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Brief Reports

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Laser vaporization of solids into an inert gas: A measure of high-temperature cluster stability

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We have studied the effects of an inert cooling gas on laser vaporization of solid sodium chloride. The unicluster decay cascades that follow the vaporizing laser pulse are rapidly quenched in helium or argon gas, generating cluster ions whose relative populations reflect their high-temperature stabilities against decay. Cluster production and thermalization are shown to occur in less than 15 ns. Abundance measurements of $[\mathrm{Na(NaCl)}_n]^+$ ions ($n = 1-157$) confirm that surface steps are the most stable additions to a cuboid base lattice.

Both particle sputtering and laser vaporization can produce atomic or molecular clusters.[1-3] Furthermore, the spectra of clusters generated by the two techniques display similar contrasts between abundant and rare cluster sizes. This similarity is explained by looking at the factors that determine observed cluster size. For dissociation into vacuum, the measured cluster size is sensitive to the amount of excess energy the original cluster had when it ceased to interact with the surface and the number of atoms or molecules it evaporates before reaching effective stability. For cluster growth in a high-pressure inert gas, the final cluster size is determined largely by collision rates and the availability of unattached atoms or molecules. In both cases, the final size distribution is strongly influenced by external statistical effects in addition to the actual energetic properties of the clusters involved.

In the experiments described in this paper, a technique is employed that avoids these statistical effects. A laser is used to vaporize the surface of solid sodium chloride into an expanding jet of helium or argon gas. The laser-generated sodium chloride particles undergo very rapid cooling, without any subsequent opportunity to grow and form larger particles. The rapid decrease in density and temperature during the jet expansion ensures that each sodium chloride particle suffers less than 1% of the collisions needed to observe significant cluster growth in the channel of conventional laser vaporization cluster sources.[4] As a result, the spectrum of cluster ions observed within the expanding jet is essentially unchanged from its status immediately following the laser pulse. Cooling reduces the random effects of initial excess energy on the final measured cluster size and immediate jet expansion eliminates the random effects of collision-limited growth.

Having removed these statistical influences from the problem, the final cluster size distribution is determined almost exclusively by high-temperature stability. Immediately after leaving the solid surface, each original cluster has a great excess of energy and evaporates atoms or molecules at a rapid rate. Between evaporations, it dwells briefly at particular sizes, exploring configuration space for a path to the next decay.[5] The particles dwell the longest at those sizes that are best able to handle the excess energy. These decay-resistant cluster sizes are either very tightly bound or have large regions of configuration space with only weak couplings to decay channels. Somewhere along this decay sequence, the cooling gas removes enough energy to prevent further decay. Thus the final spectrum of clusters shows enhanced populations for those cluster sizes that exist longest at high temperature before decaying into smaller particles.

The source apparatus (Fig. 1) used in this experiment consists of a pulsed gas nozzle, a sample of sodium chloride, and a focused laser beam. The 200-μs gas pulse (helium or argon at 1–10 atm) is produced by a Lasertechnic LPV valve and is directed across the sample from a 1.25-mm-diam orifice. The laser beam (193 or 248 nm from a Lambda Physik EMG103MSC excimer laser) is focused by a 50-cm lens to a spot 1×2 mm on the sample, centered approximately 2 mm below the nozzle. The energy density on the sample is 1–10 J/cm^2 in 15 ns, at a repetition rate of 5–50 Hz.

This source produces a pulsed molecular beam, which is skimmed 15 cm downstream from the source and its ions mass analyzed in a 10-kV pulsed Wiley and McLaren

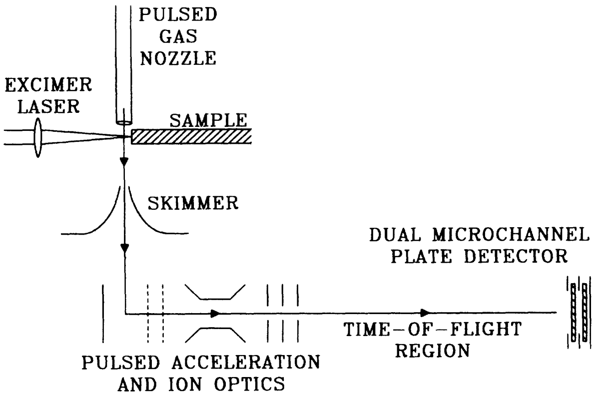

FIG. 1. Experimental apparatus: Cluster ions are produced by laser photofragmentation of the sample, cooled and entrained in the gas jet, and dispersed according to mass following acceleration to 10 keV.

time-of-flight mass spectrometer.[6] A dual microchannel plate detector registers the ion arrivals, and the resulting voltage signal is digitized for signal averaging and analysis by computer. The mass resolution of the accelerating system and time-of-flight mass spectrometer is 1 part in 500.

Two types of NaCl source samples were used. A rotating NaCl single-crystal disk was inserted under the gas nozzle at the laser focus, which produced a consistent pulsed beam of cluster ions. A packed powder source, NaCl powder between two stainless-steel disks, was also used and it produced larger clusters than could be obtained with the single-crystal sample. The powder sample appears to set a larger initial size for the fragmentation cascade. Several groups that use laser vaporization as a source for carbon clusters have reported a relative increase in the yields of large clusters after long run times[7] or at reduced laser intensities,[8,9] and they have attributed this effect to the cluster source geometry or different growth mechanisms. These observations may actually have been the vaporization of carbon powder, which had built up within the sources. At reduced laser intensity, the powder would vaporize into clusters rather than individual atoms.

The spectra of sodium chloride cluster ions present in the jet are shown in Fig. 2. Clusters of the form $[\mathrm{Na(NaCl)}_n]^+$ and $[\mathrm{Cl(NaCl)}_n]^-$ are observed, consistent with the results of previous studies.[10,11] These spectra are remarkably insensitive to experimental parameters such as laser fluence or wavelength, inert gas pressure or mass, sample geometry, and measurement time delays.

The relative cluster ion abundances vary dramatically with mass. Most of this variation results from differences in high-temperature stabilities between nearby cluster sizes. The longer a particular cluster size can withstand unicluster decomposition, given a large excess of energy, the more such clusters will be frozen into the gas jet.

Shattering of a solid *into vacuum* produces a distribution of clusters that is initially unstructured and statistical.[10,12] The clusters are generally very hot and population differences develop as clusters evaporate away atoms or molecules. The larger the internal temperature, the more complete the transition from a random initial population to one that is energetically and kinetically determined. Increasing the initial energy in alkali halide sputtering (fast-atom bombardment[13] and secondary-ion-mass spectroscopy[14]) experiments clearly increases the measured contrast between different cluster sizes.

The randomness of both the initial cluster size and the

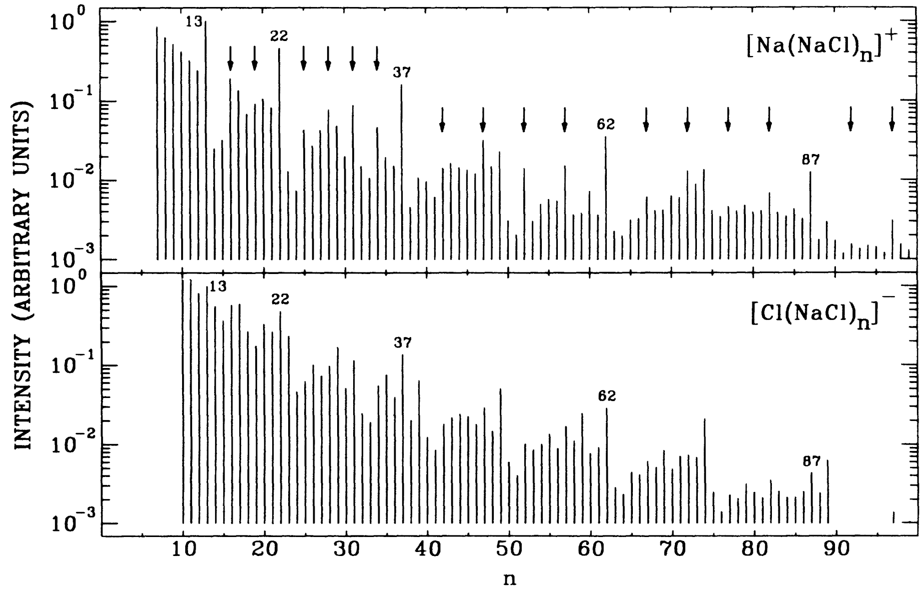

FIG. 2. Relative abundances of the positive and negative NaCl cluster ions, obtained by integrating the total charge detected at each mass. Cuboid cluster sizes at $n = 13$, 22, 37, 62, and 87 are clearly visible, along with a periodic fine structure. Single-mass population uncertainty is ±10%. For distant comparisons, there is an additional uncertainty of ±2% to the power Δn.

excess energy limits the degree to which energetics can influence the final observed cluster size. A cluster will stop decaying when it runs out of excess energy, so that each energetically favorable cluster size will have only a modestly increased likelihood of being the decay stopping point. However, the time spent at each size depends exponentially on cluster stability and excess energy.[15] By giving the clusters a large initial excess of energy and then lowering the temperature rapidly a short time later, the present experiment develops a cluster population that depends exponentially on cluster energetics and kinetics. The similarity between this experimental technique and a theoretical one, molecular-dynamics simulation, is striking. Molecular dynamics simulates the time evolution of a cluster by numerically solving the equations of motion for a given temperature. That temperature is often reduced slowly in order to search for a local or global minimum in the potential-energy surface, a process termed simulated annealing. Adaptation of previous molecular-dynamics studies of sodium chloride[16,17] and fragmentation studies in other systems[15] to model the present quenched vaporization experiment should be feasible and extremely interesting.

In contrast to recent sputtering experiments that show that a 1-torr buffer gas can freeze in the structureless initial size distribution,[18] particles in the present experiment have initial temperatures and decay rates so high that they erase any memory of the random initial size distribution, before the 1–10-bar gas can stop the decays. Varying the buffer gas pressure merely alters the time scale for cooling, without affecting the final size distribution.

Most of the observed cluster ions began as hot, ionized particles and were stability tested with their charge in place. Unfortunately, there are three additional processes that can complicate the experimental spectra if they occur after the clusters have cooled and stopped decaying—electron capture, photoionization, and photofragmentation. The first two processes convert clusters that were stability tested as neutrals, into ions, so that seemingly stable cluster ions are actually abundant neutral clusters that have acquired a charge. The third process, photofragmentation, reheats the clusters and causes further decay. So long as the cross section for photon absorption does not vary significantly between nearby clusters or is uniformly small, it will only delay the cooling process. The ion spectra in Fig. 2 contain evidence, to be discussed below, that both electron capture and photoionization occur, and that photofragmentation of cooled cluster ions is not a significant problem. Furthermore, for photoionization of cold neutral clusters to be possible, clusters must form, cool, and photoemit electrons during the 15-ns duration of the laser pulse. To understand the basis for these observations, we must analyze the spectra of cluster ions.

As seen in previous studies,[11,19] the most abundant cluster ions are those that form perfect cuboids: $n=13$, 22, 37, 62, and 87. For example, $n=13$ has 27 atoms and forms a $3\times3\times3$ atom cube. There is an additional fine structure present in the current measurements, particularly in the positive ions, which we attribute to surface steps on incomplete cuboid lattices. For example, $n=37$ is a $3\times5\times5$ atom cuboid. If we remove one row of three NaCl molecules we arrive at the abundant $n=34$, a second row leaves us at $n=31$, and so on, all the way to $n=13$. Every third cluster size in this range is unusually abundant. Above $n=37$, the faces with five atoms are also important and a periodicity of 5 begins to emerge. By $n=52$, five-molecule steps are dominant and continue so until $n=122$ $(5\times7\times7)$ where seven-molecule steps begin to appear (not shown). The stability of such surface steps has been predicted theoretically,[10,20] and the stability of a first molecular row on a cuboid base was observed experimentally.[10]

Unfortunately, some of the observed cluster ions formed as neutrals and subsequently became negative through electron attachment or positive via photoemission. The added charge neutralizes one atom of the cluster and that atom evaporates easily, being bound by only 40 meV for chlorine and 400 meV for sodium.[20,21,22] Thus some clusters which started as $[\mathrm{NaCl(NaCl)}_n]$ are observed as $[\mathrm{Na(NaCl)}_n]^+$ or $[\mathrm{Cl(NaCl)}_n]^-$. The signature of this process is clear: because cuboid neutral atom clusters are also unusually abundant, most of the charged neutral clusters have one fewer atom than a perfect cuboid.[21] For example, ion abundance peaks at $n=17$, 20, 27, 29, and 49 are due to cuboid neutral clusters, which became charged and then lost an atom. Further evidence for this charge-changing process is found by cooling with argon gas at pressures exceeding 10 bars. In this regime, we observe many $[\mathrm{NaCl(NaCl)}_n]^-$ cluster ions, because cooling occurs quickly enough to retain the sodium atom. These peaks merge smoothly with the $[\mathrm{Cl(NaCl)}_n]^-$ peaks as the argon pressure is reduced.

This charging process produces fewer positive than negative cluster ions. As a result, the positive spectrum is relatively easy to interpret. Virtually all peaks in the positive spectrum can be explained by surface steps on cuboid base lattices or by charged daughters of cuboid neutral clusters. However, there remain three anomalous and unexplained peaks: $n=60$, 70, and 85.

Finally, the existence of positive cluster ions that originated as cool cuboid neutral clusters and lost electrons to laser photoemission indicate that the cluster-formation process (vaporization and cooling) is essentially complete within the 15-ns laser pulse width. Cooling must therefore occur at a rate in excess of 10^{11} K/s. Fifteen nanoseconds is probably too short for clusters of three hundred or more atoms to grow, even in a very high-temperature and high-pressure environment. Furthermore, if either growth or photofragmentation were important, we would not observe abundant peaks for positive clusters produced by electron photoemission of cuboid neutral clusters. As soon as those neutral cuboids lose an electron and then a chlorine atom, they are not cuboids at all. Any growth or photofragmentation will quickly change their sizes. With a charge and a missing atom, these cuboid -1 clusters are extremely sensitive to growth or photofragmentation. If they are not substantially damaged, there can be no significant growth or photofragmentation present in this experiment.

In summary, vaporization of a solid into an expanding jet of inert gas produces populations of cluster ions that reflect the relative high-temperature stabilities of those ions. The clusters form by unicluster decay cascades and are not significantly affected by growth or photofragmentation. The formation and cooling process occurs in as little as 15 ns and should be directly accessible to modeling by molecular-dynamics simulations.

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