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Laser annealing of silicon clusters

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LASER ANNEALING OF SILICON CLUSTERS

by

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by

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Abstract

A miniaturized pulsed laser-vaporization supersonic cluster beam source was developed and mounted on the magnetic axis of a Fourier transform ion cyclotron resonance apparatus (FT-ICR) so that the clusters were directly injected into the ICR ion trap. Mass-selected positive silicon cluster ions were levitated in the FT-ICR, and probed in chemisorption reactions with ethylene and ammonia. Clusters in the 36-51 atom size range were effectively annealed to unique structural forms by excitation with a XeCl excimer laser followed by cooling through infrared radiation and collisions with argon. Reactions on the annealed clusters showed the variation in reactivity with cluster size was enhanced. To our knowledge this is the first reported example of a successful annealing experiment on gas phase clusters of any kind.
Acknowledgment

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I. INTRODUCTION AND BACKGROUND: Magic Numbers and Multiple Isomers

It is hoped that the study of the chemical and physical properties of clusters, such as reactivity, photofragmentation, photodetachment, structure, ground state energy, and bonding will provide insight for surface scientists in understanding the similar properties of bulk surfaces. In particular, clusters have the advantage of being discrete molecular units. This makes them significantly simpler systems to model than the bulk surface, and in some cases their physical properties can be calculated from first principles. Due to advances in parallel computing over the next ten years, it is likely that the calculation of the ground state energy of a silicon cluster of 100 atoms will be routine. Given this eventuality, we are accumulating experimental data that future calculations will be compared to. Instead of using silicon single crystals to idealize the surface, these clusters can be used as molecular models to study electronic and geometric structure. This way clusters provide a fertile testing ground for fundamental ideas and concepts about underlying principles that govern physical properties such as bonding, structure and reactivity. The idea that clusters will be useful as molecular models hinges on the premise that these clusters actually adopt unique structural forms.

For the present, minimum energy structures have been calculated for silicon clusters up to 10 atoms in size\(^1\), but beyond this the problem quickly becomes numerically intractable due to the many degrees of freedom. 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 can be several alternative structures that are isoenergetic, or nearly so\(^5\). In the worst case scenario the clusters continually change shape as they interconvert from structure to structure. Due to computational intricacies, it is important that theorists be able to impose limitations on the reasonable choices for structures of the clusters. Restrictions on what the most likely structures might be are deduced from physical insight, empirically developed models, or geometrical and symmetry arguments.
One particularly appealing example is a structure suggested by Kaxiras\textsuperscript{9} for Si\textsubscript{45}\textsuperscript{+}. It is based on the idea that the magic number clusters are relatively unreactive because the surface resembles a stable reconstruction of the bulk crystal around a core of tetrahedrally bonded atoms. Figure 1 shows the proposed Si\textsubscript{45}\textsuperscript{+} structure. The surface of this cluster is similar to the 2x1 reconstruction of the (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.

For silicon, the data generated by our group has been crucial information in the process of sorting out which configurations are favored structures, since chemical reactivity is closely related to structure. Some of the most interesting work done consisted of straightforward chemisorption experiments. Although less reactive than bulk silicon, most clusters react readily, however, there are certain unreactive ones, the "magic number" clusters that are the exception. In the case of medium-sized (20-60 atom) clusters of silicon, the magic number behavior was observed in this group a few years ago by Elkind, Alford, Laaksonen, Weiss and Smalley\textsuperscript{2}, and further expanded by Alford \textit{et.al.}\textsuperscript{3,4} (see fig. 2). Sharp variations were seen in reaction rates as a function of cluster size in reaction with ammonia. Those clusters with 21, 25, 33, 39, and 45 atoms appeared to be relatively inert while clusters with only one atom more or less reacted rapidly. Presumably, these clusters have surfaces that are constructed so as to avoid a reactive site. This was taken as evidence that clusters are not amorphous chunks of bulk material, but that each size has a favorite configuration. To a large extent these clusters had "crystallized" to particular structural forms, some of which had few if any active sites for NH\textsubscript{3} chemisorption on their surfaces. This data stimulated a substantial level of activity within the theoretical community, with a number of structures being proposed together with supporting calculations\textsuperscript{5-10}.

Due to the intricacies of the FT-ICR, this data was tedious and difficult to obtain, so we turned our attention to redesigning the cluster source. To verify and extend the ammonia
chemisorption results, we implemented a more elaborate version of the original FT-ICR apparatus\textsuperscript{3,4} whose key component is the "Minisource", a miniaturized pulsed laser-vaporization supersonic beam source. We confirmed the magic number behavior with ammonia in substantially more detail, and also observed the same trend in an extensive chemisorption study with ethylene. All clusters exhibited multiple structural isomers as indicated by changes in their chemisorption reaction rates, but Si\textsubscript{39}\textsuperscript{+} and Si\textsubscript{45}\textsuperscript{+} appear to be dominated by a particularly unreactive, stable form.

It quickly became clear that if these clusters are to be useful, it is necessary to find a reliable way either to sort them out quickly, or to anneal them to a single well-defined structure. Working on the assumption that one of the multiple isomers we observed would be more energetically stable than the other forms, we sought heating and cooling conditions that would allow these clusters to convert from less stable to the more structures. We found that such annealing is possible through laser excitation (XeCl 308 nm) and that once annealed the clusters do not interconvert at room temperature. Detailed chemisorption experiments on the annealed sample showed that Si\textsubscript{39}\textsuperscript{+} and Si\textsubscript{45}\textsuperscript{+} were now not only unreactive, but effectively inert to chemisorption by several reagents. For these two clusters, we have proved that the least reactive isomer is also the most energetically stable.

Similar experiments with nitric oxide on germanium reveal the same results. We have uncovered a trend that is real and robust to changes in experimental parameters. Since structure is critical to chemical reactivity, we take these observations as evidence that the bonding in these two elements is similar, and that the chemistry of these two systems is dictated by the unique geometrical forms that these molecules like to occupy.
Figure 1. The proposed Kaxiras structure for Si$_{45}$
Figure 2. Rate constants for chemisorption of one NH$_3$ onto silicon clusters of different sizes. Magic Numbers are unreactive compared to their neighbors.

\[ \text{Si}_n^+ + \text{NH}_3 \rightarrow \text{Si}_n\text{NH}_3^+ \]
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\(^{11-14}\). Alford et al.\(^ {15,16}\) and Kofel et al.\(^ {16,17}\) independently demonstrated that a simple einzellens 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\(^ {2,3,17-19}\). Even so the cluster beam source remained a weak point in the apparatus. In seeking to extend the mass range of clusters we could routinely generate, and also to improve the reliability of its operation, we turned our attention to devising a new external cluster beam source.

**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\(^ {20}\). 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 \(\text{L} \text{s}^{-1}\) pumping station (total volume of 219 liters). Although a major innovation at the time, this source ("Dinosource") 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.

The shortcomings of the Dinosource 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 the Dinosource 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{20} 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.

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 Dinosource.

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 focusing 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 Dinosource. 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$^{21}$, and used to provide short pulses for beam-beam scattering experiments by Gentry and Giese$^{22}$. An early version was first implemented by Liverman, Beck, Monts, and Smalley$^{23}$ for laser spectroscopy of cold molecules and radicals, and was used in the very first experiments in laser vaporization production of cluster beams$^{24}$. It was abandoned in favor of the double solenoid designs that delivered a higher gas flow$^{25}$. 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\textsuperscript{26} (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 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 degrees 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 with 25 degrees 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 misalignment 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 Dinosource 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 has a native oxide overlayer we were able to cycle the disk through five to ten surface ablations to remove the oxide and expose the pure electronics grade surface of our sample. 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 a 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 \(2\times10^{-2}\) Torr, which would have been be completely unacceptable in the Dinosource, that operated with three \(10^4\) 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 \(4\times10^{-3}\) 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 \(5\times10^{-8}\) 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.

FT-ICR cell and operation

The remainder of this FT-ICR apparatus were much the same as described in earlier publications from this group\textsuperscript{3,17}. 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.

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. Positively charged clusters travelling through the middle of this tube were effectively decelerated
Figure 4. FT-ICR Schematic
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.

Since the cluster ions are all accelerated to nearly the same $1.9 \times 10^5$ cm s$^{-1}$ velocity by the supersonic expansion, each cluster has a translational energy which is linearly dependent on its mass (For $\text{Si}_{45}^+$ 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 $\text{Si}_{36}^+$ - 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
Figure 5. Clusters *As Injected* and trapped in the ICR cell.
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\textsuperscript{28} 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 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.

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\textsuperscript{-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\textsuperscript{-9} Torr range.

**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\textsuperscript{3}. This manipulation is possible because the cyclotron frequency of a charged particle in a magnetic field varies inversely with mass. 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.

An alternative method was first discussed by Marshall29,30 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 filtered SWIFT signal is applied to the two excitation plates of the ICR cell. 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\textsuperscript{31}. The SWIFT technique was used extensively in the following annealing studies to confirm the existence of structural isomers.

The ICR transients were detected by a Stanford Research Systems model SR560 preamplifier, followed by 12 bit digitization and relatively straightforward FFT data processing\textsuperscript{32} to produce the mass spectra shown below.
III. RESULTS

Direct injection into ICR cell

Figure 5 displays a typical FT-ICR mass spectrum of positive cluster ions directly injected into the cell from the Minisource. For this experiment the vaporization laser was fired 60 microseconds after the peak of the current pulse driving the spring of the pulsed valve. This corresponds to roughly half-way up the rising edge of the gas pulse into the waiting room of the nozzle as shown in Fig. 3. We estimate that the helium gas pressure in the nozzle at the moment of laser vaporization was about 200 Torr, and that the average residence time of the clusters in the waiting room was 40 microseconds, during which time the pressure should have increased to 400 Torr. Measurements of the cluster ion arrival time distribution show the width of the ion packet is 40 microseconds as expected, and velocity slippage of the heaviest clusters is less than 10 percent.

To ensure the clusters were well thermalized in the ICR trap we typically exposed them to argon at a pressure of $2 \times 10^{-5}$ Torr for an additional 10 seconds. The FT-ICR mass spectrum shown in Fig. 5 was recorded after an additional 10 second pumping time to allow the ICR cell background gas pressure to fall below $5 \times 10^{-8}$ Torr. The fine structure seen in each main peak in the mass spectrum is due to the various isotopomers arising from the $\text{Si}^{28}$ (92.21%), $\text{Si}^{29}$ (4.70%), and $\text{Si}^{30}$ (3.09%) isotopes in natural abundance.

In order to produce the mass spectrum of Fig. 5, the injection process was repeated 50 times over a period of 5 seconds. During this time the average helium pressure in the region of the ICR cell was estimated to be in the range of $10^{-4}$ to $10^{-3}$ Torr, with the peak pressure rising to $10^{-2}$ Torr immediately after each supersonic beam pulse. Since the cluster ion packet arrives at the ICR cell within the first 50-100 microseconds of the supersonic beam pulse when the pressure is still quite low, this large average and peak gas load on the ICR is acceptable. The
Dinosource, with its slower solenoid valve, higher gas load and unreliable vacuum properties was unacceptable for mounting directly on the magnet.

After injection of the cluster packet the front and rear door voltages were ramped to 10 V over a period of 1.0 second, and then the clusters were exposed to argon at a pressure of $2 \times 10^{-5}$ Torr for 2-10 seconds in order to thermalize their motions in the ICR trap to near 300 K. The ICR transient was then excited with a computer-generated rf waveform having constant power over 50-90 kHz (equivalent to the mass range from 36 to 53 silicon atoms) and the resulting coherent ICR transient was detected and processed to produce the spectrum shown in Fig. 5. This figure displays the FT-ICR mass spectrum of silicon clusters as they appear initially after injection.

**C₂H₄ chemisorption: 2-cycle experiments show multiple isomers exist**

Since the mass of ethylene is the same as the dominant isotope of silicon, it was necessary to sweep away some of the clusters to generate a clear baseline to see the chemisorption products. We chose to keep only Si$_{36}^+$, Si$_{39}^+$, Si$_{42}^+$, Si$_{45}^+$, Si$_{48}^+$, and Si$_{51}^+$ and ejected the intermediate masses with an application of a SWIFT cycle. Careful inspection of the remaining peaks in Fig. 6 shows that we chose the SWIFT waveform to leave behind slightly different isotopomer distributions for each cluster so that their subsequent reaction products could be easily traced.

Figure 7 is the FT-ICR mass spectrum obtained by exposing the SWIFTed cluster distribution from Fig. 6 to ethylene at a pressure of $1 \times 10^{-5}$ Torr for a period of 20 seconds -- about 5,000 collisions with ethylene molecules. All the clusters show the addition of an ethylene group, but it is clear that clusters with 36, 42, and 51 atoms are considerably more reactive than those with 39, 45, or 48 atoms. This result is highly reproducible. The experiment was repeated with a wide range of thermalization conditions prior to exposure to the ethylene reactant. The same result was obtained when the argon thermalization period was varied throughout the range of 0 to over 10,000 collisions.
Figure 6. After applying a SWIFT cycle to clear a baseline in preparation for \( \text{C}_2\text{H}_4 \) reaction.
Figure 7. After 5000 collisions with C$_2$H$_4$: Si$_{39}^+$ and Si$_{45}^+$ and Si$_{48}^+$ are less reactive than Si$_{36}^+$, Si$_{42}^+$, or Si$_{51}^+$. 

![Graph showing the distribution of cluster ion masses after 5000 collisions with C$_2$H$_4$. Peaks for Si$_{39}^+$, Si$_{45}^+$, and Si$_{48}^+$ are visible.]
some experiments the clusters were allowed to thermalize as they were levitated in the trap for a period of over 100 seconds. In fact we actively sought conditions where Si_{45}^{+} would become reactive and could find none. This should have been sufficiently long for effective cooling by infrared emission alone, even in the absence of collisions. We are confident, therefore, that the observed special reactivity behavior is characteristic of the ground electronic state of the clusters at an internal temperature of near 300 K.

To find evidence that the clusters were actually reacting with more than one reaction rate, we ejected the chemisorbed products of the first reaction experiment (Fig. 7) with a second application of the original SWIFT waveform, and Fig. 8 shows the result of a subsequent exposure of these clusters to another 5000 collisions with ethylene. Note that the bare silicon clusters that survived the initial ethylene exposure are now considerably less reactive, and the clusters at 39, 45, and 48 are relatively more prominent. It would seem that a fraction of the clusters of 39, 45, and 48 atoms have a component of an isomer that reacts quickly, then has been ejected from the cell by the SWIFT. It is interesting that, in this case, the dominant isomers of these clusters are more stable to reaction with ethylene. This is clear evidence that the cluster inventories for each mass are a mixture of structural forms, some of which are easily titrated away. Therefore, multiple geometrical isomers were present to some extent in the initial cluster distribution. Further exposure to ethylene continued to sort the clusters out in accordance with their relative reactivity. We could push this reaction reliably to about 40,000 collisions which is near the maximum allowed by diffusional loss of the cluster ions from the ICR cell. The only remaining clusters detectable in this mass range were Si_{39}^{+}, Si_{45}^{+}, and (least intense) Si_{48}^{+}.

These ethylene chemisorption experiments confirm our earlier data that Si_{39}^{+} and Si_{45}^{+} can take structural forms which are specially unreactive and also show that Si_{48}^{+} is rather unreactive as well. Since the Minisource generates significantly more signal intensity than the Dinosource did, we repeated the earlier ammonia chemisorption work, now being able to push the reaction farther (more collisions).
Figure 8. Remarkably different reactivity pattern. Reactive components have been titrated away.
This data confirmed that the dominant structural isomers of Si$_{39}^+$ and Si$_{45}^+$ are relatively unreactive toward ammonia chemisorption, while Si$_{48}^+$ does ultimately react away.

It was a fortunate coincidence that this reactivity pattern was observed at all during operation with the Dinosource. Not only did the original technology generate fewer cluster ions in this size range, but all of these didn't make it into the cell. A standard Wiley-McLaren extraction stack was used to pulse the ions out of the plasma beam down the magnetic axis of the ICR. As mass of a cluster ion increases a higher extraction voltage is necessary to turn the clusters, making extraction increasingly inefficient with increasing mass. Since fewer bare cluster ions were collected in the ICR trap, the clusters could be kept around for fewer collisions with a reactant, making the reactivity differences less obvious. But, because the older nozzle technology made fewer clusters in this mass range, a laser ionization step (ArF) was required to utilize more of the cluster inventory. Although the purpose of the ArF light was to ionize the cluster beam, also unknown to us it partially annealed the clusters, making the reactivity pattern more prominent in the results.

Laser annealing of silicon clusters

Once it was established that multiple isomers of each cluster were being generated by the Minisource, we realized that we may not have made the same clusters day to day. In fact comparison of ethylene reactivity data from different days showed the amount of reactive isomer for each cluster varied 10-30 percent on any given day. We began to seek a method of preparation of these cluster ions that would give us a single isomer sample, so we could pursue other experiments without the complications introduced in the data by the multiple isomers. With the hope that one of these isomers would be more energetically stable than the others, we tried to anneal the clusters in the ICR cell with laser light. We found we could do this very reproducibly with ArF and XeCl light, in what appears to be a single photon process. Now,
instead of doing a two-cycle chemisorption experiment, we compared reactivity of the clusters before and after laser annealing.

Figure 9 is an example of the critical data for this experiment. 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 2x10^{-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. 7 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. Again the SWIFT excitation was chosen such that Si_{39}^+ and 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. 7 shows the result of exposure of these selected clusters to ethylene at 1x10^{-5} Torr for 20 seconds -- about 5000 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. This is equivalent to the data in Figure 7. The chemisorption products are marked with the symbol E_y.

The bottom panel of Fig. 9, however, demonstrates a more significant point: these reactive isomers of the special clusters 39, 45, and 48 also turn out to be 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
Figure 9. (a) Clusters as injected. (b) After SWIFTing to clear the baseline for chemisorption. (c) Reaction of ethylene with unannealed clusters. (d) Reaction of ethylene after annealing.
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 Si$_{39}^+$ and
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 Si$_{39}^+$ and Si$_{45}^+$
bear the wider isotopic width signature indicating chemisorption of one, and two ethylene
groups onto each cluster. For Si$_{39}^+$ there is even chemisorption of three ethylene groups that
appears as an isotopically wide peak that is overlying the narrow peak of Si$_{42}^+$ bare cluster
(compare to the Si$_{42}^+$ bare cluster in panel (b) ). In the bottom panel, however, the peaks
corresponding to Si$_{39}^+$E$_1$ and Si$_{39}^+$E$_2$ in panel (c) are clearly not adducts of Si$_{39}^+$ since
these peak widths are thin. These have been assigned as the chemisorption of four and five
 ethylenes onto Si$_{36}^+$, whose bare cluster peak has vanished completely. Similarly the peaks
that match up to Si$_{45}^+$E$_1$ and Si$_{45}^+$E$_2$ in panel (c) are clearly the result of chemisorption of four
and five ethylenes onto Si$_{42}^+$ in panel (d). The annealed forms of the Si$_{39}^+$ and Si$_{45}^+$ atom
clusters are effectively inert. The relative heights of Si$_{36}^+$ and 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$_{39}^+$ and Si$_{45}^+$
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. 10. In this case all injected ions except
Si$_{39}^+$ and Si$_{42}^+$ were ejected from the cell. The top panel shows the reaction with ethylene
after 5000 collisions. Again it is evident that as injected $\text{Si}_{39}^+$ 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 $\text{Si}_{42}^+$ displays no evidence of any reaction the annealed $\text{Si}_{42}^+$ remains highly reactive. A particularly significant aspect to the top and bottom panels of Fig. 10 is that they have the same vertical scale factor. The marked higher intensity of the bare $\text{Si}_{39}^+$ 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 $\text{Si}_{39}^+$ 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$^{-2}$ per pulse, and over a broad range of laser pulse rates (2.5-50 Hz). In all cases the effect on the apparent 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
Figure 10. Annealing not photofragmentation. Enhanced bare cluster signal on $\text{Si}_{39}^+$ after annealing. Note vertical scale on both spectra is identical.
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.

**NH₃ chemisorption on annealed clusters**

Figure 11 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. 9, panel (b). The top panel of Fig. 11 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 variation in apparent reactivity toward ammonia. Yet the bottom panel shows again clear evidence of laser-induced annealing: Si₃⁹⁺ and Si₄₅⁺ 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. 1 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. 1.

In general, for all silicon clusters ammonia is simply more reactive than ethylene, although both react selectively. In the initial work from this group² 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 Si₃⁹⁺ and Si₄₅⁺ clusters again being the least reactive. However, H₂O 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.
Figure 11. Ammonia reaction. Magic numbers are evident after annealing, but not before.
Jarroid and co-workers have recently reported a number of experiments with almost directly opposite results on these silicon clusters\textsuperscript{33}. Using a tandem quadrupole apparatus with an intervening flow tube reactor, they have examined the reactivity of positive silicon cluster ions with a variety of reagents such as ethylene\textsuperscript{33,34} and oxygen\textsuperscript{35}. Unlike our FT-ICR studies, they observed nothing particularly different as a function of cluster size. In fact, all their clusters react at approximately the collision rate -- to within about a factor of two. More disturbingly, they observed extensive evidence for the presence of multiple isomers in abundance for all clusters. Most recently these experiments have been extended to reactions with ammonia where similarly confounding results were obtained\textsuperscript{36}. The disagreement between the two types of apparatus is persistent. In view of our laser annealing results, we argue it is due to a difference in the conditions of formation and annealing of the clusters prior to reaction, and possibly to the observation of dissociative chemisorption in the FT-ICR and molecular chemisorption in the tandem quadrupole apparatus.

If the clusters in Jarroid's apparatus have become trapped in a large set of less well-ordered structures that seemingly have more reactive sites, consequently, differences in reactivity between cluster sizes are masked by differences in reactivity between multiple structural isomers of the same cluster size. In particular, the energetically less favored isomers of Si\textsubscript{39}\textsuperscript{+} and Si\textsubscript{45}\textsuperscript{+} are more reactive than the most stable form that they anneal to. This is consistent with Jarroid's faster reaction rates taken from the multiple isomer cluster mixture. We therefore conclude that the non size-selective reactivity behavior of silicon clusters towards ammonia and ethylene reported by Jarroid and co-workers\textsuperscript{34-36} is due to inadequate annealing of the clusters produced by their continuous jet source.

By comparing "after injection" spectra taken from different days with the Minisource and also the spectra taken with the Dinosource, it is clear that even with pulsed sources the relative
amount of poorly annealed clusters in this 30-60 atom size range can vary substantially (10-30%) as a function of minor variations in the source conditions. The proportion of the poorly annealed component produced should be sensitive to the temperature conditions in the growth region of the source, and to the relative importance of growth by single atom addition compared to growth by aggregation.\textsuperscript{36}

The Minisource was designed to form clusters in the early stages of nucleation from the laser-generated vapor where growth is predominantly by sequential addition of single atoms. Most of this growth occurs during the first few tens of microseconds while the carrier gas is still quite hot from the laser pulse. Some of the clusters appear to stay hot enough that they anneal while they grow. The laser-vaporization cluster source used by Jarrold's group, however, forms the clusters on a much longer time scale (milliseconds) in a slowly moving low pressure helium gas, efficiently cooled by thermal conduction to its walls. During this longer time interval the majority of the silicon is in the form of clusters, since most of the free silicon atoms will have diffused to the walls. Here cluster growth will rapidly be dominated by aggregation of small and medium-sized clusters with each other. Without significant reheating, these cluster aggregates may never anneal to the most energetically favored form.

We conclude that some sort of downstream annealing procedure may always be necessary with these supersonic cluster beam sources if reproducible results are to be obtained with silicon 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\(^{37}\). 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\(^{38}\), 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 \(\text{Ge}_{39}^+\) and \(\text{Ge}_{45}^+\), and the most reactive is \(\text{Ge}_{43}^+\).

Figure 12 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. 13, 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 13 shows the result of exposure of the selected clusters to nitric oxide gas at a pressure of \(1\times10^{-4}\) Torr for 10 seconds, about 30,000 collisions. Prior to the reaction the clusters had been thermalized to 300 K by roughly 2000 collisions with argon. For some clusters such as \(\text{Ge}_{43}^+\) reaction products of the
Figure 12. Germanium clusters as injected into the ICR cell. Notice 1 amu resolution on the Ge$_{45}^+$ detailed picture.
Figure 13. Reaction of Germanium clusters with NO reveals similar magic number behavior.

**Diagram Description:**
- **Upper Section:**
  - Title: Germanium Clusters
  - SWIFTed
  - No reaction

- **Lower Section:**
  - Reaction with NO
  - 10sec x $10^{-4}$ Torr

**Graph Details:**
- Plot of Relative Intensity vs. Cluster Ion Mass (amu)
- Mass values: 39, 40, 41, 42, 43, 44, 45, 46
- Mass range: 2800 to 3400

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$^{2,3,36}$ where again the 43rd cluster appears to be the most reactive and the 39th and 45th are inert. The fact seen here in Fig. 13 that a similar cluster reactivity pattern exists for germanium now supports the earlier photofragmentation evidence that germanium adopts the same structures as silicon in these small clusters. Observation of the same pattern in germanium and silicon suggests that there is an underlying systematic order to these clusters. 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.
IV. FUTURE APPLICATIONS

To pursue the apparent parallel between silicon and germanium we plan to check to see if this same behavior occurs for NO on silicon. In the original ICR experiment, NO and water seemed to react unselectively with all silicon cluster ions, but with the improved apparatus we could use a more dilute mixture of NO in argon to follow the reaction more slowly. This procedure revealed the selectivity of the water reaction on silicon, but we may run into the complication of NO etching silicon clusters.

Now that an annealed inventory of silicon clusters can readily be prepared in the ICR cell, experiments that are waiting to be performed include expanding the mass range on which the chemisorption data has been obtained. We anticipate more magic numbers in the 50-100 atom range, not the transition to bulk properties that Jarrold claims to see. In addition, we are now in a position to derive the reaction rates of annealed silicon clusters which seem to vary over about five orders of magnitude, not the three that were determined in the original experiments.

The question of molecular or dissociative chemisorption of ammonia on these clusters also must be addressed. We may be able to do this by isotopic labeling, or photodissociation of the adsorbed ammonia on the cluster. There is preliminary evidence from this group that at saturation coverage with ammonia on Si$_{10}^+$, the loss of H$_2$ is observed. This may be an indication of dissociative chemisorption on the surface, but at high coverage the cluster may reconstruct, so conclusions based on this type of information must be drawn carefully. This saturation study would be an interesting chemisorption to try on Si$_{42}^+$ or Si$_{43}^+$ since these clusters are so reactive. Similar saturation experiments with hydrogen might provide a clue as to the number of dangling bonds on each cluster surface, but this result again would be ambiguous since it is likely that restructuring of the surface may occur. Another obvious experimental parameter to investigate is the effect of charge state on the magic number trend.
Negative ions

Preliminary data on the negative silicon ions needs to be expanded to see if the magic number trend extends to a change in charge state. There have been many fewer experiments done on the negative silicon clusters. One characteristic common to the negatives and the positives is that for both charge states \( \text{Si}_{43}^{+}\cdot \) is consistently the most reactive cluster with any reagent we have tried. Like the positive ions, laser annealing of the negatives also changes their reactivity pattern. The negative ions are always less reactive, however, and we lose an additional factor of ten in signal when we do the laser treatment. The negative ion is simply more likely to photodetach its electron during the laser excitation than the positive ion is to gain an electron, then these neutral clusters will drift out of the cell.

The mass spectra for the reaction of the negatives with ammonia is shown in Figure 14. Since the ammonia adduct peaks do not overlap with other bare clusters, applying a SWIFT waveform to clear a baseline for observation of the reaction products was not necessary. By far the most reactive cluster is \( \text{Si}_{43}^- \). Unlike the positive clusters, all of which react to a degree with ammonia, clusters with 39, 40, 42, 43, 44, and 45 atoms are the only ones that show a significant reaction product. The laser annealing does have a similar affect, however, on \( \text{Si}_{39}^- \) and \( \text{Si}_{45}^- \). Both of these clusters have relatively decreased reactivity, like the positive ion, but are not completely inert. Reactivity for 42, 43 and 44 is not changed. This may be due to incomplete annealing of the clusters, which is much trickier to accomplish than with positive ions.

**Silicon negative ion TMA results**

Preliminary results of the negative ions with trimethylamine (TMA) are even more interesting. The reaction products for this experiment are shown in Fig. 15. In this case a baseline has been cleared by SWIFT ejection of some of the clusters. 36, 39, 42, 45 and 48 remain, as in the ethylene experiments, again with the isotopic width of 39 and 45 left wider than the others. Although all clusters have reacted, 39, and 45 are relatively less reactive than the others. This is
the same magic number behavior that was seen in the positive clusters. After annealing 39 and 45 are even less reactive while 36, 42, and 48 have reacted about the same amount. In fact there is no Si$_{42}^{+}$ [TMA]$_2$ peak observed after annealing.
Figure 14. Raw data from FT-ICR for negatively charged silicon clusters. The top panel is reaction with ammonia on clusters as injected. The bottom panel is the same reaction after annealing the clusters.
Figure 15. Reaction of negatively charged silicon clusters with TMA. $\text{Si}_{39}^-$ and $\text{Si}_{45}^-$ are less reactive than the remaining clusters.
V. CONCLUSIONS

To our knowledge this is the first reported example of a successful annealing experiment on gas phase clusters of any kind. These results are highly repeatable, and this technique offers great promise for the future study of single isomer cluster samples of silicon. This data convincingly shows that gas phase metal and semiconductor clusters can be annealed to energetically favored single-structure configurations. These kinds of observations will make it eventually possible to establish some rules about how clusters like to come together, and what shapes they like to stay in.

Finally, these experiments have benefited greatly from the reliable operation of the Minisource, and the simplicity of direct injection. The Minisource may find wide applications in other UHV compatible apparatuses. Its ability to produce intense atomic beams (not discussed here) may make it useful in molecular beam epitaxy and other materials applications. In particular, this source may be used to apply a variety of mass-spectrometric techniques to large biomolecules -- a project also on our list to explore.
VI. REFERENCES


27. Electroformed Nickel Skimmer, Beam Dynamics, Inc., Minneapolis, MN.


