Ab initio study of localization and excitation of an excess electron in alkali halide clusters

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Hartree-Fock calculations coupled with second-order many-body perturbation theory have been performed to study binding energies, localization, and excitation properties of an excess electron in various alkali halide clusters, Na_nF_{n-1}, Na_nCl_{n-1}, and Li_nF_{n-1} ($n = 2, 4, 5, 14$). The binding energies agree well with recent experimental data and three different modes of localization are corroborated. The position of the F-center absorption band in Na_nF_{n-1} clusters is verified, but not for Na_nCl_{n-1}. New absorption bands for Na_nCl_{n-1} and Li_nF_{n-1} clusters are predicted.

The interest in the physics and chemistry of small clusters is rapidly increasing due to their novel and hybrid properties. Recent experimental[1−3] and theoretical[4,5] work focused on the properties of an excess electron attached to a cluster since the extra electron influences the cluster stability and therefore the reactive properties. Honea et al.[1] have measured abundances and binding energies of an excess electron interacting with $(Na_nF_{n-1})^+$ clusters. Based on observed abundances and ionization threshold they classified the clusters as follows: cubic clusters consist of a filled cubic lattice of ions with the extra electron occupying a weakly bound surface state; F-center clusters consist of a nearly filled cubic lattice with an electron localized in an anion vacancy; and noncubic clusters have the excess electron bound to a single cation. The F-center and the noncubic clusters show high electron binding energies. As further evidence for electron localization, Honea et al. cite the observation of strong optical-absorption bands in F-center clusters using resonant two-photon ionization spectroscopy.

In this paper we report results of an ab initio study of localization and excitation properties of an excess electron attached to various alkali halide clusters and provide a basis for the relation between binding energies, excitation energies, and the degree of localization. With respect to localization properties, we find good agreement with earlier theoretical predictions[4,5] based on quantum path-integral molecular-dynamics calculations and corroborate the interpretation given in Ref. 1. The calculated binding energies agree well with the experimental data, and, for the noncubic cluster Na_5F_4, are in better agreement than the binding energies obtained from a cruder model.[1] For the excitation energy we verify the position of the F-center absorption band in Na_nF_{n-1} clusters, but cannot support the interpretation that the observed blue-green band in Na_2Cl cluster is associated with the excitation of the excess electron.

Calculations are performed for various Na_nF_{n-1}, Na_nCl_{n-1}, and Li_nF_{n-1} clusters where $n = 2, 4, 5$, and 14. The internuclear separation between cation and anion in the cluster is taken to be the same as in bulk solid which is 3.80, 4.36, and 5.31 bohrs for LiF, NaF, and NaCl clusters, respectively. [Preliminary cluster-geometry optimization—only bond lengths, but not bond angles—shows the lowering of total energy only in the case of "ionized clusters." For example, the $(Na_2Cl)^+$ cluster relaxes in-ward to the bond length of 4.81 bohrs, relative to the bulk value of 5.31 bohrs, lowering the total energy by 0.1 eV. No relaxation of cluster geometry from the bulk separation has been found for the neutral clusters.]

The unrestricted Hartree-Fock linear combination of atomic-orbitals method is employed. Correlation corrections are calculated using second-order many-body perturbation theory.[6] For the expansion of the atomic orbitals for Na, F, and Cl, Huzinaga Gaussian basis sets[7] are split into contractions of (421/4), (421/4), and (4321/43), respectively. For Li, a (6,1) basis set[8] is used. The excess electron in the F-center cluster is accommodated by adding another single Gaussian whose exponent is determined variationally.

Table I gives the binding energy of the excess electron in various alkali halide clusters. The binding energy is defined as the difference between total cluster energies of a neutral cluster, for example, Na_nF_{n-1}, and the ionized cluster, for example $(Na_nF_{n-1})^+$. The total cluster energies are the values obtained from Hartree-Fock calculations coupled with second-order many-body perturbation theory. As it turned out, the correlation corrections are

TABLE I. Binding energy of the excess electron in alkali halide clusters calculated by Hartree-Fock coupled with second-order many-body perturbation theory.

| | Binding energy (eV) | | |
	This work	Observed[a]	Calculated[a]
F-center clusters			
Na_2Cl	4.06	⋯	⋯
Na_4Cl_3	4.17	⋯	⋯
Na_2F	4.29	3.85+0.15	3.50
Na_4F_3	4.28	3.54+0.15	3.80
Li_2F	4.60	⋯	⋯
Li_4F_3	4.73	⋯	⋯
Noncubic cluster			
Na_5F_4	3.80	3.85+0.15	3.10
Li_5F_4	4.33	⋯	⋯
Cubic cluster			
$Na_{14}F_{13}$	⋯	1.88	⋯
$Li_{14}F_{13}$	1.20	⋯	⋯

[a]Reference 1.

quite small (0.2 eV), as one would expect for ionic systems. Table I also includes the experimental and calculated values of the binding energies obtained by Honea et al.[1] Our calculated values are in satisfactory agreement with the measured values for the Na_nF_{n-1} clusters. They show that the binding energies for F-center and noncubic clusters are quite large, i.e., about 4 eV, whereas the cubic cluster has a clearly smaller binding energy of about 1.8 eV.

Qualitative information about the charge distribution on different atoms in clusters is obtained from a Mulliken population analysis.[9] The results show that in the F-center clusters, the excess electron is always contained at the vacancy site, whereas in the noncubic clusters the electron is associated with a single cation, therefore neutralizing this ion. In the cubic cluster, the electron is distributed over all surface atoms of the cluster. Our calculation therefore corroborates the results of Landman and co-workers[4,5] and confirms three distinct modes of localization in these clusters.

The extent of localization of the excess electron can be expressed in terms of a range R for a single Gaussian by the relationship $R = (2a)^{1/2}$, where a is the exponent coefficient of the Gaussian. The range R is then the distance at which an s-type Gaussian has its squared amplitude reduced to e^{-1} of its maximum. In the F-center clusters, the range of the excess electron comes out to be about $0.65a$, $0.73a$, and $0.77a$ for the cases of LiF, NaF, and NaCl clusters, respectively. Here "a" is the internuclear separation in the cluster. This shows that the excess electron occupies the vacancy site, but is not very localized.

We discuss now the excitation properties of the excess electron in the F-center clusters. In these clusters, the electronic states of the excess electron may be labeled as $1s$, $2s$, $2p, \ldots$, which is analogous to those of one-electron atoms, in this case He^+. The first allowed optical transition is therefore between the $1s$ and $2p$ states. The electron may now be optically excited to an unrelaxed excited state such that ions retain their ground-state positions. The $1s$ and $2p$ states are then referred to as the ground and unrelaxed excited states for the optical-absorption process. Thus we compute the absorption energy by taking the difference between the total cluster energies of the ground and unrelaxed excited states of the excess electron.

The calculated absorption bands are given in Table II along with the observed bands. For NaF clusters, our calculated bands lie in the yellow-red region of the spectrum as the observed ones, showing an excellent agreement between theory and experiment. However, this agreement fails for NaCl clusters where the calculated bands lie in

TABLE II. Optical absorption energy of the excess electron in the F-center clusters.

	Absorption energy (eV)	
	This work	Observed[a]
Na_2Cl	1.55	blue-green
Na_4Cl_3	1.91	$\cdots$
Bulk NaCl	$\cdots$	2.70
Na_2F	1.89	yellow-red
Na_4F_3	2.00	$\cdots$
Bulk NaF	$\cdots$	3.60
Li_2F	2.00	$\cdots$
Li_4F_3	2.41	$\cdots$
Li_6F_5	3.29	$\cdots$
Bulk LiF	$\cdots$	5.00

[a]Reference 1.

the red-infrared region, whereas the observed ones are reported to be in the blue-green region. To confirm our predictions, we have also calculated the absorption bands for LiF clusters. Referring to Table II, we notice that the bands in clusters shift to higher energy as we go from NaCl to NaF to LiF following the same trend as observed in the bulk solids (Table II). Furthermore, the bands show size dependency approaching their bulk value with the increase in the cluster size. Hence, we believe that the observed blue-green band in Na_2Cl cluster cannot be associated with the optical excitation of the excess electron in the cluster.

The size dependency of the absorption bands is due to the fact that the F-center electron is somewhat more spread out in the excited state than in the ground state. This is confirmed by the relatively large range of the excess electron in the excited state, which is found to be about the internuclear separation in the clusters considered here.

In summary, we have demonstrated that Hartree-Fock approximation coupled with second-body many-perturbation theory is capable of predicting properties of the excess electron in alkali halide clusters successfully. We have corroborated three distinct modes of localization of the excess electron. Our calculated binding energy agrees with the observed values. We have also verified the position of the F-center absorption band in the NaF cluster and then have predicted the positions in NaCl and LiF clusters.

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