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Holding onto Electrons in Alkali Metal Halide Clusters: Decreasing Polarizability with Increasing Coordination

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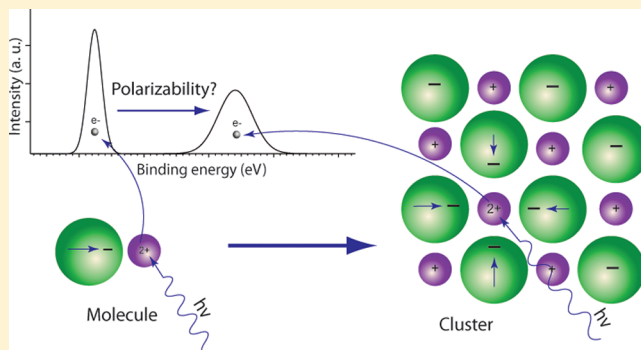
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ABSTRACT: The connection between the electronic polarizability and the decrease of the system size from macroscopic solid to nanoscale clusters has been addressed in a combined experimental and model-calculation study. A beam of free neutral potassium chloride clusters has been probed using synchrotron-radiation-based photoelectron spectroscopy. The introduction of “effective” polarizability for chlorine, lower than that in molecules and dimers and decreasing with increasing coordination, has allowed us to significantly improve the agreement between the experimental electron binding energies and the electrostatic model predictions. Using the calculated site-specific binding energies, we have been able to assign the spectral details of the cluster response to the ionizing X-ray radiation, and to explain its change with cluster size. From our assignments we find that the higher-coordination face-atom responses in the K 3p spectra increase significantly with increasing cluster size relative to that of the edge atoms. The reasons behind the decrease of polarizability predicted earlier by ab initio calculations are discussed in terms of the limited mobility of the electron clouds caused by the interaction with the neighboring ions.



I. INTRODUCTION

Alkali metal halide clusters have been an object of studies in fundamental and applied science for decades. One reason for this is that they can be seen as finite bits of the simplest ionic materials with a regular periodic structure providing a testing ground for various theories and models. More recently, another important reason has emerged: the study of the geometric and electronic structures of alkali metal halide clusters can give information on the formation and dynamics of sea-spray-originating nanoparticles in atmospheric marine aerosols. In the studies of the alkali metal halide cluster geometry and energetics, various theoretical and experimental approaches have been used, such as molecular dynamics^{1–3} and ab initio methods^{4–7} in theory and electron diffraction, mass spectroscopy,⁸ photoelectron spectroscopy,^{9–12} etc. in experiment. Lately, substantial progress in the quantum mechanics description of rather large alkali metal halide nanostructures has been made. The corresponding calculations show that though in a class of cases the cluster properties are close to those of the solid, for some types of clusters with ionic bonding the electronic and geometric structure may deviate significantly

from those adopted at macroscale. For example, for the alkali metal halide clusters containing up to 10^2 atoms the possibility of a structure with tubular geometry minimizing the energy to a degree higher than the solid-like cubic geometry continues to be a subject of theoretical investigation^{3–7} since Aguado et al. suggested it.

The present work is part of our to a large extend experimental studies of free alkali metal halide clusters using photoelectron spectroscopy.¹³ In theoretical works on such clusters it has been realized already for quite some time that the ab initio calculations of the electronic and geometric structure could be experimentally tested using photoelectron spectroscopy. For alkali metal halide clusters size-induced phase transitions⁶ and differences in the ionization energies for different sites¹⁴ have been predicted to be possible to detect by this experimental method. Indeed, our first electron spectroscopy investigation on alkali metal halide clusters,¹³ where NaCl

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has been the cluster parent material, has allowed us to obtain element- and site-specific information. Significant electron binding energy changes due to the transformation from the salt monomer to clusters have been observed by us¹³ for both core and valence levels of NaCl clusters. The electron binding energies have been shown to change with the cluster size. For differently sized clusters, the varying population of different sites (the surface, corner, edge and face sites with reduced coordination, and fully coordinated interior sites) leads to the changes in the cluster response detected by the photoelectron spectroscopy method. For calculating electron binding energies we have also suggested an electrostatic model including Coulomb and induced-dipole interaction, which has given a reasonable explanation of the experimental observations for NaCl particles of about 1 nm dimension.

Using this electrostatic model for free neutral alkali metal halide clusters/nanoparticles, it is rather straightforward to calculate the changes (relative to a monomer) in the system total energy for both the ground and the ionized state. (By definition, the difference between these two energies gives the electron binding energy.) Applying the photoelectron spectroscopy method to a free cluster beam,¹² it is possible to measure the electron binding energy differences between the molecules and the corresponding nanoparticles, thanks to the simultaneous presence of both in such a beam. In the early approaches to the electron binding energy calculations, for alkali metal halides in the “infinite” solid case a “dielectric-medium” model has been used to describe the role of the ions outside the first coordination shell of an atom under the question.^{15,16} Nowadays the theory and the calculation technique have been developed to a degree when a cluster model of any desired size can be employed to obtain not only the cluster energies but also those of the bulk. However, such an approach is a separate demanding task, so a certain virtue can still be seen in a simple, transparent electrostatic model which gives rather satisfactory numerical results.

In the present work, the question of differences in electronic polarizability and interatomic distance in nanocrystals with ionic bonding has been addressed. This has been realized in a combined experimental/computational investigation of another common salt, KCl, where the contribution of K ions (bulk polarizability $\approx 1.2 \text{ \AA}^3$) to the dipole interaction in the crystal becomes comparable to that of the chlorine ions (bulk polarizability $\approx 3.0 \text{ \AA}^3$). In contrast, the polarizability of the smaller Na ions (bulk polarizability $\approx 0.26 \text{ \AA}^3$) could be practically neglected in NaCl clusters.¹³

In our study on NaCl clusters the simple assumption of solid-state values for the reported in literature polarizability and interatomic distance has been sufficient to get a reasonable agreement between the experiment and our model calculation. In the present work, the electrostatic model has been cross-tested over a wide range of interatomic distance and polarizability values. The polarizability variation, proposed here as a way to reach better matching of our model calculation to the experiment, has been motivated by theoretical works on alkali metal halide and other systems with ionic bonding, in which the anion polarizability has been suggested to be noticeably lower than the corresponding value in a monomer and dependent on the number of the nearest neighbors.^{17–20} For the clusters with ionic bonding it has been shown¹⁹ that a change in the cluster-atom coordination number from the smallest to the largest possible leads to a gradual anion-polarizability decrease by almost a factor of 2. Experimental

observations together with the model treatment implementing the assumption of lower anion polarizability in alkali metal halide nanoscale clusters constitute the main result of the present work.

II. EXPERIMENT

Free KCl clusters were produced by the so-called “pick-up” method.¹² In the present experiment, a primary beam of argon clusters was generated by adiabatic expansion of Ar gas into vacuum in a dedicated chamber, separated from the ionization chamber by a skimmer. Having entered the ionization chamber through the skimmer, the argon cluster beam passes through alkali metal halide vapor created in an oven placed in the ionization chamber and filled with solid salt granules. Alkali metal halide clusters are formed in the process of thermal exchange between the molecular vapor and the cryogenically cold Ar clusters. The setup, as a whole named exchange metal cluster (EXMEC) source, was mounted at the end station of the beamline I411 at MAX-Lab in Lund, Sweden. The details of the setup have been described elsewhere.²¹ More information about the experiment has been given in our previous paper.¹³ To produce KCl clusters of different sizes, the number of pick-up events was varied by changing the KCl vapor density via the oven temperature, which was set to several different fixed points in the range from 350 to 450 °C. Judging on the basis of our previous results on NaCl clusters created in the same way, the size of the KCl clusters should be in the range from a few tens to a few hundreds of atoms, and thus these clusters have a characteristic dimension of about 1 nm.

The incident synchrotron radiation crossed the alkali metal halide cluster beam at 90°. The photoelectron spectra were recorded in the K 3p, Cl 2p, and valence regions using a Scienta R4000 electrostatic energy analyzer placed either at 90° or at the so-called magic angle of $\approx 54.7^\circ$ with respect to the radiation polarization plane. With acquisition at 90° we can expect a reduced surface sensitivity relative to the case of the “magic-angle” geometry. The reason for this is the effect of intracluster elastic scattering on the angular distribution of the photoelectrons. The photoelectrons from the p levels are primarily emitted in the polarization plane, i.e., perpendicular to the detection direction in this case. The bulk electrons get a more uniform angular distribution due to elastic scattering on their way out of the cluster, whereas the surface photoelectrons to a high degree preserve their initial emission direction perpendicular to the direction of detection.²² This results in a relative enhancement of the bulk signal compared to the surface signal.

An absolute energy calibration was obtained using the Ar 3p lines from the uncondensed Ar atoms in the beam. The monomer K 3p state was observed at around 25.1 eV, consistent with the literature value obtained by both experiments and model calculations.⁵

III. IONIC MODEL AND THE ROLE OF ITS MAIN PARAMETERS FOR ALKALI METAL HALIDE CLUSTERS

As mentioned in the Introduction, in our previous study of NaCl clusters,¹³ significant binding energy shifts from the monomer values were detected in both core and valence levels. The Na 2p core level was observed to have approximately 3 eV lower binding energy than the monomer. The shifts in the Cl 3p-dominated valence levels and Cl 2p core level were not as

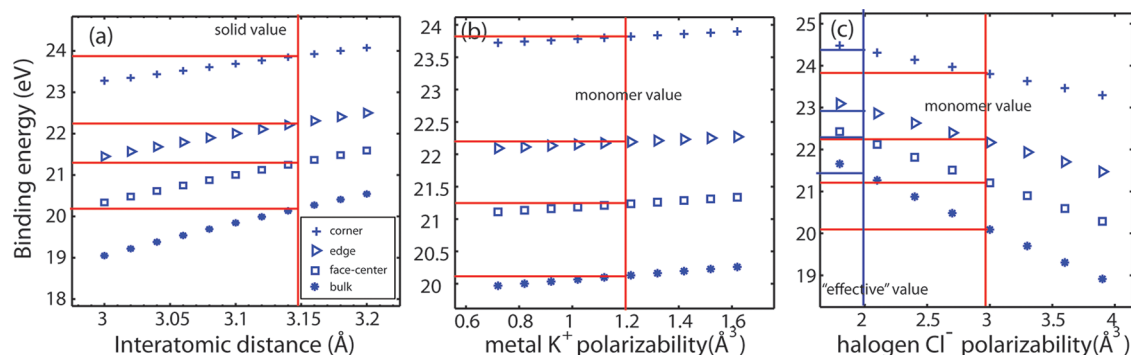


Figure 1. Calculated value of K 3p binding energy by changing three parameters in the ionic model for cubic clusters with 4 atoms along the side, denoted as $4 \times 4 \times 4$ clusters: (a) interatomic distance; (b) K ion polarizability; (c) Cl ion polarizability. The solid red lines correspond to the parameters that have been used in literature for macroscopic solid or a monomer. The effective parameters have been directly used by changing the Cl polarizability, and the results are shown by blue solid lines.

large, and they were toward the opposite direction, ≈ 1 eV to the higher binding energy relative to the monomer. In the present work on KCl clusters, similar but somewhat smaller shifts have been observed. For KCl clusters, a span of metal-site shifts for the K 3p level from 1.8 to 2.8 eV (corresponding to binding energies between 21.5 and 22.5 eV), i.e., a larger range than for NaCl clusters, has been recorded. This variation of the shifts has been attributed to different sizes of KCl clusters produced at different experimental conditions. The spectral details will be described below, in the context of the modeling of the results. Before this, however, we will first qualitatively discuss the connection between the spectral response of KCl clusters and their key, substance-specific properties: interatomic distance and polarizability. We will then proceed to use the electrostatic model described in detail in ref 13 for calculating electron binding energies, and we will try to establish whether a better quantitative agreement with the experimental data can be achieved within a reasonable range of the distance and polarizability variations. The grounds for these variations will be also discussed in more detail.

As mentioned earlier, a classical electrostatic ionic model can rather well describe the core-level electron binding energies for separate alkali metal halide monomers, dimers and clusters,^{1,13} if only Coulomb interaction and polarization interaction of distorted electron clouds with the counterions is taken into account. For clusters, a decisive point is also what kind of crystal structure they adopt in the process of self-assembling from the gas-phase monomers to (molecules). In several earlier works it has been suggested that alkali metal halide clusters were cuboids (rectangular parallelepipeds with an even number of atoms along at least one of the edges).^{4,23,24} During the later time it has been theoretically shown that for the ionic clusters with the number of atoms below 100 the ratio of the cation and anion radii, r_C/r_A , defined whether a tubular or cubic geometry would be energetically favorable.^{3,6,14} If $r_C/r_A \leq 0.5$, tubular structures occur to be more stable. Potassium chloride belongs to those alkali metal halides for which this criterion allows assuming cubic geometry for all cluster sizes because $r_C \approx r_A$ in this case. Cubic geometry makes the model calculations straightforward, and the results are quantitatively very close for cubes and cuboids constructed by adding/removing a crystal plane to/from a corresponding cube. Imperfect cuboids with molecules adsorbed on one or more plane faces should also give spectral responses close to those of the cubes.¹³ For this reason we will for simplicity consider only cubic clusters

and regard all the conclusions to be valid also for closely related cuboids. In the model, the total energy difference between the initial and final states due to Coulomb and polarization interactions between the probed atom and the rest of the atoms in an ideal cube is used as the electron binding energy of a specific atom at the corner, edge, face and bulk sites.

It is appropriate here to emphasize the somewhat different roles the polarization energy in the ground state plays at nanoscale and in macroscopic salt crystals. In the latter case, there is no polarization energy for the absolute majority of the atoms (the bulk atoms) due to the perfect symmetry of the Coulomb field, and thus no chosen direction for the electron-cloud deformation. In stoichiometric clusters with a characteristic dimension of only a few interatomic distances, the Coulomb field distribution has no local symmetry, and as the result all electron clouds are deformed. This creates polarization interaction even in the ground state of an ionic nanosolid. In the electron binding energy calculation it is important to take it into account. For example, in the KCl clusters discussed in the present work the initial-state polarization energy of the face and bulk metal atoms is calculated to be about 20% of the polarization energy of the same K atom in the final state. In the latter, doubly ionized state of the metal atoms the polarization energy becomes comparable with the Coulomb interaction, but this is valid for both nano- and macroscale solids.

The here investigated electron binding energies are influenced by several factors, such as cluster size, the geometric structure including interatomic distances and the site-dependent coordination numbers, as well as the response of the system to the removal of one electron. Interestingly, opposite to the intuitive expectations based on the results for the other types of clusters, the cluster size influences the calculated electron binding energies much less than the site: For one and the same site the binding energy remains practically constant for cluster sizes above $2 \times 2 \times 2$ atoms. For example, in NaCl clusters, when going from $2 \times 2 \times 2$ cubes to $20 \times 20 \times 20$ cubes, our calculations give a shift of only about 0.2 eV for each specific site. In other words, the size dependence is rather weak relative to the monomer–cluster separation of 2–3 eV. For the present work, the size-dependent change is close to the instrumental broadening of the spectral features which is ≈ 0.17 eV.

After geometry and size, the next two parameters defining the electron binding energies in alkali metal halide clusters are the interatomic distance, and the polarizability of the electron clouds of the metal and halide ions. For the clusters, both the

polarizability and interatomic distance can be assumed to be between the limits set by the monomer and the solid. In the calculation for NaCl clusters, the infinite-solid values of interatomic distance and polarizability²⁵ have been used by us as a reasonable first approximation, yielding calculated energies close to Na and Cl responses in the experimental photoelectron spectra of the clusters. Nevertheless, the relative energy difference between the experiment and the numerical results has been noticeably larger for NaCl clusters than for the monomers. The present work has been intended to investigate this issue using the results of extensive studies on KCl clusters. We use the binding energies for cubic clusters with 4 atoms along the side (denoted $4 \times 4 \times 4$ clusters) as an example. The size of ≤ 100 atoms/cluster has been typical for the present experiment.

Implementing the model¹³ formalism we first investigate the role of the interatomic distance. We calculate the electron binding energies for four different sites (corner, edge, face, and bulk) using interatomic distances in a range around the bulk lattice constant while keeping the polarizabilities of potassium and chlorine fixed to the solid-state values derived by Tessman et al.²⁵ from the optical refraction data. We especially focus on the K 3p level due to the large experimental shift to explain. The results for the 3.0–3.2 Å range of interatomic distances in clusters, to be compared to 2.6 Å for the monomer and 3.15 Å for the solid, are shown in Figure 1a. The calculated K 3p binding energy in clusters increases with increasing interatomic distance, and the separations between the four geometric sites become smaller. At the presently investigated cluster sizes, the edge and face sites should dominate the cluster response in the photoelectron spectra. The calculated binding energies for interatomic distances equal to or smaller than that of the solid-state interatomic distance (Figure 1a) are, however, lower than the binding energies observed in the experiments, where the main intensity is above 22 eV. A larger interatomic distance than for the solid would give better matching to the experiment, but it is not very probable as the clusters are intermediate to the monomer and the solid, and thus likely to have the interatomic distance smaller than the solid. Indeed, for example, for (NaCl)₄ clusters Yalovega et al.²⁶ calculated the interatomic distance to be 2.5 Å, between the value for the monomer (2.36 Å) and the solid (2.81 Å). Other theoretical studies of alkali metal halides, for example by Aguado et al.,²⁷ though somewhat overestimating the interatomic distance for a cubic cluster, predict values smaller than for the bulk. The systematic overestimate is caused by the neglect of the electron correlation in the calculation.

Summing up the discussion about the role of the interatomic distances in the range between the lower and upper limits, we conclude that the variation in the reasonable distance-range does not give binding energies in agreement with the experiments, provided that the same polarizability²⁵ as in the solid is assumed.

Could instead the present model–experiment discrepancies for alkali metal halide clusters be explained by the polarizabilities of the metal and halogen ions being different from those in the crystal derived by Tessman?²⁵

As briefly mentioned in the Introduction, in several theoretical works^{18–21} the electronic polarizability of the constituent atoms has been shown to change when a multiatomic alkali metal halide system was formed. In the earlier works it has been suggested that the chlorine polarizability reported to be from 3.66 Å³²⁸ to 3.94 Å³,²⁹ in a

free ion should be “quenched” already in a molecule by about 30–40%.^{17,30} For an alkali metal halide dimer the polarizability of halide anions, determining the larger part of the polarization interaction, has been estimated to decrease further by about $\approx 10\%$.¹⁷ Theory suggests that the polarizability decreases even further when the number of neighbors grows. For LiF crystal Fowler and Madden¹⁸ have calculated a decrease by a factor of 2.5 for the electronic polarizability of a fluoride ion. Recent detailed calculations by Aguado and Madden¹⁹ show a gradual decrease of the anionic polarizability with the coordination number in ionic clusters, with the limit values differing by a factor of 2. A review on the subject has been just published.²⁰ At the atomic level the polarizability is connected to the deformation of the electron density distribution by an external electric field. In the early work¹⁸ on the bulk crystal the polarizability decrease has been explained mainly by the attractive forces of the crystal field pulling the electron clouds back to their equilibrium positions, when these clouds are deformed toward the ion in question. This mechanism becomes especially clear in the final state of the photoionization process for the metal core-level. A sudden appearance of a doubly charged metal ion distorts the symmetry of the electric field distribution, and the electron clouds of the neighbor halide ions will tend to adapt to the new charge. However, the other metal ions will act in the direction away from the new doubly charged ion. This attractive force increases with the number of atoms in the surroundings.

Another reason why the polarizability in clusters should be smaller is the spatial confinement of the electrons in the cage of the neighboring ions with their electrons. Polarizability in clusters changes as the result of the orbital compression, due to the overlap with the involved electron clouds of the neighbor ions in the first coordination shell.^{4,18} The cage built by the neighbors can be complete as in the bulk, or open as on the surface. Thus for the surface atoms a larger degree of electron-cloud deformation/mobility is possible and thus the surface-atom polarizability can be higher than that of the bulk, as the ab initio calculation¹⁹ shows.

It should be added here that the solid-state chloride polarizability value of ≈ 3.0 Å³ (from ref 25) used by us was obtained in 1953 from the analysis of the optical refraction index of alkali metal halide crystals. The few later estimates found by us in the literature rely on the experimental results of the same time. From such an optical experiment it is possible to derive a pair polarizability due to the electrons of both cations and anions together. Fowler and Madden¹⁸ estimated the experimental chloride value to be 3.14 Å³ by subtracting their ab initio calculated cation polarizability from the experimental pair polarizability of NaCl. There are several ab initio calculation results for the crystal electronic polarizability, varying considerably depending on the method in use.^{18,26} The values for the monomers and dimers have been recalculated, for example, in 1991 (see ref 17), and are supported by spectroscopic data, so we consider a comparison to them as more appropriate. The anion polarizability value for the KCl dimer given in ref 17 is 2.24 Å³.

We investigate first the hypothesis of lower K⁺ and Cl[−] polarizabilities in clusters as the explanation for the discrepancies for the K 3p level cluster energy, the discrepancies between the experiment and the model using a set of measurements on KCl clusters and corresponding model calculations.

Figure 1b presents the results of the calculation for the K 3p electron binding energies in KCl $4 \times 4 \times 4$ clusters for four sites as a function of the metal-atom polarizability. The range is $\pm 40\%$ from the value for the crystal given in ref 25 as 1.2 \AA^3 . In monomers and dimers it is reported to be 1.05 and 1.09 \AA^3 .¹⁷ As can be seen from Figure 1b, the polarizability of K^+ cations has only a weak influence on the K 3p binding energy. This is due to one geometric and one electronic factor. The probed metal ions have halide ions as nearest neighbors, and the nearest other metal ions would be only in the second coordination shell. Therefore, the main screening of a core-ionized potassium atom comes from the electron clouds of the halide ions. Furthermore, polarizability of a separate atom is a function of the number of electrons per atom and the deformability of the orbitals. K^+ and Cl^- are isoelectronic: the number of electrons is the same in these ions. The key difference is the deformability of the orbitals, which should be higher for Cl^- as its 3p electrons are weakly bound, whereas the 3p electrons of K^+ are more strongly bound. Thus, the effect of the metal polarizability variation on the K 3p ionization energy can be practically neglected. It is indeed confirmed by the calculation results (Figure 1b) where the corresponding dependences are close to straight horizontal lines.

Finally Figure 1c shows the calculated results for the K 3p energy dependence on the Cl polarizability varied in the range $\pm 40\%$ around the value used earlier by us. Relative to the more recent estimates of the Cl polarizability, the range starts well below the dimer values¹⁷ and extends up to the values above the free ion polarizability. The calculations show that a decrease in Cl polarizability leads to an increase of the K 3p binding energy. This is an important feature that will help us to find what can be called the “effective” polarizability⁴ for the clusters by optimizing the matching between the model and experiment.

Summing up, one can conclude that the cluster K 3p ionization potentials may shift to higher energies and the energy differences between the four sites may become smaller mainly due to the anion polarizability decrease in clusters rather than to the interatomic distance increase.

IV. TEST OF PARAMETERS USING EXPERIMENTAL RESULTS

1. K 3p Core Level. As discussed above, using K and Cl polarizabilities from Tessman et al.²⁵ and the interatomic distance of the KCl crystal leads to too low binding energies in the calculations for the edge and face sites, when compared to the experimental cluster signal. At the same time, as explained above, these sites should dominate the cluster photoelectron signal in the investigated size range. Consequently, there is some discrepancy to explain. We have performed electrostatic model¹³ calculations varying the chlorine-ion polarizability to deduce a value giving the best agreement with the experimental results.

We will now discuss these experimental results, the core-level photoelectron spectra obtained for clusters at different experimental conditions. Figure 2a shows the K 3p photoelectron spectra and Figure 2b shows the valence-level spectra of KCl clusters recorded with the photon energy of 69.9 eV . They are in fact the parts of one and the same acquisition run that is split into two regions for the clarity of presentation. For the K 3p case, the cluster feature is observed at more than 2 eV lower binding energy than the monomer feature at $\approx 25 \text{ eV}$. The maximum of the cluster feature appears in the range

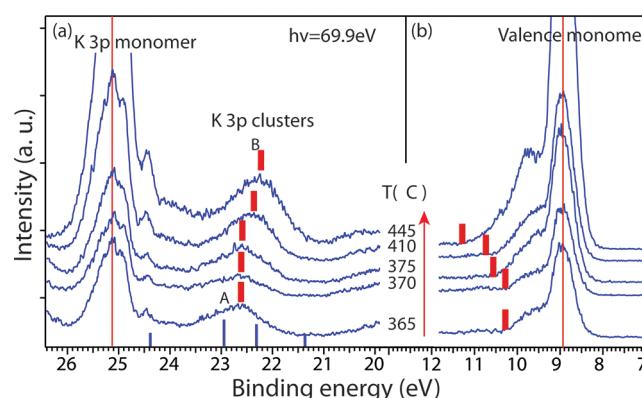


Figure 2. K 3p and valence binding energies recorded at 69.9 eV photon energy and with the spectrometer at the magic angle. Spectra from the bottom to top correspond to gradually increasing oven temperature. The red solid lines in (a) and (b) correspond to the monomer core K 3p and valence level, respectively. The short blue lines in the bottom are the calculated binding energies for different sites from Figure 1c. From the left to right are: corner, edge, face-center, and bulk.

between 22.3 and 22.6 eV depending on the cluster formation conditions. From the bottom to the top in Figure 2a, the cluster K 3p level shifts downward with increasing vapor pressure as the oven gets hotter. The shape of the cluster feature is asymmetric and changes with the cluster formation conditions. Our explanation for the spectral changes is that the experimental spectra reflect the change in the cluster size distribution, with the differences in binding energy for various sizes and sites. This also comes out from the model calculations presented in Figure 1. The feature just below the monomer (starting from $\approx 24 \text{ eV}$) rises significantly for higher temperatures. We assign this rise to be not only due to the increasing monomer and dimer concentration but also due to the contributions from the low-coordination sites, such as corners and corner-like sites (adsorbed molecules) in clusters.

The “effective” polarizability for Cl ions derived by optimizing the calculations for the experimental results occurred to be $\approx 2 \text{ \AA}^3$, as has been shown in the Figure 1c. This is close to the calculated value for a dimer of 2.24 \AA^3 by Chauhan et al.¹⁷ The four vertical lines at the bottom of the experimental spectra in Figure 2a correspond to the binding energies of the four sites calculated with this “effective” polarizability value. Despite the relatively simple model, good agreement with the experiment is observed. The contributions from the cluster corners, dimers, and monomers overlap and cannot be resolved, but they add to the total intensity in the corresponding binding energy region. It is seen that the experimental intensity is mainly located in the regions around the points where edges and faces should respond. The shift of the cluster peak maxima (when moving from the bottom to the top of Figure 2a) is not due to the increasing size in itself but can be attributed to the changes of the site distribution with cluster size, as explained above in section III. With increasing cluster size, the relative contribution from the edge sites should become smaller, and that from the face sites stronger. The face response should increase further with increasing size. The bulk contribution should also increase but would appear at a noticeably lower binding energy around 21.4 eV . Only the top spectrum in Figure 2a, representing the largest clusters, contains some intensity in this binding energy region. The

absence of the bulk response is assigned to the fact that we produce rather small clusters, as discussed in our publication on NaCl.¹³ The signal from the few bulk atoms is furthermore attenuated due to the short electron escape depth of 1–2 layers. Another possible explanation of the absence of the bulk signal at the expected calculated position could be an even lower polarizability for the inner atoms.¹⁶ The larger number of neighbor atoms in the bulk implies stronger equilibrium-restoring force, due to the crystal field and larger electron cloud mobility limitation, and thus even lower polarizability. Such a conclusion is consistent with the mentioned above theoretical results¹⁹ showing a steady decrease of the anion polarizability with the coordination number. The lower polarizability would additionally shift the bulk electron binding energy upward, so that it may even overlap with the face-atom response.

In another set of measurements, shown in Figure 3, with the electron spectrometer at 90° to the polarization plane, we have

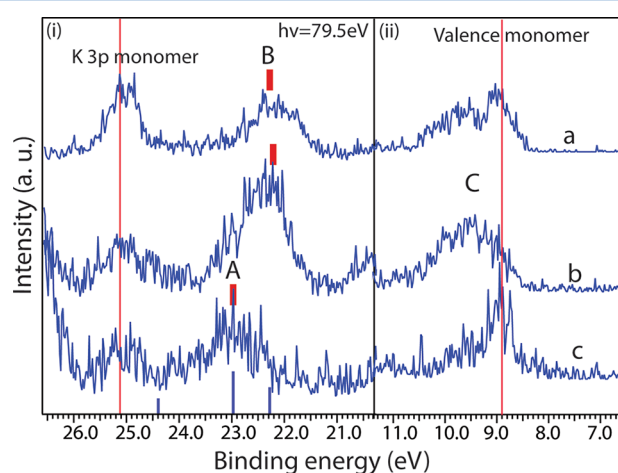


Figure 3. Photoelectron spectra of K 3p and valence states recorded at 79.5 eV photon energy and with the spectrometer at 90°. Two solid red lines on both parts of the figure are the monomer signal. Position A corresponds to the calculated value for edge, and B for face-center using effective polarizability value and solid interatomic distance. The clusters' peak maxima in the spectrum a shows 1 eV lower binding energy than that of spectrum c.

observed a wider span of K 3p cluster binding energies than in the magic-angle measurements. A close inspection of spectrum in Figure 3a shows that, using the above assignments, it is “face-rich”, whereas the spectrum in Figure 3c is “edge-rich”. The spectrum in Figure 3b corresponds to an intermediate situation, with the contribution from the faces being just a bit larger than that from the edges. The bulk response is also very weak in Figure 3.

As mentioned above, with the acquisition at 90° to the radiation polarization plane one could expect an enhanced bulk response relative to the case of the “magic-angle” geometry. However, the size of the clusters in the present case assumes only a very small fraction of bulk atoms, so the bulk signal occurs to be too weak even at this geometry.

2. Cl 2p Core Level. As in the case of NaCl clusters, the experimentally obtained cluster core-level binding energy changes of the chloride ions are much smaller than those of the alkali metal ions. The cluster signal overlaps with the dimer signal from the effusive beam of the uncondensed salt vapor from the oven. As a result, the halide cluster response is in a certain sense less informative than that of the metal ions. As

discussed in our previous work,¹³ there are two main reasons for the positive binding energy shift observed: First, in the photoionization process the halide charge goes from “−1” to “0”, whereas the alkali-metal charge goes from “+1” to “+2”. So there is no Coulomb interaction term in the Cl final state whose presence is the main reason for the negative shift for the cation energy. Second, the absence of the charge in the final state leads also to the disappearance of induced dipoles on the neighbor electron clouds, and thus to the absence of this type of polarization interaction in the final state. For cations the resulting from such interaction energy shifts the levels also (as for the anions) downward.

For the Cl 2p core-electron levels in KCl clusters, the present measurements place the cluster features at ≈ 0.7 eV higher binding energy than for the monomer. A detailed assignment of the intensities above the monomer binding energy is somewhat ambiguous because, as mentioned above, the cluster and dimer features overlap. For simplicity the spectrum has been fitted with four independent, symmetric Voigt line profiles, one pair for the 3/2, 1/2 spin–orbit components of the monomers and one pair for the dimers/clusters (Figure 4). The free fitting

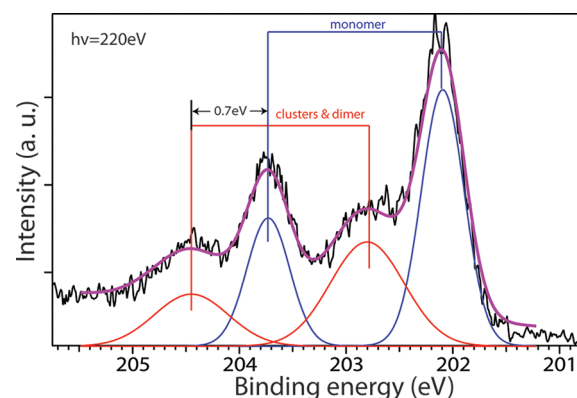


Figure 4. Photoelectron spectra in Cl 2p region of KCl clusters. Molecular lines are also present due to the existence of the monomer in the effusive beam.

parameters are the binding energy of these components, the intensity and the widths of the lines. The relative intensity of the two spin–orbit components in each pair has been fixed to the statistical ratio 2:1, and the spin–orbit splitting for clusters/dimers has been kept at the monomer value. The width of the cluster/dimer features is larger than that of the monomer. This is to be expected: First, each feature is a result of the cluster–dimer overlap; second, the cluster beam contains a distribution of cluster sizes with different sites, which all act to broaden the features similarly to the case of K 3p. In Table 1, the experimental shifts ΔE for the clusters/dimers relative to the corresponding monomer ($\Delta E = E_{\text{cluster}} - E_{\text{monomer}}$) are presented. The Cl 2p binding energies of KCl monomers and, for comparison, of NaCl monomers are given. As seen from Figure 4 and Table 1, the Cl 2p cluster feature shifts less in $(\text{KCl})_n$ than in $(\text{NaCl})_n$.

The model suggests that the main difference in Cl 2p electron binding energy between KCl and NaCl in the transition from molecules to clusters should come from the Coulomb interaction term of the initial state. This is because the interatomic distance in KCl is larger than in NaCl. The polarization-interaction terms are small both in the initial and in the final states. For example, in the initial state of the $4 \times 4 \times 4$

Table 1. Experimental and Model Binding Energies of Cl 2p for NaCl and KCl Monomers and the Shift between Clusters and Monomers

molecule	core level	binding energy (eV)	model calculated binding energy (eV)	shifts $\Delta E(\text{eV})$ ($=E_{\text{cluster}} - E_{\text{monomer}}$)	calculated $\Delta E(\text{eV})$ for face site
NaCl	Cl 2p _{3/2}	202.6	202.7	≈ 1	1.1
	Cl 2p _{1/2}	204.2	204.2		
KCl	Cl 2p _{3/2}	202.2	202.1	≈ 0.7	0.8
	Cl 2p _{1/2}	203.7	203.7		

clusters, the polarization energy for the surface sites is between 0.1 and 0.4 eV. In the final core-ionized state the chlorine atom with a hole in a rather deep electronic shell shrinks significantly, and its polarizability may well decrease further due to that. All this suggests that polarizability variations cannot influence Cl 2p energies to the same extent as K 3p energies and cannot improve the correspondence between the experiment and the model, which gives too large shifts for the chlorine 2p state in clusters relative to those observed experimentally. Only for the corners where the model shift is about 1 eV does the matching to the experiment exist. For the edge and face atoms the calculated shift is more than 2 eV. To explain this discrepancy relative to the experiment, one can try taking into account the change in the repulsion energy for the chlorine in the initial and final states. In the formulation of the model an assumption (introduced yet by the authors of the electrostatic model for the alkali metal halide monomer ionization.^{1,9,10}) of unchanged repulsion between the initial and final states has been made. Because the here measured and calculated electron binding energy results from a difference between the initial and final state, the corresponding repulsion terms cancel in the calculation of the ionization energy. In the studies,^{1,9,10} the ionization of the outermost orbitals for both the metal and halogen sites has been discussed. Taking away an electron from these orbitals should not change the radius of the atoms significantly. Thus the repulsion between the metal and halogen electron clouds should also not change much. In the present case of Cl 2p ionization it can be different: in the final state the core-ionized chlorine with 8 electrons in the outer-shell will resemble an argon atom according to the so-called $Z + 1$ approximation.³¹ The radius of the chlorine ion will correspondingly decrease.¹⁵ In its turn this should significantly decrease the repulsion energy between the resulting much smaller Cl atom and its neighbors. Indeed, in an early study¹⁵ of alkali metal halide crystals with photoelectron spectroscopy, the authors stated the absence of repulsion forces in the final state. As the repulsion energy in the initial state is subtracted and that of the final state is added in the calculation of the Cl 2p binding energy, the absence of latter energy would shift the calculated binding energy downward, i.e., closer to the experimental energy. An estimate of the value can be made using molecular constants obtained for KCl in ref 9. For the solid interatomic distance of 3.15 Å, the thus calculated initial-state repulsion energy in a molecule occurs to be 0.23 eV. Assuming simple additivity of this energy with increasing number of neighbors, one gets for the 4-coordinated edge atoms ≈ 0.9 eV, and for the 5-coordinated face atoms ≈ 1.2 eV. These estimates are not far from ≈ 0.8 eV calculated in ref 15. This repulsion correction makes the calculated Cl 2p binding energies practically coincide with the experimental binding energies for the cluster, which

can be considered as a good agreement for a classical model. One can underline that for the metal site, where it is the outermost shell that loses an electron, the repulsion terms in the final and initial states should be similar and counter-compensate each other in the difference expression and thus do not change the model calculation.

3. Valence Region. A clear cluster signal is also observed in the Cl 3p-dominated valence region both in the magic-angle and in the 90° cases. Qualitatively and even quantitatively similar processes happen on the chloride site in the case of 2p and 3p level ionization: the chlorine atom becomes neutral, so the Coulomb interaction in the final state is absent, and the binding energy of cluster/dimer is higher than in a separate molecule. The cluster valence binding energy is approximately 1 eV higher than for the monomer for the largest size in the series of measurements at the magic angle (Figure 2).

In the 90° measurement series, the monomer contribution is comparatively small, so it is possible to discern the cluster feature shape as a single peak between 8 and 11 eV. The monomer-to-cluster shift is highest in spectrum Figure 2c, and smallest in spectrum Figure 2a. The overall behavior of the valence spectrum is consistent with the changes in the K 3p spectra with the size.

Here, in the model calculation for the Cl 3p case, as for Cl 2p level, there is a larger deviation from our experimental results than for the K 3p case. In contrast to the discussed above for the Cl 2p core-level case, the repulsion energy in the Cl 3p cannot be expected to become significantly different after the valence ionization. At the same time, the removal of one valence electron has been shown to lead to almost twice higher polarizability of the chlorine atom in a KCl molecule.⁹ It can qualitatively be rationalized as due to the appearance of some free space (in the otherwise fully occupied 3p orbital) for the electron cloud deformation when the eighth electron is removed. An increase of polarizability by a factor of 2 would lead to a directly proportional final-state polarization energy increase by the same factor of 2. For a cluster of $4 \times 4 \times 4$ atoms this would mean a value just below -1 eV. Again, this correction makes the calculated and experimentally observed binding energies match well.

V. CONCLUSIONS

In summary, the size- and site-dependent electronic properties of KCl clusters have been investigated using photoelectron spectroscopy and electrostatic model calculations. Apart from the large binding energy shifts from molecular to cluster metal core levels, as has already been demonstrated for NaCl clusters, we have also recorded the changes in the shapes of the cluster spectral features with the size, and a wider span of the energy changes with more than 1 eV difference between the limiting points. These shape and position changes have been explained by the different sizes of the clusters through the change of the site distribution in them. At the KCl cluster size in question, $\leq 10^2$ atoms, the dominating contribution to their photoelectron spectra is given by the surface atoms located in the faces, edges, and corners of the KCl cluster cuboids. As the size becomes larger, the fraction of the face atoms increases faster than that of the other atoms.

A concept of “effective” electronic polarizability has been implemented for clusters. The idea behind it expressed and developed theoretically in a series of works is the decrease of the electron cloud mobility in clusters relative to the free ion and molecular cases. Mainly two types of interaction with the

ions in the surroundings cause such a decrease: (1) the equilibrium-restoring attraction force from the “crystal” field and (2) the compression of the electronic orbitals by the orbitals of the nearest neighbors. Therefore, the anion electron clouds of a monomer (molecule) are more polarizable than those of the clusters and the solids. Moreover, within a cluster the surface-atom electron clouds should be more polarizable than those in the bulk. Lowering of the anion polarizability value relative to that of the molecules improves significantly the agreement between the experiment and the calculations for the metal site. The effective polarizability has been estimated using a combined experiment-model approach. Because the clusters in the present work are created in the size range where the fraction of surface atoms is large in comparison to the bulk-atom fraction, the polarizability value derived here can be seen as an averaged property of the nanoparticles’ surface. One can also emphasize that polarization interaction plays a larger role in salt nanosolids and at the surface than for the macroscopic bulk. In the latter case the polarization energy in the ground neutral state is zero in the view of the absolute symmetry of the Coulomb field at the nodes of the crystal, and thus no asymmetric distortion of the electron clouds present. At nanoscale, the electric field is asymmetric at the nodes even in the nanoparticle interior and it varies depending on where the ion is situated. Thus the polarization energy is present even in the neutral ground state. Last but not least, the experimental results suggest a considerable change in the chlorine 3p polarizability after the ionization. And it is, for example, the dynamic electronic polarizability that determines to a great extent optical properties of nanocrystals. All in all, taking into account varying electronic polarizability in nanoparticles is of clear importance.

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Notes

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