anneals to its reactive form. The same pattern occurs for clusters larger than 33
for germanium clusters with three reagents: nitric oxide, water and TMA. Clusters of both elements display a similar fragmentation pattern. The negative ion of each is much less reactive than the positive ion. There is a correlation between thermodynamic stability and reactivity. This data builds a case for the conclusion that the structures of these clusters above 33 are the same.

These are clusters of covalently bonded materials that consist of a core and a surface that compete when forming a structure. This is in contrast to metallic clusters that are a core of closely packed atoms.

Germanium clusters are significantly less reactive than silicon clusters, indicating a different reaction barrier. There are more reconstructions that it can take on to tie up dangling bonds and become nonreactive in comparison to silicon.

Hopefully this work on germanium and the follow on effort will stimulate calculations on the structure of germanium clusters. Presently there are none, owing to the larger size of the atom and the complication of its having d-electrons. Now that we have expanded our work from silicon to germanium, interest in applying what we learn about clusters to their bulk parent surfaces will increase. For instance, when growing semiconductor films, the clustering affect is already observed as a nucleation process of growing one layer on another for heterodevices. As a result, cluster research on semiconductors is only going to get more attention.

In the longer term, we are moving toward compiling a knowledge base from which to do predictive surface science. Meaning once the forces than influence bonding and "reconstruction" in surfaces are understood, at some moment in the future a materials scientist will be able to go to a workstation and
design a semiconductor nanosurface that will behave electronically, or
catalytically like we want. Entrepreneurs will call these nanostructures "Designer
Devices". We are still a long way from this type of predictive materials science,
but it is sure that understanding novel structures will lead to unusual materials
with uncommon properties.
VII. REFERENCES


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