# Localization of an Excess Electron in Sodium Halide Clusters

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Measurements of abundances and electronic properties of neutral sodium halide clusters, $Na_nX_{n-1}$ ($n < 100$), demonstrate a remarkable range of excess-electron-dominated behavior. Clusters which can form a cubic lattice containing a single anion vacancy have the electron localized in the vacancy, stabilizing the cluster against fragmentation. For the singular values of $n$ which correspond to a filled cubic lattice, the electron is very weakly bound. A simple quantitative model of electron localization is proposed to account for the observed patterns of abundances and electron binding energies.

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The behavior of an excess electron interacting with a finite dielectric or insulator system is a problem of great current interest,[1,2] and is particularly suited to test new theoretical methods. For an excess electron in molecular clusters, there exist predictions of bulk or surface states[3] and a wide range of electron-dominated behavior influenced by the degree of electron localization.[4] In a recent Letter,[5] Landman, Scharf, and Jortner (LSJ) investigated the properties of an electron interacting with a cluster consisting of $n$ $Na^+$ and $m$ $Cl^-$ ions at finite temperatures. Several notable predictions appear in this and subsequent papers:[6] (i) An excess electron can localize in an internal $Cl^-$ anion vacancy, as in the case of an $F$-center defect in the bulk alkali halide crystal, but previously unsuspected for such small systems ($n$ of order 10); (ii) if the cluster has no favorable site in which the electron can localize, such as cubic $Na_{14}Cl_{13}$, the excess electron is very weakly bound in a cluster surface state; (iii) at finite temperature, a characteristic decay channel is that in which the electron neutralizes a $Na^+$ ion, leading to dissociation of the weakly interacting $Na$ atom
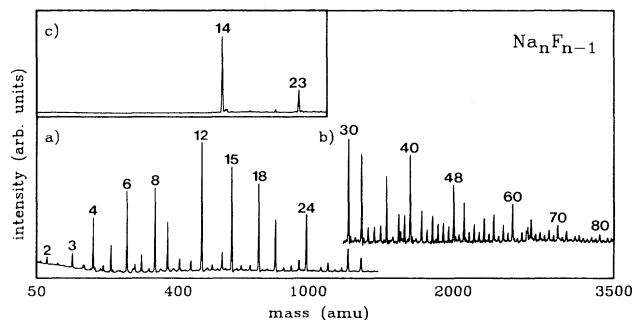
from the ionic lattice. In this Letter we describe the abundances and electronic properties of $Na_nF_{n-1}^+ \cdot e^-$ clusters, which display a remarkable range of properties determined by the excess electron. We find good agreement with the predictions above, as well as evidence of more general electron localization not foreseen in the simulations on a few cluster sizes.

Figures 1(a) and 1(b) show experimental abundances of neutral $Na_nF_{n-1}$ clusters ($n = 2$–80) in a supercooled cluster beam, measured by photoionization (5.0 eV radiation, ~2 mJ/cm$^2$) and displayed in the form of a mass spectrum. The cluster beam is formed by a Na-metal laser vaporization source of a type described previously,[7] with a small amount of a halogen containing molecule seeded in the helium carrier gas. Similar results are obtained over the energy range 5.0–5.6 eV, and for the systems $Na_nCl_{n-1}$, $Na_nBr_{n-1}$, and $Li_nF_{n-1}$ over a more limited range of $n$. In Fig. 2 the adiabatic electron binding energy (threshold photoionization energy measured with a tunable dye laser) is plotted versus cluster size ($n$) for the $Na_nF_{n-1}$ series to $n = 30$. Note that a stoichiometric $(NaF)_n$ cluster would be expected to have an electron binding energy close to 9 eV. The thresholds observed fall in three ranges, reflecting the behavior of
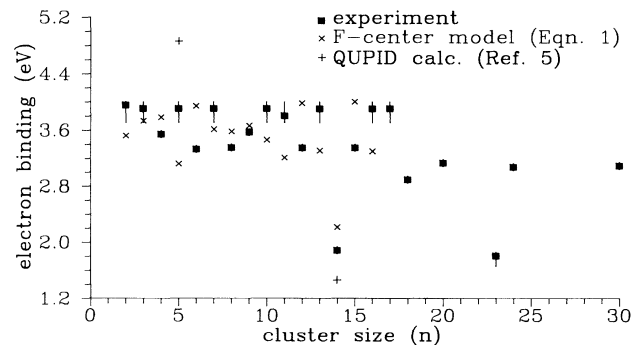


FIG. 1. Time-of-flight mass spectra of $Na_nF_{n-1}$ clusters detected by single-photon ionization. (a) Relative neutral cluster abundances: 5.0-eV ionization energy, mass spectrometer optimized for smaller clusters. (b) Similar to (a) with mass spectrometer optimized for larger clusters and increased signal amplification. (c) 2.5-eV ionization energy: only the cubic ion clusters $Na_{14}F_{13}$ and $Na_{23}F_{22}$ are efficiently ionized.



FIG. 2. Comparison of measured and predicted adiabatic binding energies of an excess electron interacting with an $Na_nX_{n-1}^+$ cluster.

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TABLE I. Characteristics of $Na_nF_{n-1}$ clusters. All energies are in eV, with the $E_b$ model from Eq. (1) and $E_f$ from Eq. (1). Only a few of the large $F$-center cluster $j \times k \times l$ designations are given as examples.

| $n, n-1$ | $j \times k \times l$ | $E_b$ model | $E_b$ expt | $E_f$ |
|---|---|---|---|---|
| | | *F*-center clusters | | |
| 2,1 | $1 \times 2 \times 2$ | 3.5 | $3.85 \pm 0.15$ | 0.7 |
| 3,2 | $1 \times 2 \times 3$ | 3.7 | 3.85 | 0.6 |
| 4,3 | $2 \times 2 \times 2$ | 3.8 | $3.54 \pm 0.05$ | 0.7 |
| 6,5 | $2 \times 2 \times 3$ | 3.9 | 3.33 | 1.0 |
| 8,7 | $2 \times 2 \times 4$ | 3.6 | 3.35 | 0.8 |
| 9,8 | $2 \times 3 \times 3$ | 3.7 | 3.57 | 0.8 |
| 12,11 | $2 \times 3 \times 4$ | 4.0 | 3.35 | 1.2 |
| 15,14 | $2 \times 3 \times 5$ | 4.0 | 3.35 | 1.2 |
| 18,17 | $3 \times 3 \times 4$ | | 2.89 | |
| 20,19 | $2 \times 4 \times 5$ | | 3.13 | |
| 24,23 | $3 \times 4 \times 4$ | | 3.07 | |
| 30,29 | $3 \times 4 \times 5$ | | 3.09 | |
| 32,31 | $4 \times 4 \times 4$ | | $< 4$ | |
| 36,35 | $3 \times 4 \times 6$ | | $< 4$ | |
| 60,59 | $4 \times 5 \times 6$ | | $< 4$ | |
| | | Cubic ion clusters (low electron binding energy) | | |
| 14,13 | $3 \times 3 \times 3$ | 2.2 | 1.88 | 0.5 |
| 23,22 | $3 \times 3 \times 5$ | | 1.80 | |
| 38,37 | $3 \times 5 \times 5$ | | | |
| | | Noncubic clusters (high electron binding energy) | | |
| 5,4 | | 3.1 | $3.85 \pm 0.15$ | 0.2 |
| 7,6 | | 3.6 | 3.85 | 0.3 |
| 10,9 | | 3.5 | 3.85 | 0.4 |
| 11,10 | | 3.2 | 3.80 | 0.5 |
| 13,12 | | 3.3 | 3.85 | 0.2 |
| 16,15 | $2 \times 4 \times 4$ | 3.3 | 3.85 | 0.6 |

the excess electron in the different cluster structures. Based on ionization thresholds and observed abundances, we define three classifications for the excess electron clusters, as summarized in Table I.

*Cubic ion clusters* are of low abundance with a filled cubic lattice of ions, and a very weakly bound electron excluded from the structure. Figure 1(c) shows the smallest of these, the $n = 14$ and 23 clusters. The photo-ionization efficiency of $Na_{14}F_{13}$ begins to decline near 2.1 eV, with a threshold of $1.88 \pm 0.05$ eV, in good correspondence with the LSJ prediction (1.5 eV) of the $Na_{14}Cl_{13}$ adiabatic electron binding energy. As has long been demonstrated,[8,9] stable cuboid ions of $j \times k \times l$ ions on each side can be formed with $2n - 1$ lattice sites if $j$, $k$, and $l$ are all odd. The $Na_{14}F_{13}$ and $Na_{23}F_{22}$ clusters thus correspond to the stable cubic forms $3 \times 3 \times 3$ and $3 \times 3 \times 5$, respectively, with the electron occupying a weakly bound surface state.

*F-center clusters* have high abundances, high electron binding energies, and optical absorption bands characteristic of a nearly filled cubic lattice with an electron localized in an anion vacancy. As can be seen by comparing Figs. 1(a) and 2, the cluster sizes with electron binding energies of 2.8–3.6 eV are also those which are most abundant and hence relatively stable. Although precise

electron binding energies have not been determined for $n > 30$, we find that all the large abundant clusters have electron binding energies $< 4$ eV. Each of these with locally very strong peaks for $n = 2$–96 are found to correspond to structures with $2n$ sites of a cubic lattice of $j \times k \times l$ ions on each side, with $j$, $k$, and $l$ nearly equal. *However, there are only $2n - 1$ ions to occupy the lattice of an $Na^+_n F^-_{n-1}$ cluster. The $2n$th charged particle to occupy the remaining anion vacancy in the cubic lattice is the excess electron.*

*Noncubic clusters* are those with low abundance and the strongest electron binding, with the excess electron probably bound to a single Na atom, increasing both the probability of dissociative attachment and the vertical electron binding energy. These clusters corresponding to $2n$ or $2n - 1$ not decomposable into $j, k, l > 1$ are the least abundant. The electron binding energies, although not precisely determined, are reduced from the atomic ionization potential[10] of 5.14 eV to approximately 4 eV. This is in accordance with the LSJ simulations where the noncubic $Na_5Cl_4$ cluster was found to have a relatively high electron binding energy of 4.9 eV and was particularly prone to dissociative attachment into the $Na_4Cl_4$ cube and neutral Na. The exception to this classification scheme is $Na_{16}F_{15}$, which could possibly be an *F*-center

cluster ($2 \times 4 \times 4$), but which is observed to be of relatively low abundance and high electron binding energy, as for a noncubic cluster.

Quantitatively, predictions by LSJ for only two clusters, $Na_5Cl_4$ and $Na_{14}Cl_{13}$, can be compared with our results. However, the implication that the excess electron occupies a site in a cubic lattice can be extended to make quantitative predictions with a very simple model. First, it is assumed that the electron distribution is sufficiently localized and spherical so that its contribution to the cluster potential energy is that of a halide anion. The magnitude of the total energy of an $Na_nX_{n-1}^+ \cdot e^-$ cluster is still less than that of the corresponding $Na_nX_n$ cluster because of the kinetic energy, $K$, of the localized electron. The total energies of neutral $Na_nCl_n$ and $Na_nCl_{n-1}^+$ ion clusters (with respect to separated ions) have been calculated by Martin.[8] We can estimate $K$ as the energy of an electron localized within a lattice site, taken to be a cube of dimension $2a$.[11] With $a$ the lattice constant of crystalline NaF, $K$ is 1.7 eV. This value is also close to the zero-temperature kinetic energy of the localized electron bound to $Na_{14}Cl_{13}$ calculated by quantum path-integral methods.[5]

Within this model, the electron binding energy $E_b$ is given by

$$E_b(n) = (E_{n,n} - K) - E_{n,n-1},    (1)$$

and is plotted versus $n$ in Fig. 2. In accordance with the localization hypothesis, $E_{n,n} - K$ approximates the energy of the excess-electron cluster. Despite the evident crudeness of the model, there is good agreement with the gross features observed.

To apply this model to abundances, a dominant fragmentation pathway must be assumed. Consideration of the energetics of several alternatives reveals that abundances should be determined by stability against the dissociative attachment process,

$$Na_nX_{n-1}^+ \cdot e^- \xrightarrow{E_f} Na_{n-1}X_{n-1} + Na,$$
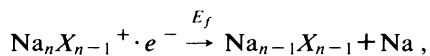
requiring the positive energy $E_f$. $E_f$ is given by

$$E_f^{(n)} = (E_{n,n} - K) - (E_{n-1,n-1} + I_{Na}),    (2)$$

where $I_{Na}$ is the ionization potential of the sodium atom. The quantity $E_f^{(n)}$, which is plotted versus $n$ in Fig. 3, ranges from barely positive (weakly bound) for clusters such as $n = 13$ to $> 1$ eV (strongly bound) for $n = 6$ or 15. Comparison to the neutral cluster abundances in Fig. 1(a) shows excellent correspondence between predicted fragmentation energy and cluster abundance. This pattern is in marked contrast to $M_nX_{n-1}^+$ mass spectra displaying ion stabilities.[8,9,12]

Finally, strong optical-absorption bands have been found by resonant two-photon ionization spectroscopy for several of the clusters which we identify as the $F$-center type: $Na_2Cl$ (in the blue green),[13] $Na_2F$, $Na_4F_3$,
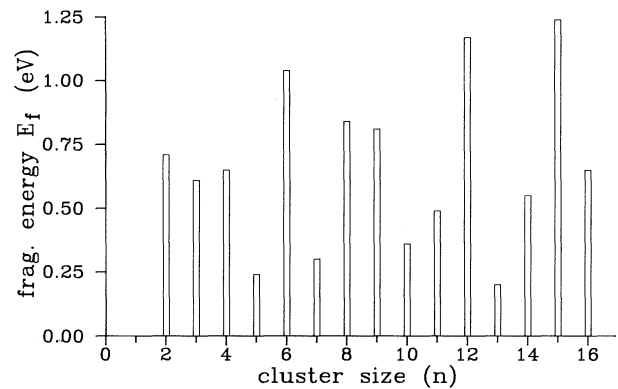


FIG. 3. Energy required for an $Na_nX_{n-1}$ cluster to fragment into an $Na_{n-1}X_{n-1}$ cluster and a neutral Na atom as calculated using the localized electron ($F$-center) model described in the text.

and $Na_8F_7$ (yellow red).[12] These spectra, which are still under investigation, may be taken as further evidence for electron localization in finite systems.

In conclusion, we find good agreement with predicted values[5] of excess-electron binding energies and with the hypothesis that dissociative attachment determines cluster stabilities. In contrast to work on metal-rich ionic clusters $Na_nCl_m$ ($m = 1$-3) (Ref. 13) and $Cs_nO_m$,[14] where the excess electrons were found to be *delocalized* in spherical shells,[15] we conclude that the electron is substantially localized, suggesting a transition at some intermediate excess metal concentration. As a start, from the metal-poor side, we have undertaken investigations of the two excess-electron series, $Na_nX_{n-2}$, the bulk analog of which has recently been investigated by Selloni *et al.*[16] It remains to be seen, however, whether quantum path-integral dynamics or other theoretical methods can accurately treat dynamical quantities of the excess-electron systems, as revealed by optical spectra, and whether the hypothesized metal-insulator transition can be observed.

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