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Alkali halide cluster dianions: metastability and threshold sizes

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Abstract. Singly and multiply charged salt clusters ($M_nX_{n\pm m}^{\pm m}$; MX = alkali halide) can be generated simply by spraying saline solutions, with or without electrical (charging) field. Dianion species ($m = 2$) show a clear threshold size at $n = 5-7$ (range) for all elements beyond the first row. These sizes ($12-16$ atoms) are much smaller than previously observed for alkali halides and are among the smallest cluster dianions yet found in gas phase. We describe the experiment and discuss the onsets in terms of ab initio density functional calculations on a number of representative sodium chloride cluster mono- and dianions.

PACS. 36.40.Qv Stability and fragmentation of clusters

1 Introduction

A long standing question in chemical physics concerns the smallest molecular entity to bind two – or more – excess electrons. Theoretical work has shown that such species may well be meta-stable with significant barriers, for example with respect to monoanion or electron loss along the repulsive coulomb potential [1]. Then one must more accurately ask what are the smallest multi-ply charged species to be: (i) thermodynamically stable relative to all possible decay channels or alternatively (ii) to have metastable lifetimes greater than the experimental time scale. Clearly, the requisite sizes will be a function of the types of molecules under consideration. Questions (i) and (ii) may also be formulated in terms of a specific cluster family – preferably clusters for which there are only minor size dependent variations in electronic structure and bonding. This is the subject of the present communication.

At this writing C_7^{2-} is the smallest dianion to have been unequivocally observed in gas-phase (with lifetime $> 10^{-5}$ s) [2]. There are reliable reports of other dianions from about eight atoms on up, e.g. $S_2O_6^{2-}$ [3]. Theory predicts significantly smaller long lived dianions in a whole range of chemical systems [1, 4, 5]. Particularly well studied have been alkali halide clusters due in part to their comparative computational tractability [6]. Calculations on free MX_m^{q-} (M = Li,Na,K; X = F,Cl; $m = 1-3$ and $q = 0-2$) have uncovered the so far smallest metastable dianion predicted to be measurable in a mass spectrometer: ionically bound MX_3^{2-} [6, 7]. Depending on the computational level, LiF_3^{2-} – as a typical example – is unstable by about 260 kJ mol^{-1} relative to $LiF_2^- + F^-$ but is prevented from dissociating by a barrier of about 15 kJ mol^{-1}. No MX_3^{2-} (MX = alkali halide) has yet been observed experimentally.

Significantly larger alkali halide cluster dianions $M_xX_{x+2}^{2-}$ have occasionally been reported in the electrospray ionization (ESI) mass spectroscopy literature [8, 9]. The recent observation of a wide series of $Cs_nI_{n+m}^{m-}$ ($m = 1-4$) polyanions obtained upon ESI of CsI solutions in CH_3CN is so far the most comprehensive [9]. While the authors of the latter study noted lower limits under their conditions for the observation of specific charge states ($Cs_{13}I_{15}^{2-}$; $Cs_{28}I_{31}^{3-}$ and $Cs_{63}I_{67}^{4-}$), they were primarily interested in these species from the point of view of mass calibration. In conjunction with the construction of a new electrospray source – time of flight mass spectrometer (ESI-TOFMS) we have attempted to assess the utility of ESI for systematic studies of alkali halide cluster polyanions and report preliminary experimental results on (lower) dianion thresholds for a variety of salts together with density functional calculations on several representative sodium chloride dianion species.

2 Experimental

Experiments were performed using a linear electrospray time-of-flight mass spectrometer (ESI-TOFMS), which will be described in more detail in a future publication [10]. Briefly, this instrument consists of an Analytica of Branford Model 104169 ESI source and a perpendicularly oriented 2.1 m drift tube Wiley-McLaren type TOFMS. The ESI source comprises an atmospheric pressure spray region. Ions are sampled through a capillary opening into a first differentially pumped chamber (1 mbar). This is followed by a skimmer into a second stage of differential pumping (10^{-1}–10^{-2} mbar) which contains a hexapole ion guide. The latter extends into stage 3 (2×10^{-4} mbar)

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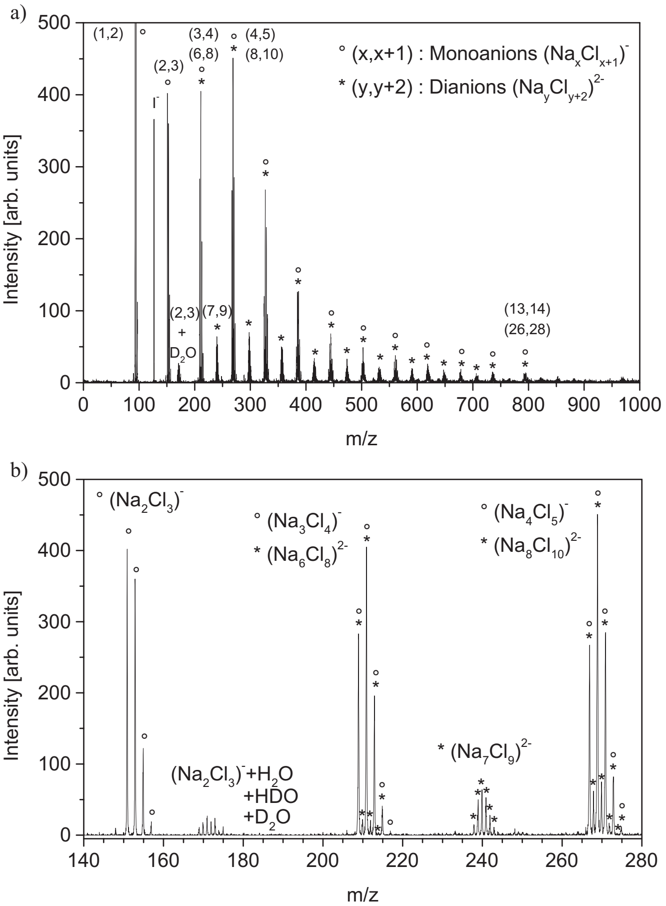

Fig. 1. Negative ion ESI-TOF mass spectrum obtained upon electrospraying a 0.04 M NaCl in D_2O solution. (a) shows the complete mass spectrum. Note the presence of a series of monoanion ($Na_xCl^-_{x+1}$) and dianion ($Na_yCl^{2-}_{y+2}$) signals. (b) highlights the dianion onset region. Note that the lightest resolvable dianion in this system is $Na_6Cl_8^{2-}$ [11].

from which ions exit through a 3 mm opening into the detector chamber (stage 4 (10^{-6} mbar)). The overall needle to TOFMS centre-line distance was ∼ 40 cm. The corresponding integral transit time is highly dependent on source parameters and difficult to quantify. Typical transit times of ions through the collisionless stages 3 and 4 were on the order of 30–50 μs. Ions were pulse extracted from the primary (ESI) beam at repetition rates > 1000 Hz, yielding > 2% duty cycle. Typical extraction voltages for repeller and extractor were −8 and − 7.7 kV, respectively. Ions were detected with an MCP detector and signals were processed with a fast multichannel scaler.

We studied alkali halide solutions in H_2O (bidistilled) or in the case of NaCl also D_2O (99.9%). Alkali halides were from commercial sources. Typical salt concentrations were 0.04 M except for the seawater sample (Mediterranean, ca. 0.5 M in NaCl). Solutions were delivered to the ESI needle by a syringe pump at flow rates of about 2 ml/h. Two types of measurement were performed: (i) "electrospray" – the ESI needle (grounded) was positioned slightly off axis, approximately 2 cm from the 600-μm diameter, 24-cm length dielectric capillary orifice (front end: 1100 V; vacuum side: −150 V) and (ii) "spray" – ESI needle (grounded) either on-axis or only slightly off-axis, 0.5–2 cm from the capillary (front and back grounded; no other applied potentials in the atmospheric pressure region). Room temperature N_2 was used for desolvation and shroud gas in both types of measurement.

Table 1. Onset sizes for $M_nX^{2-}_{n+2}$ dianion formation[a].

	Li	Na	K	Rb	Cs
F	(15,17)	?[b]	(8,10) $\cdot 5H_2O$	(6,8) $\cdot 6H_2O$	(6,8) $\cdot 7H_2O$
Cl	(9,11)	(6,8)	(6,8)	(6,8)	(6,8)
Br	(11,13)	(6,8)	(6,8)	(6,8)	(5,7)
I	(10,12)	(7,9)	(6,8)	(5,7)	(5,7)

[a] Plotted are $(n, n+2)$ values corresponding to the lightest dianion species unequivocally identified above the noise (or over contaminants) in each MX system. The corresponding experiments were carried out at sensitivities and mass resolutions comparable to Fig. 1.

[b] Doubly charged species could not be clearly identified due to a dense spectrum of singly charged solvent adducts and undetermined contaminants.

3 Results

(a) Experimental observations

A typical ESI-TOFMS mass spectrum of anions obtained upon electrospraying a sodium chloride solution in D_2O is shown in Fig. 1. Electrospray conditions have been chosen to optimize dianion cluster formation while at the same time minimizing solvent adducts. Note the presence of a dominant series of $Na_nCl^-_{n+1}$ and $Na_nCl^{2-}_{n+2}$ peaks. The latter commences at a threshold size of $Na_6Cl_8^{2-}$ which can be distinguished from $Na_3Cl_4^-$ on the basis of the isotopic structure [11]. Beyond threshold, the intensity of $M_nX^{2-}_{n+2}$ is comparable to or even larger than that of $M_nX^-_{n+1}$ (same n). We have observed similar behavior for a wide variety of alkali halides electrosprayed from H_2O solutions (M = Na, K, Rb, Cs; X = Cl, Br, I). Table 1 provides a summary of the observed threshold sizes for dianions. For heavier, (more polarisable) atoms we see onsets at $M_5X_7^{2-}$ rather than $M_6X_8^{2-}$. Lithium salts appear uncharacteristic in that onsets are shifted to larger cluster sizes. Fluoride thresholds are also uncharacteristic in that it was not possible to completely desolvate the smallest dianions. While they appear lower than previously reported [9] we have not yet attempted to systematically determine threshold sizes for trianion species in this study. Similarly, while singly and multiply charged cationic clusters ($M_nX^{m+}_{n-m}$) can also be readily generated by the same procedure, we have not been concerned with them here. Interestingly, (smaller amounts of) cluster mono- and dianions were also formed under

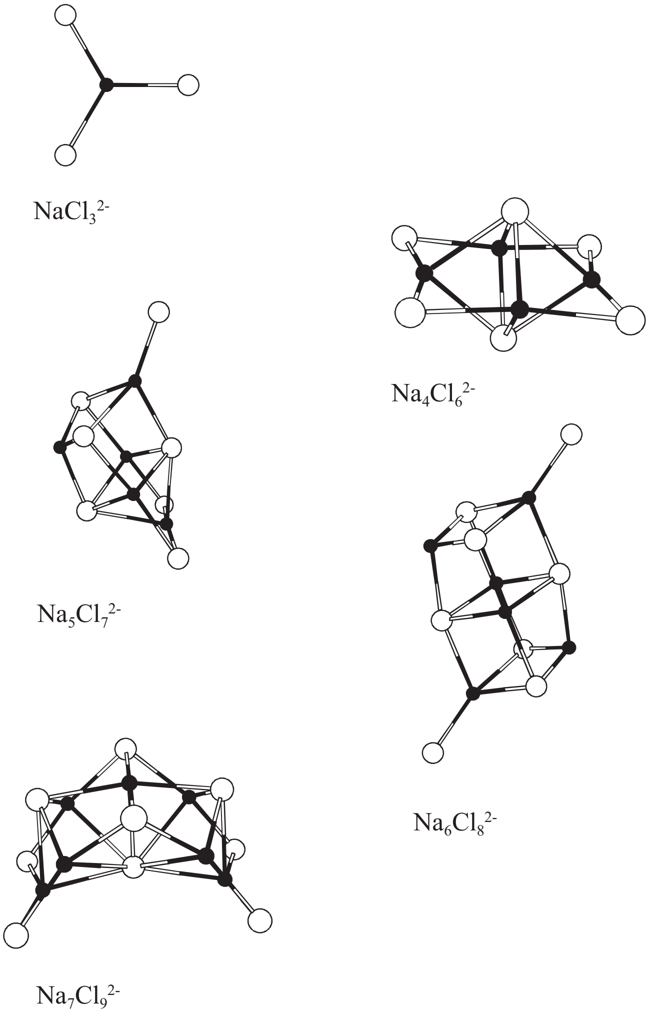

Fig. 2. Optimum structures determined by DFT calculations for a variety of $Na_nCl_{n+2}^{2-}$ (see text for details).

"spray" conditions, without electric fields applied in the atmospheric pressure region. In particular, spraying seawater in this fashion also readily generates charged salt clusters. This may have environmental implications.

(b) Theory

Density functional and ab initio-SCF calculations were performed on a number of ionic mono- and dianions in the sodium-chloride system (see Fig. 2 and Table 2). This halide system was chosen to provide an optimum of minimal computational effort and maximal experimental generality. All calculations were performed with the TURBOMOLE package [12] and will be reported in more detail elsewhere [10]. For both chlorine and sodium we used the "TZVPP" basis set implemented in the package. This consists of a $(14s9p2d1f)/[5s4p2d1f]$ basis on chlorine and a $(14s8p1d)/[5s4p1d]$ basis on sodium. For $NaCl_3^{2-}$ and $NaCl_2^-$ we performed calculations at the Hartree-Fock, DFT-BP, and MP2 level. The resulting minimum geometries agree to within 0.05 Å, the reaction energies (for $NaCl_2^- + Cl^- \rightarrow NaCl_3^{2-}$) to within 5% (+169/+173/+166 kJ/mol respectively). Therefore all the larger clusters were calculated at the density functional level with the Becke–Perdew (BP) parameterization [13]. All the structures presented here represent local minima, i.e. all their vibrational frequencies are non-imaginary.

Table 2. Computed dissociation energies for $Na_nCl_{n+2}^{2-}$ [a].

	Cl^--loss	$NaCl_2^-$-loss	$Na_2Cl_3^-$-loss	$Na_3Cl_4^-$-loss
$NaCl_3^{2-}$	−173.3	−173.3		
$Na_4Cl_6^{2-}$	−49.5	−81.8	−28.2	−81.8
$Na_5Cl_7^{2-}$	−32.9	−102.4	−60.0	−60.0
$Na_6Cl_8^{2-}$	7.7	−82.2	−77.0	−88.2
$Na_7Cl_9^{2-}$	−7.3	1.5	−13.7	−62.1

[a] All energies are in kJ mol^{-1}. They were obtained as the difference of DFT total energies (BP parameterization, triple zeta + polarization basis set) corresponding to parent dianion and fragment sum, respectively. Zero point energies were not taken into account. Negative energies mean that the respective dianions are thermodynamically unstable with respect to fragmentation. Note however that all species are metastable towards fragmentation due to a large barrier (often > 100 kJ mol^{-1} [10]).

Structures, Monoanions: The optimum structures for all $Na_nCl_{n+1}^-$ $(n \leq 7)$ were determined. $NaCl_2^-$ and $Na_2Cl_3^-$ are linear, $Na_3Cl_4^-$ represents a 2 × 2 × 2 cube with one Na^+ vacancy, it has C_{3v} symmetry. The lowest energy structure for $Na_4Cl_5^-$ is a square pyramid with the sodium atoms on top of the triangular faces (C_{4v} symmetry), $Na_5Cl_6^-$ and $Na_6Cl_7^-$ can be derived from a 2 × 2 × 3 cuboid by removing one Na^+ or adding one Cl^- ion respectively.

Dianions: We investigated the structures and energies of all $Na_nCl_{n+2}^{2-}$ $(n = 1, 4-7)$. $NaCl_3^{2-}$ is planar with D_{3h} symmetry, in agreement with the structure proposed by Cederbaum [6]. The structure of $Na_4Cl_6^{2-}$ is a square bipyramid (D_{4h}) while $Na_5Cl_7^{2-}$ can be derived from a 2 × 2 × 3 cuboid by adding a Cl^- ion on one corner and removing a Na^+ on the opposite corner, see Fig. 2. For $Na_6Cl_8^{2-}$ the optimum structure is that of a 2 × 2 × 3 cuboid with two Cl^- ions attached on opposite corners. Note that another isomer with O_h symmetry is 26 kJ mol^{-1} higher in energy. The minimum structure for $Na_7Cl_9^{2-}$ has C_{2v} symmetry, see Fig. 2. An isomer derived from a 2 × 2 × 4 cuboid is only 6.3 kJ mol^{-1} higher in energy.

Energetics: For the dianions studied, we calculated reaction energies (ΔE_e, i.e. at 0 K without zero point vibrations) for all fragmentation channels leading to two monoanions:

$$Na_nCl_{n+2}^{2-} \rightarrow Na_{n-y}Cl_{n-y+1}^- + Na_yCl_{y+1}^- \; (0 \leq y \leq n)$$

The results are summarized in Table 2. Except for $Na_6Cl_8^{2-}$ (stable against Cl^- loss) and $Na_7Cl_9^{2-}$ (stable against $NaCl_2^-$ loss), all dianions investigated were found to be energetically unstable with respect to all monoanion pair dissociation channels. Note however that even the energetically least favorable dianion, $NaCl_3^{2-}$, shows a significant barrier of more than 15 kJ/mol against Cl^- loss and that preliminary calculations for the larger systems show comparable barriers to fragmentation that are in the range of 100 kJ/mol [10].

4 Discussion

The thrust of previous experimental work has been to make large alkali halide cluster anions and cations for mass calibration over a wide m/z range [8, 9]. From this point of view the aqueous solutions used in this study were previously judged to be deleterious, with CH_3CN/CH_3OH mixtures instead preferred [8]. It is ironic that in electrospraying aqueous solutions it has now been possible to significantly lower the experimental threshold size for alkali halide cluster dianion detection. In fact at 12 atoms, $M_5X_7^{2-}$ (MX = RbI, CsBr and CsI) are among the smallest dianions yet observed in any cluster system except carbon [1].

Detected dianion threshold sizes are of course a function of chemical system, ESI source conditions and detector configuration/sensitivity. We make no claim to have detected the smallest dianion possible, which in this system appears to be metastable MX_3^{2-} based on calculations [6, 7]. The high experimental mass resolution obtained provides a (lower) lifetime limit of about 1 μs for the dianion species detected here (significantly shorter lifetimes towards electron loss or fragmentation would become comparable with the TOFMS extraction time scale, thus leading to peak broadening).

It is interesting that the onset size for dianions is typically in the range of $M_6X_8^{2-}$, **independent** of M and X (excepting Li and F). The extensive literature on ionically bound stoichiometric alkali halide cluster cations and (mono)anions suggests that global cluster size dependent trends in structure and (scaled) energetics do not depend strongly on M or X (again excepting Li and F) [14]. This suggests that there may be an alkali halide specific rather than purely instrumental explanation for the dianion thresholds observed.

Our calculations for $Na_6Cl_8^{2-}$ show it to be metastable towards $NaCl_2^-$, $Na_2Cl_3^-$ and $Na_3Cl_4^-$ loss, respectively. Consequently, the dianion onset cannot be explained purely in terms of thermodynamic stability [15]. $Na_6Cl_8^{2-}$ is however the smallest dianion species to be (barely) bound with respect to Cl^- loss. Note that for several MX sprayed from CH_3CN solutions we observe a local abundance minimum at $M_{13}X_{15}^{2-}$ ($3 \times 3 \times 3$ cube + X^-) which among dianions likely reflects a local stability minimum with respect to X^- loss [10, 14]. In future experimental work on these systems it will be of interest to test the generality of such a relaxation channel.

From the computational point of view one would like to know the relative heights of barriers to X^- loss vs. molecular anion scission. Note that all such barriers will be strongly influenced by the mediating role of water molecules which must be present as the atomic ions settle into their final positions in the "drying" ESI droplet. It will therefore be of particular interest to study the computational dynamics of $M_5X_7^{2-}/M_6X_8^{2-}$ and their (partially) solvated congeners.

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11. The singly spaced peak multiplet commencing at $m/z = 169$ is not a doubly charged species but instead corresponds to a superposition of $Na_2Cl_3^- \cdot H_2O$, $Na_2Cl_3^- \cdot HDO$ and $Na_2Cl_3^- \cdot D_2O$ – as an experiment with H_2O solution shows. This is the only water adduct observed. The H_2O/HDO contamination likely originates from the N_2 desolvation gas and from surfaces previously exposed to H_2O
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15. Of course for large enough n, there will be $M_nX_{n+2}^{2-}$ isomers more stable than any possible fragment pair. However, preliminary calculations suggest that this occurs beyond the size range of interest here