

Shattering of Clusters Upon Surface Impact: An Experimental and Theoretical Study

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The shattering transition expected upon ultrafast heating has been observed in size selected $(\text{NH}_3)_{n-1}\text{NH}_4^+$ clusters, $n = 4$ to 40, upon impact at supersonic velocities on a graphite surface. As a function of the impact velocity, the transition is between the recoil of the intact parent cluster and the appearance of small, $n = 1, 2, \dots$ charged fragments. As the cluster size increases, the transition becomes a sharper function of the impact velocity. The experimental fragmentation pattern is well accounted for by a distribution of maximum entropy subject to conservation of energy, atoms, and charge.

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It is an unwelcome but common experience that a china plate that drops to the floor shatters into a large number of small pieces. The same is true for other high velocity impact phenomena [1]. In this Letter we report the observation of this transition on a molecular scale under controlled conditions. Specifically, both the velocity of impact and the molecular size of the projectile can be varied. The generalization, supported by the theory [2], is that a superheated cluster does not evaporate, but shatters. By evaporation we mean the sequential loss of small (one, two, etc.) monomeric subunits. Shattering is the limiting behavior when the cluster breaks into many small fragments. The technique of cluster impact [3–5] enables us to vary the amount of energy supplied, on a sub-ps time scale, to the cluster. It is thereby possible to demonstrate the shattering transition.

At sonic velocities of impact, the initially directed energy of the cluster, which upon impact is converted to random motion, is low. The rate of heating of the cluster is therefore moderate, and the cluster has the time to cool down by evaporation [6]. Experimentally, this is the regime where it is the intact parent cluster, or a cluster which lost one or two subunits, which rebounds from the surface. At higher velocities, energy which is sufficient to fully dissociate the cluster is provided on a time scale comparable to that of molecular motion. The cluster then shatters, and the experimental signature proposed herein is the disappearance of the charged parent cluster the simultaneous observation of small ionic fragments and hardly any ions of intermediate size. Moreover, as suggested by the theory, the onset of shattering is already a steep function of the collision velocity for fairly small (say, $n = 10$) parent clusters. The present experiment, which detects only charged clusters, cannot, however, establish that the neutral fragments, which must accompany the disappearance of the parent ion, are small.

The theoretical expectation [2] is that the transition to shattering has the characteristics of a phase transition. This is not unreasonable because of two aspects. First,

the simultaneous breaking of the cluster into its constituents is clearly a collective event. Then, the transition has to have a size dependence which will make it sharper for larger clusters. The reason is that it is due to an interplay between energetic and entropic effects as follows: Configurational entropy favors the larger clusters because the number of possible isomers increases exponentially with the size of the cluster. Other things being equal, the cluster is therefore expected to rebound intact from the surface. As the energy content per cluster unit E/n increases, the entropy associated with the volume in mechanical phase space favors fragmentation. Hence one has opposing trends, both of exponential order. When the relative importance of the two effects changes, the swing from one mode of behavior to the other is abrupt.

The detailed experimental results are reported for protonated clusters of ammonia (NH_3), and similar results were obtained for protonated clusters of methanol (CH_3OH). These clusters are produced by electron impact ionization of a supersonic jet generated by a pulsed valve (0.5 mm conical nozzle, the expansion gas, 70% Ne and 30% He, contained 10% NH_3 at a total pressure of 1 bar). The pulsed electron beam (≈ 100 eV, from a heated tungsten filament) crossed the molecular beam 2 mm downstream from the nozzle exit. The ammonia clusters were softly ionized by collisions with excited carrier gas atoms. An intense cluster beam (up to 10^7 ions/pulse), containing clusters of up to 100 ammonia molecules with one added proton, were produced. A coaxial, pulsed, time of flight mass spectrometer accelerated the ions to an energy of 1000 eV with an energy spread of ≈ 10 eV. The accelerated clusters were reflected, at 45° , by a planar, pulsed, ion mirror that acted also as a mass gate. The mass selected ion clusters collided with a highly oriented pyrolytic graphite surface at normal incidence. The base pressure in the target chamber was better than a μPa . The collision energy (in the range 20–300 eV) is defined by maintaining the target surface at a controlled high voltage. Ions reflected from the surface were pulse deflected and

collected by a second time of flight mass spectrometer. The total ion count rate was low (3–30 ions/shot). Pulse sequences for the experiment were generated by a home-built computer controlled timer card with a resolution of 100 nsec. At each collision energy, the mass spectra reported are averages over several hundred pulses.

The experimental observation is that at low velocity of impact it is the intact parent cluster ion that is reflected from the surface. No other charged species are detected, and the intensity of the parent ions is essentially independent of the energy of impact. As the velocity is increased, there is a sharp decline in the number of rebounding parent cluster ions which is accompanied by a corresponding steep increase in the number of small charged clusters. Ionic clusters of intermediate size are observed only in the narrow velocity range, over which the transition from parent to small cluster ions takes place. Even in that range, their number is a very small fraction of the total number of reflected ions.

Figure 1 shows the count rate of parent, $(\text{NH}_3)_{n-1}\text{NH}_4^+$ clusters that rebound from the surface as a function of impact velocity, for $n = 4, 10, 20,$ and 30 . It is evident that by $n = 10$, the width of the shattering transition is narrower than the spread ($\propto 1/n$) in the velocity of impact which is due to the uncertainty ($\approx 1\%$) in the initial energy of the ions. The decrease in the intensity of the reflected parent clusters is accompanied by the observation, Fig. 2 below, of an increase in the count rates of very small ionic fragments. Also shown in Fig. 1 is the comparison with the theory [7].

The experimental and theoretical complete fragmentation pattern vs velocity of impact are shown in Fig. 2 for $n = 10$. The results for the other values of n are very similar. The theoretical results, as shown in Figs. 1 and 2, are a somewhat sharper function of the energy than the experimental pattern. Convoluting the theoretical results with a window function representing the spread in the ini-

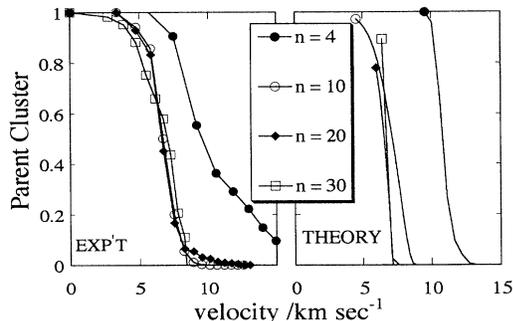


FIG. 1. The experimental and theoretical results for the fraction of parent ions reflected from the surface vs the velocity of impact. The experimental spread in velocity is larger for smaller clusters. The theoretical results have not been convoluted with a window function representing the spread in energy and hence are sharper.

tial energy is sufficient to account for the somewhat larger spread of the experimental results.

The analytical expression for the number of clusters (ions or neutrals) of size p is [2]

$$X_{pm} = \sum_k g_{pkm} \exp(-\beta \epsilon_{pkm} - \gamma p - \mu m).$$

Here p is the number of ammonia molecules and m ($m = 0, 1$) the number of protons, and only the charged species ($m = 1$) are experimentally detected. The computed results shown in Figs. 1–3 are all for $m = 1$. β , γ , and μ are Lagrange multipliers whose values are determined by three conservation conditions: energy, number of ammonia molecules [8], and charge. Note that the total number $X = \sum_{pm} X_{pm}$ of clusters is not imposed as a constraint. k is the number of ammonia-ammonia bonds in the cluster. g_{pkm} is the number of different isomers of a cluster of p ammonia molecules and m protons with k bonds. It is computed, using the graph theoretic technique introduced by Uhlenbeck and Ford [9], in the theory of gas imperfection. For larger (say, $p > 5$) clusters, g_{pkm} is exponentially large in p and so, in the absence of conservation constraints, larger

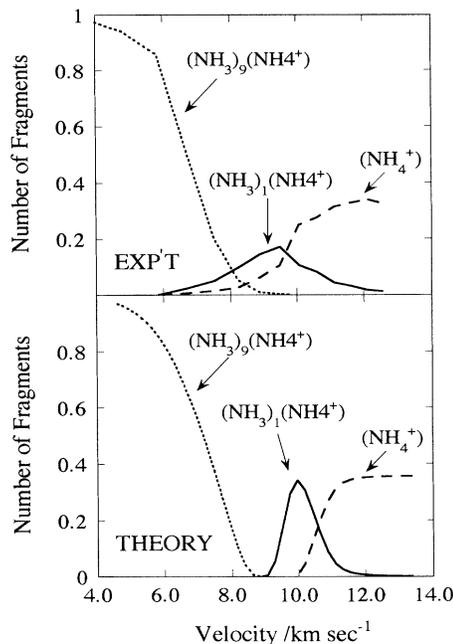


FIG. 2. The experimental and theoretical results for the fragmentation pattern, upon collision of $(\text{NH}_3)_9\text{NH}_4^+$, vs the velocity of impact. Other details are as in Fig. 1. Ionic clusters of intermediate size are observed only in the narrow velocity range, over which the transition from parent to small cluster ions takes place. Even in that range, their number is a very small fraction of the total number of reflected ions. The theoretical results shown in Fig. 3 suggest that the small contribution of evaporation occurs at velocities of impact just below the shattering transition.

clusters will be favored. The actual size distribution is very sensitive to the magnitude of γ which, from the equation, has the significance of the (Planck) chemical potential of ammonia. The signature of the shattering transition is the discontinuity in γ as a function of the energy of impact. The detailed fragmentation pattern depends on the energy, ε_{pkm} , of a cluster of a given size and composition [10].

The input to the computation of the Lagrange multipliers is as follows: the energy available after the impact, the number n of ammonia molecules in the parent cluster, and the charge (one) on the parent. The values of the parameters are determined by maximizing the entropy subject to these constraints [11]. The details are provided elsewhere [2]. Here we comment that, at the velocity range of interest, there is sufficient time for more than several hard-sphere-like collisions between the constituents of the cluster. As can be expected [12], this is sufficient to approach equilibrium for the interconstituent motion. Simulations verify that this is the case. Hence the use of a maximum entropy formulation is subject only to conservation laws.

Figure 3 shows different theoretically computed measures that characterize the shattering transition [13]. The top panel shows the increase in the total number, X , of fragments vs the collision energy. To show that it is a shattering transition rather than an "evaporation," the fig-

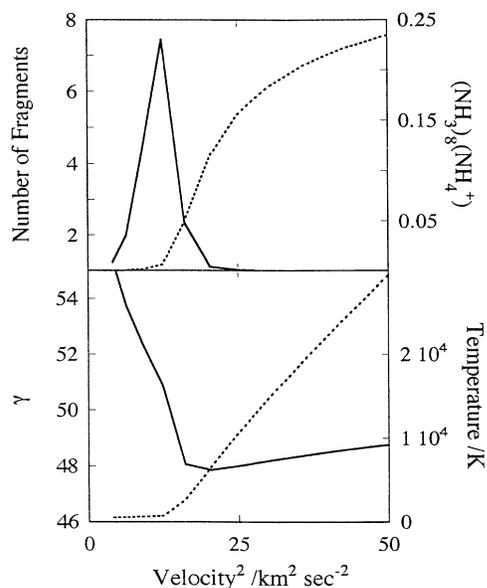


FIG. 3. Additional theoretical characterization of the shattering transition vs the impact velocity for $n = 10$. Top panel: the total number of fragments (10, if the cluster is fully dissociated into its elementary constituents) (dashed line, left ordinate) and the number of parent minus one fragments, $(\text{NH}_3)_8\text{NH}_4^+$ (solid line, right ordinate). Note the scale difference. Bottom panel: γ , the chemical potential of ammonia, solid line; and the temperature, dashed line.

ure also shows the (small) number of clusters that lost one ammonia molecule. It is evident that, as the energy of the cluster is increased, there is a regime where it cools by evaporation. But, as a function of energy, this evaporative regime is narrow. That is not to say that the evaporative regime is a narrow one on a temperature scale. Figure 3 also shows the temperature (i.e., β^{-1}) as a function of the available energy. In the regime of interest, small increments in the available energy cause large increases in the temperature.

The point about the technique of cluster impact is that it enables one to "heat" the cluster on a time scale, short compared to that needed for evaporation. In this way one can prepare "superheated" clusters with enough energy for breaking most or all intermolecular bonds so that the cluster shatters into its constituents. The behavior of the chemical potential γ is also shown in Fig. 3. The discontinuity at the shattering point (which is the point where X begins its rapid increase) is evident.

Experimental results suggesting that, upon ultrafast heating, molecular clusters will shatter have been presented. Similar experimental results have been obtained for other ionic molecular clusters. Further experiments are needed to monitor the size distribution of the neutral fragments. Molecular dynamics simulations also exhibit the shattering transition. The analytical theory has, however, the advantage that it can show the transition to be due to the interplay of two contributions to the entropy: the configurational term, favoring large clusters, and the translational entropy, favoring many fragments. Both terms are exponentially large. The available energy determines which effect dominates, and because of the exponential scaling, the transition between the two modes is a rather sudden one even for small clusters.

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energy after the impact at the surface. For the collision of a single fast atom with the surface, the simulations [T. Raz *et al.*, J. Chem. Phys. **101**, 8606 (1994)] show that the fractional energy loss is constant, and this can be understood and quantitatively accounted for in terms of a binary collision model between the atom and an effective oscillator representing the surface. For a cluster, the energy loss is expected to be size dependent because only those atoms (or molecules) which are at the front of the cluster actually reach the surface and are reflected from it. The rest of the cluster collides with the rebounding front. The bigger the cluster, the lower the fraction of atoms which are out front and the smaller is the fractional energy loss to the surface. The required scaling is that for $n = 10$; the available energy after impact is 45% of the initial kinetic energy, and the available energy scales with $n^{2/3}$. On the other hand, the bigger the cluster, the more energy needed to fragment it. The net outcome is that the experimental velocity range over which the shattering occurs is not very size dependent. The theoretical results, when plotted vs the available energy after impact, are that bigger clusters shatter at higher energies..

- [8] The theory assumes no fragmentation of ammonia. For impacts above 10 km/s, this is no longer completely realistic.
- [9] G.E. Uhlenbeck and G.W. Ford, in *Studies in Statistical Mechanics*, edited by J. De Boer and G.E. Uhlenbeck (Interscience, New York, 1962).
- [10] There is a considerable literature on the energetics of protonated ammonia clusters and the recent paper [A.W. Castleman, Jr. *et al.*, J. Chem. Soc. Faraday Trans. **86**, 2417 (1990)] provides a guide to it. Note that in principle, different isomers of given p and k can differ in their energy. See T.D. Märk and A.W. Castleman, Jr., *Adv. At. Mol. Phys.* **20**, 65 (1985).
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