Electron detachment energies in high-symmetry alkali halide solvated-electron anions

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We decompose the vertical electron detachment energies (VDEs) in solvated-electron clusters of alkali halides in terms of (i) an electrostatic contribution that correlates with the dipole moment (μ) of the individual alkali halide molecule and (ii) a relaxation component that is related to the polarizability (α) of the alkali halide molecule. Detailed numerical *ab initio* results for twelve species $(MX)_n^-$ (M=Li,Na; X=F,Cl,Br; $n=2,3$) are used to construct an interpolation model that relates the clusters' VDEs to their μ and α values as well as a cluster size parameter r that we show is closely related to the alkali cation's ionic radius. The interpolation formula is then tested by applying it to predict the VDEs of four systems [i.e., $(KF)_2^-$, $(KF)_3^-$, $(KCl)_2^-$, and $(KCl)_3^-$] that were not used in determining the parameters of the model. The average difference between the model's predicted VDEs and the *ab initio* calculated electron binding energies is less than 4% (for the twelve species studied). It is concluded that one can easily estimate the VDE of a given high-symmetry solvated electron system by employing the model put forth here if the α, μ and cation ionic radii are known. Alternatively, if VDEs are measured for an alkali halide cluster and the α and μ values are known, one can estimate the r parameter, which, in turn, determines the ''size'' of the cluster anion. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1580113]

I. INTRODUCTION

It is known that a cluster of polar molecules is able to host an excess electron in at least two ways.[1,2] The first possibility is that the electron can be tethered to the cluster via its interaction with the net dipole moment of the cluster. In such cases, the polar molecules tend to align head-to-tail to maximize their dipole moment and thus their binding energy. In such so-called ''dipole-bound'' anions, the extra electron is localized primarily *outside* the molecular framework on the positive side of the neutral parent, as demonstrated long ago by Jordan and Luken.[3] Alternatively, an excess electron can be trapped *inside* the cluster, in which case at least two of the polar molecules align their dipole toward one another. The existence of the latter species, commonly referred to as *solvated electron* (SE) anions, has been known for more than 100 years when their bulk analogs were identified in solids and liquids.[4,5] Since then, a very large number of the SE species have been investigated experimentally and theoretically.[2,6-19] Among other differences between dipole-bound anions and solvated electrons, the latter species are known to possess relatively large vertical electron detachment energies and to undergo large geometrical rearrange-

ments upon electron detachment because having dipoles directed toward one another is highly unfavorable in the absence of the electron.[2,9,14,18]

Large vertical electron detachment energies (VDEs) characterizing SE species have been reported in the literature recently. For example, the urea dimer ''solvating'' an excess electron has been found to possess a VDE of ~0.2, 0.5, and 0.9 eV, when two ''canonical,'' one canonical and one zwitterionic, or two zwitterionic urea tautomers are involved, respectively.[15] For a solvated electron trapped in a cluster consisting of two or three NaCl molecules, even larger VDEs have been found. In particular, the linear $D_{\infty h}$-symmetry sodium chloride negatively charged dimer cluster (in which two NaCl molecules are aligned in a head-to-head manner) binds an extra electron by 2.64 eV[18] while the D_{3h}-symmetry $(NaCl)_3$ cluster has a VDE of 4.2 eV.[19]

The proposal that we intend to explore in the present work is that the large electron binding energies characterizing alkali halide SE systems can be correlated with two fundamental physicochemical properties (i.e., μ and α) of the monomers that constitute such clusters. To examine this hypothesis, we needed to undertake *ab initio* calculations of the VDE values for various SE species in order to generate the necessary VDE data. In so doing, we studied several previously unreported cluster anions, so our data represent new findings in these cases. To restrict the systems for which we

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develop correlations between VDEs and μ and α values, we limited our studies to electrons solvated by high-symmetry alkali halide dimers and trimers. We believe the approach described here provides a step toward understanding and predicting the large electron binding energies in the SE alkali halide anions.

II. METHODS

The equilibrium geometries of the anionic species have been optimized at the second-order Møller–Plesset (MP2) level of theory. In these calculations, the values of $\langle S^2 \rangle$ never exceeded 0.7526 for the doublet anionic states, so we are confident that spin contamination effects are not serious. The electronic binding energies (D) of the anions were calculated using second-order Møller–Plesset perturbation theory as well as the coupled-cluster method with single, double, and the conventional[25] perturbative noniterative triple excitations (CCSD(T)).[20] However, in the case of trimers containing bromine atoms [i.e., $(LiBr)_3^-$ and $(NaBr)_3^-$] we had to limit our treatment to the CCSD level because even the perturbative inclusion triple excitations for these species was not feasible with the computer resources available. The choice of the atomic orbital basis set used to describe the neutral molecule and the excess bound electron is very important for reproducing the correct value of the electron binding energy. In this contribution we employed aug-cc-pVDZ basis sets[21] whose usefulness for describing various molecular anions has been documented previously.[22] The diffuse character of the orbital describing the ''solvated'' (excess) electron necessitates the use of extra diffuse basis functions having very low exponents and therefore our geometry optimization calculations were performed with the aug-cc-pVDZ+$5s5p$ basis sets, while the electron binding energies were calculated with the aug-cc-pVDZ+$6s6p4d$ basis sets. The additional $5s5p$ (or $6s6p4d$) sets of diffuse functions were centered in the middle of the cluster (i.e., in the symmetry center) in each case, where the excess electron is localized (see Fig. 1). The extra diffuse functions do not share exponent values, and for calculating electron binding energies we used even-tempered[23] six-term s, six-term p, and four-term d basis sets. The geometric progression ratio was equal to 3.2,[24] and for each orbital symmetry, we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in the aug-cc-pVDZ basis set for lithium or sodium. As a consequence, for lithium-containing species we used lowest exponents of $8.046\,627\,031 \times 10^{-6}$, $1.725\,554\,466 \times 10^{-6}$, and $6.914\,138\,794 \times 10^{-4}$ a.u., for the s, p, and d symmetries, respectively, and for sodium-containing systems we employed lowest exponents of $6.752\,088\,4 \times 10^{-6}$, $5.895\,271\,8 \times 10^{-6}$, and $4.463\,195\,6 \times 10^{-4}$ a.u., for the s, p, and d symmetries, respectively. We should note that, because the electron binding energies of the alkali halide clusters studied here are substantial (at least 2 eV), it likely is not necessary to use such a large set of diffuse basis functions. We employed these bases to make sure that our basis was adequate; our interest was not in determining the smallest basis that would be needed to obtain reasonable results.
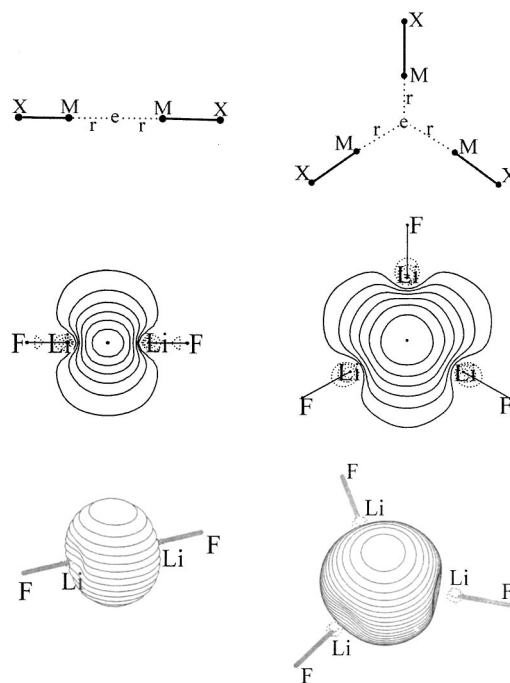

FIG. 1. Singly occupied molecular orbitals (shown as a two-dimensional map and as a contour plot) holding the excess electron in the SE system formed by LiF dimer (left) and trimer (right). The corresponding schemes depicting the monomer orientations in high-symmetry clusters are also given.

All calculations were performed with the GAUSSIAN 98 program[25] on Intel Pentium IV and AMD Athlon computers and a Compaq Sierra numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program.[26]

III. RESULTS

A. *Ab initio* geometries and electron binding energies of the solvated electron species

In order to construct our model for interpolating (and extrapolating) the electronic stabilities of SE species, we selected several molecular clusters that form negative ions with the excess electron localized *inside* the cluster. Since the anions formed by alkali halide clusters had been the subject of an earlier extensive study of ours, we decided to use these species in our present study. Hence, we considered twelve clusters (dimers and trimers): $(NaF)_2^-$, $(NaF)_3^-$, $(NaCl)_2^-$, $(NaCl)_3^-$, $(NaBr)_2^-$, $(NaBr)_3^-$, $(LiF)_2^-$, $(LiF)_3^-$, $(LiCl)_2^-$, $(LiCl)_3^-$, $(LiBr)_2^-$, and $(LiBr)_3^-$. We first verified that all of these clusters have the ability to form SE species with the monomers directed inward and the extra electron localized inside the cluster. We recall that, to simplify the problem, only high-symmetry clusters were considered (i.e., linear $D_{\infty h}$-symmetry structures in the case of the dimers and triangular D_{3h}-symmetry structures in the case of the trimers). Noting this limitation is important because it is known that at least some such clusters also form alternative lower-symmetry structures, such as the X–M__e__M–X__M–X trimers (where e denotes the extra electron and M and X represent the alkali and halogen atom, respectively).[14,19]

TABLE I. The MP2 equilibrium bond lengths (R_m) and corresponding dipole moments calculated for the neutral monomers with the aug-cc-pVDZ $+6s6p4d$ basis sets. The CCSD(T) vertical electron binding energies ($D^{\text{CCSD(T)}}$) for the corresponding anions are also given (in eV). Bond lengths in Å, dipole moments in debyes, polarizabilities in bohr^3. The values of α correspond to the $\alpha_{\parallel}$ terms of the polarizability tensor.

Species	μ	$\alpha_{\parallel}$	R_m (M–X)	$D^{\text{CCSD(T)}}$
NaF	8.6059	10.1086	1.9888	0.4862
NaCl	9.5029	31.8206	2.4256	0.6874
NaBr	9.6161	43.6802	2.5646	0.9409
LiF	6.5542	9.3891	1.6093	0.3759
LiCl	7.4210	27.0680	2.0849	0.5880
LiBr	7.4272	36.7106	2.2058	0.6287

Due to the significant polarity of the monomers in each cluster (see Table I for monomers' properties), we expected each of these species to form an electronically stable anion. The calculated *ab initio* electron binding energies for the twelve clusters holding an extra electron confirmed this expectation (see Table II).

For each dimer anion, we found its local minimum (corresponding to the SE species) to possess $D_{\infty h}$ symmetry as depicted in Fig. 1. Similarly, for each trimer we obtained a local minimum at D_{3h} symmetry (see Fig. 1). The relevant geometric parameters describing these anions are collected in Table II where we show the intramonomer M–X distance (R) and the metal-to-cluster-center distance (r). While the former is the bond length of the monomer in the cluster, the latter may be interpreted as an approximate distance from the alkali atom M (representing the positively charge site of the monomer) to the site where the excess electron is localized. In addition, in Table II we give the self-consistent field (SCF) dipole moments [the SCF dipole moments of the neutral alkali halides are similar to those calculated from the MP2 electron densities and the largest difference (0.2 D) we found for NaF species] and polarizabilities of the neutral monomers

TABLE II. Geometrical parameters (in Å) defining the MP2 equilibrium geometries of the SE species studied in this work and their vertical electron binding energies ($D^{\text{CCSD(T)}}$ or D^{CCSD}). See Sec. III A and Fig. 1 for the definitions of R and r. The corresponding μ/r^2 and α/r^4 values are also given (in a.u.), where μ indicates the dipole moment of the neutral monomer and α is the $\alpha_{\parallel}$ term of the polarizability tensor calculated for the neutral monomer. The vertical electron binding energies are given in eV. All results were calculated with the aug-cc-pVDZ $+6s6p4d$ basis sets.

Species	R (M–X)	r (M$\cdots e$)	μ/r^2	α/r^4	$D^{\text{CCSD(T)}} \approx D^{\text{exact}}$
$(\text{NaF})_2^-$	1.0345	2.0231	0.2373	0.047	2.196
$(\text{NaCl})_2^-$	1.2636	1.9561	0.2778	0.170	2.642
$(\text{NaBr})_2^-$	1.3413	1.8961	0.2999	0.265	2.784
$(\text{LiF})_2^-$	0.8353	1.7221	0.2495	0.084	2.123
$(\text{LiCl})_2^-$	1.0884	1.6405	0.3099	0.293	2.759
$(\text{LiBr})_2^-$	1.1601	1.6431	0.3105	0.395	2.888
$(\text{NaF})_3^-$	2.0381	2.3668	0.1730	0.025	3.739
$(\text{NaCl})_3^-$	2.4810	2.3465	0.1931	0.082	4.222
$(\text{NaBr})_3^-$	2.6268	2.2757	0.2080	0.128	4.407[a]
$(\text{LiF})_3^-$	1.6490	1.9674	0.1910	0.049	3.914
$(\text{LiCl})_3^-$	2.1328	1.9343	0.2230	0.152	4.653
$(\text{LiBr})_3^-$	2.2558	1.8846	0.2360	0.228	4.818[a]

[a]$D^{\text{CCSD}} \approx D^{\text{exact}}$.

(see Table I) divided by appropriate powers of the equilibrium distance r. The latter data are used later in approximating specific contributions to the electron binding energies of the SE species as we discuss later.

It can be seen that the r distances calculated for the SE species are in the 1.6–1.7 and 1.9–2.0 Å range for the lithium-based dimers and trimers, and 19–2.0 and 2.3–2.4 Å for the sodium-based dimers and trimers, respectively (see Table II). As expected, the corresponding VDEs are large and cover the 2.1–2.9 eV range for the dimers and the 3.7–4.8 eV range for the trimers. The largest electron binding energy among the systems studied is that for $(\text{LiBr})_3^-$ which binds an extra electron by 4.818 eV (as calculated at the CCSD level, see Table II). This is likely related to the fact that $(\text{LiBr})_3^-$ involves the smallest alkali metal atom and the largest halogen atom. Not surprisingly, the electron binding energy increases when the ''sizes'' of the alkali metal and halogen atom decrease and increase, respectively.

Having the *ab initio* electron binding energies of several SE species calculated, we now move on to discuss the interpolation–extrapolation model that we propose in this contribution.

B. Constructing the model

The exact value of the electron binding energy (D^{exact}) we approximate by the electron binding energy calculated at the CCSD(T) level,

$$D^{\text{exact}} \approx D^{\text{CCSD(T)}} = E_N^{\text{CCSD(T)}} - E_A^{\text{CCSD(T)}}, \qquad (1)$$

where $E_N^{\text{CCSD(T)}}$ and $E_A^{\text{CCSD(T)}}$ are electronic energies of the neutral and anionic species, respectively, calculated at the CCSD(T) level with the aug-cc-pVDZ $+6s6p4d$ basis sets for the MP2 equilibrium geometry of a given solvated electron species. Recall that our electron binding energies are ''vertical'' values (i.e., calculated for the same geometry of the neutral and anionic species), and since the anionic structures were used to calculate these values, our vertical electron binding energies (D) correspond in fact to vertical electron detachment energies (VDEs).

D^{exact} (approximated by $D^{\text{CCSD(T)}}$) can be partitioned into various contributions, for example:

$$D^{\text{exact}} \approx D^{\text{CCSD(T)}} = D^{\text{KT}} + \Delta D^{\text{SCF}} + \Delta D^{\text{MP2}} + \Delta D^{\text{HTSO}}, \qquad (2)$$

where D^{KT} indicates the electron binding energy calculated at the Koopmans theorem[27] level while ΔD^{SCF}, ΔD^{MP2}, and ΔD^{HTSO} represent the corrections to D obtained at the SCF, MP2, and higher-than-second-order (HTSO) levels, respectively. In particular, the HTSO term is given as

$$\Delta D^{\text{HTSO}} = D^{\text{CCSD(T)}} - D^{\text{MP2}}. \qquad (3)$$

On the basis of our experience[18,19] with high-symmetry SE species formed by alkali halides dimers and trimers, we postulate that the electron binding energy for a SE system can be approximated by the MP2 electron binding energy (D^{MP2}). In other words, we assume the ΔD^{HTSO} contributions to the total D are not important. To support this assumption we present in Table III results for the sodium chlo-

TABLE III. The MP2 and CCSD(T) vertical electron detachment energies calculated with the aug-cc-pVDZ+$6s6p4d$ basis sets with the higher-than-second-order (HTSO) contribution to D separated (labeled ΔD^{HTSO}). The electron binding energies are given in eV (see Sec. III B for the definition of the ΔD^{HTSO} term).

Species	D^{MP2}	ΔD^{HTSO}	$D^{CCSD(T)}$	ΔD^{HTSO} contribution to $D^{CCSD(T)}$
$(NaF)_2^-$	2.184	0.012	2.196	0.55%
$(NaF)_3^-$	3.727	0.012	3.739	0.32%
$(NaCl)_2^-$	2.634	0.008	2.642	0.30%
$(NaCl)_3^-$	4.218	0.004	4.222	0.09%
$(NaBr)_2^-$	2.776	0.008	2.784	0.29%
$(NaBr)_3^-$	4.389	0.018	4.407[a]	0.41%
$(LiF)_2^-$	2.096	0.027	2.123	1.27%
$(LiF)_3^-$	3.881	0.033	3.914	0.84%
$(LiCl)_2^-$	2,747	0.012	2.759	0.43%
$(LiCl)_3^-$	4.646	0.007	4.653	0.15%
$(LiBr)_2^-$	2.877	0.011	2.888	0.38%
$(LiBr)_3^-$	4.800	0.018	4.818[a]	0.37%

[a]D^{CCSD}.

ride dimer and trimer as well as for the lithium fluoride dimer and trimer (forming SE structures). After analyzing the data in Table III it becomes clear that the ΔD^{HTSO} terms are indeed not significant and responsible at most for 1% of the total electron binding energy (D). Therefore, we conclude that the inclusion of these terms is not necessary to estimate the electronic stabilities of the SE species with decent accuracy (although their consideration would be required if one wants to calculate very precise values of D for such systems).

The *ab initio* results calculated for the twelve SE dimers and trimers used to construct our model indicate that, in fact, the electron binding energy is quite well reproduced even at the SCF level since the ΔD^{MP2} term is always very small (see Table IV). This is due to the (partial) cancellation of the second-order dispersion and nondispersion terms as shown in Table IV (ΔD^{MP2} can be partitioned into ΔD_{disp}^{MP2} and $\Delta D_{no\text{-}disp}^{MP2}$, see Ref. 9). It can be concluded that the ΔD^{MP2} term does not exceed 0.05 eV in most cases and is usually smaller than 2% of D. Therefore, we decided to focus on

TABLE IV. The dispersion (ΔD_{disp}^{MP2}) and nondispersion ($\Delta D_{no\text{-}disp}^{MP2}$) components of the net MP2 contribution (ΔD^{MP2}) to the total electron binding energy. All energies are given in eV. The ΔD^{MP2} term can be partitioned into ΔD_{disp}^{MP2} and $\Delta_{no\text{-}disp}^{MP2}$ as described in Ref. 9.

Species	ΔD_{disp}^{MP2}	$\Delta D_{no\text{-}disp}^{MP2}$	$\Delta D^{MP2}=\Delta D_{disp}^{MP2}+\Delta D_{no\text{-}disp}^{MP2}$
$(NaF)_2^-$	0.032	−0.080	−0.048
$(NaCl)_2^-$	0.064	−0.059	0.005
$(NaBr)_2^-$	0.088	−0.076	0.013
$(LiF)_2^-$	0.042	−0.042	0.000
$(LiCl)_2^-$	0.078	−0.055	0.023
$(LiBr)_2^-$	0.101	−0.072	0.028
$(NaF)_3^-$	0.036	−0.124	−0.088
$(NaCl)_3^-$	0.076	−0.103	−0.027
$(NaBr)_3^-$	0.111	−0.141	−0.030
$(LiF)_3^-$	0.046	−0.079	−0.033
$(LiCl)_3^-$	0.088	−0.095	−0.006
$(LiBr)_3^-$	0.121	−0.130	−0.009

reproducing the D^{SCF} values for the SE systems while constructing our model. In other words, we assume that relating the D^{SCF} values to the μ and α properties of the monomers is adequate, because, as we have just shown, $D^{SCF}\approx D^{exact}$ for such species. We should note that the neglect of dispersion contributions to the binding energy may be acceptable for the alkali halide cluster anions treated here, but it would not be appropriate when treating clusters of species with much lower dipole moments [e.g., $(HCN)_n^-$ or $(H_3C\text{-}CN)_n^-$] for which it is known that dispersion terms are crucial fractions of the total binding energies.[28]

Since we concluded that reproducing the D^{SCF} binding energies would be satisfactory to make relatively good estimates of the electron binding energies for our SE species, we now move on to discuss how such binding energies are obtained. One needs to recall that

$$D^{SCF}=D^{KT}+\Delta D^{SCF} \qquad (4)$$

(as described in Ref. 9) and therefore, to reproduce the D^{SCF} energies one has to find a way to estimate D^{KT} and ΔD^{SCF}.

We found that the KT electron binding energies (D^{KT}) for our SE species correlate well with μ/r^2, where μ is the dipole moment of the neutral monomer that the SE species contains (see Table I) while r is the distance between the symmetry center of the SE system (where the excess electron is expected to reside) and the alkali atom. In Table II we provide the μ/r^2 values and in Figs. 2(a) and 2(b) we illustrate the correlation between D^{KT} data and μ/r^2 values for the dimers and trimers. The observed correlation arises because the electron–dipole interaction potential is given by $\mu\cos\theta/r^2$ and the KT binding energy involves primarily the electrostatic interaction of the extra electron with the dipole potential of the neutral parent molecule. Of course, the value of r reflects the eventual balance between electron–dipole attraction and the repulsion between the dipoles. In this sense, r relates to the ionic radius of the alkali cation as we show in Fig. 3.

The D^{KT} data points obtained from the *ab initio* calculations performed for the dimers fit a first-order polynomial that was found (via linear regression) to be

$$D^{KT}(\mu/r^2)=9.208\,78\mu/r^2-0.037\,16 \qquad (5)$$

with the regression correlation coefficient equal to 0.969 [see Fig. 2(a)]. The data points obtained from the *ab initio* calculations performed for the trimers fit a first-order polynomial of the form:

$$D^{KT}(\mu/r^2)=11.420\,39\ \mu/r^2+1.745\,48 \qquad (6)$$

with the regression correlation coefficient equal to 0.979 [see Fig. 2(b)]. The fact that the linear slope shown in Fig. 2(b) is larger than that of Fig. 2(a) simply reflects the fact that there are three electron–dipole attractive potentials operative in the trimer and only two in the dimer.

The fact that the D^{KT} correlates well with the corresponding μ/r^2 values lets us approximate the *ab initio* D^{KT} binding energies of the SE species by using the above-given formulas [Eqs. (5) and (6)] if we have available the monomer's μ value and if we can obtain an r value [e.g., by using
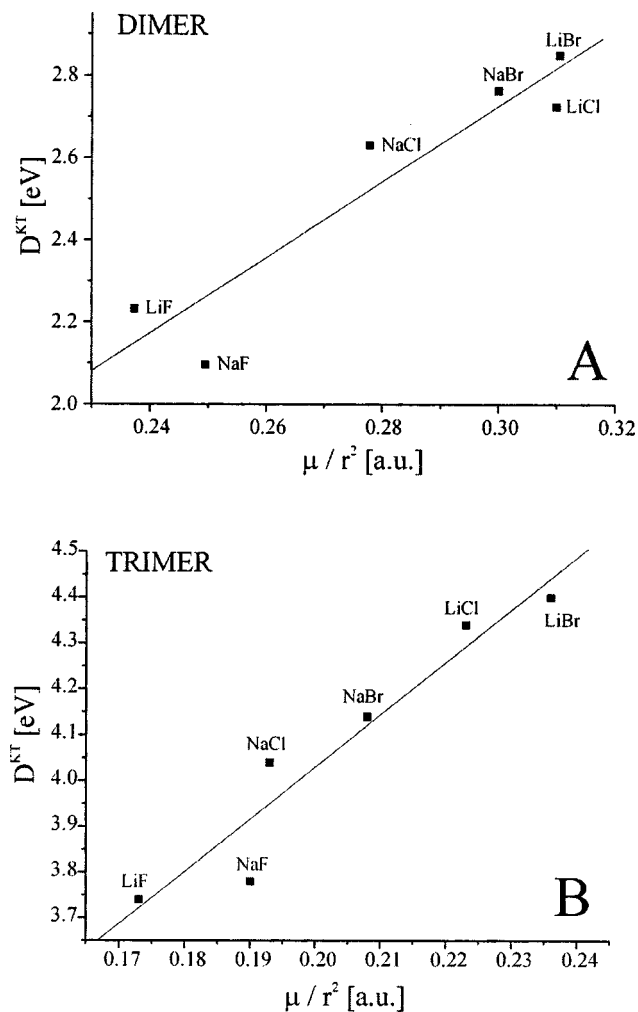
FIG. 2. The KT electron binding energy (D^{KT}) of the SE dimers (a) and trimers (b) as a function of μ/r^2 (see Tables I and II, as well as Sec. III B for details). The regression correlation coefficient is 0.969 [for the dimers, see (a)] and 0.979 [for the trimers, see (b)].
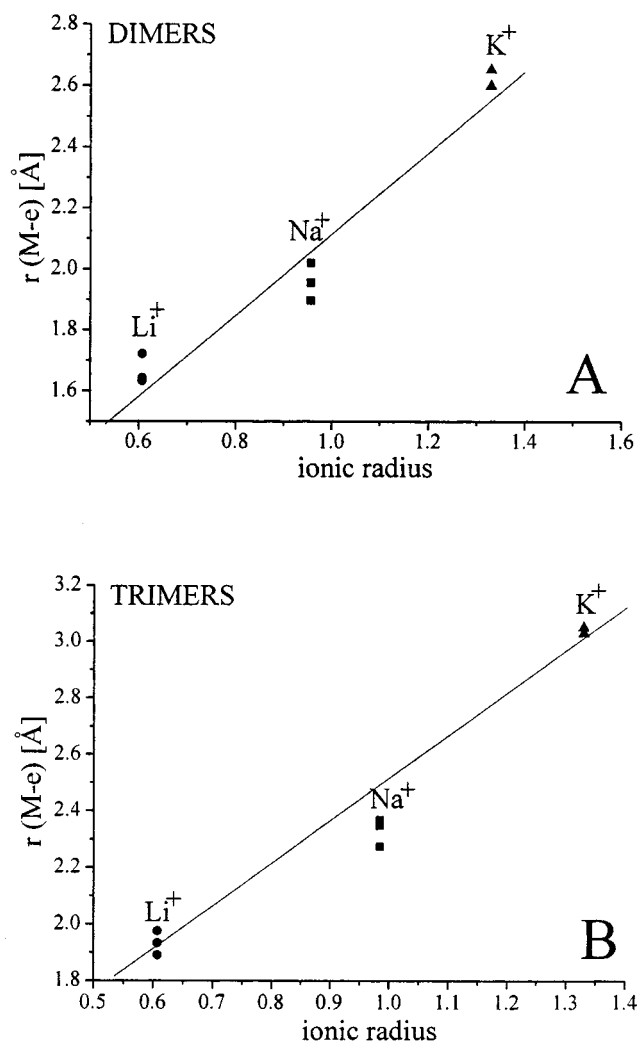

FIG. 3. The MP2 equilibrium metal-to-cluster-center distance (r) between for the SE clusters studied. The data for the dimers fit a first-order polynomial that was found to be 1.330 84 r^{ion} + 0.781 16 with the correlation coefficient of 0.984 [see (a)], while those for the trimers fit a first-order polynomial that was found to be 1.504 39r^{ion} + 1.010 49 with the correlation coefficient of 0.991 [see (b)]. The symbol r^{ion} indicates the Pauling ionic radius of the metal atom.

the relationship between the cation's ionic radius and the r values reflected in Figs. 3(a) and 3(b) and discussed in the following].

Next, we observed that the ΔD^{SCF} contributions to the electron binding energies for the SE species correlate well with α/r^4, where α is the polarizability (specifically it is the parallel component, $\alpha_\parallel$) of the neutral monomer that the SE system contains (see Table I). In Table II we list the α/r^4 values and in Figs. 4(a) and 4(b) we show how the ΔD^{SCF} data correlate with the α/r^4 values for the dimers and trimers. The data points obtained from the *ab initio* calculations performed for the dimers fit a first-order polynomial that was found (with the linear regression) to be

$$\Delta D^{SCF}(\alpha/r^4) = 0.655\,90 \ \alpha/r^4 + 0.025\,51 \qquad (7)$$

with the regression correlation coefficient equal to 0.998 [see Fig. 4(a)]. The results obtained from the *ab initio* calculations performed for the trimers fit a first-order polynomial that was found to be

$$\Delta D^{SCF}(\alpha/r^4) = 1.629\,12 \ \alpha/r^4 + 0.054\,71 \qquad (8)$$

with the regression correlation coefficient equal to 0.997 [see Fig. 4(b)].

The fact that the ΔD^{SCF} correlates well with the corresponding α/r^4 values lets us predict the *ab initio* ΔD^{SCF} binding energies using the above-given formulas if we know the monomer's α value and the r value (or, the alkali cation's ionic radius).

We have already shown why we assume $D^{SCF} \approx D^{exact}$ for the SE species and the above-given analysis shows that the D^{SCF} electron binding energy consists of two terms [D^{KT} and ΔD^{SCF}, see Eq. (4)] that can be obtained in a very simple manner when the μ/r^2 and α/r^4 values are known [see Eqs. (5)–(8)]. Therefore, it seems natural to rewrite Eq. (4) for the *dimers* as

$$D_2^{model} \approx D^{SCF} = D^{KT} + \Delta D^{SCF}$$

$$\approx 9.208\,78 \ \mu/r^2 - 0.037\,16$$

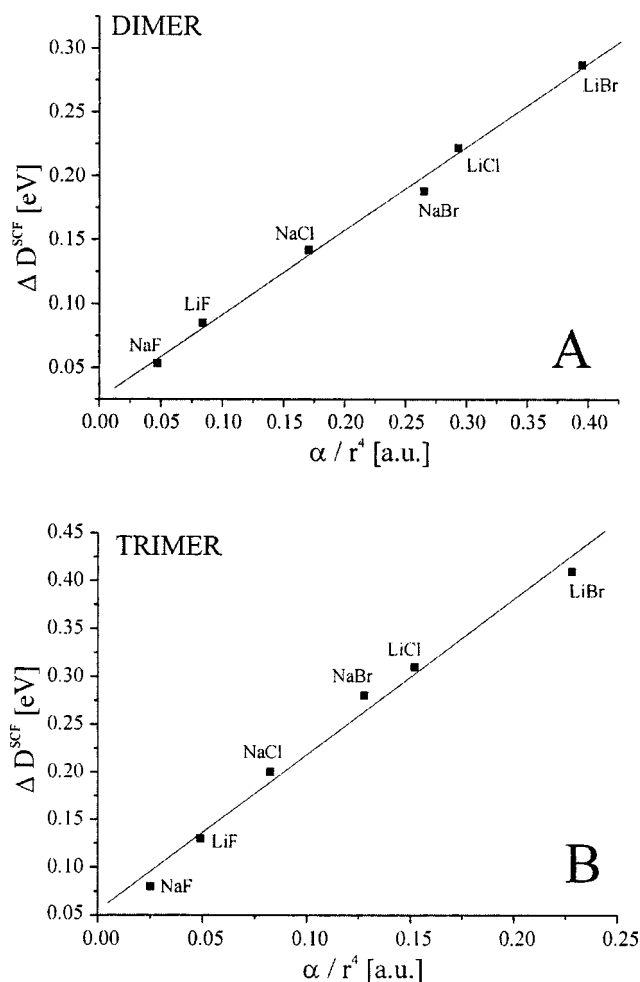$$+ 0.655\,90 \ \alpha/r^4 + 0.025\,51 \qquad (9)$$

FIG. 4. ΔD^{SCF} contribution to the electron binding energy of the SE dimers (a) and trimers (b) as a function of α/r^4 (see Tables I and II, as well as Sec. III B for details). The regression correlation coefficient is 0.998 [for the dimers, see (a)] and 0.997 [for the trimers, see (b)].

TABLE V. The comparison between the electron binding energies estimated by implementing the model described in this work (D^{model}) and the *ab initio* [CCSD(T) or CCSD] calculated values ($D^{CCSD(T)}$ or D^{CCSD}). All energies are given in eV.

Species	D^{model}	$D^{CCSD(T)} \approx D^{exact}$	Deviation
$(NaF)_2^-$	2.204	2.196	0.4%
$(NaCl)_2^-$	2.658	2.642	0.6%
$(NaBr)_2^-$	2.924	2.784	5.0%
$(LiF)_2^-$	2.341	2.123	10.3%
$(LiCl)_2^-$	3.034	2.759	10.0%
$(LiBr)_2^-$	3.107	2.888	7.6%
$(NaF)_3^-$	3.817	3.739	2.1%
$(NaCl)_3^-$	4.139	4.222	2.0%
$(NaBr)_3^-$	4.384	4.407[a]	0.5%
$(LiF)_3^-$	4.061	3.914	3.8%
$(LiCl)_3^-$	4.595	4.653	1.2%
$(LiBr)_3^-$	4.867	4.818[a]	1.0%

[a]$D^{CCSD} \approx D^{exact}$.

formula to the extrapolation domain, keeping in mind that the model is expected to work when applied to high-symmetry SE clusters (dimers and trimers) consisting of alkali halides but not species such as $(HCN)_n^-$ for which electrostatic and relaxation affects do not dominate the electron–molecule interaction.

C. Testing the model

First, let us examine how the D^{model} values [i.e., calculated from Eq. (10) for the dimers and from Eq. (12) for the trimers] compare to the corresponding *ab initio* D values for the twelve SE species *that were used to construct the model equation*. In Table V we show the deviations (in %) calculated as $|D^{model} - D^{exact}|$ divided by D^{exact} [where D^{exact} corresponds to the electron binding energy calculated at either CCSD(T) or CCSD level]. Clearly, the model works reasonably well because the average error is only 4% and the largest error (obtained for the LiF anionic dimer) is 10%.

Next, let us examine how well the model works when applied to SE species *that were not used to construct the model equations* [Eqs. (10) and (12)]. We considered four high-symmetry solvated electron species [i.e., $(KF)_n^-$ and $(KCl)_n^-$, $n = 2,3$) and we both (i) calculated their MP2 equilibrium geometries and electron binding energies at the CCSD(T) level[29] as we did for the other systems discussed in this work, and (ii) estimated their electronic stabilities by using the model embodied in Eqs. (10) and (12). The results collected in Table VI indicate that the deviations between the estimated and *ab initio* calculated electron binding energies are substantial yet not very large (except in the case of KF trimer where the deviation is 34%). In particular, our VDE (i.e., D) estimate for the $(KF)_2^-$ (5% deviation from the *ab initio* calculated value) is satisfactory, while those for $(KCl)_2^-$ and $(KCl)_3^-$ (deviations of 15% and 14%, respectively) are significantly worse yet still qualitatively correct (see Table VI).

It has to be stressed, however, that the model proposed utilizes the distances (r) between the alkali metal atom and

[in which Eqs. (5) and (7) were used and D_2^{model} indicates the electron binding energy obtained for the dimers (subscript "2") with the model proposed]. This gives (for the *dimers*)

$$D_2^{model} = 0.655\,90 \ \ \alpha/r^4 + 9.208\,78 \ \ \mu/r^2 - 0.011\,65. \quad (10)$$

Exactly the same procedure can be used to get the formula for the *trimers* [by using Eqs. (4), (6), and (8)]. This gives (for the *trimers*)

$$D_3^{model} \approx D^{SCF} = D^{KT} + \Delta D^{SCF}$$
$$\approx 11.420\,39 \ \mu/r^2 + 1.745\,48$$
$$+ 1.629\,12 \ \ \alpha/r^4 + 0.054\,71 \quad (11)$$

[in which D_3^{model} indicates the electron binding energy obtained for the trimers (subscript "3") with the model proposed], or

$$D_3^{model} = 1.629\,12 \ \ \alpha/r^4 + 11.420\,39 \ \ \mu/r^2 + 1.800\,19. \quad (12)$$

Having discussed the model interpolation–extrapolation formulas, Eqs. (10) and (12), we now move on to compare the results obtained with our formulas to *ab initio* calculated electron binding energies for species that were not used to construct our formula. That is, we extend this interpolation

TABLE VI. The comparison between the electron binding energies estimated by implementing the model described in this work (D^{model}) and the *ab initio* (MP2) values (D^{MP2}) for anions not used in constructing the model. All energies are given in eV.

Species[a]	D^{model}	$D^{CCSD(T)} \approx D^{exact}$	Deviation
$(KF)_2^-$	1.395	1.472	5.2%
$(KCl)_2^-$	1.747	2.065	15.3%
$(KF)_3^-$	3.123	2.322	34.4%
$(KCl)_3^-$	3.410	2.998	13.7%

[a]The corresponding equilibrium distances (r) are 2.6566, 2.6010, 3.0540, and 3.0370 Å for $(KF)_2^-$, $(KCl)_2^-$, $(KF)_3^-$, and $(KCl)_3^-$, respectively.

the center of the cluster (i.e., the site where the excess electron is expected to be localized). It may appear that the distance r for a given alkali halide dimer or trimer solvating the extra electron is not available unless one first performs the proper *ab initio* geometry optimization calculation on the anion. However, we notice (see Tables II and VI) that the equilibrium r distances found in the SE systems studied likely correlate with the ionic radius of the alkali metal atom. In particular, for the dimers containing lithium, sodium, and potassium the r values are in the range of 1.64–1.72, 1.90–2.02, and 2.60–2.66 Å, respectively, while for the trimers containing Li, Na, and K atoms the r distances are in the range of 1.88–1.97, 2.28–2.37, and 3.04–3.05 Å, respectively. In fact, knowing that the Pauling ionic radii of Li^+, Na^+, and K^+ are 0.607, 0.958, and 1.331 Å, respectively,[30] we note that the r values can be obtained by using a simple first-order polynomial (see Fig. 3) relating r to the cation's ionic radius.

IV. CONCLUDING REMARKS

We conclude that the model put forth here works reasonably well for several SE species and the average errors it produces are quite acceptable considering the approximations made in constructing it. This model approximates the Koopmans' theorem electron binding energy in terms of the dipole moments of the monomer building blocks and a size parameter r that we show can be related to the Pauling ionic radius of the cation. It approximates the ΔSCF detachment energy in terms of these same quantities and the parallel component of the alkali halide monomer's polarizability. We envision this model being used in either of two ways:

(1) to estimate the electron binding energies of new dimer or trimer cluster anions by using dipole moment and polarizability data on the monomers as well as the cation's ionic radius, or

(2) to estimate the size (i.e., r value) of a dimer or trimer cluster using measured electron detachment energies and the dipole moment and polarizability of the constituent monomers.

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