Doubly charged cluster ions $[(NaCl)_m(Na)_2]^{2+}$: magic numbers, dissociation, and structure

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Abstract

Doubly charged sodium chloride cluster ions $[(NaCl)_m(Na)_2]^{2+}$ with $m = 11$–62, were produced by electrospray ionization and examined by tandem mass spectrometry in a quadrupole ion trap. Variations in the ion intensity with cluster size indicate the existence of magic numbers at $m = 11$, 12, 17, 20, 21, 26, 30, 34, 36, 44, 54, and 61. The magic number clusters were studied by collision-induced dissociation (CID). The largest clusters ($m > 35$) fragment mainly by neutral losses. Cluster ions containing 19–35 NaCl molecules are prone to fission with charge separation to form a singly charged magic number cluster ion (a regular crystallite comprised of $a \times b \times c$ ions, where a, b, and c are small odd integers) along with other lower abundance singly charged clusters. Small doubly charged clusters ($m < 19$) could not be isolated for study by tandem mass spectrometry unless an unusually large isolation window (10–30 mass/charge units) was used. Structures of three types are proposed to account for the dissociation behavior of the magic number clusters: (1) combination blocks, where a block is a singly charged magic number cluster $a \times b \times c$, including the special case of a perfect sheet ($a \times b \times 1$), (2) merged blocks, and (3) regular crystallites with single-point defects ($a \times b \times c - 1$, where a, b, and c are small odd integers). Electrospray ionization (ESI) proves to be a good way to generate salt clusters in the gas phase and ion trap tandem mass spectrometry is well suited to their characterization. (Int J Mass Spectrom 195/196 (2000) 667–684) © 2000 Elsevier Science B.V.

Keywords: Clusters; Doubly charged clusters; Magic numbers; Sodium chloride; Tandem mass spectrometry; Electrospray ionization (ESI); MS/MS

1. Introduction

The study of clusters has attracted substantial attention during the past two decades. Clusters differ considerably from bulk matter in at least two important aspects [1]. First, a large fraction of their constituent atoms are present on the surface. For example, a cluster composed of 125 units, if spherical, has approximately 80% surface units [2]. Second, the electronic and chemical properties of clusters are distinct from those of their bulk or atomic counterparts, leading to size-dependent physical and chemical properties. Examples are the ionization energy and electron affinity of small copper clusters that exhibit strong odd/even dependence on the number of atoms forming the cluster due to the alternation between fully paired and unpaired valence electrons. For these and other reasons, clusters are sometimes called the

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A tribute to the memory of Robert R. Squires.

fifth state of matter [3], the interesting properties of which have stimulated sustained investigation.

An often-stated goal of cluster studies has been to gain understanding that will ultimately bridge the knowledge of the gaseous and condensed states of matter [4]. Understanding of phase transitions, crystal growth, chemical catalysis, microelectronics, and thin film preparation [5–7] may all benefit from the cluster studies. An important discovery in cluster science is the identification of magic numbers [8–12] in the intensity distribution of clusters (usually ionized clusters). Cluster abundance distributions are generally considered a direct reflection of their relative stabilities [8–16] so magic numbers represent clusters with special structural stability [8–10]. For example, magic number metal clusters have closed electronic shells [17,18]; most magic numbers in hydrogen-bound clusters arise as a consequence of solvation shells [19], and the magic numbers observed in carbon clusters include the specially stable "Buckminster-fullerene" C_{60} [20–23] and Met-Car [24,25] structures.

Although many analytical techniques and theoretical methods have been exploited in cluster studies [26], mass spectrometry stands out as a major experimental technique that offers advantages for studying size-dependent cluster properties with unparalleled sensitivity, specificity, and versatility [27–29].

Alkali halide clusters have been extensively studied since the late 1970s [11,12,30,31]. As model ionic compounds, alkali halides have simple binding properties and their preparation in pure form is trivial. Naturally occurring nanocrystals of salts such as NaCl and NaBr are also important in environments such as the marine atmosphere, where they crystallize from salt-water droplets formed as aerosols as a result of ocean wave action. These natural alkali halide clusters are of growing interest because their reactions with nitrogen oxide pollutants provide one source of the halogen that is believed responsible for catalytic ozone depletion [32,33].

Most reported studies on alkali halides deal with singly charged clusters, especially cation excess clusters of the type $[(CA)_nC]^+$, where C and A represent the cation and anion of the molecule. There are only a few reports on the doubly charged clusters, $[(CA)_mC_2]^{2+}$ [34,35]. It is self evident that the presence of two net charges in the doubly charged clusters makes them inherently less stable than their singly charged counterparts. Whereas singly charged clusters as small as $n = 1$ can be generated, electron ionization studies of NaI clusters by Sattler et al. [36] suggested that there is a critical size for stable doubly charged clusters, a number they suggested to be $m = 18$ for $[(NaI)_m(Na)_2]^{2+}$. Shortly after this, Martin [34] presented calculations for $[(NaCl)_m(Na)_2]^{2+}$, $m = 1–18$, to rationalize the absence of these doubly charged clusters in the mass spectrum. It was found that for cluster ions with m less than 8, the removal of a Na^+ from the doubly charged cluster is exothermic, thus these clusters are not thermodynamically stable. However, the calculation also indicated that there exists at least one metastable configuration for each of these cluster ions. Martin concluded that the absence of small doubly charged clusters in general could be attributed to their inherent instability, short lifetime compared to the time for the ions to reach the detection system, or the fact that some metastable configurations are not accessible following vertical ionization. Note that in these early studies, the clusters were generated by vertical ionization such as electron impact ionization. By photoionization of very cold $[(CA)_nC_2]^+$ ions or photo-ejection of a halogen atom from $[C_{n+2}A_{n+1}]^+$ ions followed by photoionization as a second step, Li and Whetten [35] generated doubly charged cluster ions of KBr and CsI below the so-called critical size, $m = 18$. The finding of a "stability island" around $m = 11–12$ is especially interesting [35], and the stability of $m = 12$ was attributed by these authors to a highly symmetric "cage" structure that can be formed by removing the central Cl^- from a singly charged cube $[(NaCl)_{13}Na]^+$ to generate the doubly charged ion $[(NaCl)_{12}Na_2]^{2+}$. In the nomenclature we introduce below, this is a point-defect structure.

As a soft ionization technique, electrospray ionization [37] has greatly extended the range of compounds that can be studied by mass spectrometry and also provided new possibilities for cluster studies [38–42]. For example, water clusters have recently been pro-

posed for mass calibration purposes [40] due to well-spaced cluster peaks that cover a wide *m/z* range. New findings of residue-specific peptide solvation in the gas phase and the corresponding occurrence of water magic numbers (clathrate formation) by Beauchamp and his research group [43], as well as the hydration of doubly protonated peptide ions and the observation of magic numbers of attached water molecules by Williams et al. [44], suggest the emergence of useful new diagnostic tools in peptide analysis. Formation of sodium chloride and many other salt clusters has been exploited in studies of the electrospray mechanism [39,45,46], however, until recently [47] only singly charged cluster ions had been reported.

Using NaCl as a model compound at relatively high concentrations, we find it possible to form abundant doubly charged cluster ions by electrospray ionization. In addition, magic number effects in the doubly charged cluster ion distribution were observed. These doubly charged cluster ions therefore were examined individually by collision-induced dissociation (CID) and an effort was made to elucidate their structures.

2. Experimental

An LCQ (Finnigan Corporation, San Jose, CA) ion trap mass spectrometer was employed in the positive ion electrospray mode for all studies. A PM-80 solvent delivery system (BAS, West Lafayette, IN) with a divert valve was used for sample introduction. The mobile phase was a mixture of water and methanol (1:1 by volume) and the flow rate was 0.2 mL/min. The capillary temperature was 120 °C, and the electrospray voltage was 4.0 kV. Nitrogen was used as both the sheath and auxiliary gas for the electrospray source at flow rates of 1.35 L/min and 1.5 L/min, respectively.

The Mathieu parameter, q_z, values selected for isolation, resonance excitation, and ejection were 0.83, 0.25, and 0.9, respectively. The ion excitation time for collision-induced dissociation (CID) was 30 ms. The amplitude of the excitation ac used for CID was optimized in each experiment and both this value and the manufacturer's nominal relative collision energy (%) are reported. (The range from 0–100% relative collision energy corresponds to 0–2.5 V zero-to-peak resonant excitation potential.) Data were acquired using the LCQ software in the full-scan MS or MS/MS mode and spectra were generated after appropriate background subtraction, when necessary. The spectra reported represent averaged data taken over the period of sample introduction that was typically 30 s or approximately 20 scans. Data are shown in Thomson, where 1 Thomson (Th) = 1 Da per charge [48].

Sodium chloride (99.2%) and methanol (HPLC grade) (Mallinckrodt Baker, Paris, KY) were used without further purification. Deionized water was used throughout the experiments. Solutions were prepared at 0.1 M in 1:1 water/methanol to match the mobile phase composition used for electrospray.

3. Results and discussion

As shown in Fig. 1, abundant cluster ions are observed in the electrospray mass spectrum when 0.1 M sodium chloride in a 1:1 water/methanol matrix is sprayed. Examination of the spectrum reveals that both singly charged and doubly charged cluster ions are present. The singly charged cluster ions have the formula $[(NaCl)_nNa]^+$, and form a series of peaks in the mass spectrum differing by one NaCl unit (Fig. 1); the chlorine isotopic pattern is evident from the 2 Th spacing. A second series of cluster ions is present in the mass spectrum, as evidenced by ion signals located between each singly charged ion cluster. These correspond to a doubly charged series of the form $[(NaCl)_m(Na)_2]^{2+}$. The separation between component ions of each doubly charged cluster, shown in the insert in Fig. 1, is 1 Th, conclusive evidence for the doubly charged nature of these ions. Because the spacing of doubly charged clusters is half that of their singly charged counterparts, overlap of the two series occurs at positions where $m = 2 \times n$. Overlapping signals are observed for most of the even *m* clusters in the mass spectrum. The other feature to note is that
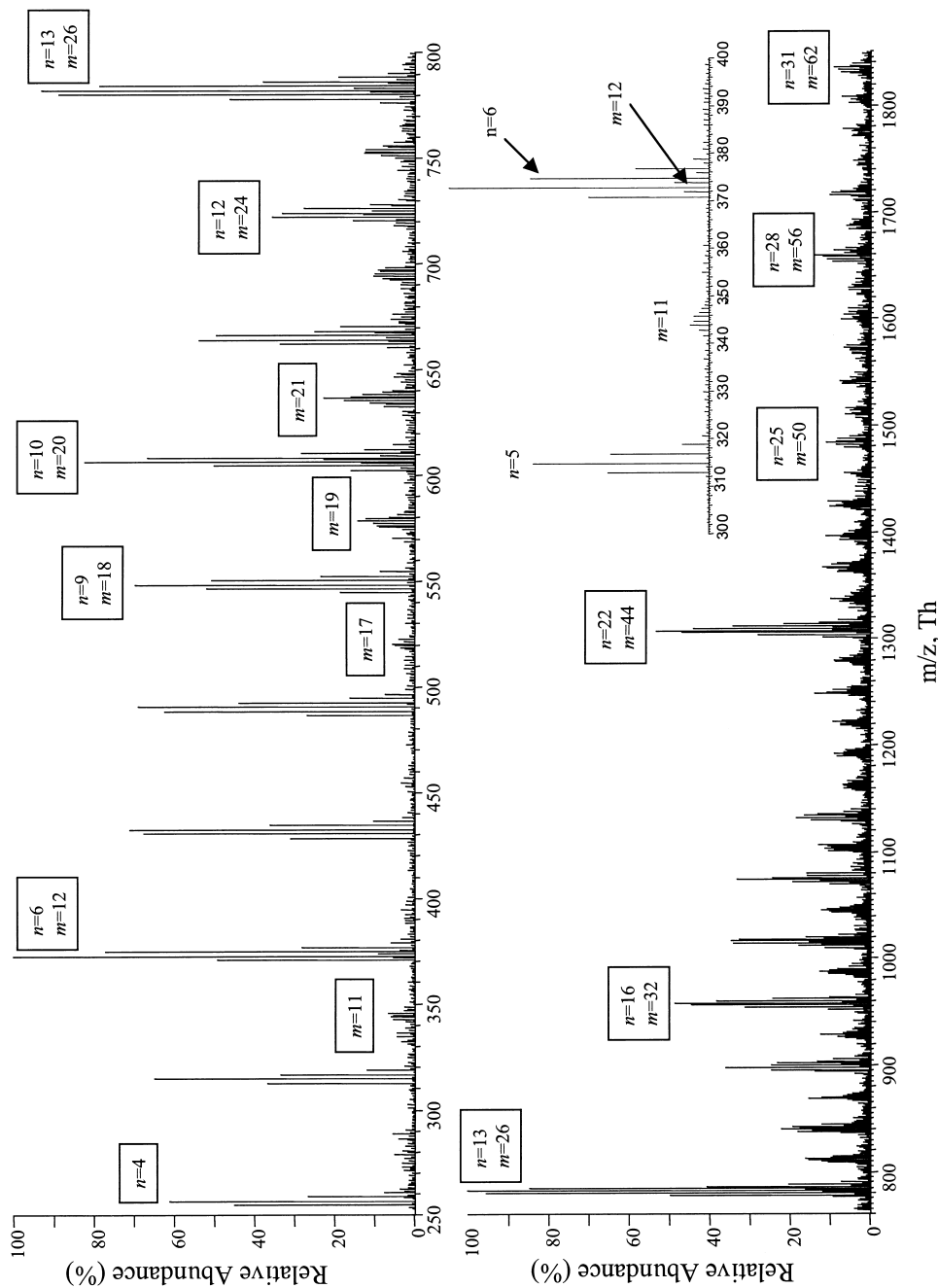
Fig. 1. Full-scan mass spectrum of 0.1 M NaCl solution under positive ion electrospray conditions. The top section shows both singly charged and doubly charged cluster ions in the range 250–800 Th, and the bottom section shows those present in the range 760–1860 Th. The overlap of the two sections facilitates comparison of relative abundances. Inset shows one of many regions in which both singly charged and doubly charged ions appear. Values n and m are used to designate singly charged and doubly charged cluster ions in the forms $[(NaCl)_n Na]^+$ and $[(NaCl)_m (Na)_2]^{2+}$, respectively.

the intensity distribution, as shown in the mass spectrum, is not uniform and magic number effects appear to exist for the doubly charged as well as the singly charged cluster ions.

The effects of sample concentration, temperature of the heated capillary in the ESI source, and the extraction voltage were examined. The concentration of analyte appears to play a pivotal role in the formation of cluster ions, especially that of the doubly charged cluster ions. By varying the salt concentration in the sample from 10^{-4} to 10^{-1} M, we found that 10^{-4} M is roughly the onset for singly charged cluster ion formation, whereas 10^{-2} M is the onset for the production of doubly charged cluster ions. Higher concentrations favor the formation of both singly and doubly charged clusters, but solutions above 0.1 M can block the heated capillary by salt crystallization. The temperature of the heated capillary also has some effect on the distribution of the cluster ions formed. Capillary temperatures were varied from 125–200 °C in steps of 25 °C, at a fixed concentration of 0.1 M sodium chloride, and it was observed that (1) the overall doubly charged cluster ion intensities decreased and (2) the smallest observable doubly charged cluster ion increased in size from $m = 11$ to $m = 17$. The elevated temperature also affected the congeneric produced singly charged cluster ions and caused the most abundant member of this series to shift down to a lower n value. All these observations are consistent with the assumption that more energetic conditions decrease cluster stability. Finally, the skimmer voltage effect was also examined but found to be insignificant.

3.1. Critical size

An important property of multiply charged clusters is the so-called "critical size." From theory and available experimental studies, it is known that the long-range interactions between a pair of positively charged fragments from a multiply charged cluster are always repulsive [49,50]. However, as the two fragment ions are brought within chemical bonding distances, there should be a transition from unstable to kinetically stable (or metastable) clusters, just as there

is even in such small doubly charged ions as He_2^{2+} [51]. The "critical size," although a fundamental property, is usually defined operationally by this transition, i.e. by the smallest observable multiply charged cluster [52]. It apparently depends on experimental conditions, as shown by the effect of heated capillary temperature where the smallest observable cluster shifted from $m = 11–17$ when the temperature was elevated. Doubly charged clusters of some alkali halides have been examined by photoionization methods [36] and a critical size of $m = 18$ was observed [36] for $[(NaI)_m Na_2]^{2+}$; the same value was found for doubly charged KBr and CsI clusters [35]. In our experiments, the smallest doubly charged cluster observed is $m = 11$, smaller than the values observed for other alkali halides in the earlier experimental investigations. We ascribe this to the fact that electrospray is a very gentle ionization process. The stability of the small clusters observed is in agreement with the calculations by Martin [34], except that $m = 14$ (which was predicted to have similar stability to $m = 11$ and 12) is not observed in our experiments.

3.2. Magic numbers

The mass spectrum of doubly charged sodium chloride clusters shows clear variations in intensity with cluster size, signaling magic number effects. To better express the size dependence of the intensities of doubly charged cluster ions, they are plotted separately from other charge states in Fig. 2. The intensities of odd m clusters were measured directly from the low resolution mass spectrum, whereas those for the even m clusters were measured at higher resolution in order to resolve the isotopes. Note that despite the overlap of the singly and doubly charged cluster ions at positions where $m = 2 \times n$, the isotopic pattern of doubly charged clusters (1 Th separation) allows their distinction. In Fig. 3, the intensities of individual clusters are compared to those of their neighbors by plotting $I_m^2/(I_{m-1} \times I_{m+1})$ as a function of the cluster size, m, where I is the intensity of the corresponding doubly charged cluster ion and the subscript represents the cluster size. Such a differential scaling enhances the magic number effects (which we take to
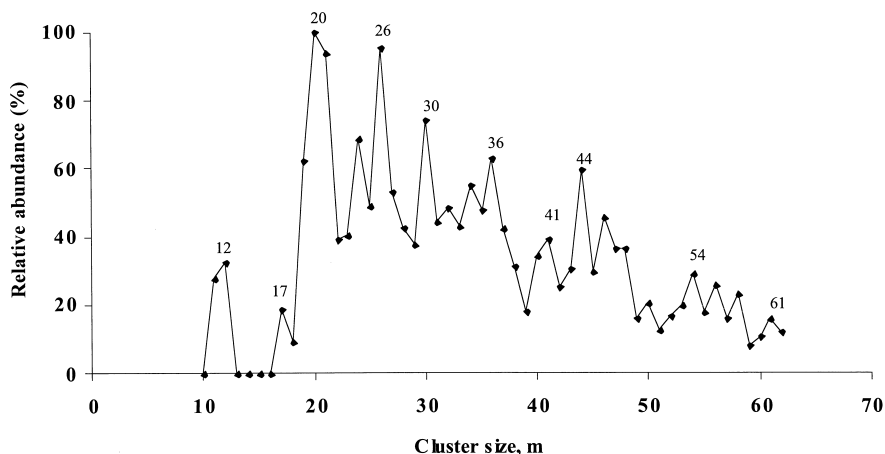
Fig. 2. The relative abundances of doubly charged clusters observed in the NaCl ESI mass spectrum showing magic number effects for certain cluster sizes.

be indicated by values greater than 1). This treatment, carried out on a single set of data, shows that magic numbers appear to exist at $m = 11, 12, 17, 19, 20, 21, 24, 26, 32, 34, 36, 40, 41, 44, 46, 48, 50, 52, 54, 56, 58$, and 61. However, there is experimental scatter in the data and this was accounted for by recording five intensity distributions of the doubly charged clusters on different days, and measuring the probability of each cluster being a local maximum (enhanced stability). A probability of 80% or higher was assigned as an indication of a magic number cluster. The magic numbers after this treatment were
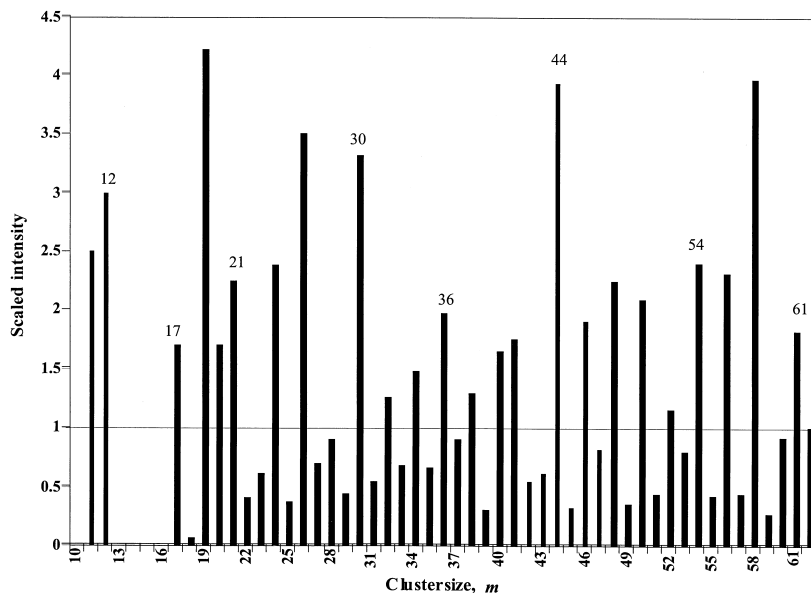

Fig. 3. Plot of $I_m^2/(I_{m-1} \times I_{m+1})$ vs. cluster size, m. In this comparative plot based on cluster abundance relative to neighboring clusters, magic numbers are identified by values greater than 1; $m = 11, 12$, and 17 are undefined because they have zero abundance neighbors, so they are given arbitrary values (compare Fig. 2).
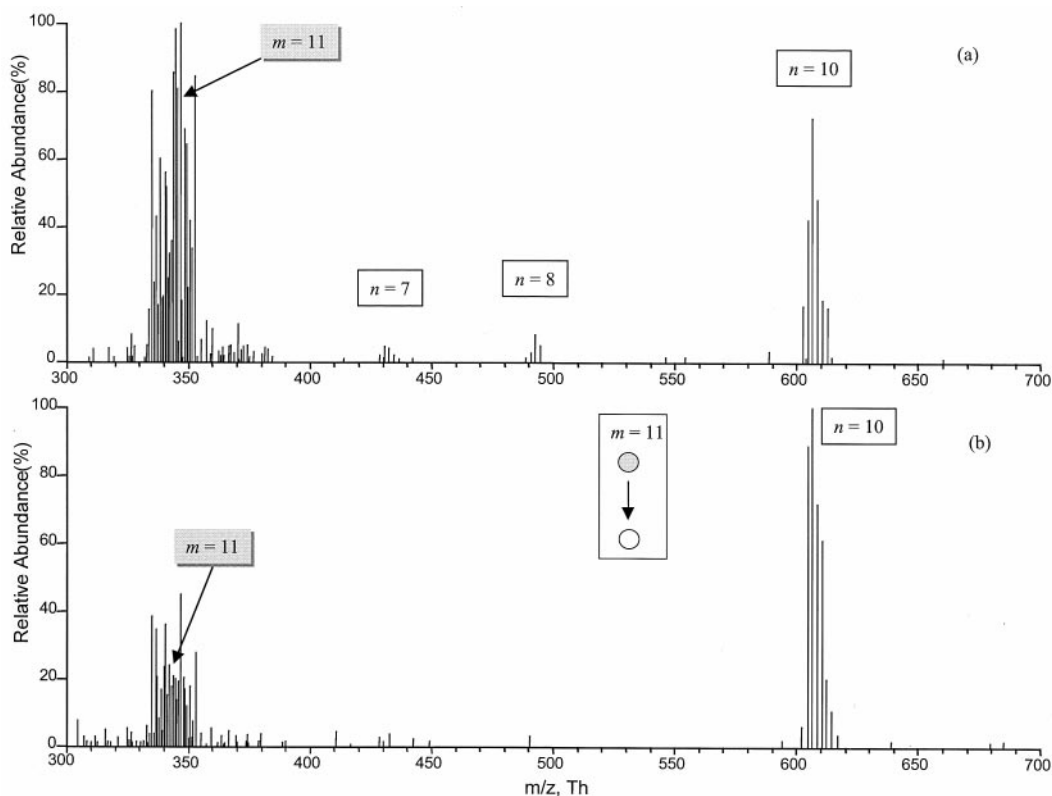
Fig. 4. MS/MS spectra recorded using an isolation delay and by CID of doubly charged clusters: (a) isolation spectrum of $m = 11$ and (b) CID spectrum of $m = 11$. A 20-Th isolation window was used in both cases. Note that the mass spacings reveal the charge states of the fragment ions.

reduced to those at $m = 11, 12, 17, 20, 21, 30, 34, 36, 44, 54,$ and 61. In addition, clusters $m = 24, 28, 32,$ and 58 showed a 60% probability as local maximum whereas some other cluster ions such as $m = 41, 46, 47, 52,$ and 56 were found to have a 40% probability being a local maximum. None of these ions is considered a magic number cluster although they might exhibit some enhanced stability.

3.3. Fragmentation of doubly charged clusters

It is well known that collision-induced dissociation (CID) is an excellent way to study the structures of gas-phase ions. For this reason, CID has often been used to study the structure, stability, and fragmentation behavior of various types of cluster ions [53–60].

To probe the structures of the doubly charged cluster ions generated from NaCl, we examined their fragmentation by CID in the ion trap mass spectrometer. This required isolation of individual clusters using an excitation waveform tailored to include frequencies for all ions except those of interest which remain trapped in stable orbits. In the course of this isolation experiment, a strong dependence on the m/z window chosen for isolation was observed. Typical isolation windows in the range of 1–3 Th resulted in a very poor signal, so larger windows were required to improve the isolation efficiency. A similar phenomenon was observed in a previous study [61] where proton-bound amine dimers could only be isolated using windows as large as 6 Th in width. This phenomenon appears to be due to excitation induced in ions that have resonance frequencies close to those at the edges of the range used to make up the isolation
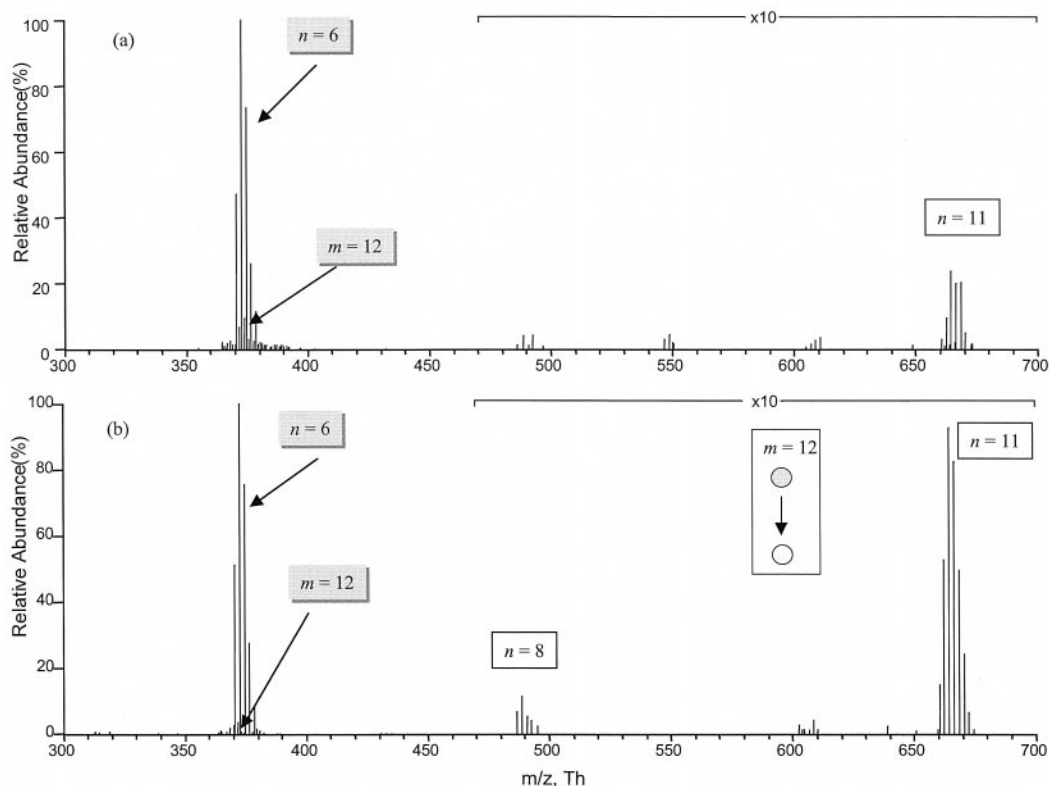
Fig. 5. MS/MS spectra recorded using an isolation delay and by CID of doubly charged clusters: (a) isolation spectrum of $m = 12$ and (b) CID spectrum of $m = 12$. A 20-Th isolation width was used in both cases. Note the overlap between $m = 12$ and $n = 6$ as shown in (a).

waveform. In the course of resonance excitation, acceleration, and ejection of the undesired ions, nearby ions that should be retained in the trap also pick up some energy and are lost. The absence of low mass doubly charged cluster ions in the isolation experiment suggests that they must be unusually fragile to dissociation (their dissociation products would, of course, be lost to the action of the isolation waveform). It was found that clusters with $m > 19$ can be isolated for further investigation with a 6 Th isolation window, but smaller clusters require a much greater window and 20 Th was chosen to achieve adequate isolation efficiencies for MS/MS studies.

As shown in Fig. 4(a), the isolation spectrum of $m = 11$ contains not only $m = 11$ but also $n = 8$ and 10, which are apparently spontaneous fission products arising after isolation. The CID spectrum of $m = 11$, on the other hand, shows the fragment ion

$n = 10$, due to loss of $(Na_2Cl)^+$ from $m = 11$, as the major product ion [Fig. 4(b)]. Similarly, $m = 12$ was isolated using a 20 Th window but $n = 11, 10, 9, 8$ also occur in the isolation spectrum although the degree of fragmentation was lower [Fig. 5(a)]. An MS/MS spectrum of $m = 12$, illustrated in Fig. 5(b), displays $n = 11$ and $n = 8$ singly charged product ions. These results imply that $m = 11$ and $m = 12$ are structurally very different from one and the other, as discussed further below.

The four cluster ions, $m = 13, 14, 15,$ and 16 were not observed in the ESI mass spectrum so no doubly charged clusters were available to be isolated. The cluster ion $m = 17$ occurs but is fragile and exhibited extensive fragmentation ($\sim$60%) during isolation, as shown in Fig. 6(a). When this cluster was subjected to CID, the singly charged cluster ion $n = 4$ was produced in addition to singly charged cluster
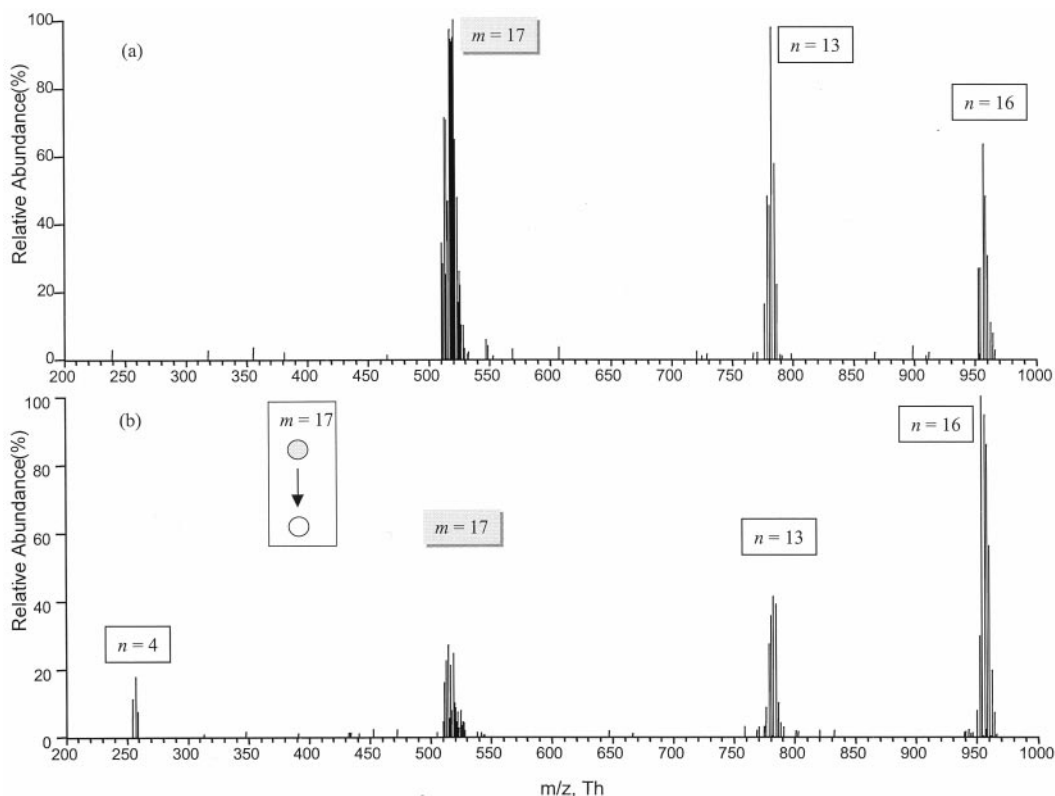
Fig. 6. MS/MS spectra recorded using an isolation delay and by CID of doubly charged clusters: (a) isolation spectrum of $m = 17$ and (b) CID spectrum of $m = 17$. A 20-Th isolation width was used in both cases.

ions at $n = 13$ and 16 that also occurred in the isolation spectrum, Fig. 6(b). Note that the clusters $n = 4$ and $n = 13$ are complementary fission products of $m = 17$, and that $n = 4$ has special stability and is identified as a magic number from both calculation and experiments [62–64]. Cluster ion $m = 18$ produces $n = 13$ and 17 as both spontaneous decay and CID products, as indicated in Table 1. On the other hand, the cluster $m = 19$ shows extensive fragmentation (~35%) under isolation conditions as shown in Fig. 7(a). It is noteworthy that the singly charged analog, $n = 19$ was present in both the isolation and the CID spectrum [Fig. 7(b)], to a small extent. Because $n = 19$ is formed from $m = 19$ by the ejection of a Na^+ atom, an uncommon dissociation pathway for doubly charged clusters, the product is assumed to be unusually stable.

MS/MS results for other odd-m cluster ions indicate that those in the range $m = 21$–35 tend to fission

upon CID and form at least one singly charged magic number fragment, along with other less abundant ions. For example, CID of $m = 25$ is dominated by the singly charged fragment $n = 22$ which is a magic number cluster ($5 \times 3 \times 3$), whereas the CID spectrum of $m = 33$ features $n = 31$ ($7 \times 3 \times 3$) as shown in Fig. 8 (a) and (b). For m greater than 35, however, MS/MS only results in neutral losses in the range of observation. The CID spectra of $m = 35$ and 41 are shown in Fig. 9 (a) and (b). Detailed MS/MS data for all the odd m clusters examined are presented in Table 2.

Because of the inability to separately isolate $[(NaCl)_m(Na)_2]^{2+}$ from $[(NaCl)_nNa]^+$ when m is an even number and $m = 2 \times n$ (because they have the same m/z), the behavior of even-m clusters was examined in two ways. In the first approach, the mixture of ions at the same m/z value was isolated and

Table 1
Fragmentation of small doubly charged clusters[a]

Parent cluster m	CID[b] energy (%)	Doubly charged fragments, m	Singly charged fragments, n	Notes
11	0	N.O.[c]	10(85), 8(10), 7(7)	~50% S.D.[d]
	10	N.O.	10(100)	
12	0	N.O.	11(25), 10(4), 9(5), 8(4)	~30% S.D.
	10	N.O.	11(100), 10(4), 8(12)	
17	0	N.O.	13(100), 16(65)	~60% S.D.
	10	N.O.	16(100), 13(42), 4(18)	
18	0	N.O.	17(100), 13(16), 16(11)	~30% S.D.
	10	N.O.	17(100), 13(18), 16(19)	
19	0	N.O.	13(35), 16(10), 17(3), 18(3), 19(2)	~35% S.D.
	10	N.O.	13(100), 16(63), 6(50), 17(6), 18(11), 19(3), 3(3)	

[a] Both isolation and CID were performed using an isolation width of 20 Th to ensure adequate signal.
[b] Collision is induced by a dipolar ac excitation; 100% corresponds to 2.5 V zero-to-peak ac voltage.
[c] N.O. = not observed.
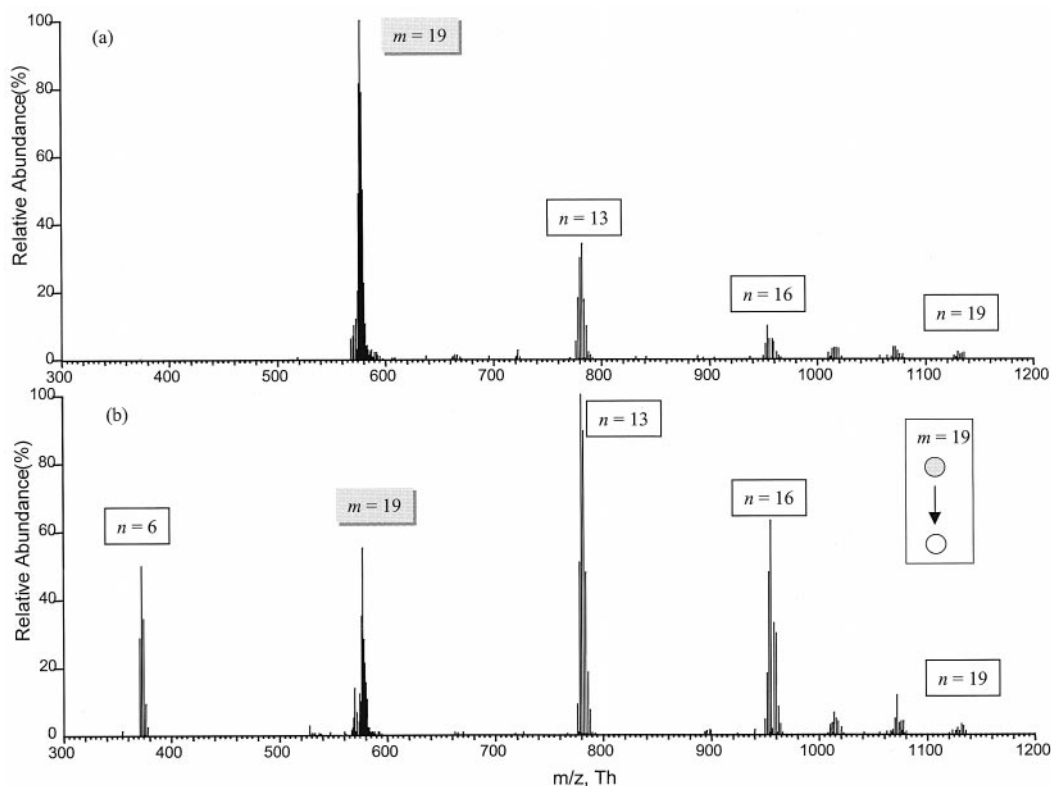[d] S.D. = spontaneous decay.

Fig. 7. MS/MS spectra recorded using an isolation delay and by CID of doubly charged clusters (a) isolation spectrum of $m = 19$ and (b) CID spectrum of $m = 19$. A 20-Th isolation window was used in both cases. Note that $n = 19$, which comes from the loss of Na^+ only, is clearly seen in the spectra.
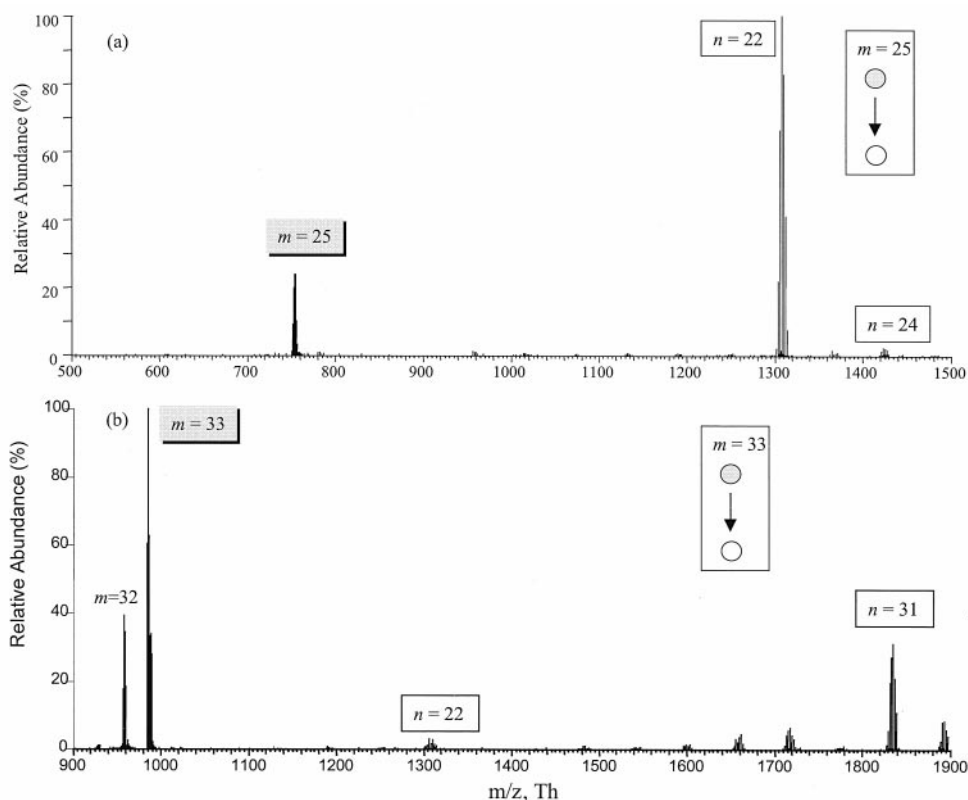
Fig. 8. CID spectra of doubly charged clusters (a) $m = 25$ and (b) $m = 33$. Note that whereas only fission products were observed for $m = 25$, neutral losses was also observed from $m = 33$. In addition, singly charged magic numbers such as $n = 22$ and 31 are dominating in the spectra.

spontaneous dissociation allowed to occur for a period of time (30 ms). A subsequent analytical scan revealed two kinds of fission products for even-m clusters between 18 and 34: one or more singly charged magic number clusters and the fragment corresponding to the loss of a unit of $[Na_2Cl]^+$ from the parent cluster. When these clusters were examined by CID, instead of being allowed to fragment spontaneously, fission products composed of a singly charged magic number cluster (e.g. $n = 13, 22, 31$) and other singly charged clusters, were usually observed. Clusters with even larger m showed greater stability toward fission and only doubly charged fragment ions due to neutral losses (up to five NaCl molecules) were observed in CID. The detailed results are summarized in Table 3.

The overall MS/MS results indicate that cluster ions having m between 11 and 35 are unstable toward

fission and fragment to form singly charged cluster ions, whereas cluster ions with m larger than 35 are stable toward fission and exhibit only neutral losses upon collisional activation.

3.4. Structural aspects of magic number clusters

It is well known that magic number clusters are usually associated with special structural properties, therefore we attempt in the following to rationalize the observed doubly charged magic number clusters based on the present experimental evidence. For small clusters [2], most of the constituent ions will be located on the surface, moreover, because both Na^+ and Cl^- have very small polarizabilities, excess charge in a doubly charged cluster ion can be represented by two excess sodium cations with localized charges. Moreover, because coulombic repulsion fa-
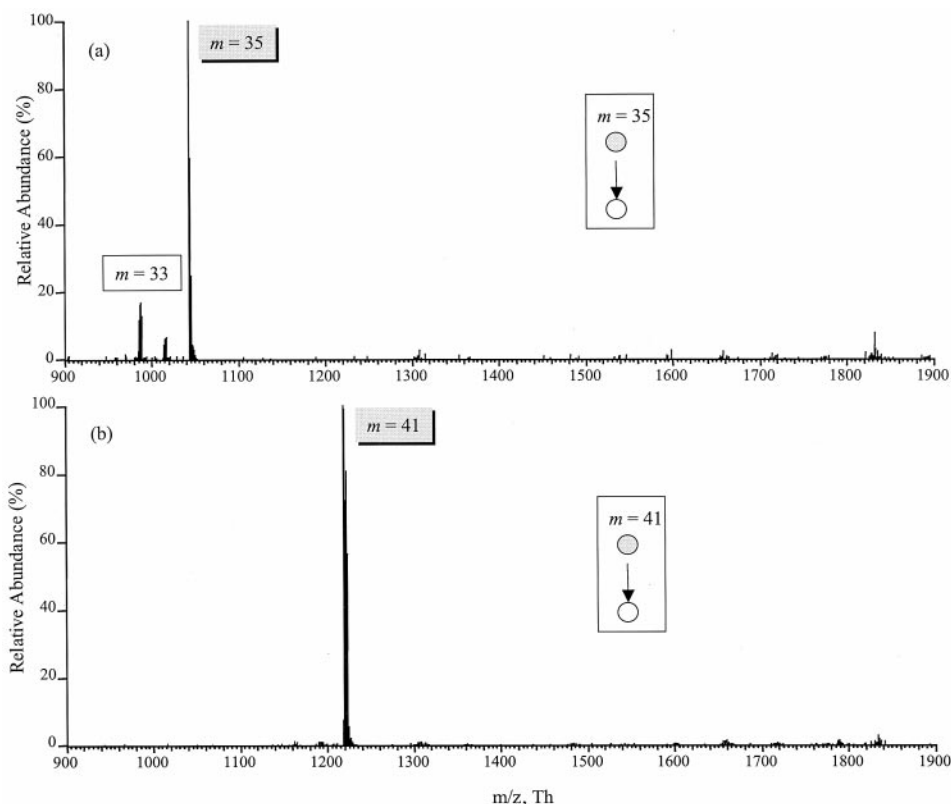
Fig. 9. CID spectra of doubly charged clusters (a) $m = 35$ and (b) $m = 41$. Note that little fragmentation is observed with these larger clusters.

vors charge separation, the formal charges in small doubly charged clusters must be well separated to maximize stability. These properties are accommodated in the structures proposed by Martin [34] for such clusters as $m = 8$ and $m = 11$, the latter shown in Fig. 10. This type of structure can be viewed as a combination of two blocks (or sheets) or singly charged clusters and they feature well-separated charges. For example, the structure of the cluster $m = 11$ can be viewed as the result of combining two singly charged sheets of ions, $5 \times 3 \times 1$ and $3 \times 3 \times 1$. This structure also explains the cleavage of a $(NaCl)Na^+$ unit, a process well represented by the presence of $n = 10$ in the CID spectrum of $m = 11$, as shown in Fig. 4(b). Similarly, $m = 8$ can be viewed as a combination of two $3 \times 3 \times 1$ ($n = 4$) blocks. We believe that this structural type also explains the magic number at $m = 17$. The cluster

ion $m = 17$ is shown to be quite stable, but no structure has been proposed previously. Because the dissociation of this cluster readily gives $n = 16$ and 13, it is suggested that its structure likely contains the structures represented in $n = 13$ and 16. A structure is proposed in which an $n = 13$ ($3 \times 3 \times 3$) unit is combined with a perfect $3 \times 3 \times 1$ sheet in an offset fashion, as shown in Fig. 10. The $3 \times 3 \times 1$ unit stretches away from and is stabilized by the $3 \times 3 \times 3$ array but the binding is not as strong as between the other ions. Cleavage along plane (a) should be easy and result in the formation of $n = 16$, whereas direct cleavage of the $3 \times 3 \times 1$ array along plane (b) will lead to $n = 4$ and 13 formation. These features are all present in the CID spectrum of $m = 17$, as illustrated in Fig. 4(b) and they provide evidence for the proposed structure. This type of combination block structure also applies to $m = 26$ and 44. In short, $m = 26$

Table 2
Fragmentation of odd-number doubly charged clusters[a] upon CID

Parent m	CID[b] energy (%)	Singly charged fragments n (relative abundance, %)	Doubly charged fragments m (relative abundance, %)
19	12	6(50), 13(100), 16(72) 17(8), 18(12)	N.O.[c]
21	15	8(64), 13(100), 17(58), 20(50) 4(14), 6(5), 16(6), 19(10)	N.O.
23	15	22(100)	N.O.
25	15	22(100) 24(3)	N.O.
27	15	22(100), 26(96) 5(6), 23(12), 25(22)	26(32)
29	15	28(100)	N.O.
31	18	28(60), 29(36), 30(100) 31(6)	30(8), 29(8)
33	18	31(100) 22(6), 28(8), 29(20), 30(3), 32(18)	32(78)
35	18	22(5), 31(16)	34(40), 33(100)
37	18	N.O.	36(100), 35(5)
39	18	N.O.	38(42), 37(100)
41	18	N.O.	39(5)
43	24	N.O.	42(100), 41(60)
45	25	N.O.	44(100), 43(32), 42(43), 41(18)
47	25	N.O.	46(100), 45(38), 44(22)
49	25	N.O.	48(100), 47(60), 46(15)
51	25	N.O.	50(24), 49(20), 48(100), 47(52), 46(18)
53	25	N.O.	52(62), 51(100), 50(6), 48(6)
55	25	N.O.	54(100), 53(12)
57	25	N.O.	56(100), 55(22), 54(8)
59	30	N.O.	58(34), 57(30), 56(100), 55(32), 54(22)
61	30	N.O.	60(100), 59(54), 58(38), 57(18), 56(18), 55(4)
63	30	N.O.	62(100), 61(90)
65	30	N.O.	64(56), 62(72), 61(100)
67	30	N.O.	66(100)

[a] Odd number clusters are those in which m in the formula $[(AC)_m C_2]^{2+}$ is an odd number.

[b] The CID energy is chosen so that most of the parent ions are fragmented; 100% CID corresponds to 2.5 V zero-to-peak ac activation voltage.

[c] N.O. = not observed.

is assigned as a combination of $3 \times 3 \times 1$ ($n = 4$) and $5 \times 3 \times 3$ ($n = 22$) blocks whereas $m = 44$ is assigned to a combination of blocks of $5 \times 3 \times 1$ ($n = 7$) and $5 \times 5 \times 3$ ($n = 37$).

The special stability of $m = 12$, on the other hand, comes from the highly symmetrical structure that can be considered as a point defect in the singly charged microcrystallite $n = 13$, as proposed previously by others [34,35]. Ejection of the central Na^+ from the singly charged $n = 13$ cluster, leads to a doubly charged ion of high symmetry and probably high stability. This is consistent with the isolation spectra

of $m = 11$ and 12 where the higher stability of the cluster $m = 12$ is reflected in the smaller extent of spontaneous fragmentation (30% for $m = 12$ versus 60% for $m = 11$, see Table 1). In addition, these two doubly charged ions show quite different fragmentation behavior that also indicates different structural types. To seek further examples of the point defect type of structure, it is logical to assume that other doubly charged magic numbers arise by ejection of an internal Na^+ from singly charged magic number clusters such as $n = 22(5 \times 3 \times 3)$, $31(7 \times 3 \times 3)$, $37(5 \times 5 \times 3)$ and $62(5 \times 5 \times 5)$. Upon exam-

Table 3
Fragmentation of even-number doubly charged clusters[a] upon CID

m, doubly charged clusters being co-isolated	CID energy (%)	Singly charged fragments n (relative abundance, %)	Doubly charged fragments m (relative abundance, %)
20	20	13(3.5), 16(2.1), 19(4.5)	N.O.[b]
24	20	22(7), 23(6)	N.O.
26	20	22(3), 25(1)	N.O.
28	20	22(4), 25(1), 27(2)	27
30	20	29(4)	N.O.
32	20	31(2.6)	N.O.
34	20	31(1.5)	33, 32
36	20	N.O.	35, 34, 33
38	20	N.O.	37, 36
40	20	N.O.	39
42	20	N.O.	41
44	20	N.O.	43, 42
46	20	N.O.	45
	30		45, 44, 43
48	20	N.O.	47, 46
	30		47, 46, 45
50	20	N.O.	49
	30		N.O.
52	20	N.O.	51,
	30		51, 50, 49, 48
54	20	N.O.	53, 52
	30		53, 52, 51
56	20/30	N.O.	55, 54
58	20/30	N.O.	57, 56
60	20	N.O.	59
	30		59, 58, 57, 56, 55
62	20/30	N.O.	61
64	20	N.O.	63
	30		61, 60, 59
66	20/30	N.O.	N.O.

[a] Even number clusters are those in which m in the formula, $[(AC)_mC_2]^{2+}$ is an even number.

[b] N.O. = not observed.

ining all the magic number clusters, we find all the corresponding doubly charged clusters ($m = 12, 21, 30, 36$, and 61) to be present. Such an excellent correlation is convincing evidence of the correctness of the proposed point-defect structures.

If we set aside the magic numbers already assigned, only $m = 20, 34$, and 54 are left uncharacterized. We believe that they must belong to some other type of structures and it is possible to rationalize structures based on the types of clusters discussed so

far. Recall that $m = 17$ is a combination of blocks of $3 \times 3 \times 3$ and $3 \times 3 \times 1$, and larger clusters can be viewed as involving additions of units to $m = 17$. A logical sequence would therefore be to add the less coordinated ($3 \times 1 \times 1$) unit to $m = 17$ to form $m = 18, 19$, and 20 with the tentative structures shown in Fig. 11. It is easy to recognize that $m = 18$ is probably not very stable, owing to the existence of an imperfect sheet on the surface. More interestingly, though, is the structure shown for $m = 19$. Cleavage along plane (*a*) is likely and can result in the formation of singly charged clusters of $n = 18, 17$, and 16 whereas further cleavages along plane (*b*) will ultimately result in $n = 13$. Note, however, there is one di-coordinated Na$^+$ in this structure, and this cation, therefore, has a chance to be cleaved directly leading to the formation of $n = 19$. Interestingly enough, all these ions, including small amounts of $n = 19$, are observed in the CID spectrum and this provides evidence for the proposed structure. Furthermore, if one more molecule unit is added to the $m = 19$ structure, a second perfect $3 \times 3 \times 3$ array would form, partially superimposed on the first, and it is expected that $m = 20$ would be particularly stable. This is in excellent agreement with the experimental results. As shown in Figs. 1 and 2, $m = 20$ is one of the most abundant doubly charged cluster ions in the ESI mass spectrum and this further validates our speculations on these structures. To view the structure of $m = 20$ in a different perspective, we can describe it as a merged structure of two $3 \times 3 \times 3$ ($n = 13$) arrays with part of the structure being shared by the two blocks. Further examination of the other two remaining magic numbers show that they also belong to this category. Thus, $m = 34$ can be viewed as consisting of merged blocks of two $n = 22$ ($5 \times 3 \times 3$) units, whereas the cluster $m = 54$ can be assigned to a merged blocks of two $n = 37$ ($5 \times 5 \times 3$). These results are summarized in Table 4.

Although the three types of special structures (combination blocks, merged blocks, and point-defect structures) have allowed us to rationalize the magic numbers encountered, it is likely there are still other types of structures also relatively stable. This would account for the stability effects observed (compare
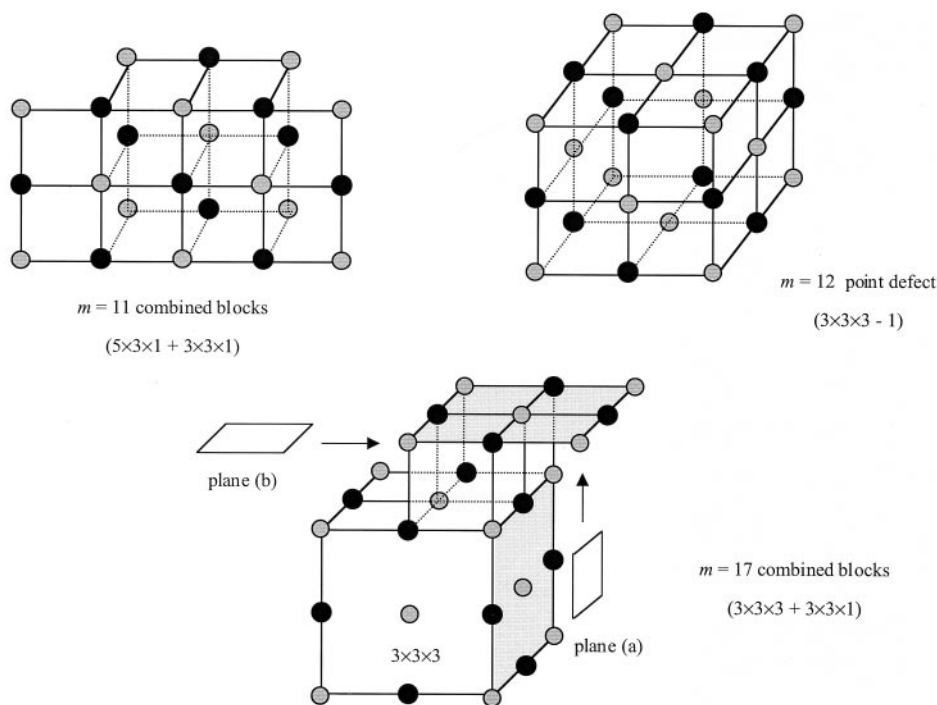
Fig. 10. Proposed structures for magic number clusters: $m = 11$, 12, and 17 which represent combination blocks ($m = 11$ and 17) and defect ($m = 12$). Filled dark circles represent chloride anions and shaded circles represent sodium cations.

Fig. 2) for clusters such as $m = 24$, 28, 32, 41, 46, 47, 52, 56, and 58. For example, $m = 32$ could be assigned to a structure of merged blocks of $n = 22$ and $n = 22$. (This can be viewed as adjacent 5×3 and 3×3 faces of $n = 22$ ($5 \times 3 \times 3$) being connected by a bent $7 \times 3 \times 1$ sheet.) Note that $m = 34$ is also the result of merging two $n = 22$ blocks, but in this case a bent $5 \times 5 \times 1$ sheet connects two adjacent 5×3 faces. The greater overlap in the latter case is also consistent with its higher stability. In similar fashion, $m = 41$ could be a combination of $n = 37$ ($5 \times 5 \times 3$) and $n = 4$ ($3 \times 3 \times 1$). Finally, $m = 28$ ($3 \times 4 \times 5 - 2$), 46 ($6 \times 4 \times 4 - 2$), 52 ($3 \times 6 \times 6 - 2$), and 58 ($4 \times 5 \times 6 - 2$) could all be accommodated by the general formula ($l \times j \times k - 2$), resulting from the loss of two chloride anions from a neutral microcrystallite. This last type of structure seems increasingly likely in large clusters; moreover, as the clusters grow bigger, the number of possible structures for a certain cluster size increases and the differences in stability between

clusters of similar size are likely to be smaller, thus making for a more featureless distribution at higher m values. These considerations are also reflected in the observed size-dependent intensity distribution, where the lower mass clusters show much more pronounced magic number effects.

In spite of the good correlation between the structure and the MS/MS results, we do not rule out isomeric structures for some of these clusters. The possibility also exists that isomerization may occur during cluster ion excitation. A recent study of singly charged NaCl anion nanocrystals using ion mobility measurements by Jarrold and co-workers [65] showed that the Arrhenius activation energy is remarkably low (<0.6 eV) for some of the structural transformations of clusters generated by laser vaporization. Nonetheless, experimental evidence (e.g. the occurrence of $m = 11$) suggests that the cluster ions generated in electrospray ionization are much less internally excited and thus likely to assume the most stable low-energy configuration.
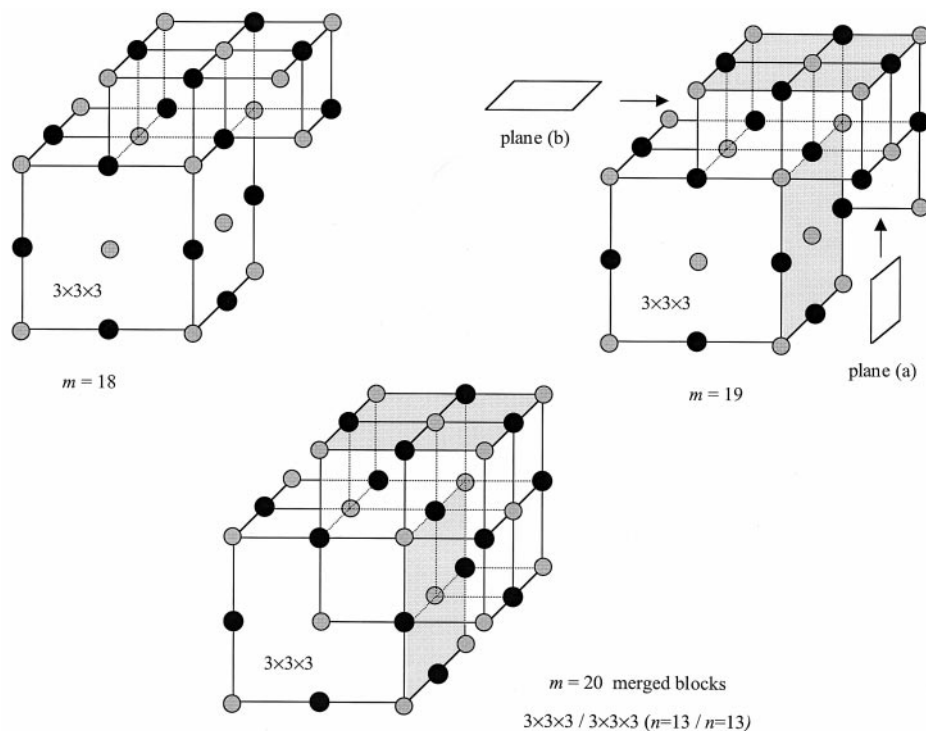
Fig. 11. Structures proposed for $m = 18$, 19, and 20 where $m = 20$ represents two merged blocks both of $n = 13$, as shown. Filled dark circles represent chloride anions and shaded circles represent sodium cations.

4. Conclusions

Doubly and singly charged clusters of sodium chloride, $[(NaCl)_m(Na)_2]^{2+}$ and $[(NaCl)_nNa]^+$, can be generated by positive ion electrospray ionization. Whereas a high sample concentration (>0.01 M) is required for the formation of doubly charged cluster ions, high capillary temperatures cause a reduction in

Table 4
Proposed structures of doubly charged magic number cluster ions

Parent cluster m	Atomic array structures proposed	Type of structures proposed
11	$3 \times 3 \times 1 + 5 \times 3 \times 1$	Combination blocks $\{4, 7\}$[a]
12	$3 \times 3 \times 3 - 1$	Point defect
17	$3 \times 3 \times 3 + 3 \times 3 \times 1$	Combination blocks $\{13, 4\}$
19	$3 \times 3 \times 3 + 4 \times 3 \times 1 + 1$	Point defect
20	$3 \times 3 \times 3 + 5 \times 3 \times 1$	Merged blocks $\{13/13\}$
21	$5 \times 3 \times 3 - 1$	Point defect
26	$5 \times 3 \times 3 + 3 \times 3 \times 1$	Combination blocks $\{22, 4\}$
30	$7 \times 3 \times 3 - 1$	Point defect
34	$5 \times 3 \times 3 + 5 \times 5 \times 1$	Merged blocks $\{22/22\}$
36	$5 \times 5 \times 3 - 1$	Point defect
44	$5 \times 5 \times 3 + 5 \times 3 \times 1$	Combination blocks $\{37, 7\}$
54	$5 \times 5 \times 3 + 7 \times 5 \times 1$	Merged blocks $\{37/37\}$
61	$5 \times 5 \times 5 - 1$	Point defect

[a] Numbers in brackets indicate the corresponding singly charged clusters as expressed in n values. "/" between numbers is used to indicate overlapping or merging.

intensity for lower members of the doubly charged cluster series and a decrease in the overall cluster ion intensity.

Doubly charged cluster ions containing as few as 11 sodium chloride molecules, which is below what had previously been suggested to be the critical size, were observed. Magic number effects exist for the doubly charged cluster ions at $m = 11, 12, 17, 20, 21, 26, 30, 34, 36, 44, 46, 54,$ and 61. Examination of these magic number clusters by tandem mass spectrometry shows that small clusters are prone to fission in CID to form singly charged magic number clusters, whereas larger clusters undergo neutral losses after collisional activation. Detailed consideration of the dissociation data reveal that the doubly charged cluster ions can be classified into three types of structures: (1) combination blocks, (2) merged blocks, and (3) point defects in regular crystallites. Strong correlations were found between the structures of the singly charged and doubly charged cluster ion series.

The combination of electrospray ionization and ion trap tandem mass spectrometry has proved to be a useful alternative technique for producing and studying ionic clusters.

Acknowledgements

References

[1] H. Haberland, in Springer Series in Chemical Physics, J.P. Toennies (Ed.), Springer-Verlag, Berlin, 1994, Vol. 56, p. 3.

[2] A.W. Castleman, T.D. Mark, in Gaseous Ion Chemistry and Mass Spectrometry, J.H. Futrell (Ed.), Wiley, New York, 1986, p. 259.

[3] G.D. Stein, Phys. Teach. Nov. (1979) 503.

[4] A.W. Castleman, R.G. Keesee, Acc. Chem. Res. 19 (1986) 413.

[5] T.D. Mark, A.W. Castleman, Adv. At. Mol. Phys. 20 (1985) 65.

[6] T.D. Mark, Int. J. Mass Spectrom. Ion Processes 79 (1987) 1.

[7] A.W. Castleman, Int. J. Mass Spectrom. Ion Processes 118/119 (1992) 167.

[8] O. Echt, K. Sattler, E. Recknagel, Phys. Rev. Lett. 47 (1981) 1121.

[9] O. Echt, A.R. Flotte, M. Knapp, K. Sattler, E. Recknagel, Ber. Bunsenges. Phys. Chem. 86 (1982) 860.

[10] J. Muhlbach, K. Sattler, P. Pfau, E. Recknagel, Phys. Lett. A 87 (1982) 415.

[11] T.M. Barlak, J.E. Campana, R.J. Colton, J.J. DeCorpo, J.R. Wyatt, J. Phys. Chem. 85 (1981) 3840.

[12] T.M. Barlak, J.R. Wyatt, R.J. Colton, J.J. DeCorpo, J.E. Campana, J. Am. Chem. Soc. 104 (1982) 1212.

[13] L. Friedman, R.J. Beuhler, J. Chem. Phys. 78 (1983) 4669.

[14] M.Y. Hahn, E.C. Honea, A.J. Pauguia, K.E. Schriver, A.M. Camarena, R.L. Whetten, Chem. Phys. Lett. 130 (1986) 12.

[15] C. Lifshitz, F. Louage, J. Phys. Chem. 93 (1989) 5633.

[16] M.T. Coolbaugh, J.F. Garvey, Chem. Soc. Rev. (1992) 163.

[17] W.D. Knight, K. Clemenger, W.A. Deheer, W.A. Saunders, M.Y. Chou, M.L. Cohen, Phys. Rev. Lett. 52 (1984) 2141.

[18] W.A. Deheer, W.D. Knight, M.Y. Chou, M.L. Cohen, Solid State Phys., Adv. Res. Appl. 40 (1987) 93.

[19] J.F. Garvey, W.J. Herron, G. Vaidyanathan, Chem. Rev. 94 (1994) 1999.

[20] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.

[21] H.W. Kroto, Science 242 (1988) 1139.

[22] R.F. Curl, R.E. Smalley, Science 242 (1988) 1017.

[23] R.E. Smalley, Sciences-New York 31 (1991) 22.

[24] S. Wei, B.C. Guo, J. Purnell, S. Buzza, A.W.J. Castleman, Phys. Chem. 96 (1992) 4166.

[25] B.C. Guo, K.P. Kerns, A.W. Castleman, Science 255 (1992) 1411.

[26] H. Haberland, in Springer Series in Chemical Physics, J.P. Toennies (Ed.), Springer-Verlag, Berlin, 1994, Vol. 52.

[27] A.S. Stamatovic, T.D. Mark, Rapid Commun. Mass Spectrom. 5 (1991) 51.

[28] T.D. Mark, Adv. Mass Spectrom. 13 (1995) 71.

[29] R.G. Cooks, G. Chen, P. Wong, H. Wollnik, in Encyclopedia of Applied Physics, VCH, New York, 1997, Vol. 19, p. 289.

[30] F. Honda, G.M. Lancaster, Y. Fukuda, J.W. Rabalais, Int. J. Mass Spectrom. Ion Phys. 32 (1978) 363.

[31] J.E. Campana, B.N. Green, Int. J. Mass Spectrom. Ion Processes 55 (1984) 281.

[32] B.J. Finlayson-Pitts, Res. Chem. Intermed. 19 (1993) 235.

[33] K.W. Oum, M.J. Lakin, D.O. DeHaan, T. Brauers, B.J. Finlayson-Pitts, Science 279 (1998) 74.

[34] T.P. Martin, J. Chem. Phys. 76 (1982) 5467.

[35] X. Li, R.L. Whetten, Chem. Phys. Lett. 196 (1992) 535.

[36] K. Sattler, J. Muhlbach, O. Echt, P. Pfau, E. Recknagel, Phys. Rev. Lett. 47 (1981) 160.

[37] J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong, C.M. Whitehouse, Science 246 (1989) 64.

[38] D.R. Zook, E.P. Grimsrud, J. Am. Soc. Mass Spectrom. 2 (1991) 232.

[39] S.L. Zhou, M. Hamburger, Rapid Commun. Mass Spectrom. 10 (1996) 797.

[40] D.W. Ledman, R.O. Fox, J. Am. Soc. Mass Spectrom. 8 (1997) 1158.

[41] V.Q. Nguyen, X.G. Chen, A.L. Yergey, J. Am. Soc. Mass Spectrom. 8 (1997) 1175.

[42] G. Wang, R.B. Cole, Anal. Chem. 70 (1998) 873.

[43] S.W. Lee, P. Freivogel, T. Schindler, J.L. Beauchamp, J. Am. Chem. Soc. 120 (1998) 11 758.

[44] S.E. Rodriguez-Cruz, J.S. Klassen, E.R. Williams, J. Am. Soc. Mass Spectrom. 8 (1997) 565.

[45] P. Kebarle, L. Tang, Anal. Chem. 65 (1993) A972.

[46] D.R. Zook, A.P. Bruins, Int. J. Mass Spectrom. Ion Processes 162 (1997) 129.

[47] M. Gamero-Castano, J.F. de La Mora, personal communication (1999).

[48] R.G. Cooks, A.L. Rockwood, Rapid Commun. Mass Spectrom. 5 (1991) 93.

[49] O. Echt, T.D. Mark, in Clusters of Atoms and Molecules, H. Haberland (Ed.), Springer-Verlag, Berlin, 1994, Vol. 52, p. 267.

[50] O. Echt, T.D. Mark, in Clusters of Atoms and Molecules II, H. Haberland (Ed.), Springer-Verlag, Berlin, 1994, Vol. 56, p. 183.

[51] M. Guilhaus, A.G. Brenton, J.H. Beynon, M. Rabrenovic, P.V. Schleyer, J. Phys. B 17 (1984) L605.

[52] O. Echt, K. Sattler, E. Recknagel, Phys. Lett. A 90 (1982) 185.

[53] N.F. Dalleska, K. Honma, P.B. Armentrout, J. Am. Chem. Soc. 115 (1993) 12 125.

[54] S. Goebel, C.L. Haynes, F.A. Khan, P.B. Armentrout, J. Am. Chem. Soc. 117 (1995) 6994.

[55] M.B. Sowaresat, P.A. Hintz, S.L. Anderson, J. Phys. Chem. 99 (1995) 10 736.

[56] R.B. Huang, Z.Y. Liu, H.F. Liu, L.H. Chen, Q. Zhang, C.R. Wang, L.S. Zheng, F.Y. Liu, S.Q. Yu, X.X. Ma, Int. J. Mass Spectrom. Ion Processes 151 (1995) 55.

[57] H.T. Deng, K.P. Kerns, A.W. Castleman, J. Phys. Chem. 100 (1996) 13 386.

[58] K.P. Kerns, B.C. Guo, H.T. Deng, A.W. Castleman, J. Phys. Chem. 100 (1996) 16 817.

[59] S. Kruckeberg, G. Dietrich, K. Lutzenkirchen, L. Schweikhard, C. Walther, J. Ziegler, Int. J. Mass Spectrom. Ion Processes 155 (1996) 141.

[60] J.M. Lisy, Int. Rev. Phys. Chem. 16 (1997) 267.

[61] D.X. Zhang, L.A. Gill, R.G. Cooks, J. Am. Soc. Mass Spectrom. 9 (1998) 1146.

[62] T.M. Barlak, J.E. Campana, J.R. Wyatt, R.J. Colton, J. Phys. Chem. 87 (1983) 3441.

[63] B.I. Dunlap, J.E. Campana, Org. Mass Spectrom. 21 (1986) 221.

[64] A. Aguado, A. Ayuela, J.M. Lopez, J.A. Alonso, Phys. Rev. B: Condens. Matter Mater. Phys. 58 (1998) 9972.

[65] R.R. Hudgins, P. Dugourd, J.M. Tenennbaum, M.F. Jarrod, Phys. Rev. Lett. 78 (1997) 4213.