a mixture of ions having the phenol and the cyclohexadienone structures. If tautomerization occurs, it applies only to part of the ions and is complete within a few milliseconds.

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**Registry No.** Phenol, 108-95-2; phenetole, 103-73-1; bicyclo[2.2.2]-oct-2-ene-5,7-dione, 17660-74-1; 2-phenoxyethyl chloride, 622-86-6; phenol radical cation, 40932-22-7; 1,3-cyclohexadien-5-one radical cation, 34481-01-1.

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# Secondary Ion Mass Spectrometry of Metal Halides. 2. Evidence for Structure in Alkali Iodide Clusters

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**Abstract:** Recently, we reported extended-mass secondary ion mass spectrometric data of the alkali iodide (MI) cluster species $[M(MI)_n]^+$, which indicated that certain species in the series ($n$ = 1-22) have different intrinsic stabilities. The cluster ion intensity distribution exhibited anomalies at certain $n$ values rather than the expected monotonic decrease of ion intensity with increasing $n$. The structures of cluster ions at certain $n$ values, which have enhanced ion intensity, were postulated to have "cubic-like" atomic arrangements. This report presents ultrahigh mass spectral data ($>m/z$ 18 000 and $n$ = 1-70) of CsI clusters, induced by xenon ion bombardment and analyzed by a high-performance secondary ion mass spectrometer. These high-mass cluster ions are the largest mass-resolved ions ever produced and observed using a conventional mass analyzer, and they are more than 20 times more massive than those ions reported with other secondary ion mass spectrometers. These new data support our former hypothesis, which deals with the structures of certain alkali iodide cluster ions, and they confirm predictions based on it. The hypothesis and its relationship to previous work are discussed. The similarity of the body-centered cubic salt, CsI, ion intensity distribution with the ion intensity distributions of the simple cubic salts (NaI, KI, RbI) is also addressed. We conclude from these data that one type of stable configuration of the alkali iodide cluster ions is the "cubic-like" structure, which is reminiscent of the bulk crystal structure.

## Introduction

The mechanism of cluster ion formation and the secondary ion emission process of the alkali halides has been the subject of current investigation in this laboratory[1] utilizing a specially designed high-performance secondary ion mass spectrometer.[2] Collision-induced sputtering mechanisms of the metal halides have been studied by the measurement of energy distributions of sputtered neutral species,[3] the recent investigation of sputtered cluster ions by secondary ion mass spectrometry (SIMS),[1,4] bombardment with neutral beams,[5] and theoretical investigation[6,7] including molecular dynamics.[8] The commonality of these studies is the search for the mechanisms of secondary particle emission, ionization, and cluster formation. These phenomena have profound implications in fundamental and applied research in such disciplines as astrophysics, combustion chemistry, materials research, and radiation chemistry. This is a significant field of research because of the direct connection it provides between the transition of gas-phase species to the condensed phase.[9]

Various models for the secondary ion emission process and associated cluster ion formation have been proposed, based on experimental evidence[1,3,4,10] and trajectory computations using molecular dynamics.[8,11] A recent and comprehensive review of molecular SIMS discusses the various models and research trends in this area.[12] The formation of molecular and other polyatomic ions or cluster species by ion bombardment can be broadly viewed either as the direct emission of species originating at the surface or the recombination of sputtered species to form new structures. The direct emission model can include processes such as ejection through momentum transfer in collision cascades,[13] thermal spikes,[14] thermal evaporation,[14] and even agglomeration in the selvedge region[10] or any other unrealized process that can eject species from contiguous sites. On the other hand, the recombination model includes processes like agglomeration, nucleation, or association reactions which form species containing constituents from nonadjacent sites.

Recently, we have reported SIMS spectral evidence for the direct emission of certain high-mass alkali iodide (MI) cluster species during ion bombardment. Positive ions[1,2] of the type $[M(MI)_n]^+$, negative ions[2] $[I(MI)_n]^-$, and metastable ion decompositions of these species have been reported.[1,2] The high-performance instrumental capabilities of the SIMS instrument used in these studies[2] allowed the observation of noteworthy anomalies in the ion intensities at high-mass values in the positive ion SIMS spectra of CsI ($n$ = 19), RbI ($n$ = 16), KI ($n$ = 22), and NaI ($n$ = 22), where $n$ is the largest cluster ions species observed.

Similar anomalies were observed for all of the above alkali iodides. The characteristic features of the mass spectra previously reported[1] are the following: (1) the plot of the log ion intensity vs. log $n$ decreased linearly; (2) the $n$ = 13 species was equal to or more intense than the $n$ = 12 species; (3) the $n$ = 14 and 15 species were dramatically absent or of decreased intensity relative

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to the $n = 13$ and 16 species; additionally, in the spectra of NaI and KI, (4) the $n = 22$ species was equal to or more intense than the $n = 21$ species; and (5) ions were not observed beyond the $n = 22$ species. These striking features in the SIMS spectra led us to postulate that the increased stability of the $n = 13$ cluster ion, indicated by ion intensity enhancement relative to its neighbors ($n = 12, 14, 15$), could be attributed to the symmetrically stable 3 × 3 × 3 "cubic-like" structure (where the numbers refer to the number of atoms on the side of a parallelpiped). Likewise, the ion intensity enhancement observed at $n = 22$ was explained by a 3 × 3 × 5 "cubic-like" structure. Although ions beyond $n = 22$ were not observed, we assumed that the ion intensity anomaly observed at $n = 13$–15 recurred at $n = 22$–24. The decreased ion intensity of the cluster ions immediately following the stable $n$ values ($n = 13, 22$) indicated a barrier to the formation mechanism (e.g., addition of one or two more salt molecules to these symmetrically stable bulk-like structures, bond-breaking, crystal cleaving) or inate instability.

The proposal of simple "cubic-like" structures for the observed enhanced cluster ion species led to the hypothesis that ion intensity enhancements would be observed at other high values of $n$ corresponding to "closed structures" such as the 3 × 3 × 7 ($n = 31$) and the 3 × 5 × 5 ($n = 37$) simple "cubic-like" structures. Our preliminary results indicated that some stable alkali iodide cluster ion configurations correspond to bulk "cubic-like" structures even for CsI which has a body-centered cubic (bcc) structure. In contrast to our hypothesis, research on cluster formation processes indicates that small polymers and larger clusters, formed by nucleation, do not obtain bulk characteristics until the number of atoms in the cluster becomes significantly greater than those observed with our SIMS instrument.[6,15,16] In this report we present new data which support our hypothesis[1] on the structure of certain alkali iodide clusters.

## Experimental Section

All experimental conditions[1] and instrumentation[2] were as described elsewhere unless noted in this section. The alkali iodide samples were prepared by pressing pellets from reagent grade salts.[1] It must be emphasized that these samples contained an extremely high density of surface defects relative to cleaved or single-crystal surfaces.

The high-performance secondary ion mass spectrometer is based on a conventional (Consolidated Electrodynamics Corp.) double-focusing (Mattauch-Herzog geometry) mass analyzer. CsI and NaI SIMS spectra were obtained by bombardment of the sample with 4-keV $Xe^+$ ions ($10^{-6}$ A/cm$^2$) and with a 1-kV secondary ion accelerating voltage. The primary ions impinge upon the sample at 30° with respect to the sample surface. The ion-focusing electronics were modified so as to facilitate operation of the spectrometer and the focusing of ions at low secondary ion accelerating voltages, specifically at 300 and 500 V. This was required because the mass range at 1 kV accelerating voltage was limited to about $m/z$ 5400 by the 1.1-T magnetic field maximum. Spectra were obtained at each of the low accelerating voltages with 4.7- and 4.5-keV $Xe^+$ ions, respectively. The primary ion energy was always the difference between the initial primary ion energy (5 keV) and the energy of the secondary ions.[2] The secondary ion emission from NaI did not significantly increase with primary ion beam mass and energy. Extended NaI SIMS spectra could not be obtained beyond $n = 36$ even at lower acceleration voltages; therefore, only the 4.0-keV primary ion beam energy results are reported here. These data are an average of at least three mass spectral peak maxima. We have shown that peak maxima are a good measure of ion abundances with this instrument and that these data can be used to calibrate conventional quadrupole SIMS instrument.[17]

Nominal mass measurement was accomplished both by the measurement of the magnetic field with a Hall probe and by digital control of the magnet to give linear mass spectra for manual mass-to-charge interpolation (and interpretation).

## Results

Increasing the mass of the primary particle usually results in an increase in the sputter and secondary ion yields.[18] Xenon ions were used in these studies as the primary ion, and thus we expected that the secondary ion yield would increase significantly such that high-mass, previously unobserved, cluster species might be produced and detected. These expectations necessitated operation of the SIMS instrument at lower secondary ion accelerating voltages in order to extend the mass range, since the mass range is inversely proportional to the accelerating voltage.

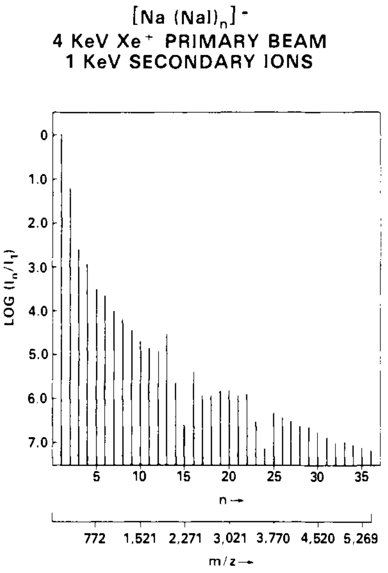

**Figure 1.** SIMS spectrum of NaI cluster species to $n = 36$ at 1 kV accelerating voltage. Evidence for stable "cubic-like" structures are evident at $n = 13$, 22, and possibly 31.

Figure 1 summarizes the NaI mass spectrum obtained at 1 kV accelerating voltage. This is the first time that alkali iodide cluster ions beyond $n = 22$ have been observed. The ion intensities at $n = 22$–24 (Figure 1) reinforce our previous interpretation of a recurrent ion intensity anomaly observed initially at $n = 13$–15 and support the previous assignment of the stable 3 × 3 × 5 structure at $n = 22$ as consistent with our postulate. The ion intensity information in this mass spectrum suggests a stable structure at $n = 31$ (3 × 3 × 7). There is a minor decrease in the ion intensity of the $n = 32$ species; however, we do not preclude or assume the existence of the 3 × 3 × 7 structure of $n = 31$ on the basis of this mass spectrum. This mass spectrum extends to $n = 36$ which is just short of the next logical prediction, $n = 37$ (3 × 5 × 5), in the progression.

Since for identical ion bombardment conditions CsI is much more emissive (increased secondary ion yield) than NaI,[19] ultrahigh mass SIMS spectra could be obtained by operation of the mass spectrometer at still lower secondary ion accelerating voltages.

The mass spectrum of CsI at 500 V accelerating voltage is reproduced in Figure 2 and was recorded from $n = 16$ to 41; the high mass limit shown is at $m/z$ 11 000. Here, the anomalous ion intensity behavior at $n = 22$–24 is observed. In this spectrum, anomalous ion intensity behavior at $n = 37$–38 (3 × 5 × 5) is conspicuously evident; furthermore, the intensity anomaly at $n = 31$–33 supports the postulate of a 3 × 3 × 7 structure.

Finally, the accelerating voltage was decreased to 300 V to further increase the mass range. The results of this experiment are summarized in Figure 3, where cesium iodide cluster ions were observed to $n = 70$ or $m/z$ 18 320 (S/N = 1.5). The next obvious "island of stability" and anomalous region about the $n = 62$ species or the 5 × 5 × 5 "cubic-like" structure are apparent. In addition,

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(19) Ion bombardment of CsI produces a bright blue fluorescence of the sample where NaI emits a faint organge glow. Although this light emission is fundamental to the understanding of the secondary ion formation and emission processes, it is not currently understood how this light emission is related to the internal energy state of the cluster ions.

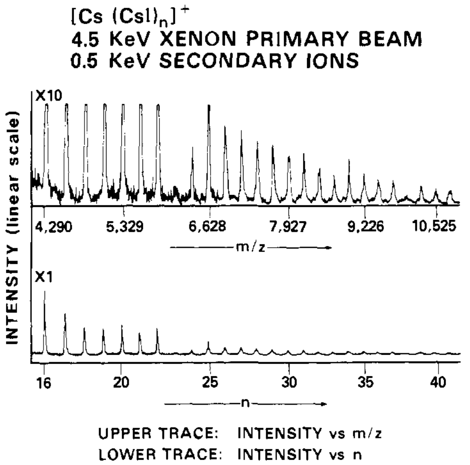

**Figure 2.** SIMS spectrum of CsI cluster species from $n = 16$ to 41 at 500 V accelerating voltage. The notable decrease in intensity of the species following stable structures at $n = 22$ and 37 is apparent. This mass spectrum extends to almost $m/z$ 11 000.

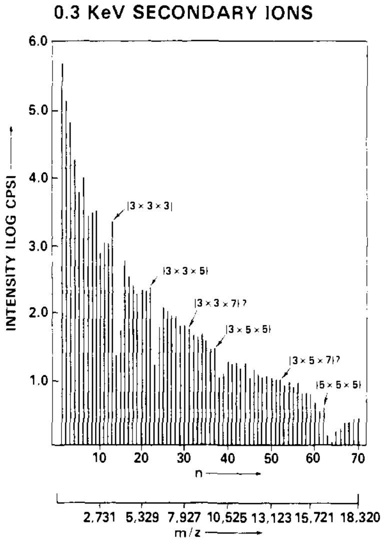

**Figure 3.** SIMS spectrum of CsI at 300 V accelerating voltage. Spectral evidence for several stable "cubic-like" structures is apparent at $n = 13$, 22, 31, 37, 52, and 62. This mass spectrum extends beyond $m/z$ 18 000.

there is mass spectral evidence for the stable species at $n = 52$ ($3 \times 5 \times 7$ structure); however, that corresponding ion intensity enhancement is less dramatic as is the $n = 31$ ($3 \times 3 \times 7$ "cubic-like" structure) species.

## Discussion

The anomalous cluster ion intensity behavior observed in the ultrahigh mass spectra of this work confirms the predictions of an earlier hypothesis based on low-mass results.[1] These extended mass spectra and the high-mass cluster ions were obtained by bombarding the sample with more massive and more energetic primary ions ($Xe^+$, 4.7 keV) than used in our previous work ($Ar^+$, 4.0 keV).[1] The alkali iodide cluster ion intensity enhancements predicted and observed in our investigations and the corresponding stable "cubic-like" structures are summarized in Table I. Although an enhanced ion intensity for the $n = 4$ species was not observed for the alkali iodides, we have observed this ion intensity enhancement for the other sodium halides.[20] Additionally, Martin has shown the $1 \times 3 \times 3$ ($n = 4$) structure to be thermodynamically stable for NaCl.[6] Our mass spectral data indicate increased formation or enhanced stability of certain cluster species, especially at $n = 13$, 22, 31, 37, 52, and 62, and barriers to formation or instability of the cluster species immediately following the stable form. These enhanced ion intensities can be explained by "cubic-like" cluster species not to preclude other unrealized molecular arrangements.

Table I. Summary of Stable "Cubic-Like" Alkali Iodide Cluster Ion $[M(MI)_n]^+$ Structures Observed by SIMS

| $n$ value | total no. of atoms | "cubic-like" structure | ion intensity enhancement |
|---|---|---|---|
| 4 | 9 | 1 × 3 × 3 | no |
| 13 | 27 | 3 × 3 × 3 | yes |
| 22 | 45 | 3 × 3 × 5 | yes |
| 31 | 63 | 3 × 3 × 7 | yes? |
| 37 | 75 | 3 × 5 × 5 | yes |
| 52 | 105 | 3 × 5 × 7 | yes? |
| 62 | 125 | 5 × 5 × 5 | yes |

An immediate curiosity of our results is that the CsI (bcc) SIMS spectra show anomalies in the cluster ion intensity distribution at the same $n$ values as the simple cubic alkali iodides (NaI, KI, and RbI). Similar ion intensity anomalies for the bcc and simple cubic salts can be interpreted as consistent with current theoretical, experimental, and crystallographic data.

Martin has shown through modeling that the $(CsCl)_{12}$ bcc structure transforms spontaneously into a more stable arrangement of three stacked-octagonal rings.[15] A further generalization of his findings is that in the initial stages of crystal growth or nucleation the bcc clusters possess a simple cubic or wurtzite form; as many more molecules are agglomerated, a transformation is made to the bcc structure. These suggestions for structural transformations in small clusters are in agreement with experimental evidence presented by DeBoer and Stein.[16] Their experiments using a molecular beam apparatus coupled with X-ray diffraction indicate that a large number of atoms (>500) must be agglomerated before homogeneous clusters assume bulk properties.[16] The similarity of the intensity distributions of the simple cubic and bcc alkali iodides observed in our work may imply that the small bcc CsI clusters are spontaneously transformed into stable cubic structures during the emission process or as microcrystals are formed on the surface by ion bombardment, condensation, or otherwise.

A more compelling explanation of the spectral similarities is that the bcc CsI crystallite contains a primitive cubic structure, the rhombohedron, which can be viewed as a skewed cube. Therefore, it is likely that the stable "cubic-like" structures of CsI are rhombohedral, rather than cubic (NaI, KI, RbI).[21]

Therefore, the principal conclusion drawn from our results and hypothesis is that one type of stable configuration for certain small alkali iodide cluster species produced by sputter-emission mechanisms is the close-packed, "cubic-like" geometry. Furthermore, the postulated "cubic-like" structures are intrinsic to the bulk crystal structure. We have recently interpreted these SIMS results by a simple bond-breaking model or more appropriately a crystal-cleaving picture,[21] which involves cluster-ion surface energies.[7,22]

These data are best interpreted by a direct emission mechanism of sputtering in the alkali iodides as reported earlier.[1] This conclusion is based on the following: (A) nonstatistical ion intensity distribution and (B) experimental and theoretical evidence. These factors will be discussed in detail.

**A. Nonstatistical Ion Intensity Distribution.** Cluster species formed by statistical recombination or growth statistics are expected to yield an ion intensity distribution which falls off monotonically with $n$ value since the distribution represents the probability of forming clusters from larger numbers of constituents.

Several alkali iodide cluster ions show enhanced ion intensity and hence enhanced ion stability whose size correlates with bulk "cubic-like" atomic arrangements. These ion intensity en-

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hancements are evident as positive deviations in the decreasing ion intensity distribution obtained from the SIMS and other cluster data. Similar positive deviations have been observed in the SIMS data of frozen water[23] which yield cluster species of the type $[H(H_2O)_n]^+$. In this case, ions intensity enhancements were noted at $n = 3$, 4, and 21, where the $n = 21$ species was postulated to be a clathrate structure, i.e., a pentagonal dodecahedron. These ion intensity enhancements were previously observed in the ionized products of the free jet adiabatic expansion of water.[24,25] Hence, the interpretation of the SIMS results of frozen water has been viewed as a localized thermal activation followed by an irreversible adiabatic expansion of the lattice species into the vacuum to relieve the nonequilibrium situation with concomitant recombination of species in the selvedge region.[23]

Our alkali halide results differ from the water cluster distribution in that negative deviations of the decreasing ion intensity distribution are also observed. These negative deviations correspond to the cluster species immediately following the stable species. This phenomenon indicates a *dependent* relationship between various cluster ions, e.g., $n = 13-15$, of the alkali iodides and not the structural independence expected from recombination, e.g., water clusters.

Sattler et al. have noted[26] in their study of metal clusters ($Sb_n$, $Bi_n$, and $Pb_n$), formed by metal vapor condensation and detected by time-of-flight mass spectrometry, that for $n < 20$ the ion intensity distributions are dependent on the stability of the clusters. They conclude[26] from data extending to $n = 500$ that the ion intensity distribution for $n > 20$ is a function of the "formation conditions" and is mainly determined by growth statistics; that is, intensity anomalies are negligible in the cluster ion spectra above $n = 20$. While the frozen water cluster ion intensity distribution[23] is in agreement with Sattler's observations[26] and free jet expansion results,[24,25] our alkali iodide intensity distributions continue to deviate from the expected distribution even at high values of $n$. A dramatic and recurrent anomaly is observed in the $n = 13$, 22, 37, and 62 regions (see Table I and Figure 3).

In summary, these systems (alkali iodides, frozen water and heavy metals) are inherently different. While the alkali iodide results are better interpreted by a direct emission model, the frozen water and heavy metal results are best explained by recombination and growth statistics.

**B. Experimental and Theoretical Evidence.** Experimental[27] and theoretical[11] evidence exist for the direct secondary ion emission of discrete organic molecules and covalently bonded anionic species[28] from surfaces. In such systems, the relative intermolecular bond strengths may dictate the nature of the emission process.[12] Species that have stronger covalent or ionic bonds many undergo direct emission and those that have weaker metallic or van der Waals bonds may undergo recombination.

Most recently Heyes et al. have presented a two-dimensional molecular dynamics (MD) study of the sputter mechanism[8] which models experimental conditions similar to our study. These results are applicable to our study because (1) a metal halide (KCl) was modeled, (2) primary ion beam energies were 2 keV, (3) the primary ion angles of incidence are ~20 and 45° relative to the sample surface, (4) bombardment-induced surface defects were modeled, and (5) a suitable well depth of the bulk pair potential was used (4 eV).

The conclusion of the MD study was that cluster ions are more likely to represent the undistributed surface as the primary ion beam impinges at smaller angles relative to the sample surface. The results of a primary ion beam incident at 20° demonstrated a "peeling effect" where a large portion of the crystal about the impact zone was emitted from the surface. On the other hand, ion bombardment at 45° to the surface results in a smaller probability of forming clusters from nearest neighbors. Heyes et al. conclude that at small angles of primary ion incidence emitted clusters are unarranged units of the original interface, i.e., direct emission.

This two-dimensional MD study was reconfirmed by Foley and Garrison[29] using three-dimensional MD modeling of a Cu single crystal. They find that more nearest-neighbor dimers result (direct emission) from a "shearing mechanism" operative at a primary ion beam ($Ar^+$, 600 eV) angle of incidence of 45° (compared to normal incidence) in the $\langle 100 \rangle$ direction of the model Cu crystallite. (This study did not consider lower angles of primary ion incidence or damaged surfaces.)

These considerations, especially the molecular dynamics results,[8] corroborate our interpretation of direct emission of "cubic-like" alkali iodide cluster ions.

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## Addendum

The mass capability of this high-performance SIMS instrument[2] is demonstrated with these data. These SIMS data provide ultrahigh mass references for SIMS[17] and our system ranks similarly with state-of-the-art mass spectrometers and the high-mass references provided by field desorption ionization of polymers.[30,31] Notable is the mass range in Figure 3 extending beyond $m/z$ 18 000, the highest mass-resolved ions observed by a conventional mass analyzer to date. (Mass spectrometric detection of unresolved ions beyond $m/z$ 50 000 have been reported.[26,32])

These SIMS studies of cluster formation processes may provide a link between the microscopic phenomena of secondary particle sputtering and the macroscopic phenomena of chunk sputtering.[33] These experimental results should be of considerable interest to theorists as researchers continue to probe the secondary ion emission process and the associated formation of cluster species, the "fifth state of matter".[34]

**Registry No.** NaI, 7681-82-5; CsI, 7789-17-5.

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