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by

Hyun Jin Hwang and M. A. El-Sayed

University of California
Department of Chemistry and Biochemistry
Los Angeles, California 90024

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DYNAMICS OF EVAPORATION OF CsI MOLECULES FROM INDIVIDUAL $[Cs(CsI)_n]^+$ CLUSTERS

HYUN JIN HWANG[†] and M. A. EL-SAYED
Department of Chemistry and Biochemistry,
University of California
Los Angeles, California 90024, USA

Abstract

A brief review is first given of the different types of clusters and their synthesis. The results on the determination of the mechanisms of the evaporation of one and two CsI molecules from individual mass selected $[Cs(CsI)_n]^+$ clusters (made by sputtering techniques) are discussed in terms of their observed stabilities, their observed average kinetic energy released and its distribution during the evaporation process. It is found that the stability towards evaporation, rather than formation rates, is the origin of observing clusters with magic numbers. Furthermore, comparison with theoretical models showed that the evaporation process of CsI molecules from these clusters is statistical. Finally, it is shown that the evaporation of two CsI molecules involves the fission of a dimer rather than a sequential evaporation of two CsI monomers.

†Department of Chemistry, University of California, Berkeley, California 94720, USA

I. Introduction; Cluster Types, Synthesis and Detection:

It is usually accepted that the study of clusters gives us a systematic understanding of the physical and chemical properties of matter as a function of its size. It is hoped that questions such as how many atoms one needs to have a metal or how many molecules are required to have the properties of a molecular liquid or solid can be answered. Of course, the answer will depend on the length or time scale of the experiment used to measure such a property as a function of size.

Clusters are classified according to the type of bonding believed to hold the cluster together or the type of entity that leads to cluster formation. Van der Waals clusters[1] are formed between rare gas atoms or stable neutral molecules or between rare gas atoms and stable molecules. Small van der Waals clusters (in particular dimers) have received a great amount of attention in the field of molecular dynamics,[2] as they represent an interaction between these entities during "half" collisions. The flow of energy between intramolecular vibrations and the motion along the van der Waals dissociation coordinate has been, and is, of great theoretical and experimental interest. They have recently been used to define zero time in rapid biomolecular photochemical reactions[3] between the cluster components using femtosecond spectroscopy. Van der Waals clusters have been studied by mass spectrometry, infrared, Raman and optical spectroscopy. Clusters in which hydrogen bond might play a role in the binding, e.g., those involving organic acids, or alcohols, NH_3, H_2O, are termed H-bonded clusters.[4]

Clusters made of metal atoms are termed metallic clusters. Here the name is based on the fact that atoms resulting from evaporated metals form the cluster. Certainly, the bonding in small metallic clusters is not exactly of the metallic type found in bulk metals. For alkali and noble metals, the "shell" or Jellium model is found[5] to explain the observed clusters with magic numbers (those with extra stability compared to the ones following them in size). Recent studies[6] in mercury clusters (Hg_n), suggest that for $n \leq 13$ van der Waals forces are involved, at $30 \leq n < 70$ covalent bonds are formed and for $n \geq 100$ metallic bonding takes over. A large number of studies on physical and chemical reactivity of transition metal clusters has been carried out.[7,8] Detailed structural calculations for large transition metal clusters have not yet been attempted. Due to the large number of unpaired electrons, these clusters possess a large number of electronic states that are sufficiently close in energy to allow too many structures (isomers) of comparable energy.

Nonmetallic clusters,[9] those made of nonmetals, e.g., carbon, silicon, are covalently bonded. Active work was carried out by Smalley and Kroto[10] and their groups to study C_{60}, a cluster which is expected to have a structure with special stability and is thus observed with high intensity in the mass spectrum of carbon ion clusters. A solid which is mostly C_{60} and some C_{70} has recently been isolated[11] in the laboratory by condensing the vapor formed from the sublimation of carbon rods in helium atmosphere by passing high electric currents through it. Studies of clusters made from semiconducting material,[9] e.g., CaAs have also been carried out.

Clusters made from ionic solids, e.g., alkali halide salts, have also been studied,[12] both experimentally and theoretically. Clusters with magic numbers are

found to fit a lattice with sides having integer number of ions. Clusters of equal number of cations and anions (i.e., neutral clusters) or with excess cations (e.g., $[M(MX)_n]^+$), with excess anions $[X(MX)_n]^{-1}$ or with excess electrons[13] $[M_nX_{n-1}].e$ have all been observed and studied.

Over the years, a number of techniques have been used to synthesize clusters. In solution, metallic-containing clusters are synthesized by use of colloidal and electrochemical techniques.[14] Metal clusters are formed from their polynuclear complexes by different ligand stripping methods.[15] Metal ion clusters have also been made in liquid metal ion sources[16] by applying a high electric field to a tungsten tip dipped in the liquid metal of which cluster ions are to be made.

Clusters are made by aggregation on a support, e.g. in the rare gas matrix isolation method[17] or on different types of support, e.g., molecular sieve host and functionalized polymers.[18] Matrix isolation methods are shown to be especially useful in the study of the structure of very small clusters using spectroscopic methods.

A number of methods have been used to synthesize gaseous clusters, by continuous effusive expansion of oven-heated vapors of elements in the pure phase or in rare gases[19] (oven gas aggregation technique[20]). Pulsed supersonic cooling expansion techniques in rare gases (He or Ar) have been most useful for the making of many of the weak van der Waals or H-bonding clusters. The pulsed mode allows the use of high backing pressures of the rare gas used and thus leads to much lower temperatures for the clusters formed. The mole fraction of the gas or vapor of which the clusters are to be made is adjusted so as to allow for collisions between them to take place as they cool off during the expansion process. Dimers, trimers and higher clusters as well as clusters with the rare gas atoms used are formed under appropriate expansion conditions. For nonvolatile material, pulsed laser ablation, with[21] or without[22] supersonic expansion of the vapor in rare gases, is used to produce clusters and their positive and negative ions. The use of supersonic expansion in conjunction with pulsed laser ablation has greatly increased the size and types of the clusters made.

Another technique used for making gaseous clusters from nonvolatile material is by use of the sputtering technique in which high energy particles, e.g., electrons, rare gas cations or atoms, are used for heating the material. Next to the oven technique, making clusters from RF spark sources[23] followed shortly in time the use of ovens. Rare gas ion sputtering[24] and now fast atom bombardment (FAB)[24] using netural xenon are very useful in studies of alkali halides and high boiling metals.

The most common ways of determining the cluster distribution and its changes upon reaction are quadrupole[25] and time-of-flight mass spectrometers.[25] If a pulsed laser is used for ionization, time-of-flight is the spectrometer of choice since the whole mass spectrum is recorded for each laser shot. This eliminates the laser pulse-to-pulse intensity fluctuations. Cluster reactivity and its size dependence is best studied by use of ion-cyclotron resonance mass spectrometry.[26]

In this article we make a detailed study of the evaporation dynamics of one and two CsI molecules from mass selected $[Cs(CsI)_n]^+$ ionic cluster ions. From measurement of evaporation probability, kinetic energy released and its distribution

upon evaporation as a function of cluster size, the following conclusions are reached: 1) the rate of evaporation from the clusters, rather than the rate of their initial formation from sputtering techniques, is the origin of the appearance of clusters with magic numbers in the mass spectrum, 2) the evaporation process is statistical, and 3) the loss of two CsI molecules is found to result from a fission of a cesium iodide dimer rather than a sequential loss of two CsI molecules. An account of this observation is given.

II. DYNAMICS OF EVAPORATION OF CsI MOLECULES FROM $[Cs(CsI)_n]^+$ CLUSTERS:[27-29]

Alkali halide cluster ions of the form $[M(MX)_n]^+$ have been extensively studied both theoretically[12,30] and experimentally.[31] The ease of their formation by fast atom or ion bombardment[24] (by sputtering methods) have made them attractive to study experimentally. The simple polarizable ionic bonding model is found to yield good values for their formation energies.[12,30]

A strong size dependence was observed for the cluster yield observed in the mass spectrum of the clusters made from sputtering methods.[12,31] For example, for clusters of the composition $[M(MX)_n]^+$, mass peaks at n = 6, 9, 13, 22, 31, 37 ... were found to have unusually high intensities compared to those following them in mass. In earlier studies,[31,32] there was an attempt to attribute the high yield to larger rates of formation of these clusters during the sputtering process. However, Ens et al.[33] showed that the mass spectrum obtained shortly after the cluster formation (as opposed to the much longer time scale of observation in the conventional method using a sector-field mass spectrometer) has no magic numbers, i.e., the mass peak intensity is found to decrease exponentially with size.

In our studies, we have moved away from a study of the total mass spectrum. We examine the evaporation pattern of size-selected $[Cs(CsI)n]^+$ after a flight of a fixed distance. The evaporation probability during this time is determined as a function of the cluster size. Furthermore, by using a high resolution sector-field mass spectrometer, the kinetic energy released during the evaporation process as well as its distribution are determined for the evaporation of one or two CsI molecules. A number of questions we have attempted to answer in our studies are: a) Can variation in the evaporation probability with size account for the observed clusters with magic numbers? b) Is the evaporation process statistical and independent of size? c) Does the loss of two CsI molecules occur sequentially or as a result of a dimer fission?

A. Experimental:[27-29]

We have used a VG analytical ZAB-SE mass spectrometer fitted with a fast atom bombardment gun (model FAB11B) in the single focus mode. Cluster ions are produced with 7 keV Xe atom bombardment of CsI target prepared by evaporating aqueous salt solution on Ni foil. Positively charged cluster ions are accelerated to 8.1 keV through a two stage acceleration plate and analyzed by a 66 cm radius 35° magnetic sector. The observed mass spectrum showed sharp mass peaks

corresponding to the parent cluster ions $Cs(CsI)^{n+}$, and diffuse mass peaks corresponding to the daughter cluster ions formed mainly by evaporation of one or two CsI molecules in the field free drift region (between the acceleration region and the magnetic sector). Evaporation pathways of the (size-selected) parent clusters $[Cs(CsI)^n]^+$ with $1 \le n \le 17$ were determined from the observed nominal mass values m_* of the daughter cluster ions $[Cs(CsI)^m]^+$ with $m = n-1$ or $n-2$, by using the relation $m^* = m_2^2/m_1$ where m_1 and m_2 are the actual mass values of the parent and daughter cluster ions. To measure the kinetic energy release distribution as well as the evaporation probability for each evaporation pathway, spectra of the daughter and corresponding parent ions were taken by scanning the acceleration voltage V^a after tuning the magnetic sector field to the mass value of each ion at the acceleration voltage of 8.1 kV. During the experiments, the pressure is kept at $\sim 2 \times 10^{-6}$ Torr in the acceleration region and at $\sim 5 \times 10^{-8}$ Torr in the analyzer or field-free region. Thus no collisions occur during the evaporation process. Under our experimental conditions, one calculates that the cluster with $n = 13$ spends 57.1 μs in its flight through the field-free region.

B. Clusters with Magic Numbers: Variation in Evaporation Probability:[27]

The mass peaks corresponding[31] to n = 13, 22, 37, 52, 62, are found to be followed by weaker mass peaks, suggesting special stability for clusters having these values of n, the magic numbers. Interestingly enough the numbers of atoms in these magic number clusters agree with "cube-like" structures with edges of k x ℓ x m, where k, ℓ, and m are integers. This suggests a rectangular or cubic ionic lattice that maximizes the electrostatic interaction energy per atom (ion) for the clusters with magic numbers. Of the clusters with magic numbers, those having cubic lattices with $k = \ell = m$ are found to have more intense mass peaks [e.g., those for n = 13 (3x3x3) and 62 (5x5x5)]. All these observations are in agreement with the polarizable-ion model calculations.[12]

The question that arises is whether this unusual stability manifests itself in an increased rate of formation of these clusters during the sputtering process, or if the probability of formation decreases smoothly with the cluster size, thus allowing the variation in the evaporation probability to be the origin of clusters with magic numbers. Indeed Ens et al.[33] have demonstrated that, initially, the cluster yield decreased smoothly with size. Below we show that the variation in the probability of evaporating one or two CsI molecules can lead to mass intensity distributions showing the magic number characteristics.

Figure 1 shows two plots. In one (the circles), the size dependence of the total decomposition probability is given. In this plot, the ratio of the sum of the mass peak intensities of all the daughter ions formed from evaporation from a certain cluster to the sum of the mass peak intensities of all the daughter ions and the remaining parent cluster ion is given as a function of the cluster size. This is taken as a measure of the size dependence of the total evaporation probability. In the other plot (the triangles), the size dependence of the total cluster yield (i.e., the relative intensity of the mass peaks of the different parent clusters in the mass

spectrum) is given. It is significant to observe the "anticorrelation" between the two plots. Clusters that have high yield in the mass spectrum (e.g., the ones with magic numbers 6,9,13) also show low evaporation probabilities. This strongly suggests that clusters that are stable towards evaporation indeed show relatively high mass peak intensities.

Figure 2 shows the size dependence of the formation probability of the daughter cluster ions $[Cs(CsI)_m]^+$ by the loss of either one (circles) or two (given by x) CsI molecules from a parent ion cluster in which $n=m+1$ and $m+2$ respectively. Again, the relative mass peak intensity of a daughter ion $[Cs(CsI)_m]^+$ to the sum of the mass peak intensities of a parent ion and all the daughter ions is taken as a measure of the formation probability of the daughter ion cluster. This figure again shows that whenever m is a magic number (e.g. 6,9,13...) the probability of formation of this daughter ion by evaporation is relatively high.

Both of the above two types of results strongly support the proposal that the relatively high mass peak intensities of clusters with magic numbers result from their low evaporation probabilities as well as their high formation probabilities from larger clusters by evaporating one or more CsI molecules.

C. Is the Evaporation Process Statistical?[29]

Does the evaporation of one or two CsI molecules occur statistically or not? Does it occur from an energy equilibrated cluster? In our studies on evaporation probability, we have observed[27] a good anticorrelation between the calculated heat of evaporation and the evaporation probability. This suggested statistical evaporation processes with no reverse activation energies. This conclusion is not surprising as the condensation process (i.e., the reverse reaction) represents an ion-molecule reaction, known to have zero activation energy in general.

Klotz, in a number of important papers,[34] discussed the evaporation process from clusters. The results of his evaporative ensemble model[34] (EEM) for statistical evaporation can be used to obtain[29] the following relation:

$$e_t/\Delta = 3/(2\gamma_k) - 3k_B/[4c(2n+1)] \qquad (1)$$

where e_t is the average kinetic energy release; Δ is the heat of evaporation; k_B is the Boltzmann constant; $\gamma_k = (\Delta/k_BT)_k$ is Gspan parameter for a given microcanonical rate constant k (can be taken[29] as 22 for $k \sim 10^5 sec^{-1}$, the rate constant estimated in the first field-free region in our experiment); and c is the heat capacity for each monomer unit (i.e., for each atom or ion). T is the arithematic mean of the temperature of the cluster at the equilibrium geometry T and that at the transition state $T^\ddagger$.

Temperature is used in the EEM as an index to the internal energy E of a cluster that evaporates in a given time window (or with a specified microcanonical rate constant k), as defined by $E = CT$ and $T^\ddagger = T - \Delta/C$ where C is the heat capacity of the cluster [i.e., $C = c(2n + 1)$]. If the Gspan parameter, γ_k is constant and independent of the cluster size, e_t/Δ goes as $1/2n+1$ for statistical evaporation. γ_k is proportional to Δ/T which has the functional form of ΔS_{evap}[34]. Thus its constancy for the evaporation of molecules from clusters resembles somewhat

Trouton's Rule for the evaporation of liquids or the sublimation of solids.

The general form of equation (1) above can be derived in a simple manner as follows. The average kinetic energy released e_2 can be expressed as follows:

$$e_t = \frac{E - \Delta}{N}$$

(2)

where E, Δ and N are the internal energy of the cluster; its heat of evaporation and its internal degrees of freedom, respectively. For a $[Cs(CsI)_n]^+$ cluster, $E = cT(2n+1)$ (where C is a constant and T is the absolute temperature) and $N = 3(2n + 1) - 6 \sim 3(2n+1)$. Substituting for E and N in equation (2) gives:

$$e_t = \frac{cT}{3} - \frac{\Delta}{3(2n+1)}$$

(3)

$$or \quad \frac{e_t}{\Delta} = \frac{cT}{3\Delta} - \frac{1}{3(2n+1)}$$

(4)

if $\frac{T}{\Delta}$ is constant and size independent, then (4) becomes

$$\frac{e_t}{\Delta} = constant - \frac{1}{3} \frac{1}{(2n+1)}$$

(5)

which is of the same form as equation (1).

Figure 3 shows the high resolution mass peak spectra[29] of the parent cluster ion $[Cs(CsI)_6]^+$ (bottom), and two of its daughter ions formed by the evaporation of one and two CsI molecules in the field free region. For the following decomposition:
$$AB^+ \rightarrow A^+ + B$$
the average kinetic energy release can be calculated for Gaussian peak shape (as observed in our spectra) from the following equation:[35]

$$e_t = \frac{m_{A^+}}{16 m_B} V_a \left[\left(\frac{\Delta V_{A^+}}{V_a} \right)^2 - \left(\frac{\Delta V_{AB^+}}{V_a} \right)^2 \right]$$

(6)

where V_a is the acceleration voltage at the peak center (zero kinetic energy release) which is ≈ 8.1 keV in our experiment; m represents mass, ΔV_{A+} and ΔV_{AB+} are the

width at 0.223 of the maximum for each of the daughter and parent mass peaks measured in eV, respectively. The subtraction in brackets corrects for the instrumental broadening as well as the velocity and the angular distribution broadening due to the parent ion clusters prior to evaporation.

The heat of evaporation, Δ, can be calculated by use of the theoretical values of the formation energies of the clusters[12] and that of the CsI monomer or the dimer[30]. If one uses these calculated values of Δ and the values of e_t determined from the observed high resolution mass peaks and equation (6) for different clusters, one can calculate e_t/Δ values for the evaporation of a monomer or a dimer (since our results discussed below suggest that the loss of two CsI molecules results from a fission of a CsI dimer). The plot of the e_t/Δ values for different clusters is given in Figure 4 for the evaporation of a CsI monomer (circles) and the dimer (crosses). The theoretical curve obtained by using equation (1) for statistical evaporation predicts the solid curve for $\gamma_k = 22$ and $c = 3k_B$. The agreement is indeed very good and strongly suggests a statistical evaporation of either a monomer or the dimer from these ionic clusters. The points, outside the predicted lines except for n = 3 → 2, can be reproduced (see Figure 5) if we assume that the temperature T instead of γ_k is constant.[20] This seems to indicate that clusters of different sizes under evaporation in a given time window possess the same amount of energy per each monomer unit. Although the assumption of a constant T is in a slight deviation from the EEM, the much better agreement obtained with the experiments shown in Figure 5 supports the validity of this assumption and the similar dynamical characteristic "statistical" nature of the evaporating clusters of differrent sizes (except for n = 3 → 2). The large deviation observed for n = 3 (see Figure 5) might suggest either a nonstatistical evaporation or else an evaporation with large reverse activation energy (i.e., the actual evaporation process has an activation energy larger than the thermodynamic heat of evaporation). The latter is the most probable cause of the deviation and results from large energy of nuclear reorganization in the evaporation-condensation process involving this cluster.

D. THE EVAPORATION OF TWO CsI MOLECULES: SEQUENTIAL LOSS OF MONOMERS OR FISSION OF A DIMER?[28]

The evaporation from the different selected cluster ions usually gives daughter mass peaks resulting from the loss of one or two CsI molecules that are comparable in their mass peak intensities. If the evaporation was sequential, one would expect the evaporation of the second CsI molecule to be slower than that of the first one and thus during the time-of-flight less formation of "granddaughter" ions. This is because the evaporation of the first molecule is expected to cool off the resulting daughter ion cluster from which the evaporation of the second CsI molecule will take place. Thus, as long as the evaporation is statistical with no reverse activation energy, and in the absence of collisions during the flight time, one expects the mass peak intensity of the second daughter to be much weaker than that for the first (perhaps, except for the few cases when the evaporation of the second CsI molecule leads to a daughter ion with a magic number). Since this is not observed, one could

conclude that the evaporation of two CsI molecules occurs via a fission of a $(CsI)_2$ molecule. Below we present even more quantitative results that substantiate this conclusion.

a. From the Values of the Kinetic Energy Released in Evaporation:[28]

In the absence of collisions, it is expected that the evaporation of the first CsI molecule would cool off the first daughter ion formed. The evaporation of a second CsI molecule from this cold daughter is thus expected to release less kinetic energy than that released during the loss of the first CsI molecule from the parent ion, except perhaps in some cases when the daughter resulting from the second evaporation has a magic number.

We have determined[28] the average kinetic energy release when a mass selected $[Cs(CsI)_n]^+$ parent ion evaporates to give $[Cs(CsI)_{n-1}]^+$ and $[Cs(CsI)_{n-2}]^+$. Using equation (6), the average kinetic energy release for the evaporation of one CsI molecule is calculated by using quantities for AB^+, A^+, and B corresponding to $[Cs(CsI)_n]^+$, $[Cs(CsI)_{n-1}]^+$ and CsI, respectively. In order to calculate the average kinetic energy release for the evaporation of a second CsI from the daughter formed, we use in equation (2) the observed quantities for $[Cs(CsI)_{n-1}]^+$, $[Cs(CsI)_{n-2}]^+$ and CsI for AB^+, A^+ and B, respectively. However, if we want to calculate the average kinetic energy release in the evaporation of a dimer directly from the parent, we use in equation (2) the quantities for $[Cs(CsI)_n]^+$, $[Cs(CsI)_{n-2}]^+$ and $(CsI)_2$ for AB^+, B^+ and A, respectively. The results[28] of these three different calculations, i.e., the evaporation of the first CsI, and the evaporation of the two CsI assuming sequential evaporation and assuming the fission of a dimer, strongly indicates that the dimer fission is the most probable. The sequential evaporation mechanism gave average kinetic energy release for the evaporation of the CsI molecule that is greater than (or comparable to in a few cases) that for the first one and in one case gave a negative number for the value of the kinetic energy release of the second molecule evaporation. Fission evaporation gave values that are consistent with simple physical intuition. These results strongly support that the loss of two CsI molecules from a parent ion involves the fission of a dimer rather than the sequential evaporation of two CsI monomers.

b. From the Distribution of Kinetic Energy Released[28]

The distribution of the kinetic energy release in the statistical dissociation (evaporation) process is modulated by the long range coupling between the departing fragments. Thus the shape of the high resolution mass peak is expected to reflect the type of the long range interaction between, and thus the structures of, the fragments produced.

In sequential evaporation from an ionic species, the long range interaction is expected to be an ion-dipole coupling between the remaining ionic fragment and the CsI dipolar molecule. If this were the mechanism of evaporating two CsI molecules, one would expect the mass peak shapes of the "granddaughter" ion $[Cs(CsI)_{n-2}]^+$ to be similar to that of the daughter ion $[Cs(CsI)_{n-1}]^+$. In both cases, ion-dipole

interaction will be the dominant long range coupling. On the other hand, if dimer fission dominates the mechanism of evaporating two CsI molecules, the shape of the mass peak of the granddaughter ion, $[Cs(CsI)_{n-2}]^+$, will be very different from that of the daughter ion ($[Cs(CsI)_{n-1}]^+$). This is because ion-quadrupole coupling will be the long range interaction involved in the process:

$$[Cs(CsI)_n]^+ \rightarrow [Cs(CsI)_{n-2}]^+ + (CsI)_2$$
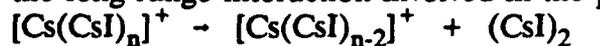
but ion-dipole coupling will be involved in

$$[Cs(CsI)_n]^+ \rightarrow [Cs(CsI)_{n-1}]^+ + CsI.$$
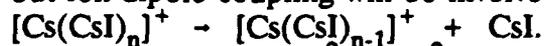
The ratio $W_{0.22}{}^2/W_{0.50}{}^2$, where $W_{0.22}$ and $W_{0.50}$ are the mass peak width at 0.22 and 0.50 of the maxima (after correcting for the parent ion mass peak width), is known as the shape factor and is a good indication of the shape of the high resolution mass peaks, and thus of the distribution of the kinetic energy released in the evaporation process. Table I lists[28] this value for $[Cs(CsI)_{n-1}]^+$ and $[Cs(CsI)_{n-2}]^+$ resulting from the evaporation of one and two CsI molecules from clusters of different sizes (different values of n). Independent of the cluster size, it is clear that all the mass peaks of the daughter ion resulting from the evaporation of one CsI molecule have similar shapes, with a shape factor of 2.30 ± 0.05. Similarly, all mass peaks of daughter ions resulting from the evaporation of two CsI molecules have similar shapes, with a shape factor of 2.16 ± 0.03, again independent of n. This result strongly confirms that the dissociating partner of the final daughter ion resulting from the loss of two CsI molecules ($[Cs(CsI)_{n-2}]^+$) does not interact with a CsI molecule (which is the case in the formation of the first daughter ion ($[Cs(CsI)_{n-1}]^+$). Thus it must involve the interaction with a dimer, which has a zero dipole moment. The values of the shape factor indeed suggest that the loss of two CsI molecules involves a much shorter range interaction than the loss of one CsI molecule, which is consistent with an ion-quadrupole and not an ion-dipole type interaction.

The question is why would the process of fission of a dimer dominate the mechanism of evaporating two CsI molecules? Sequential mechanisms have indeed been observed to dominate the evaporation from some Cu and Al metal cluster ion.[34,35] There are several reasons for this observation: 1) The loss of one CsI molecule reduces the temperature of the resulting daughter ion cluster sufficiently to reduce the rate of evaporating the second CsI molecule so that it is not observed in the time window remaining for it during its flight to the detector. 2) The CsI dimer is a stable species, which makes the heat of evaporation (and thus the evaporation activation energy) for the dimer much smaller than that for the sum of two sequential evaporations of two monomers. It is actually not different from the heat of evaporation of one monomer. This makes the evaporation of the dimer compete well with the evaporation of the monomer from the parent cluster ion. This is the reason for the observed comparable intensity of the mass peaks for $[Cs(CsI)_{n-1}]^+$ and $[Cs(CsI)_{n-2}]^+$ that results from evaporation of one and two CsI molecules from the parent ion cluster $[Cs(CsI)_n]^+$ (except for cases when clusters of magic numbers are produced).

Acknowledgment

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Table I. The Band Shapes (as measured by the ratio of $(Width_{0.22})^2/(Width_{0.5})^2$) of the Corrected Metastable Peaks of $[(Cs(CsI)_n]^+$ after Loss of One or Two CsI Molecules by Evaporation.

| n	monomer	dimer
2	2.25	-
3	2.26	2.14
4	2.31	-
5	2.40	2.17
6	2.30	2.16
7	2.30	2.19
8	2.28	2.19
9	2.29	2.18
10	2.24	2.11
11	2.31	2.16
12	2.32	2.21
13	2.26	2.16
average	2.30 ± 0.05	2.16 ± 0.03

Figure Captions

Figure 1:   Anticorrelation between the observed intensity of the different mass peaks in the mass spectrum of the sputtered $[Cs(CsI)_n]^+$ clusters (▲) and the evaporation probability of the mass selected clusters (•) The latter is determined by allowing mass selected cluster ions to evaporate during their flight to the detector and then calculate the relative mass peak intensity of all the daughter ions formed to the total intensity of these mass peaks and that of their remaining parent cluster. This anticorrelation suggests that magic numbers observed in the mass spectrum result from the stability of the corresponding clusters toward evaporation.

Figure 2:   Size dependence of the probability of formation of daughter ions from sputtered mass selected parent $[Cs(CsI)_n]^+$ clusters by evaporation of one (solid lines) and two (broken lines)CsI molecules. The fact that daughter ions with magic numbers (m = 6, 9, 13) have the highest formation probability suggests that clusters with magic numbers in the mass spectrum have relatively higher intensity because they don't evaporate to make others (as shown in Figure 1) and also because other clusters of higher mass evaporate to make them.

Figure 3:   Typical results of the high resolution mass peaks obtained from the evaporation of a mass selected parent cluster ion (e.g., $[Cs(CsI)_6]^+$) to give the first and second daughter ions ($[Cs(CsI)_5]^+$ and $[Cs(CsI)_4]^+$, respectively). From the width of these mass peaks at 0.22 of the maximum intensity, the average kinetic energy released upon the evaporation of one or two (by sequential or fission type processes) CsI molecules can be determined (see text). The band shape (see Table I) of $[Cs(CsI)_5]^+$ and $[Cs(CsI)_4]^+$, which reflects the kinetic energy distribution and thus the mechanism of evaporation of one and two CsI molecules, is different. This strongly suggests that the evaporation of two CsI ion molecules is not sequential and that the kinetic energy distribution of $[Cs(CsI)_5]^+$ is modulated by ion-dipole interaction while that of $[Cs(CsI)_4]^+$ is modulated by ion-quadrupole (due to the neutral dimer) interaction.

Figure 4:   Comparison of experimental data and predicted (given by solid curve and assuming statistical evaporation) ratio of the average kinetic energy release to the theoretical heat of evaporation for a CsI monomer (o) and dimer (x). The predicted curve is obtained by using Eq. (1) with γ_k = 22 and c = $3k_B$. The agreement suggests statistical evaporation. The points outside the predicted line can be explained (see text).

Figure 5:   Comparison of the measured (0) and the predicted (--) ϵ_t / Δ. The predicted curve is obtained by using Eq. (1) assuming T is constant (T = 790K) and c = $3k_B$.

Figure: Formation Probability, % versus Size of Fragment Cluster Ion, m.

$[Cs(CsI)_n]^+ \rightarrow [Cs(CsI)_m]^+ + CsI$ ——

$\rightarrow [Cs(CsI)_m]^+ + (CsI)_2$ ——

$[C_s(C_sI)_4]^+$

×200

$[C_s(C_sI)_5]^+$

ΔV_2

×200

$[C_s(C_sI)_6]^+$

ΔV_1

8040 8060 8080 8100 8120 8140 8160

V_a
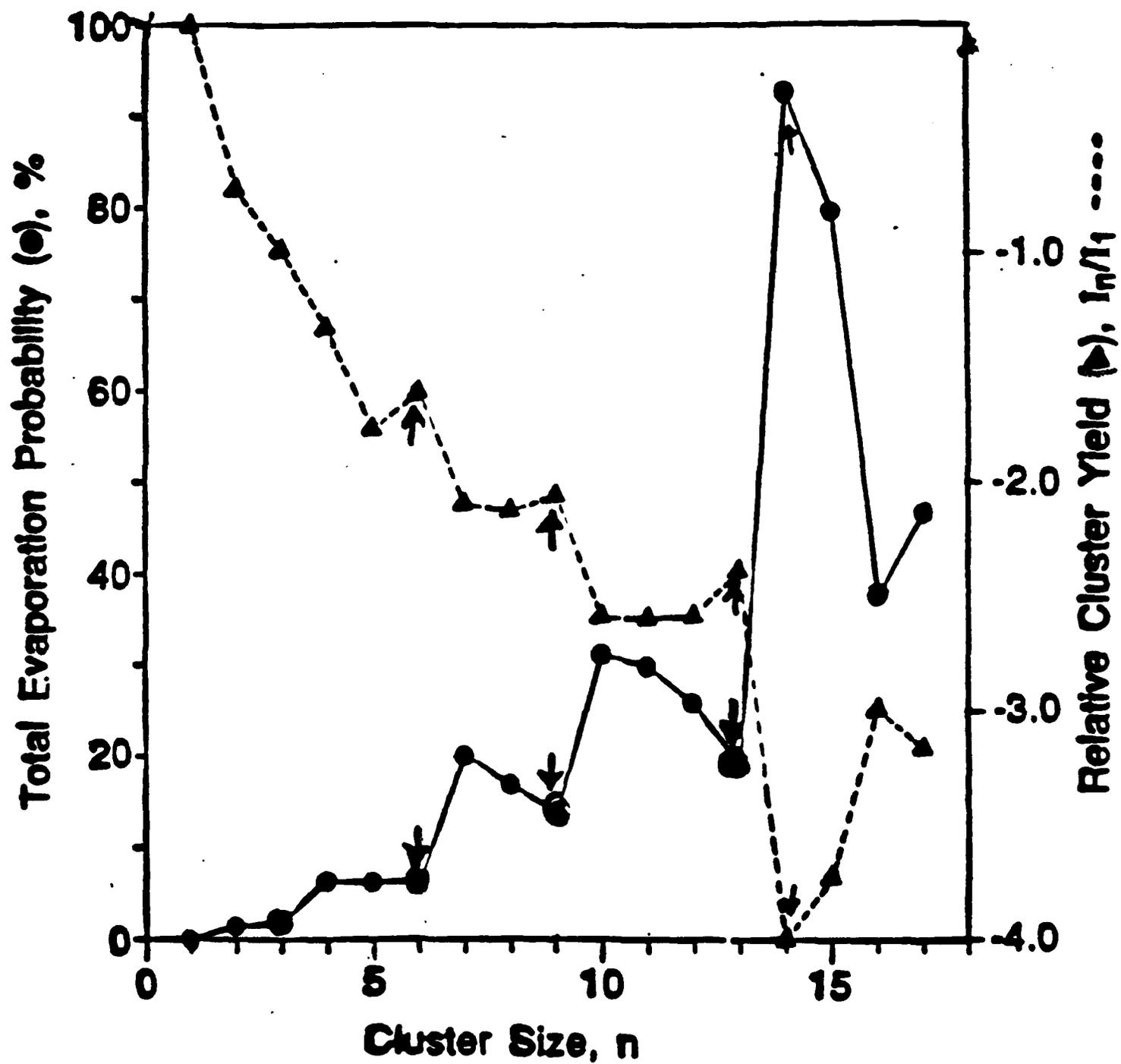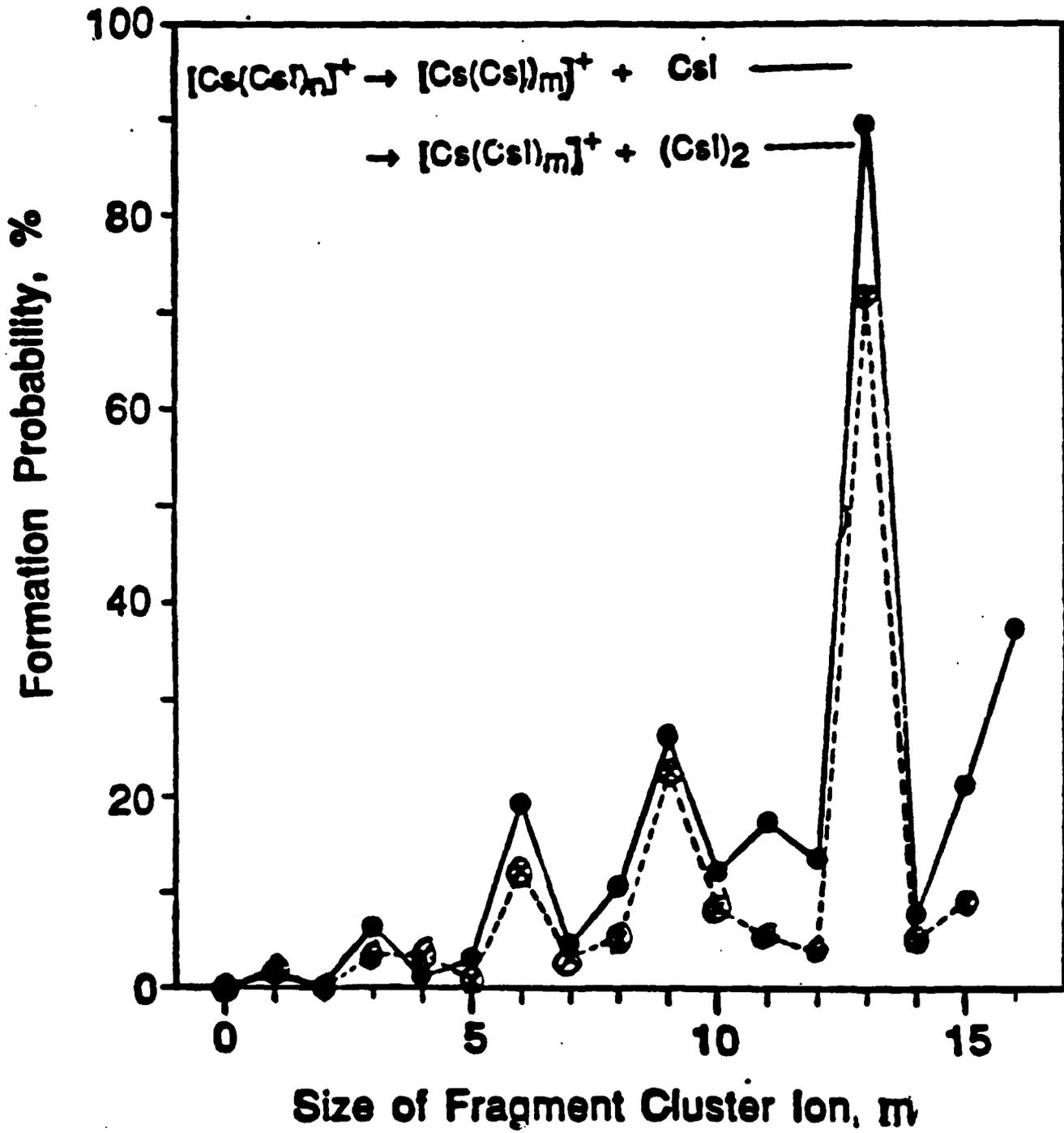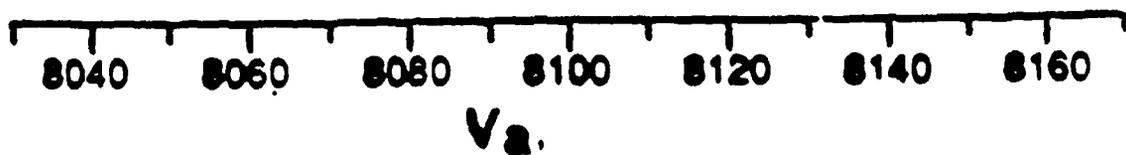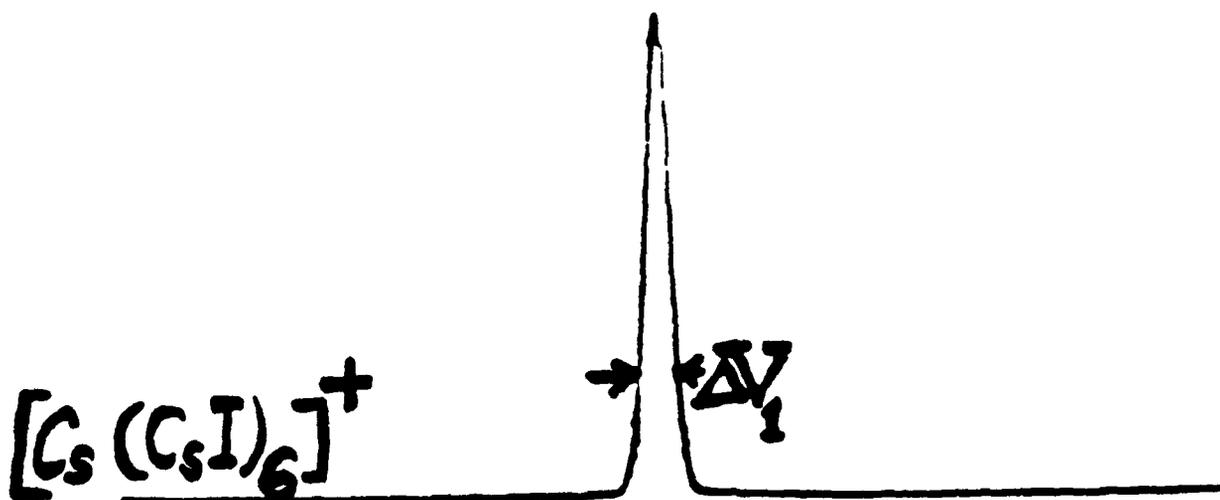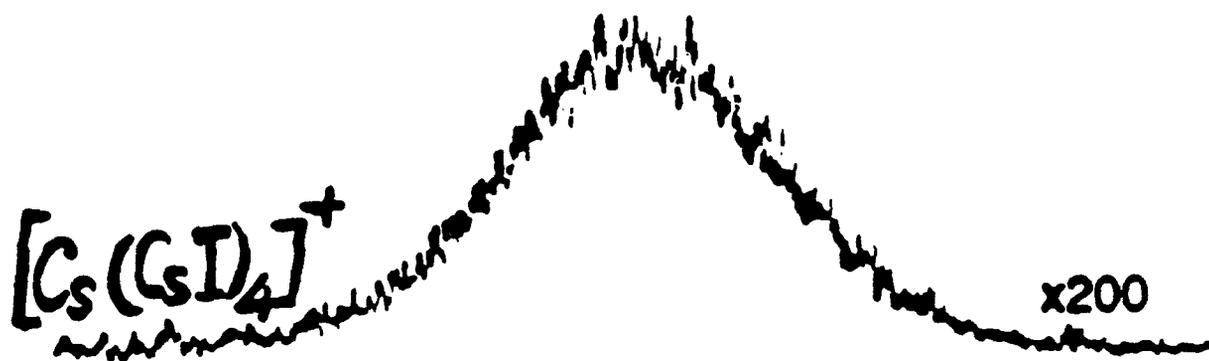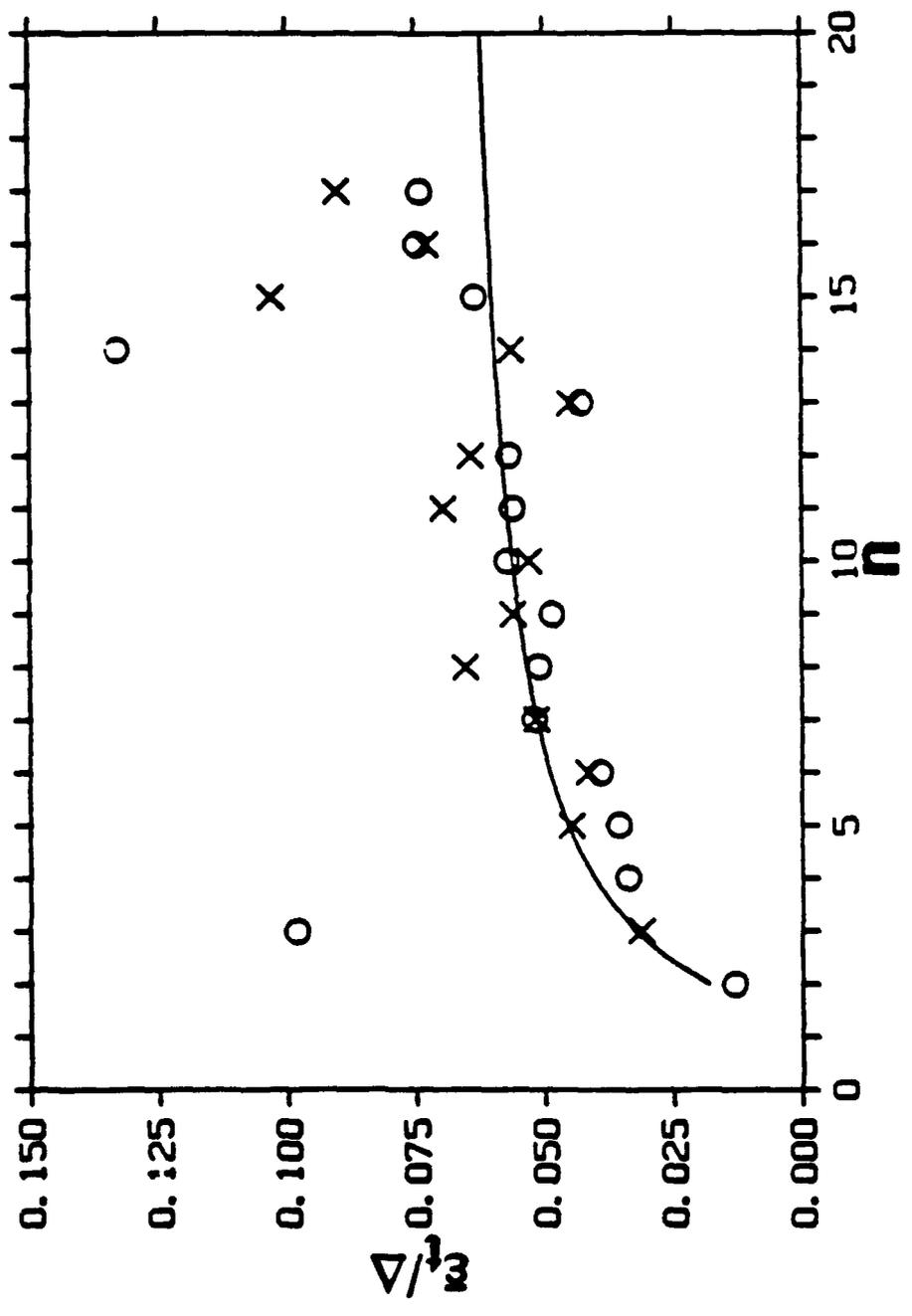
(a) Evaporation of CsI
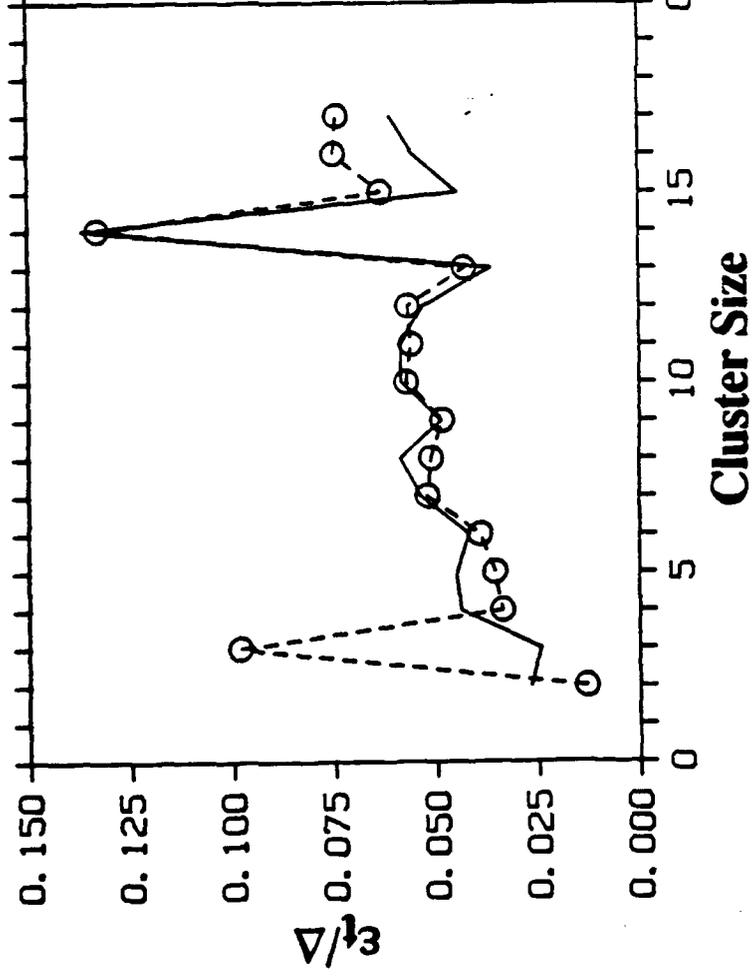
(b) Evaporation of (CsI)₂

Cluster Size

ϵ_t/Δ
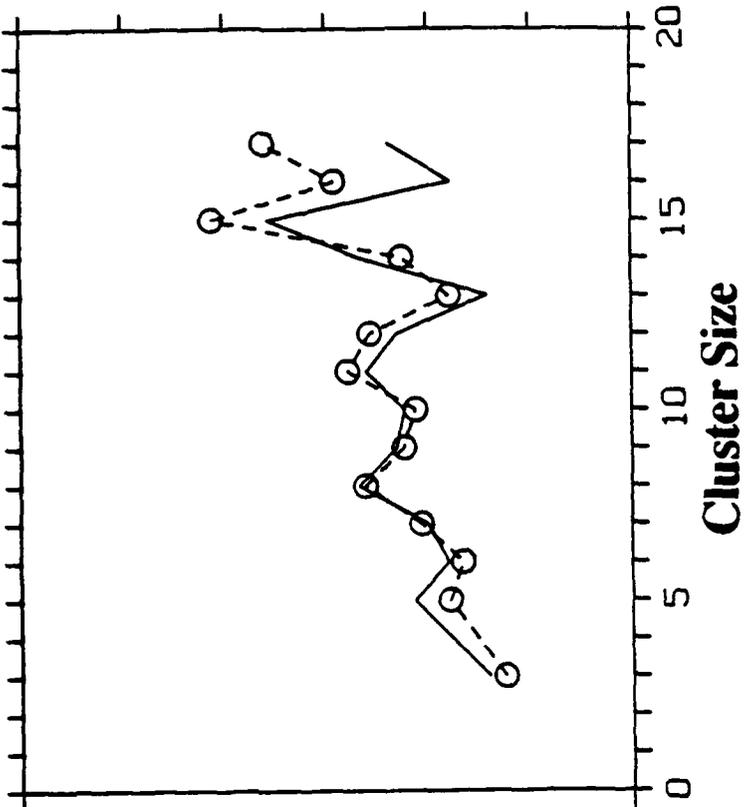
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