Metallization of Ionic Clusters

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The energetics and structure of multiple excess electrons in halogen-deficient Na_nF_m clusters are studied starting at the stochiometric ionic limit Na_nF_n and ending with pure metallic clusters Na_n (for $n=4,3,2$ and partially for $n=14$). The results exhibit structural transitions upon metallization, odd-even oscillations in $n-m$ and possibly shell-closing effects portrayed in formation and ionization energies, and excess-metal face segregation for the larger system.

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Recent theoretical and experimental studies provided significant information pertaining to single-excess-electron localization modes, dynamics, and spectroscopy in polar molecular (water and ammonia) [1], rare-gas (Xe) [2], and ionic (alkali-halide) [3] clusters. The extension to alkali-halide clusters containing *multiple excess electrons* (i.e., those electrons which substitute F^- anions in Na_nF_m, $m<n$) opens a new dimension for investigations of excess-electron localization and bonding in clusters since the process of "metallization" of an initially stoichiometric ionic cluster (i.e., starting from an ionic cluster with $n=m$, and successively substituting anions by electrons, ultimately resulting in a neutral metallic cluster Na_n) may portray a transition from an insulating to a metallic state in a finite system. In this context we note that while transitions from *F*-center to metallic behavior have been observed in bulk molten alkali halides at high excess-metal concentrations [4], experimental data on metal-rich alkali-halide clusters are preliminary in nature [5].

Our investigations reveal systematic trends of the metallization process in small clusters, exhibiting a structural and energetic substitutional nature of excess electrons in halogen-anion-deficient alkali-halide clusters, structural transitions (which can involve a change in dimensionality) upon reaching the metallization limit, electronic structure odd-even and shell-closing effects portrayed in formation energies and ionization potentials, and layer metallization (i.e., segregation of the excess metallic component on a face of the cluster) in an intermediate-size cluster ($Na_{14}F_9$).

The technique which we have developed [6] combines classical molecular dynamics and energy minimization on the electronic Born-Oppenheimer potential energy surface with electronic structure calculations via the local spin-density-functional method. For the purpose of this study the capability to explore the dynamical evolution of the system is not exploited, except in searching for the optimal (minimum energy) nuclear configurations. In our simulations the interionic interactions are described by the Born and Huang parametrized potentials [7] which we have tested in previous studies [3(b)], the interaction between the electrons and Na^+ is given by the $l=0$ term of the Hamann-Schluter-Chiang norm-conserving pseudopotential [8], and a Coulomb repulsive potential describes the interaction between the electrons and F^-. The local spin-dependent exchange-correlation is described via the interpolation formula of Vosko and Wilk [9]. All electronic structure calculations are performed on 32^3 grids, with a grid spacing of $1.0a_0$ (we have verified that this choice provides an accurate description of the spatial electronic distribution).

We begin with metallization sequences (MS's) of small clusters: Na_4F_m ($0\le m\le 4$), which for $m=4$ is a stable ionic cuboid and at the other extreme ($m=0$) is a stable planar rhombohedral Na_4 cluster [6] [see Figs. 1(a)-1(e)]; Na_3F_m ($0\le m\le 3$), which for $m=3$ is a two-dimensional hexagonal ring and when fully metallized (Na_3, i.e., $m=0$) is an isosceles triangle [6] [see Figs. 1(f)-1(i)]; Na_2F_m ($0\le m\le 2$), which for $m=2$ and 1 has a two-dimensional rhombus structure, converting to a linear diatomic Na_2 ($m=0$). The structures exhibited by these MS's, as well as by the MS's of ionic species [see Figs. 1(j)-1(p)], demonstrate a systematic trend: Structures of neutral (and charged) small clusters belonging to a MS are of the same dimensionality and symmetry of the corresponding parent cluster [e.g., cuboids in the case of Na_3F_m and $Na_4F_m{}^+$ ($1\le m\le 4$ and $1\le m\le 3$, respectively), 2D hexagonal rings for Na_3F_m ($1<m\le 3$), and linear chains for $Na_3F_m{}^+$ ($1\le m\le 2$)], converting to the structure of the corresponding metal cluster upon complete metallization ($m=0$). Furthermore, the excess electrons in these clusters, substituting for halide anions, maintain the cohesion and structural integrity of the clusters and their distributions exhibit a delocalized, metallic character (with the regions occupied by the remaining anions, i.e., for $0<m<n$, excluded).

The MS for a larger cluster $Na_{14}F_m$ ($9\le m\le 14$), whose $Na_{14}F_{13}$ member is a particularly stable cluster [$Na_{14}F_{13}{}^+$ is a "magic number" ionic cluster [3(a)-3(c)], i.e., a $3\times3\times3$ filled cuboid structure, with three ions of alternating charges on an edge] exhibits another novel result: face (or atomic layer) metallization (segregation), as seen in Fig. 2(a). The *optimal metallization sequence* of this cluster proceeds via *successive removal of neighboring halogens* from *one face* of the cluster, re-

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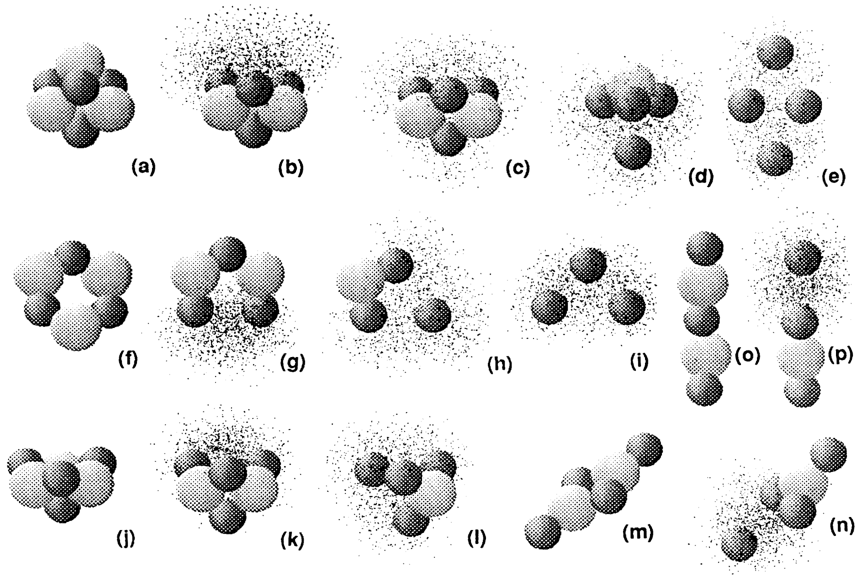

FIG. 1. Optimal structures of Na_nF_m clusters. Large light and smaller dark spheres denote F^- and Na^+, respectively, and the small dots represent the total excess-electronic distribution. The metallization sequence (MS) for Na_4F_m $(0 \le m \le 4)$ is shown in (a)-(e); Na_3F_m $(0 \le m \le 3)$ in (f)-(i); $Na_4F_m{}^+$ $(1 \le m \le 3)$ in (j)-(l), $Na_4{}^+$ is a two-dimensional rhombus [6]; $Na_4F_m{}^{++}$ $(1 \le m \le 2)$ in (m) and (n), $Na_4{}^{++}$ fragments spontaneously [6]; and $Na_3F_m{}^+$ $(1 \le m \le 2)$ in (o) and (p), $Na_3{}^+$ is an equilateral triangle [6]. Note the substitutional nature of the excess electrons and the structural transition upon complete metallization in each of the MS's.

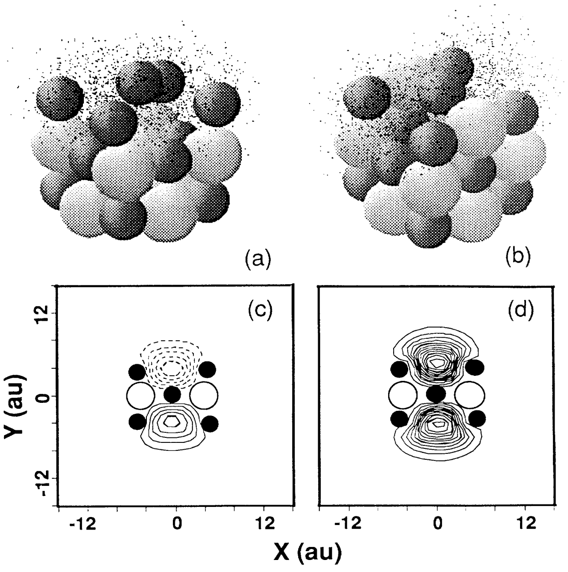

FIG. 2. (a) Structure of $Na_{14}F_9$, exhibiting a metallized (segregated) layer with the five sodium atoms (dark spheres) forming a rectangular pyramid. (b) Structure of an isomer of $Na_{14}F_{11}$, with F atoms removed from opposite edges of a face. (c),(d) Contours of spin-polarization density distribution for $Na_{14}F_{11}{}^+$ and the $Na_{14}F_{11}$ isomer [see (b)], demonstrating a transition from a delocalized [in (d)] to a spin-paired localized [in (c)] distribution. Solid and dashed lines correspond to positive and negative values, respectively. Solid and empty circles denote the positions of Na^+ ions and F^- ions in the top face of the cluster.

sulting (for $Na_{14}F_9$) in a segregated metal layer. These results suggest further structural and electronic (binding, spectra, and collective excitations) studies of larger clusters and of alkali-metal overlayer(s) on alkali-halide substrates.

Inspection of the energetics of these systems, displayed in Table I for the neutrals, reveals several trends.

(i) The interionic interactions (E_I) and the excess electrons' interactions with the ion cores (given, per electron, by u_e in Table I) constitute the major contribution to the total energy. Note that for highly metallized clusters in a given MS, E_I increases with increasing metal concentration [becoming repulsive for Na_n $(n > 1)$ and for Na_4F] while binding due to u_e increases.

(ii) The combined contribution of the Hartree $(e_H > 0)$ and exchange-correlation $(e_{xc} < 0)$ energies is repulsive (i.e., positive), slowly increasing with the number of excess electrons in a MS. Note the small values for $e_{xc}+e_H$ for the one-electron systems $(Na_nF_{n-1}, n = 14,4,3,2)$, indicating rather small self-interaction corrections in these systems.

(iii) The electron kinetic energy $e_k \sim 2$ eV [the low value for $Na_{14}F_{13}$ corresponds to a diffuse, weakly bound state [3(a),3(b)]; see Table I].

(iv) The F-center formation energies (E_f) (i.e., the difference between the total energies of Na_nF_{m-1} and Na_nF_m) are between 2.3 to 3.3 eV. It is of interest that within a MS the formation energies exhibit odd-even oscillations in $n-m$ (although the effect is small for the

TABLE I. Energetics of Na_nF_m clusters (in eV). The total energy of the clusters is given by $E_t = E_I + (n-m)e_e$, where E_I is the total interionic interaction and e_e is the electronic energy per electron; $e_e = u_e + e_{xc} + e_H + e_k$, where the terms on the right are the (per-electron) electron-ion, exchange-correlation, Hartree, and electron kinetic-energy contributions. vIP and aIP are the first vertical and adiabatic ionization potentials, E_f is the formation energy $E_f = E_t(Na_nF_{m-1}) - E_t(Na_nF_m)$, and μ is the magnitude of the total permanent dipole (in a.u. =2.5242 D). For $Na_{14}F_{12}$, results for two isomers are given [the one denoted by (i) corresponds to an internal biopolaron]. The energies (E_I) of the stoichiometric clusters Na_nF_n are −15.94, −25.05, −34.26, and −125.70 eV for n=2, 3, 4, and 14.

n	m	E_I	u_e	$e_{xc}+e_H$	e_k	e_e	vIP	aIP	E_f	μ
4	3	−26.59	−6.27	−0.011	1.89	−4.39	4.39	3.47	3.27	0.94
4	2	−13.63	−11.57	2.39	1.80	−7.38	4.59	4.22	2.61	1.02
4	1	3.28	−15.79	4.15	2.01	−9.63	3.97	3.84	2.78	0.30
4	0	24.76	−20.26	4.95	2.11	−12.01	4.40	4.38	2.32	0.0
3	2	−16.78	−7.34	0.039	2.15	−5.15	5.15	3.55	3.12	0.08
3	1	−3.21	−12.74	2.61	1.91	−8.22	5.30	4.40	2.28	0.59
3	0	12.98	−16.32	4.27	2.03	−10.03	4.26	4.08	2.57	0.0
2	1	−9.06	−5.67	−0.17	1.70	−4.14	4.14	3.72	2.73	0.07
2	0	4.91	−12.52	2.55	1.80	−8.16	5.26	5.15	1.79	0.0
14	13	−120.51	−2.76	0.21	0.87	−2.16	2.16	2.07	3.03	4.20
14	12	−106.85	−10.83	2.53	1.89	−6.41	3.42	2.82	3.00	4.89
14	11	−91.03	−14.57	4.01	2.04	−8.51	3.17	2.85	3.10	4.42
14	10	−71.34	−18.30	5.64	2.09	−10.58	3.68	3.32	2.99	3.69
14	9	−47.68	−22.15	7.42	2.13	−12.60	3.60	3.22	2.99	4.00
14	12(i)	−103.84	−13.47	3.25	2.53	−7.47	3.86	2.38	3.89	0.0
5	0	38.19	−23.14	7.50	2.13	−13.51	4.33	4.11	···	0.0
1	0	···	−7.28	0.014	1.99	−5.26	5.26	···	···	0.0

$Na_{14}F_m$ sequence), indicating that perhaps these excess-metal systems may be regarded [5(a)] as composed of a "metallic" component and a molecular-ionic one, symbolically represented by $Na_nF_m \equiv Na_{n-m}(NaF)_m$. Comparison of the total electronic energy (e_e) for Na_{n-m} in a sequence with that of the corresponding bare metal (e.g., Na_4F_2 with Na_2, Na_4F with Na_3, etc.) allows an estimate of the perturbation due to the ionic component. In this context it is instructive to observe the systematic trends revealed when cross-correlating results for a given value of $n-m$ for Na_nF_m clusters in different MS's (i.e., different n).

(v) The first ionization potentials (vertical and adiabatic, vIP and aIP, respectively) of the clusters in each metallization sequence, $Na_{n-m}(NaF)_m$, are lower than the corresponding bare-metal (Na_{n-m}) values. For each of the MS's the IP's exhibit odd-even oscillations [10] in $n-m$ and possibly shell-closing effects [10]. Our results (structural and energetic) for the bare metal and mixed clusters are in good agreement with experimental data and previous calculations, when available [10,11].

(vi) The energetics of MS's of charged clusters $(Na_nF_m{}^+, 0 \leq m \leq n$; see Fig. 1) show similar trends to those exhibited by the corresponding neutral ones. For example, vIP is equal to 8.69, 9.06, and 8.40 eV and E_f=3.35, 2.40, and 2.86 eV, for $Na_4F_m{}^+$, m=2,1,0, respectively, and vIP is equal to 9.20 and 9.88 eV and E_f=3.12 and 2.28 eV for $Na_3F_m{}^+$, m=1,0.

(vii) For the MS of a larger cluster, $Na_{14}F_m$, a number of isomers are found, differing by the locations of the removed F^- anions. The data given in Table I correspond to the most stable ones, starting with $Na_{14}F_{13}$, where the excess electron forms a diffuse surface state localized on one of the faces of the cube [3(b)], and proceeding by removing successively *neighboring* F^- anions from *one face*, ultimately yielding a metallized (segregated) layer for $Na_{14}F_9$ [see Fig. 2(a)].

While a full discussion of the various isomers will be given elsewhere, we comment on the particular case of $Na_{14}F_{12}$ where in addition to the minimum-energy cluster [with the two excess electrons localized in a bipolaronic spin-paired state at the vacancy left by removing an edge (external) F^- anion] we give the results for the isomer, where the bipolaron is localized at the location of the internally removed F^-, whose total energy is larger by 0.89 eV than that of the external bipolaronic cluster. The formation of bipolarons in $Na_{14}X_{12}$ (X=F,Cl) clusters was inferred from abundance spectra [5(b)]. We note that while for $Na_{14}F_{12}{}^{++}$ the cluster containing an internal vacancy is somewhat more stable (E_t = −111.47 and −111.02 eV for $Na_{14}F_{12}{}^{++}$ containing internal and external F^- vacancy, respectively), the reverse is true for $Na_{14}F_{12}{}^+$ (not shown) and $Na_{14}F_{12}$. Thus the smaller interionic reorganization energy when an external F^- is replaced by the excess electrons underlies the stability of that structure. Additionally, the external bipolaronic cluster possesses a large permanent dipole (see Table I) and thus may be separated from the internal-bipolaronic isomer via deflection in an inhomogeneous electric field [10].

Finally, we exhibit in Fig. 2(b) an isomer of $Na_{14}F_{11}$, which differs from the most stable one (where the F^- anions are removed from neighboring edges on one face) by removal of anions from two opposite edges, and whose formation energy $E_f=3.47$ eV is larger than that of the lowest-energy isomer (3.10 eV, see Table I). The spin-polarization contours $[\rho_\uparrow(\mathbf{r})-\rho_\downarrow(\mathbf{r})]$ for the $Na_{14}F_{11}$ isomer, in the plane of the defective face, shown in Fig. 2(d), exhibit a *p*-like distribution with a *delocalization* (driven by on-site interelectronic repulsion) of the three excess electrons over the two F-vacant sites. In contrast, the distribution for the ionic isomer, $Na_{14}F_{11}{}^+$ ($E_f=3.78$ eV) shown in Fig. 2(c), corresponds to spin-paired electrons, *each localized* in one of the vacant sites [the ionic configuration is similar to that of the $Na_{14}F_{11}$ isomer, shown in Fig. 2(b)].

(viii) Metal-rich clusters possess permanent dipole moments, whose magnitudes reflect the diffuseness and symmetries of the excess electron distribution, as well as the structural organization of the ions.

To address issues pertaining to the evolution of a metallic state in our systems, it would be of interest to explore, in addition to structure and energetics, their spectroscopic and response characteristics. Most recently we have begun such studies by including in the Hamiltonian interactions with a static electric field (of strength 10^{-4}-10^{-3} a.u., to warrant response in the linear regime). The spherically averaged static electronic polarizabilities [10] calculated by us for Na_4F_m are 256, 316, 386, and 427 a.u., for $m=3$, 2, 1, and 0 demonstrating a monotonic increase towards the fully metallized state (calculated values for the Na_n clusters are 141, 223, and 365 a.u. for $n=1$, 2, and 3, respectively). These results together with the predicted ionization potentials and dipole moments (Table I) provide the impetus for experiments on these novel systems.

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