"Textbook" Adsorption at "Nontextbook" Adsorption Sites: Halogen Atoms on Alkali Halide Surfaces

Bo Li, Angelos Michaelides,* and Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
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Density-functional theory and second order Møller-Plesset perturbation theory calculations indicate that halogen atoms bond preferentially to halide substrate atoms on a series of alkali halide surfaces, rather than to the alkali atoms as might be anticipated. An analysis of the electronic structures in each system reveals that this novel adsorption mode is stabilized by the formation of textbook two-center three-electron covalent bonds. The implications of these findings to, for example, nanostructure crystal growth, are briefly discussed.

Alkali halides are classic wide band gap insulating materials. They have long been studied as model systems to better understand basic notions in solid state physics [1] and because of their important optical properties [2]. In recent years there has been increased interest in the surface properties of alkali halides due to their potential role in emerging nanoscale technologies [3,4] and because of their importance to environmental chemistries such as ozone depletion and precipitation [5,6].

Most alkali halides have the rocksalt structure and expose flat stoichiometric (001) surfaces. However, the surfaces of alkali halide crystals are notoriously difficult to characterize at the atomic level with standard surface science approaches because of the challenges posed by surface charging and electron-stimulated dissociation [7]. Experimental procedures to circumvent these problems by, for example, growing thin films of alkali halides on conducting (metal) substrates, have been developed and used to great effect recently [4,8]. Vogt and Weiss, for example, followed such a procedure to perform a quantitative low energy electron diffraction (LEED) analysis of NaCl(001) and KCl(001) [9]. The small relaxations of the surface atoms from their ideal bulk truncated values observed in that study are in good agreement with available theoretical data [10–12]. Nonetheless, our basic understanding of such surfaces remains shallow, certainly when compared to that for metal or even metal-oxide substrates. Thus, one of the simplest questions one could ask concerning adsorption at such surfaces remains unanswered: how do (additional) halogen adatoms adsorb? This question is important to answer for the materials science technologies mentioned above and for understanding alkali halide crystal growth and dissolution as well as understanding basic principles of adsorption and bonding. Conventional wisdom would lead one to conclude that the halogen adatoms should bond to alkali substrate atoms since this is the correct location for continued crystal growth. However, we show here for a series of sodium halide surfaces—NaF(001), NaCl(001), and NaBr(001)—that first principles calculations predict halogen adatom adsorption and bonding to halide substrate

atoms instead. The explanation for this "nontextbook" adsorption is that covalent bonds are formed. Specifically, a two-center three-electron bond is created in each system. Effectively the bonding in these systems resembles that of an "embedded molecular ion," an analogy that proves to be helpful also in explaining the subtle differences observed between each adsorption system as well as the dynamical properties of the NaCl adsorption system. The above conclusions are reached based on a series of density-functional theory (DFT) and second order Møller-Plesset perturbation theory (MP2) calculations for halogen adsorption on sodium halide slabs and sodium halide clusters.

First let us discuss the periodic slab calculations that were performed within the plane-wave pseudopotential formalism of DFT and with the Perdew-Burke-Ernzerhof (PBE) [13] generalized gradient approximation (GGA). Six layer thick slabs were used to examine F on NaF(001), Cl on NaCl(001), and Br on NaBr(001) within a square unit cell comprised of 8 sodium and 8 halide atoms per layer [14]. Table I lists the adsorption energies and adsorbate-substrate distances for each system at the high-symmetry atop sites. It is clear from Table I that the halogen adatoms bind most strongly at the halide sites, rather than at the Na sites. In every case there is a preference of 0.2–0.4 eV for adsorption at the halide site. Two

TABLE I. Adsorption energies, E_{ad} (eV/atom), and optimized adatom-substrate distances, d (Å), for F/NaF(001), Cl/NaCl(001), Br/NaBr(001), and Cl on the Na_9Cl_9 cluster all with the PBE functional and the plane-wave pseudopotential method. The bond strengths and bond lengths of the corresponding gas phase molecular ions, i.e., F_2^-, Cl_2^-, and Br_2^-, calculated within the same computational framework, are given in parentheses.

Binding site		NaF(001)	NaCl(001)	NaBr(001)	Na_9Cl_9
Halide	E_{ad}	1.07(2.07)	0.72(1.73)	0.58(1.58)	0.77
	d	1.97(2.05)	2.61(2.66)	2.87(2.91)	2.61
Na	E_{ad}	0.70	0.41	0.31	0.47
	d	2.25	2.72	2.87	2.75

interesting trends are also apparent from Table I, which we discuss again below: the halide atom adsorption energies decrease and the adsorbate-substrate bond lengths increase as one moves down the halogen group from F to Cl to Br.

Noting that the energy difference between the two high-symmetry adsorption sites on each surface is on the order of $0.2-0.4$ eV it is not inconceivable that the theoretical approach employed here may simply be incorrectly predicting the halide site as the preferred one for adsorption. We make this seemingly overcautious statement because, as we will show below, the adsorption bonds above the halide sites (but not above the Na sites) are comprised of two-center three-electron bonds. Almost all density functionals on the market, including the PBE functional used here and the popular B3LYP hybrid functional, significantly overestimate the strength of such bonds [15]. MP2, on the other hand, and the hybrid "BH&HLYP" functional [16] generally yield accurate predictions for two-center three-electron bond strengths when compared to high-level quantum chemical methods such as coupled cluster [15,17].

We now employ these alternative quantum chemical methods to test the trends identified here. Specifically a series of all-electron DFT BH&HLYP and MP2 calculations for Cl adsorption on NaCl clusters were performed. The NaCl system was selected because it is the one most likely to be representative of the three systems under consideration and, of course, is the most generally interesting of the three. First we used the plane-wave pseudo-potential method to identify a suitable cluster model that would faithfully mimic Cl adsorption on NaCl(001), and then used the same cluster to compute Cl adsorption at the BH&HLYP and MP2 levels. The plane-wave pseudo-potential calculations reveal that the frozen two layer Na_9Cl_9 cluster shown in Fig. 1 is a good model since the adsorption energies and adsorption structures obtained with it for Cl adsorption at both types of adsorption site are close to those obtained with the periodic slab model (see Table I). All-electron calculations were then performed for Cl adsorption on the Na_9Cl_9 cluster with a $6\text{-}311 + G(2df)$ Gaussian-type function basis set. As is clear from Table II the BH&HLYP and MP2 calculations fully support the binding site preference predicted by the GGA-PBE pseudopotential approach; with BH&HLYP the site preference is 0.25 eV and with MP2 it is 0.23 eV [18].

More confident in the validity of the binding site assignment made here, we now ask: why do halogen adatoms bond preferentially to halide substrate atoms? This result is unexpected for the reasons outlined above and, furthermore, from a simple comparison of the relative bond strengths of alkali halide dimers versus halogen dimers in the gas phase which reveals that for the systems examined here the strength of the alkali halide dimer (i.e., NaF, NaCl, or NaBr) always exceeds that of the respective halogen dimer (i.e., F_2, Cl_2, or Br_2) [19]. An analysis of the electronic structures obtained from our DFT-PBE slab calculations reveals the answer for the predicted binding site
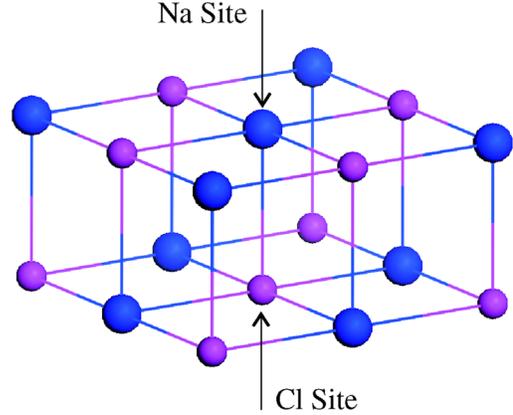

FIG. 1 (color online). The Na_9Cl_9 cluster model used. Cl atom adsorption was considered above the central Cl (bottom) or central Na (top). The Na atoms are the larger blue (darker) spheres.

preference. In all three adsorption systems a covalent bond forms when the halogen atoms bond to the halide substrate atoms. The total densities of states (DOS) and projected densities of states (PDOS) plots displayed in Fig. 2 reveal this. For each system the energy range in the vicinity of the alkali halide valence band is shown. Prior to adsorption the valence band is comprised of a single (large) peak of p orbital character. After adsorption new peaks are visible at the top and bottom edges of the valence bands [Fig. 2(a)]. Inspection of the individual Kohn-Sham eigenstates in each system reveals that a series of adsorbate-substrate bonding and antibonding states of p(adatom) and p(substrate) character are created within this energy interval. Specifically, a set of σ-type bonding $(p_z + p_z)$ and antibonding $(p_z - p_z)$ states and a set of π-type bonding $(p_{x/y} + p_{x/y})$ and antibonding $(p_{x/y} - p_{x/y})$ states are formed. In each case the bonding and antibonding states of π character are fully occupied and reside within the valence band (or in the case of NaF also below the valence band) [Fig. 2(a)]. Hence the fully occupied π-type states do not contribute to the overall net bonding. The σ-type states, on the other hand, straddle the valence band and are the key states responsible for bonding because one of the antibonding σ-type states remains unoccupied. Or, more precisely, within the spin-polarized PDOS picture of Fig. 2(b) there is a single unoccupied one-electron state

TABLE II. Adsorption energies, E_{ad} (eV/atom), and optimized adatom-substrate distances, d (Å), at the all-electron BH&HLYP and MP2 levels for Cl at the central Na or central Cl site of the Na_9Cl_9 cluster shown in Fig. 1.

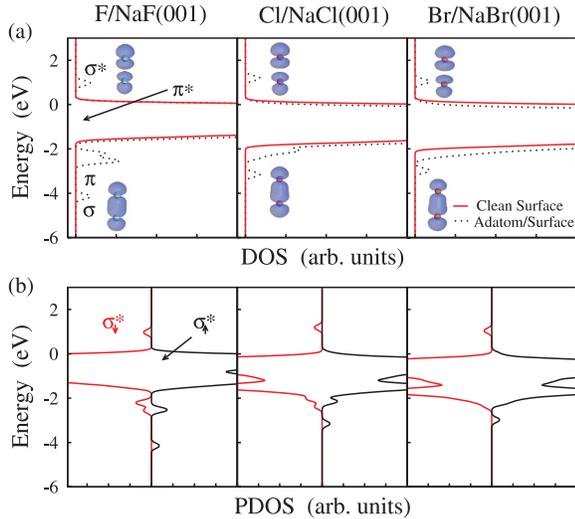| Binding site		BH&HLYP	MP2
Cl site	E_{ad}	0.35	0.39
	d	2.69	2.58
Na site	E_{ad}	0.10	0.16
	d	2.98	2.97

FIG. 2 (color online).   (a) Density of states (DOS) for clean and adsorbate covered alkali halide (001) surfaces. The insets display isosurfaces of constant electron density for individual Kohn-Sham eigenstates and the labels indicate the character of certain key adsorbate-substrate states. (b) Spin resolved partial density of states (PDOS) for the three adsorption systems in (a). All results in (a) and (b) have been obtained with the PBE functional and the plane-wave pseudopotential method. The energy zero has been set to the highest occupied Kohn-Sham eigenstate in each system.
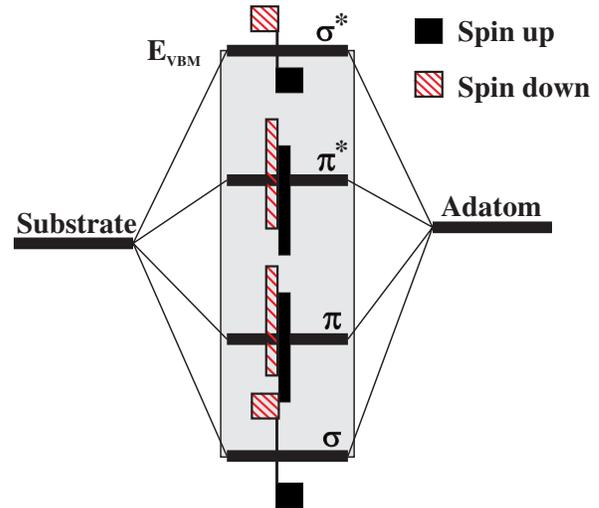

FIG. 3 (color online).   Schematic illustration of the bonding model proposed here for halogen adatom adsorption at the halide sites of alkali halide (001) surfaces. The gray rectangle designates the substrate valence band. A solitary σ-type orbital resides above the valence band maximum (E_{VBM}) and is not occupied.

of σ-type antibonding character above the valence band maximum. Examples of the eigenstates of σ-type bonding and antibonding character from each system are shown in Fig. 2(a) and a schematic diagram of the bonding picture that has emerged is shown in Fig. 3.

The σ-type covalent bond formed between the adatom and the substrate is also clear from the electron density difference plot for Cl on NaCl(001) [Fig. 4(a)]. Furthermore, the electron density difference plot for Cl adsorbed at the unfavorable Na site of NaCl(001) [Fig. 4(b)] illustrates the clear difference between the adsorption bond at each site. The covalent bonding character is absent when Cl is at the Na site [20]. Instead there is an indication of an electrostatic interaction, illustrated by the (small) charge transfer from the substrate toward the adsorbate [Fig. 4(b)]. One might then expect that if the halogen adatom gains an electron to become a halide anion, X^-, the covalent bond at the halide site will be weakened and conversely the electrostatic attraction at the alkali (Na) site will be strengthened. It is plausible that this will result in a switch in adsorption site with the alkali site becoming the preferred one for anion adsorption. Indeed, a site switch is precisely what we see when we model the adsorption of a Cl^- by either adding an extra electron to our simulation cell or by replacing the Cl atom on the underside of the NaCl(001) slab with a neutral Na atom. In the latter case, for example, the Na site is favored over the Cl site by 0.45 eV/Cl adatom. Further, the bond length of the adsorbed Cl^- to the underlying Na is

>0.10 Å shorter than it is for neutral Cl atom adsorption, and 0.64 Å shorter than the bond length for Cl^- adsorption at the (now unfavorable) Cl site. Thus we see that when the system has enough charge to have all the atoms assume their formal (integer) charges it behaves as anticipated. When this is not the case the system forms the most appropriate charged ion, by way of a textbook covalent bond.

The basic physical picture that has developed for the bonding at the preferred sites in these systems is thus that of a textbook two-center three-electron covalent bond. Essentially each adsorption system is equivalent to an X_2^- (X = F, Cl, or Br) species adsorbed upright at a halide vacancy on the surface. Indeed this analogy of an "embedded molecular ion" proves to be illuminating in two key respects. First, the trend of both the adsorption energies and adatom-substrate bond lengths correlate with the computed gas phase X_2^- bond strengths. Specifically, for the gas phase X_2^- and the respective adsorption systems the computed PBE bond strength decreases and the bond length increases upon going from F to Cl to Br (Table I). The correspondence is particularly striking between the bond lengths since each adsorption bond is within 0.1 Å of its respective molecular ion bond length (Table I). Second, the short-time dynamics, as determined from a 12.5 ps *ab initio* molecular dynamics simulation [21] for the Cl/NaCl(001) system, resembles that of an adsorbed chlorine molecule in a vacancy rather than an adsorbed atom on a flat surface. The motion of the two chlorine atoms is strongly correlated: they rotate and vibrate in concert in the "Cl vacancy." The dynamics also reveals that the potential energy surface for tilting the embedded Cl_2^- is rather flat. Indeed as confirmed by subsequent
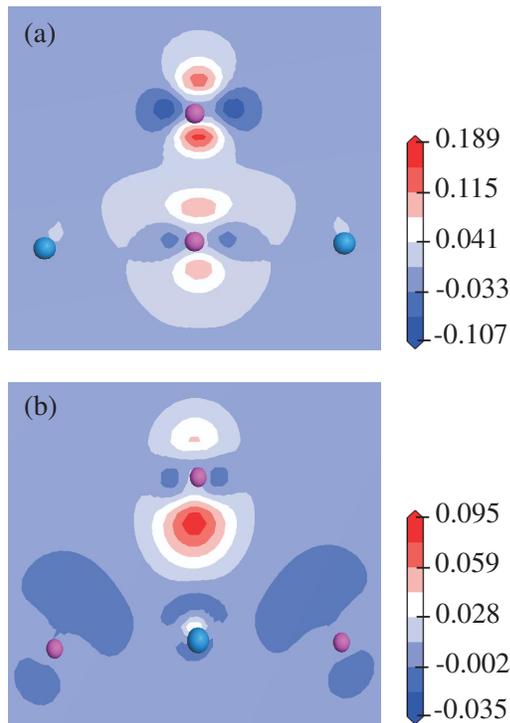
FIG. 4 (color online). Electron density difference ($\Delta\rho$) for Cl adatom adsorption at the Cl substrate site (a) and the Na substrate site (b) of NaCl(001). $\Delta\rho$ is defined as $\Delta\rho = \rho_{Cl/NaCl} - \rho_{NaCl} - \rho_{Cl}$, where $\rho_{Cl/NaCl}$, ρ_{NaCl}, and ρ_{Cl} are the electron densities of the total system, the isolated NaCl(001) surface, and the Cl atom in the gas phase, respectively. The plane of the cut is along the (100) direction, perpendicular to the surface and the units of both legends are $e \cdot Å^{-3}$.

structure optimization 75 meV can be gained by tilting the Cl_2^- by ~ 30 degrees from the surface normal.

In summary, DFT slab calculations predict textbook covalent bond formation at the nontextbook halide adsorption sites on some prototype ionic materials. For the case of Cl on NaCl(001), this binding site preference is supported by BH&HLYP and MP2 cluster calculations. Aside from the clear esoteric interest, the present results are significant because they dictate the initial binding site for epitaxial alkali halide crystal growth and possible intermediate states in alkali halide dissolution. If, for example, empirical potentials are to accurately describe such processes then they too must be able to capture this novel mode of adsorption.

*Electronic address: michaeli@fhi-berlin.mpg.de
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[20] This is also clear from inspection of the density of states and Kohn-Sham eigenstates when Cl is adsorbed at the Na site.
[21] The Born-Oppenheimer *ab initio* molecular dynamics simulation was run in the canonical ensemble at 300 K for a total of 12.5 ps with a 2 layer NaCl(001) slab.