PHYSICAL REVIEW B VOLUME 51, NUMBER 3 15 JANUARY 1995-I

Nature of bonding of alkali metals to Si(111)

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(Received 19 April 1994; revised manuscript received 7 September 1994)

The nature of the chemisorption bond between alkali metals, Li to Cs, on the Si(111) surface has been studied by means of the *ab initio* Hartree-Fock cluster-model approach. A comparative and systematic study has been carried out for a variety of cluster models simulating the high-symmetry sites of this surface. In all cases we found the bond highly ionic with a small participation of covalent effects to the interaction energy, which ranges from $\approx 20\%$ for chemisorbed Li to less than 10% for Rb and Cs above the different active sites. This result is consistent with several analyses of the interaction focused on the interaction energy, the final Hartree-Fock wave function, the analysis of the dipole moment, and of its variation with the adsorbate-surface distance. We show that the dipole moment for chemisorbed alkali metals is smaller than the one expected from an ionic bond because of the substrate polarization. Consequently we argue that changes in the measured work function are not adequate to extract information about the ionicity of a given interaction. This is in agreement with previous works considering a metal substrate. Here we show that the same mechanism holds for semiconductor surfaces as well.

I. INTRODUCTION

Mainly because of the possible technological applications of the alkali-metal–semiconductor interfaces, a large amount of research work has been devoted to the study of alkali-metal adsorption on silicon surfaces. It is nowadays well known that alkali metals chemisorbed on a semiconductor surface have something special and differ from other metals chemisorbed on the same surface.[1,2]

In spite of the large body of work already in the literature, many open questions remain and some features of these systems are still a matter of discussion. The discussion does not only appear from the theoretical point of view, but it grows up with data provided by almost all surface spectroscopic techniques (see Refs. 3–8 and references therein). It is important to quote that the key question seems to be the nature of bonding between alkali atoms and a silicon surface and that many other questions can be more or less related to it. Alkali-metal atoms have only one valence electron and the simplicity of their electronic structure seems to provide the simplest case for a metal-atom–semiconductor interaction. Contrary to what may be thought from this apparent theoretical simplicity, this unique valence electron centers the whole discussion of the system. At a first sight, one may think that this electron is completely transferred to the surface atoms and the interaction will correspond to that of an ionic bond. However, many intermediate situations have also been suggested and the real situation is far from being understood.[3]

The nature of bonding between alkali metals and a semiconductor has relevance also to theories of metallization. Complete charge transfer has been associated with a mechanism in which metallization, as a function of coverage, is caused by a partial filling of the semiconductor surface state bands.[9–13] A partial electron donation from alkali metal to silicon surface atom(s) can also be related to surface metallization. In this case, the interaction is viewed as a weak polarized covalent bond which also explains the strong work-function reduction by a polarization-dependent interaction.[14–16] Generally, these two cases are also related to the adatom coverage.[17] When the number of chemisorbed atoms is small (low coverage) it appears that the interaction is purely ionic, and that when the coverage grows the nature of the bonding corresponds to a weak covalent one.[18,19] In the case of moderate to high coverage it is necessary to discriminate whether alkali-metal–alkali-metal or alkali-metal–surface interaction is dominant.

It is now obvious that the proper interpretation of previous theoretical results and, especially, of many experimental data needs the answer to a number of well-defined questions. Hence it is necessary to determine in a unique way whether the interaction corresponds to a purely ionic interaction or is best described as a polarized covalent bond. Also, it is essential to quantify the degree of charge transfer and, of course, to find how the magnitude of the charge transfer depends on a specific alkali metal. A correct understanding of the metal-semiconductor interface cannot be achieved until these questions have been definitively solved. However, to answer these questions is not a simple task because of the complex nature of the system. As pointed out above, a rather large number of experimental works point out that the ionic or covalent nature of the bond depends on the alkali metal, the adsorption site, the coverage, and the silicon surface used in the experiments. In spite of these facts, the equivalence of different alkali metals on silicon surfaces (generally lithium is studied separately) is generally as-

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sumed in a number of studies.[17] Hence, calculations made of an alkali metal are often compared with experimental data for another alkali metal, and vice versa; this is especially true in the case of potassium and cesium. In other cases, experimental data obtained using a well-defined Si(111) surface are compared to theoretical results corresponding to Si(100) simply because there are fewer calculations on Si(111) than on Si(100). In order to be able to properly compare theory and experiment for each alkali metal on the same surface a systematic theoretical study appears to be necessary. The need for such study has been a strong chain in some recent experimental works.[3–5]

Finally, it is worth pointing out that even the adsorption site is a point of controversy. This is because there is not a clear relationship between the nature of bonding and preferred positions of the alkali metal on a silicon surface. Hence the preferred site does not seem to depend only on the nature of the bonding but also on the particular surface and on whether this is an ideal or a reconstructed-type surface.

From the arguments above described it is now clear that a systematic theoretical study is highly desirable. Such study will therefore clarify the nature of bonding between alkali-metal atoms and the silicon surface. To this end we have started a research project which involves the alkali metals, from Li to Cs, several adsorption sites, and several silicon surfaces. Of course, a large number of theoretical calculations will be necessary to quantify the importance of each physical effect and what is the relationship between different effects. The present work is centered on the study of the interaction of alkali metals above Si(111) and intends to be a systematic contribution in the direction above described.

This work relies on the *ab initio* Hartree-Fock self-consistent-field (SCF) cluster model approach. Hence, the calculation of the electronic wave functions does not need any external empirical parameter. The method is purely based in first principles and is particularly powerful in describing the nature of the chemical bond and to obtain reliable estimates of local properties. General details about the approach can be found in Refs. 20 and 21 whereas applications concerning silicon surfaces, and in particular for chemisorption above Si(111), have been reported in Refs. 22–32.

This paper is organized as follows. The cluster models used to simulate different adsorption sites are presented and discussed in Sec. II. Details concerning the computation and analysis of the SCF wave functions are given in Sec. III. Section IV reports the structural parameters derived from the study of the potential energy curves. The analysis of the interaction is discussed in Sec. V. For this purpose, we will use a set of theoretical techniques recently proposed to analyze the chemisorption bond.[20,21,32,36] These techniques permits one to quantify the amount of charge transfer from alkali atom to silicon surface or, at least, to establish whether major or minor differences between alkali metals exist. Also the use of these theoretical techniques avoids naive interpretations of the nature of the bond such as those based solely on Mulliken population analysis or on the interpretation of electron-density contour maps.[33–35] The effect of the cluster size on the nature of the chemisorption bond is analyzed in Sec. VI. Finally, in the last section, Sec. VII, we present our calculations.

II. SURFACE CLUSTER MODELS

For this initial step towards a better understanding of the alkali-metal–semiconductor interface we have chosen the unreconstructed Si(111) surface. On this surface, we have explicitly considered the main adsorption sites. These are the onefold atop site T_1, where the adsorption takes place directly above a Si surface atom; and the threefold eclipsed, T_4, and open, H_3, sites where the adatom interacts with three surface dangling bonds with or without a second-layer Si atom below the considered site (see Fig. 1). Moreover, we have considered the adsorption of a single alkali-metal atom. We must point out that, although the clusters used to represent each adsorption site have a reasonable size, it is not possible to use these reduced models to obtain information about coverage effects on the nature of the chemisorption bond. Therefore we will use the models to try to represent low-coverage situations. The effect of alkali-metal—alkali-metal interactions on the nature of the chemisorption bond will be reported in the near future.[37]

The cluster models are a simplified representation of the adsorption site. Ideally, one should use a cluster as large as possible; in practice, the cluster size is limited because of the computational facilities. Even using modern powerful workstations the number of atoms that can be explicitly taken into account in *ab initio* calculations is limited to 25–50 atoms depending on the level of accuracy. In the case of surface models simulating a silicon surface there is an additional problem due to the cluster edge atoms which introduce undesired dangling bonds. The easiest way to overcome this difficulty is to saturate the free valences with hydrogen atoms; this has been indeed the common strategy in the literature.[22–32] A possible drawback with the use of these embedding hydrogen atoms arise from the different electronegativity of hydrogen and silicon atoms. Redondo *et al.*[38] have suggested to modify the hydrogen basis set in order to have embedding atoms having an electronegativity as close as possible to that of silicon; the resulting basis-set modified embedding hydrogen atoms are usually termed siligens. Siligens have been used in some applications with apparent success.[39] In our previous study of the interaction of atomic Al on Si(111) we used both unmodified and modified hydrogen atoms and the results were almost identical.[31,32] This prompted us to perform a systematic study of the influence which those siligens may have in the results from an *ad initio* cluster-model study. The results obtained in that study revealed that neither the electronic structure of the isolated cluster models nor the nature of the chemisorption bond depend on the kind of embedding hydrogen atoms used to saturate the free valences of the cluster edge atoms.[40] It is worth pointing out that the previous conclusions are not affected by the Si-H distance chosen in the particular cluster model. Also, we must add that a recent semiempirical study using the Austin model 1 (AM1) approach has found substantial different conclusions.[41] Even the optimum Slater exponent defining the siligens was different from the *ab initio* Hartree-Fock value obtained using a double-ζ plus polarization atomic basis set. This means that the description of the siligens depends on the method used. This example clearly indicates the deficiencies which may appear when using such kind of oversimplified electronic wave functions; this is avoided in the *ab initio* cluster-model approach used here.

In the view of the previous discussion and of the results obtained using siligens as embedding atoms[40] we have decided not to use this approach and to saturate the free valences of the cluster silicon edge atoms with unmodified atomic hydrogen atoms placed at the usual Si-H distance. Many of the clusters used in this work contain only an active site per center; this is to avoid problems associated with the surface dangling bonds which remain after interaction with the adsorbate. However, we will also present selected results for a larger cluster involving many surface sites and, consequently, many dangling bonds. Such larger clusters are now currently being used in our laboratory to study coverage effects on the nature of the chemisorption on silicon surfaces.[37]

To represent the T_1 site of the Si(111) surface we use a $Si_{10}H_{15}$ cluster model (Fig. 1) having four silicon layers and with the edge atoms saturated with hydrogen atoms. A four-layer cluster is also used to simulate the H_3 open site; the resulting model may be written as $Si_{10}H_{13}$. Finally, the threefold T_4 eclipsed site has been represented by a Si_5H_9 cluster model. Results for the isolated clusters, with and without using siligens, have already been reported in our recent study and we will not report them here again (for a complete set of results, see Refs. 31, 32, and 40). We will only add the electronic ground state of the different cluster models using the irreducible representations of the C_{3v} point group. For $Si_{10}H_{15}$ the elec-

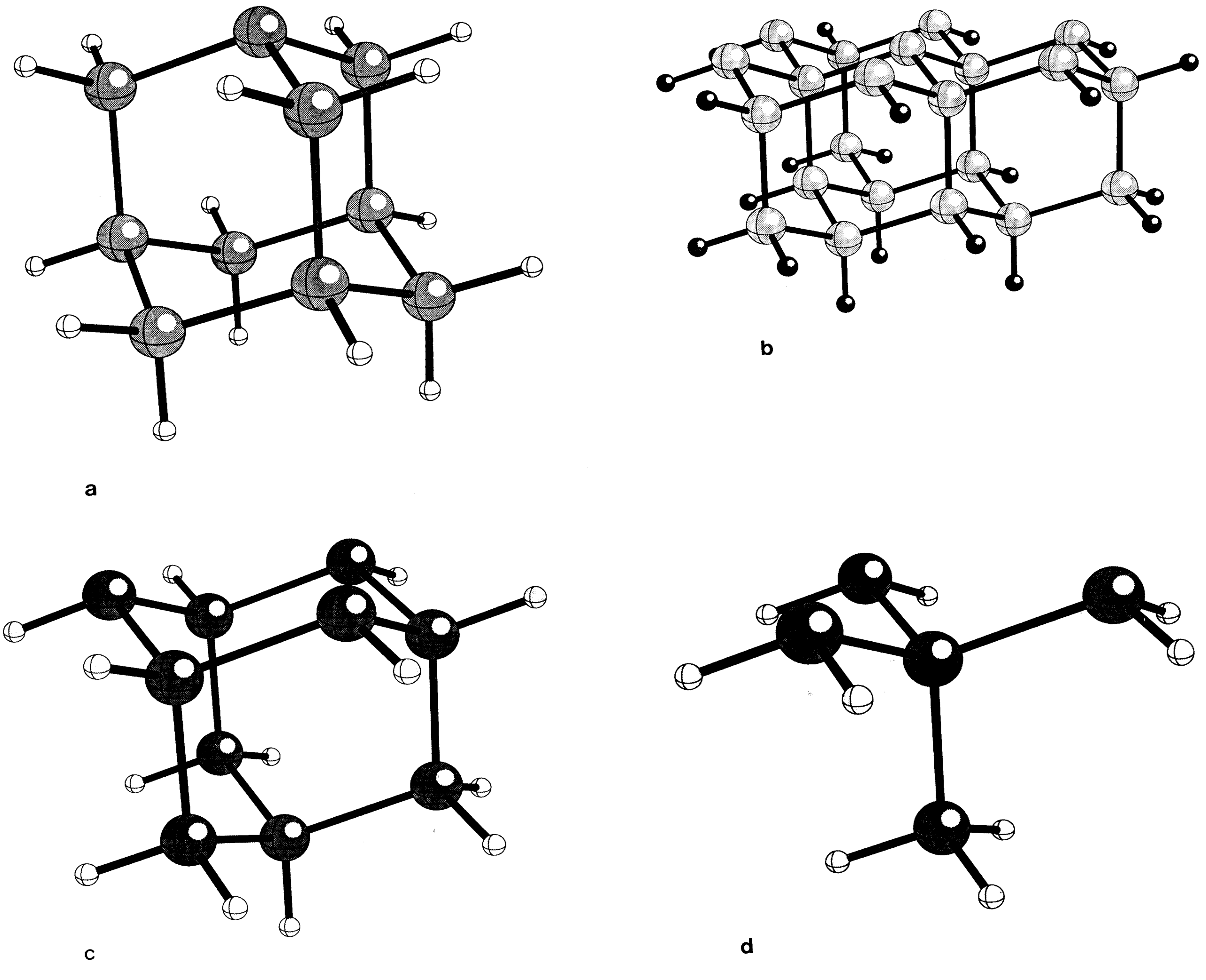

FIG. 1. Schematic representation of the $Si_{10}H_{15}$ and $Si_{22}H_{21}$ cluster models used to represent the atop site [T_1, (a) and (b)], the $Si_{10}H_{13}$ cluster representation of the threefold hollow open site [H_3, (c)], and the Si_5H_9 model for the threefold hollow eclipsed site [T_4, (d)].

tronic ground state is a $^2A_1$, which upon interaction with an alkali-metal atom leads to a closed shell $^1A_1$, whereas for both $Si_{10}H_{13}$ and Si_5H_9 the ground state is $^4A_2$, leading to $^3A_2$ after interaction with the adsorbate. For the above cluster models, low spin coupling has always been assumed for the adsorbate-surface model interaction. This spin coupling is not biased to any particular physical description; it permits the formation of both covalent and ionic bonds and the final description will be that contained in the *ab initio* Hartree-Fock wave function.

In order to investigate possible artifacts in the description of the nature of the interaction of alkali-metal atoms above Si(111) arising from the limited cluster size, we have also used a rather larger model to represent the T_1 atop site. We have chosen this site to illustrate that the present description of the chemisorption bond is not affected by the cluster size. This larger model has seven surface silicon atoms and hence seven surface sites and seven dangling bonds. It contains four layers of silicon atoms, seven in the first, six in the second and third, and three in the fourth layer. The cluster edge atoms are again saturated using embedding hydrogen atoms. Following our previous notation, this cluster will be denoted as $Si_{22}H_{21}$ [Fig. 1(b)]. For such a large cluster there is no previous experience on how to deal with the several surface dangling bonds. In fact, this is probably the largest cluster used to represent the Si(111) surface at the *ab initio* Hartree-Fock level. To deal with the problem originated by the surface dangling bonds we have considered two extreme electronic states. The first one is a high spin coupling of the seven dangling-bond electrons. This choice ensures that there is one electron per dangling bond. It may be properly argued that this is not a realistic state of the Si(111) surface because this is a nonmagnetic surface. Therefore we have also considered the low spin coupling case where the final electronic state is a nondegenerate doublet with the maximum number of doubly occupied orbitals. We must point out that, because the dangling-bond electrons are very separated spatially, the resulting system is strongly correlated. The proper electronic state will also be a doublet but with seven open shells and cannot be described by a single electronic configuration. Our choice of the high-spin case is an approach to the proper electronic state and the use of the nondegenerate doublet with the maximum number of doubly occupied orbitals will only serve to illustrate that the chemical contributions will not depend on the particular choice of the cluster electronic state *(vide infra)*.

III. COMPUTATIONAL DETAILS

In this work we have obtained *ab initio* self-consistent-field wave functions for all alkali-metal–Si_nH_m cluster models previously described. The electronic wave function has been obtained in the well-known linear combination of atomic orbitals molecular orbital (LCAO-MO) framework where the molecular orbitals are expressed in terms of a given basis set. Here we make use of the experience gained in previous works from our group (see, for instance, Refs. 24, and 29–32). Therefore we use nonempirical pseudopotentials to describe the [Ne] cores of the cluster Si atoms and deal explicitly with the $3s^23p^2$ electrons of each Si atom. The nonempirical pseudopotentials used in this work have been obtained from large-basis-set all-electron atomic SCF calculations following the procedure outlined by Durand and co-workers.[42–44] For the alkali metals we use an all-electron description mainly because a one-electron pseudopotential approach is not appropriate to study a system in which the valence electron is likely to be transferred to the cluster representation of the "surface bands."

The choice of the atomic basis set used to describe the MO's completely determines the final SCF wave function. Following our previous works[24,29–32] we use a mixed-basis-set approach. The valence electrons of nonsurface Si cluster atoms are described by a double-ζ basis set, which may be schematically represented as $(4s4p/2s2p)$, whereas the basis set used to describe the cluster surface atoms directly interacting with the adsorbate includes also a single d polarization and the final basis set is $(4s4p1d/2s2p1d)$. For the embedding hydrogen atoms we use a $(4s/2s)$ double-ζ basis set for all clusters except for the Si_2H_{21}, where a minimal $(4s/1s)$ basis is used for the embedding hydrogen atoms. As shown in previous works, larger basis sets on these atoms do not contribute appreciably to the description of the chemisorption bond.[30,40]

For the alkali-metal atoms the contracted Gaussian-type orbitals (CGTO) basis set is as follows. For the Li atom we use the $(11s5p/4s3p)$ basis set of Krishnan *et al.*,[45] whereas for atoms going from Na to Cs we have used the basis sets reported by Huzinaga *et al.*[46] which all are of triple- or quadruple-ζ quality for the valence shell and for the most external nonvalence shell, and minimal to describe the other core electrons. Final basis sets for Na to Cs are Na $(9s4p/7s4p)$, K $(12s7p/8s5p)$, Rb $(15s9p3d/9s5p1d)$, and Cs $(18s12p6d/10s6p2d)$. Finally, let us point out that, in order to ensure the validity of the above described basis sets, we have studied the effect of the basis-set superposition error (BSSE) in the energies and equilibrium distances. For all systems, the BSSE is very small, <0.2 eV, compared to the SCF calculated binding energies of $\approx 4-5$ eV.

Using the basis sets just described we have obtained SCF wave functions for the interaction of each alkali metal above each active site. Calculations have been carried out at several distances of the adsorbate to the surface and from the potential energy curves several structural parameters have been obtained; these include the equilibrium distance above the surface, r_e, the vibrational frequency of the adsorbate for the normal mode perpendicular to the surface, ν_e, and the interaction energy (BE), with respect to the isolated interacting systems. As usual, the vibrational frequency has been obtained from a polynomial quartic fit of the calculated potential curve assuming infinite substrate mass while the interaction energy has been computed with respect to the charged, $Si_nH_m{}^-M^+$ ($M=$Li–Cs), isolated systems and corrected to the neutral asymptote using the experimental alkali-metal ionization potential and the surface work function. For an ionic bond this is a better approximation than using the neutral fragments at infinite separation. This is because the main effect of electronic correlation, not included in the *ab initio* SCF wave function, is precisely in the description of the ionization potential and the electron affinity of the charged systems at the equilibrium distance (see Ref. 47). Moreover, the choice of the experimental surface work function instead of the cluster electron affinity permits an approximate correction to the limited cluster size.[48] It may be properly claimed that the present approach to the BE does not discriminate the possible different binding mechanism because full ionicity is assumed. In the forthcoming sections we will use different theoretical techniques to quantify the degree of ionicity of the interaction of each alkali metal above each surface site. Then we will make use of this information to obtain a more reliable estimate of the interaction energy.

Information about the nature of the chemisorption bond can be extracted from the wave function obtained for an adsorbate interacting with a surface cluster model.[20,21] In this work we will make use of a set of rather recent theoretical techniques to analyze the nature of the chemical bond between alkali metals and the different surface cluster models. These techniques include the analysis of the energetics of the interaction by means of the constrained space orbital variation (CSOV) method,[49–51] the analysis of the ionicity by means of the dipole moment curves and their CSOV decomposition,[52] and the analysis of the SCF wave function. In this last case we will make use of a projection technique which, starting from a purely ionic picture, permits us to obtain the contribution of this ionic wave function to the cluster SCF wave function.[53] This projection technique is similar to that used by Clotet *et al.*[54] to perform a valence-bond analysis of a MO configuration-interaction (CI) wave function.

IV. STRUCTURAL PARAMETERS

Equilibrium distances of each alkali-metal adatom above each active site have been obtained from the SCF potential energy curves; the corresponding results are reported in Tables I–III. As expected there is a monotonic increase of r_e on going from Li to Cs. Unfortunately, there are only a few previous studies and it is difficult to make comparisons with either theoretical or experimental values. For Na above the T_1 site of Si(111) the *ab initio* SCF distance is in good agreement with the one reported by Moullet, Andreoni, and Parrinello[4] using an *ab initio* molecular dynamics simulation; 5.34 bohrs in the present work to be compared with 5.37 as reported in Ref. 4. However, the SCF distances for Na above H_3 and T_4 sites are somewhat larger that those reported in Ref. 4; the present values are 4.51 and 4.62 bohrs, respectively, whereas those reported in Ref. 4 are 4.05 and 3.80 bohrs. The *ab initio* SCF values for r_e are usually in good agreement with experiment so differences are likely to be due to the relaxation and reconstruction of the substrate which is allowed in Ref. 4 or to limitations of the molecular dynamics approach. For Cs on the 7×7 Si(111) surface there is a rather recent surface extended x-ray-absorption fine-structure (SEXAFS) study by Batchelor and King;[16] the experimental result for the Cs distance at low coverage is 7.16±0.04 bohrs for the adatom site which is to be compared with the atop site of our model for the 1×1 unreconstructed surface. The present value for the T_1 site is 7.06 bohrs, in good agreement with the SEXAFS measurements. This gives additional support of the cluster-model results for the equilibrium position.

TABLE I. Calculated values for the equilibrium distance above the surface, r_e, vibrational frequency corresponding to the normal mode perpendicular to the surface, ν_e, and binding energy corrected [see Eq. (1)] with respect to the neutral separated system, BE, for the atop chemisorption of alkali metals above the atop T_1 site of the Si(111) surface.

Alkali atom	r_e (bohr)	ν_e (cm^{-1})	BE (eV)
Li	4.76	416	4.85
Na	5.34	197	4.34
K	6.26	124	4.16
Rb	6.60	79	4.05
Cs	7.06	58	4.04

TABLE II. Same as Table I for alkali metals above the H_3 threefold open site.

Alkali atom	r_e (bohr)	ν_e (cm^{-1})	BE (eV)
Li	3.95	225	4.43
Na	4.51	127	4.23
K	5.63	94	4.15
Rb	5.98	64	4.03
Cs	6.59	48	4.03

In order to understand the trend observed in the calculated r_e values above each site we have compared them with the expectation values $\langle r \rangle$ of some alkali-metal orbitals computed by using the same basis sets as in the cluster calculations. These include the *ns* orbital of the neutral atom and also the $(n-1)s$ and $(n-1)p$ of the neutral metal and of the corresponding cation. In all cases we have obtained an almost linear plot, indicating that the r_e grows linearly with the atomic size. In Fig. 2 we show the plot of r_e against $\langle r_{(n-1)p} \rangle$ for Na to Cs. In this case the linear relationship is particularly good. This might be taken as an indication of the ionicity of the interaction. However, similar linear relationships are obtained when comparing with the size of the *ns* orbital of the neutral atom. Therefore it is not possible to use the linear relationship to extract any conclusion about the nature of the bond.

TABLE III. Same as Table I for alkali metals above the T_4 threefold eclipsed site.

Alkali atom	r_e (bohr)	ν_e (cm^{-1})	BE (eV)
Li	3.86	238	4.74
Na	4.62	138	4.51
K	5.70	97	4.41
Rb	6.00	67	4.25
Cs	6.59	51	4.23

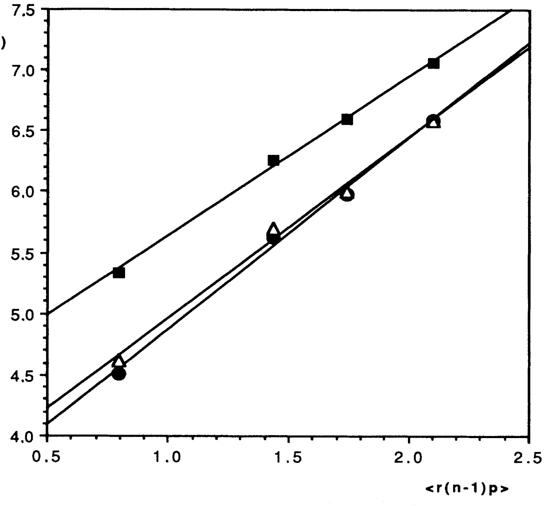

FIG. 2. Plot of the equilibrium distance r_e of each adatom above each active site against the expectation value of the $(n-1)p$ orbital, $\langle r_{(n-1)p} \rangle$, of each atom (computed using the same basis set as in the rest of the calculations). Full square, full circle, and open triangle for the atop, open, and eclipsed sites, respectively.

Reported in Tables I–III are also the values for the vibrational frequency ν_e corresponding to the normal mode for the perpendicular motion of the adsorbate above the surface. The ν_e values always decrease monotonically when going from Li to Cs. In this case we have plotted ν_e versus the inverse of the square root of the adsorbate mass. Again a linear relationship is obtained (Fig. 3). The meaning of the results in Fig. 3 is simply that the force constant, or the shape of the potential curve near r_e, is approximately the same for the different alkali metals. The decrease in ν_e is then due to an inverse of the atomic mass only and not to a variation in the curvature of the potential energy curve. Again, the analysis of the ν_e values along the series does not permit one to extract information about the nature of the bond. However, the calculated ν_e for the one- and threefold sites is different enough to experimentally confirm the actual chemisorption site.

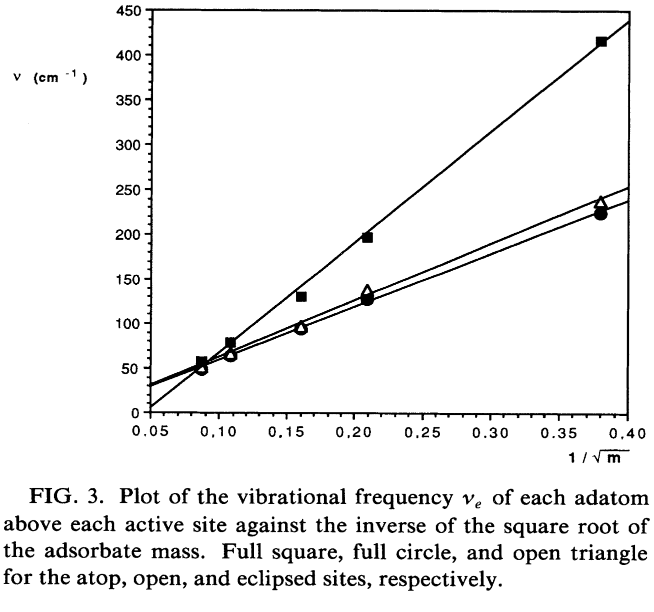

FIG. 3. Plot of the vibrational frequency ν_e of each adatom above each active site against the inverse of the square root of the adsorbate mass. Full square, full circle, and open triangle for the atop, open, and eclipsed sites, respectively.

To conclude this section we will discuss the binding energies of the alkali metals above the different cluster models. As stated above, the BE values have been computed as follows:

$$E_B = -\{E(\mathrm{Si}_n\mathrm{H}_m M) - E(M^+) - E(\mathrm{Si}_n\mathrm{H}_m^-) - V_i(M) + \Phi_{\mathrm{Si}(111)}\}\ , \tag{1}$$

where all the energies are computed at the SCF level, M=Li, Na, K, Rb, and Cs, V_i is the experimental ionization potential of the alkali metal, and $\Phi_{\mathrm{Si}(111)}$ is the experimental work function. The above expression assumes that at r_e the interaction is best described as an ionic bond and the use of experimental values for $V_i(M)$ and $\Phi_{\mathrm{Si}(111)}$ corrects for deficiencies of the SCF wave function[47] and, also, for the limited cluster size.[48] As we will show in the forthcoming sections the nature of the bonding is highly ionic. Therefore, this is a reasonable approach to the computation of the BE values. These values will be further corrected to take into account the degree of ionicity of each adsorbate above each site *(vide infra)*. Results for the BE are reported in Tables I–III for the T_1, H_3, and T_4 sites, respectively.

The BE's are very similar for a given adsorbate on a given site; this is in agreement with a recent experimental study which points out a multisite occupancy of alkali metals on the Si(111) surface.[55] Because of the limited cluster size, even after corrected as indicated above, we think that it is not possible to make strong claims based on the SCF calculated BE's. At this point we only point out the qualitative agreement between our results and the available data. For Na on Si(111) we can compare our results with those obtained from a molecular dynamics simulation[4] and also with those reported by Northrup.[10] The three studies agree in that the T_4 site is the preferred one, the H_3 lying higher by 0.06, 0.12, and 0.28 eV for the results in Ref. 4, Ref. 10, and the present work. Considering the different approaches the agreement is very good.

We would like to point out the difficulty in determining the nature of the interaction from the analysis of the bonding or structural parameters such as r_e, ν_e, or the BE. However, we would like to point out that the two last terms in Eq. (1) represent the cost to form an ionic bond. This cost ranges from +0.79 eV for Li to −0.71 eV for Cs, a negative value indicating that the formation of the ions from the separated system is energetically favorable. Even in the unfavorable cases (Li and Na) the cost is largely overcome by the benefit from the interaction arising from the remaining terms in Eq. (1). Therefore, this cost/benefit analysis indicates that the formation of an ionic bond is always possible. The analysis reported in the forthcoming sections will add further evidence of this ionic interaction.

Qualitative information about the nature of the chemisorption bond could be extracted from a Mulliken population analysis. However, one must keep in mind that this analysis suffers from well-known deficiencies especially when large basis sets are used (see, for instance, Ref. 56). Mulliken populations indicate net charges on the adatoms that range from $0.3e$ for Li on the T_4 site to $0.9e$ for Cs on the T_1 one. This may be taken as a first indication of a trend in the ionicity of alkali metals adsorbed on Si(111). The Mulliken net charge on the adatom does, in fact, increase from Li to Cs for all the sites considered. While this is the fingerprint of a trend it cannot be taken as a quantitative measure of the ionicity. The forthcoming sections will be devoted precisely to the analysis of the interaction.

V. ANALYSIS OF THE INTERACTION

In this section we will make use of different theoretical techniques to characterize the interaction of an alkali metal above a surface cluster model. Here, we will be concerned with the cluster models represented in Figs. 1(a), 1(c), and 1(d). Results concerning the largest $\mathrm{Si}_{22}\mathrm{H}_{21}$ cluster will be presented in the next section.

We start our analysis by using the constrained space orbital variation method[49–51] to decompose the interaction energy in various contributions. Our CSOV analysis starts from a superposition of two frozen electron densities. From the various possible choices we find it convenient to start by superimposing the electron density of the cation M^+ and of the $\mathrm{Si}_n\mathrm{H}_m^-$ systems. The resulting frozen-orbital (FO) description accounts for the initial Pauli repulsion and for the electrostatic attractive interaction between both charged fragments. The energy associated with this FO wave function is higher than that of the unconstrained variational SCF wave function. Additional contributions to the energy are obtained by removing the constraints imposed to the FO wave function. In this work we have used the following steps. First, we have allowed the cluster-model occupied orbitals to vary in their own virtual space V(Si;Si), to account for the substrate polarization in response to the presence of the cation. Next, we allow the occupied orbitals of the surface cluster model to vary in the full virtual space V(Si;all); this variation accounts for the charge donation from the surface cluster model and the energy gain associated with this step is a clear measure of the importance of covalent effects. In the two next steps we allow the cation to be polarized in response to the presence of the fixed (but already polarized) electron density of the surface cluster model, $V(M;M)$, and to back-donate the charge to the surface, $V(M;\text{all})$. After this last variation the energy of the system is very close to that of the unconstrained SCF wave function. This is a clear indication that all the bonding mechanisms have been included in the energy decomposition and that the different mechanisms are not coupled to each other.

The CSOV analysis of the interaction is very similar for the different alkali metals above the different clusters. In all cases we found that the FO wave function already accounts for an important part of the final BE [calculated as indicated in Eq. (1)]. Once the different variations are permitted there are only two significant additional contributions. These are the substrate polarization V(Si;Si) and V(Si;all). The remaining contributions concern mainly $V(M;M)$, $V(M,\text{all})$, and also possible coupling between the different CSOV steps. The sum of all these contributions is very small; it ranges from 0.01 to 0.08 eV. The fact that these contributions are so small can be easily understood. The term due to the cation polarization should be, and indeed is, small because cations have a rather compact electronic density and hence a small polarizability. The contribution due to charge donation from the cation to the substrate should also be very small because the formation of a dative covalent bond will imply donation from the negatively charged surface to the cation and this is achieved in the V(Si;all) step. After this variation the electronic density of the cation has varied and the resulting charge will be less than $+1$. Therefore a contribution due to donation back to the surface cluster model has no physical meaning and can only be due to BSSE artifacts. The fact that the contribution from $V(M;\text{all})$ is very small indicates a small BSSE.

Concerning the different contribution to the BE other than the one obtained from the FO wave functions, the most important contribution is the one due to V(Si;Si) or the substrate polarization. Its importance decreases from Li to Cs because the polarization is smaller when the cation is placed at a larger separation from the surface. For the three active sites, the V(Si;Si) contribution ranges from 1.00 to 0.30 eV when going from Li to Cs. The remaining contribution, V(Si;all), can be attributed to a covalent bond. As a general trend this contribution is small when compared with the total BE and shows that the chemisorption bond of alkali metals above Si(111), at low coverage, is rather ionic. From Li to Cs, this covalent contribution ranges from 0.41 to 0.07 eV at the atop site, from 0.67 to 0.19 eV at the open site, and from 0.94 to 0.30 eV at the eclipsed site. For Li and Na, the covalent contribution accounts for $\approx 20\%$ of the total BE and it is much less for the remaining alkali-metal atoms. Therefore, we can conclude that interaction of alkali metals with Si(111) above all sites can be described as an ionic bond.

The CSOV analysis above reported permits one to decompose the BE into various contributions of physical significance but it does not permit one to obtain information about the amount of charge transfer that is donated to the metal cation at the V(Si;all) step. In order to have a measure of the changes introduced in this variational step we have followed the procedure suggested by Sousa, Illas, and Pacchioni.[53] The main idea is to investigate how the wave function changes when a variation is permitted. This may be accomplished by computing the overlap between the FO wave function and the wave function obtained at a given CSOV step. Here, because no noticeable changes are introduced after the V(Si;all) variation, we will use the overlap between the FO and the final SCF wave function:

$$\Omega = \langle \Psi_{\mathrm{FO}} | \Psi_{\mathrm{SCF}} \rangle \; ; \tag{2}$$

this is the overlap integral between two Slater determinants each written in a different set of molecular orbitals. Obviously, these two sets of molecular orbitals are nonorthogonal and the computation of Ω requires one to compute the determinant of the overlap integrals between the two sets of molecular orbits [see Eq. (39) in Ref. 57]. Since the FO corresponds to a purely ionic description of the chemisorption bond any deviation of Ω from unity will indicate a deviation from the ionic picture. This analysis can be thought of as a valence bond (VB) decomposition of the SCF wave function. In fact, the square of Ω represents in percent the contribution of the ionic VB resonating forms to the total SCF wave function (see Refs. 53, 54, and 58). More useful than the overlap integral Ω is its square which indicates the percent of ionic character of the bond. We must notice that the percent of ionic character thus obtained is surely a lower bound. This is because the final SCF wave function contains the two important contributions to the chemisorption bond, substrate polarization and charge donation. The results reveal again a trend of increasing ionicity in going from Li to Cs. The results are in agreement with the different contributions to the BE discussed above. The less ionic system is Li above the T_4 site, with 81% of ionic character, whereas Rb and Cs have on all sites more than 90% of ionic character, K is an intermediate case, and Na exhibits also less than 90% of ionic character.

An analysis of the ionicity has also been carried out by transforming the MO-SCF wave function to an identical wave function but written in terms of the valence bond theory. In the VB wave function one can directly see the contribution of ionic and covalent resonant forms.[54] Results from such analysis are in full agreement with those based on the overlap integral and we will not report them in the present paper; details concerning this VB analysis will be reported elsewhere and are available upon request to the authors.

From the previous analysis it is clear that the approach used to compare the BE's [Eq. (1)] is essentially correct. One can further correct these values by taking into account the contribution of the full ionic wave function of the SCF wave function as suggested by Spiegelmann *et al.*[59] The corrected values differ from those in Tables I–III by less than 0.15 eV; hence corrected values will not be reported. The aim of this study is to analyze the nature of bonding and have a qualitative idea about bonding parameters and binding energies. The accurate calculation of the BE will probably need larger models and to include electronic correlation effects. While such a study is now feasible it will hardly modify the above conclusions. It is nowadays well known that electronic correlation effects have noticeable effects on the calculated binding energies but do not introduce substantial changes in the SCF description of the remaining structural parameters or in the nature of the chemisorption bond.[36,54]

The picture of the bonding emerging from the previous analysis is that the bond is essentially ionic, especially for Rb and Cs, with some covalent contributions for Li, Na, and K although the last can be considered as an intermediate case. The differences in the nature of bonding when going from Li to Cs are in agreement with the findings of Reihl *et al.*[3] in the sense that there is not an isoelectronic behavior. However, we must point out that the picture of the chemisorption bond above described is in agreement with some experimental results but in disagreement with others. The disagreement concerns, in particular, the experiments based on work-function measurements. In fact, the small work-function decrease obtained for Na on Si(111) seems to suggest that the bond is highly covalent.[60] This picture agrees with the one arising from a theoretical study by Ossicini, Arcangeli, and Bisi[61] but contrasts with the present findings, based on the *ab initio* Hartree-Fock approach, which attribute not less than 83% ionic contribution to either the total interaction energy or the final SCF wave function. At this point we would like to point out that, although commonly used, changes in the work function cannot be used as a measure of the adsorbate ionicity.[52] This is because the work function depends on the surface dipole but this is influenced by the surface polarization. The above conclusions were deduced for an adsorbate on a metal surface but it is likely that the same physical mechanism holds for a semiconductor surface; we will indeed prove that this is the case.

To avoid the problems derived from the substrate polarization it has been suggested to use the dipole moment curve, or more precisely the slope of the dipole moment curve, rather than the magnitude of the dipole moment itself.[52] Here we will use the same approach to add further support to the picture of the chemisorption bond above described. This analysis will prove that, on a semiconductor surface also, the surface dipole moment, and consequently changes in the work function, cannot be used to obtain information about the ionicity of the interaction. In other words, we will show that a small work-function decrease is not incompatible with the formation of an ionic bond, or of a bond with a high ionic contribution. To achieve this goal we have computed the dipole moment for each adsorbate above each active site at a number of points and expanded the resulting dipole moment curve in Taylor series around r_e such as

$$\mu = M_0 + M_1(r - r_e) + M_2(r - r_e)^2 + \cdots \ . \tag{3}$$

One can relate the net charge on the adsorbate to the slope of the dipole moment curve;[20,47,62] for a point-charge dipole we will have $\mu = qd$ and therefore (3) will exhibit a linear shape with $M_1 = q$. However, because the surface polarizes in response to the charge on the adsorbate it is not correct to compare directly with the charge; especially if the adsorbate is very close to the surface.[48,63] To use the dipole moment curves as a guide to the ionicity of the interaction it is better to compare the dipole moment curve obtained at several steps of the CSOV decomposition.[52] At the FO step we know that the wave function corresponds to an ionic description. We also know that the V(Si;Si) variation only introduces the substrate polarization whereas V(Si;all) accounts for a charge transfer to the cation. Results for the CSOV decomposition of the dipole moment curve are reported in Tables IV and V for the T_1 and H_3 sites; results for the T_4 are very similar to those of the H_3 one and will not be reported.

Concerning the results reported in Tables IV and V we first notice that, in all cases, the value of M_2 is small; the resulting dipole moment curves are nearly linear. This is a first indication that the bond contains a high degree of ionic character. Now, let us analyze the absolute value of the dipole moment; M_0 in Tables IV and V. In all cases there is a rather large decrease in the dipole moment when going from the FO to the SCF wave function. The change of the dipole moment for the interaction of alkali metals above the atop site is large. The dipole moment for Li at the T_1 site is nearly halved from FO to SCF and the SCF dipole moment of Cs also on the T_1 site is 0.75 of its FO value. For the H_3 and T_4 sites there is an even larger reduction in the dipole moment when going from the ionic FO wave function to the SCF one. In these two latter cases the FO dipole moment for chemisorbed Li is about three times larger than that of the SCF wave function. For Cs on the three hollow sites the reduction is smaller but significant; the FO dipole moment is ≈ 1.5 times that of the final SCF wave function. The reduction of the surface dipole moment is the origin of the small decrease in the surface work function. Hence our calculations are consistent with such recent experiments as those reported by Jeon *et al.*[60] However, a further analysis of the results in Tables IV and V will show that the large decrease of the surface dipole moment, and hence the observed small reduction in the measured work function, are consistent with a highly ionic bond. In fact, the CSOV decomposition of the dipole moment shows that the largest change already appears at the V(Si;Si) step. At this step, the alkali-metal atom is still adsorbed as a cation because no charge donation has been allowed. Therefore the dipole moment reduction is largely due to the substrate polarization and not to the formation of a covalent bond. In our previous discussion about the nature of the bond we have shown that the less ionic cases correspond to Li and Na but even in these cases the ionic contribution to the formation of the chemisorption bond is $\approx 80\%$. For chemisorbed Li the reduction of dipole moment from FO to SCF due to substrate polarization is 80% of the total for the T_1 site and $\approx 70\%$ and 50% when chemisorption takes place above the H_3 and T_4 sites, respectively. For the extreme cases, Rb and Cs, we found similar contributions to the decrease of the dipole moment. The decrease in μ is larger for chemisorbed Li because it is closer to the surface but the substrate polarization contribution to this decrease (in percent) is similar for the different adsorbates. Consequently, we cannot conclude from the dipole moment only that the bond is more or less ionic for the different alkali metals. However, these results clearly show that the changes in the surface work function cannot be used to measure the ionicity of a given chemisorption bond because of the large importance of the substrate polarization contribution to the dipole moment decrease. This fact has been previously described for adsorbates on metal surfaces[52] but it has not previously been recognized for adsorbates on semiconductor surfaces.

TABLE IV. CSOV decomposition of the dipole moment curve [see Eq. (3)] corresponding to alkali metals above the atop T_1 site of Si(111).

Alkali atom	CSOV step	M_0	M_1	M_2
Li				
	FO	7.293	0.920	0.033
	V(Si;Si)	4.397	1.224	0.109
	V(Si;all)	3.655	0.550	0.010
	SCF	3.641	0.546	0.014
Na				
	FO	7.840	0.917	0.038
	V(Si;Si)	5.241	1.202	0.087
	V(Si;all)	4.256	0.670	−0.002
	SCF	4.227	0.672	−0.006
K				
	FO	8.867	0.894	0.047
	V(Si;Si)	6.696	1.166	0.057
	V(Si;all)	5.929	0.821	0.023
	SCF	5.876	0.834	0.019
Rb				
	FO	9.177	0.888	0.049
	V(Si;Si)	7.118	1.152	0.047
	V(Si;all)	6.454	0.862	0.037
	SCF	6.377	0.887	0.028
Cs				
	FO	9.673	0.896	0.044
	V(Si;Si)	7.769	1.155	0.035
	V(Si;all)	7.301	0.902	0.035
	SCF	7.204	0.938	0.027

TABLE V. CSOV decomposition of the dipole moment curve [see Eq. (3)] corresponding to alkali metals above the atop H_3 of Si(111).

Alkali atom	CSOV step	M_0	M_1	M_2
Li				
	FO	5.894	0.990	−0.001
	V(Si;Si)	3.245	1.177	0.046
	V(Si;all)	2.061	0.748	−0.054
	SCF	2.057	0.764	−0.020
Na				
	FO	6.448	0.982	0.003
	V(Si;Si)	3.941	1.196	0.036
	V(Si;all)	2.660	0.817	0.016
	SCF	2.641	0.813	0.016
K				
	FO	7.582	0.956	0.010
	V(Si;Si)	5.376	1.209	0.009
	V(Si;all)	4.231	0.952	0.013
	SCF	4.203	0.950	0.016
Rb				
	FO	7.991	0.949	0.013
	V(Si;Si)	5.890	1.207	0.002
	V(Si;all)	4.917	1.026	−0.001
	SCF	4.860	1.025	0.004
Cs				
	FO	8.595	0.945	0.015
	V(Si;Si)	6.645	1.202	−0.004
	V(Si;all)	5.823	1.070	−0.004
	SCF	5.757	1.079	−0.001

In order to quantify the degree of the ionicity of the different adsorbates above the different sites we will now analyze the slope of the dipole moment curves. As shown elsewhere (Refs. 20, 47, 48, and 62, and references therein) the slope of the dipole moment curve is an excellent measure of the ionicity of a given chemisorption bond. Notice that at the FO step the value of M_1 is always $\approx +1$ as it must be because of the construction of the FO wave function. The value of M_1 is increased when substrate polarization is allowed. This is simply because the cluster-model electron density polarizes in response to the charge of the adsorbate. The value of M_1 at this step may then be taken as a reference for a purely ionic bond. It is now clear that a large value of M_1 is representative of an ionic interaction. This is precisely the case for Rb and Cs above the three active sites. For the threefold hollow sites we found that M_1 only exhibits a modest change from the value corresponding to a full ionic bond; the reduction is only 10–15 %, a clear indication of a large degree of ionicity. Again, K represents an intermediate case with a reduction of $\approx 20\%$ in the value of M_1 with respect to that considered as a reference. Finally, for Li and Na the reduction is larger ($\approx$25–35 %) indicating a larger participation of covalency in the bond but with a significant ionicity. At the atop site, we found a similar behavior although the reductions are larger, ranging from 25% for Cs to 60% for Li. The analysis of the slope of the dipole moment curve reveals that there is a different behavior in going from Li to Cs with an increase of the ionicity in the same sense. This analysis is in perfect agreement with that arising from the cost/benefit analysis given in the previous section, with the CSOV energy decomposition, and with the projection of the SCF wave function in the FO one.

Finally, we would like to point out that from the previous analysis one can interpolate net charges on the different adatoms. In our opinion, the important point is to understand the basic physics of the bonding mechanism, to interpret experimental facts, and to establish the ionicity trend along the series. However, if an approximate net charge is desired, it can be directly obtained by simply taking the percent of ionicity deduced from the overlap integral Ω as a percent of the charge in the adsorbate; i.e., for an interaction with $\Omega = 0.9$ we have $\% = 81$ and the net charge will be approximately $0.81e$.

VI. THE EFFECT OF THE CLUSTER SIZE

In this section we will discuss the case of Li above two cluster models representing the atop site of the Si(111) surface. We have chosen Li because it is the case where covalent effects appear to be more important and where cluster-size effects might be expected to be relevant. Also, we have selected the atop site because it is the case where it is easier to grow up the cluster model to include more active sites and dangling bonds. As shown in the previous section, the character of the chemisorption bond does not depend on the particular site. This is a consequence of the strongly ionic character of this interaction; mainly because ionic bonds do not exhibit a specific directionality. Therefore we feel that the conclusions of our study of cluster-size effects will hold as well for the rest of the cases described above. Here we will then discuss the interaction of atomic Li above the $Si_{10}H_{15}$ and $Si_{22}H_{21}$ cluster models.

First of all, we must point out that as expected from previous works[23,29–32] the calculated values for the structural parameters r_e and ν_e are almost independent of the cluster size. This is found to be the case for either the low-spin (LS) or the high-spin (HS) electronic states considered. The calculated r_e for $Si_{22}H_{21}$ is 4.75 bohr for the LS case and 4.77 bohr for the HS to be compared with 4.76 bohr for the $Si_{10}H_{15}$ cluster. A similar behavior is found for the vibrational frequencies.

Now let us analyze the different contributions to the bond as obtained from the CSOV analysis of the interaction for both $Si_{10}H_{15}$ and $Si_{22}H_{21}$ clusters including the LS and HS cases of the $Si_{22}H_{21}$ model. In all cases we found that only the cluster polarization V(Si;Si) and the covalent contributions V(Si;all) are important. This is in agreement with the results reported in the previous section for the whole series of alkali metals above the three active sites. This is a first clear indication that the present description in not biased by the cluster size.

The V(Si;Si) contribution for $Si_{10}H_{15}$ is 0.96 eV and that for $Si_{22}H_{21}$ is 1.88 and 2.01 eV for the LS and HS cases respectively. The cluster polarization is larger because the cluster model is also larger; this is a contribution which must depend on the cluster size. Also, notice that the LS and HS states exhibit different polarizations because they must also have a different initial Pauli repulsion. Now let us focus on the V(Si;all) covalent contribution. This appears to be surprisingly similar for both clusters and both electronic states of $Si_{22}H_{21}$: 0.41 eV for the $Si_{10}H_{15}$ cluster and 0.36 or 0.41 eV for the LS and HS cases of the $Si_{22}H_{21}$ model. This result is significant especially if one realizes that, at the Hartree-Fock SCF level, the LS and HS electronic states of $Si_{22}H_{21}$ are separated by ≈ 7 eV. This is a strong indication of the locality of the chemical interactions and of the validity of the cluster-model approach. The fact that two different electronic states of a given cluster give similar values of the chemical contributions has been discussed in detail in a recent work for CO on a metal surface.[64] Our results show that the same conclusion holds for semiconductor surfaces as well.

Finally, we will compare the dipole moment curves for both clusters. Overall, the behavior is the same reported for the smaller cluster models. Again we find a linear plot of the dipole moment curve against the distance, a reduction of the dipole moment at the V(Si;Si) step, and a large value for the slope of dipole moment curve, M_1. Here we will only comment that the calculated values for M_1 at the V(Si;Si) step are 1.09 and 1.11 for the LS and HS electronic states of $Si_{22}H_{21}$, to be compared with 1.22 for $Si_{10}H_{15}$. At this step the difference is again due to the different polarizability of both clusters. The unconstrained SCF value is 0.73, 0.63, and 0.55 in the same order. If we take the value at the V(Si;Si) step as the reference for a purely ionic bond we will find that for the interaction of Li above Si(111) as represented by the LS and HS cases of $Si_{22}H_{21}$, there is a reduction of 70% or 60% of the reference value, in perfect agreement with that obtained for the smaller $Si_{10}H_{15}$ cluster.

Results in this section can be summarized very briefly. The description of the chemisorption bond given in this work is rather insensitive to the cluster-model size and to the number of active centers explicitly considered in it. Therefore small clusters such as those depicted in Figs. 1(a), 1(c), and 1(d) can be used to appropriately represent low-coverage situations.

VII. CONCLUSIONS

The *ab initio* SCF cluster-model approach to the low-coverage chemisorption of alkali metals on different sites of the ideal unreconstructed Si(111) surface presented in the previous sections permits one to extract some definitive conclusions about the nature of the chemisorption bond and clarifies some previous discrepancies.

First, we have shown that the study of the structural parameters does not permit us to obtain information about the nature of the bond. The calculated equilibrium geometries are in agreement with the available experimental data and, also, with previous theoretical approaches. The equilibrium distances for chemisorbed alkali-metal atoms increase from Li to Cs as expected but the relationship between equilibrium distance and the atomic size is linear no matter if we consider the neutral atom or the cation. The binding energies for a given adsorbate above different sites are very similar, indicating a possible multisite adsorption, also in agreement with previous experimental findings,[55] but from their value we cannot obtain further information about the bonding mechanism.

Secondly, we have used the CSOV technique to show that if one starts from a purely ionic description there are only three contributions to the bond. The most important one is the sum of Pauli repulsion and electrostatic interaction. The two additional contributions are the substrate polarization and charge transfer from the substrate to the cation. The last one is the dative covalent contribution to the bond. It is very small for Cs and Rb, moderate for K, and significant for Na and Li. However, the covalent contribution to the binding energy is only 20% of the total value in the case of Li and decreases when going to Cs. Therefore the bonding mechanism might be viewed as largely ionic with a covalent contribution which decreases from Li to Cs. The same conclusion is reached from the analysis of the SCF wave function and, in particular, from the projection of the purely ionic FO wave function in the SCF one. The above-described mechanism holds for all the active sites studied in the present work. We would like to add that recent experimental results for K/Si(111)-(2×1) based on charge-transfer satellites in the K L_{23} x-ray-adsorption spectra indicate a strong ionic bond but without a complete charge transfer.[65] This is in perfect agreement with the results of the present work.

Finally, we have shown that the surface dipole moment of chemisorbed alkali metals on Si(111) is significantly smaller than the one expected from an ionic bond; i.e., the one obtained from the FO wave function. The CSOV decomposition of the dipole moment has allowed us to show that this decrease is mainly due to the surface polarization and not to the formation of a covalent bond. According to the previous discussion one must expect a small work-function decrease for chemisorbed alkali metals at low coverage, as really occurs.[60] However, we must point out that this small decrease in work function is not incompatible with the formation of an ionic bond. In fact, the analysis of the dipole moment curves leads to a description of the chemisorption bond of alkali metals on Si(111) which fully agrees with the picture presented above. Therefore changes in the work function do not provide a convenient measure of the ionicity. This fact has been previously recognized for ionic adsorbates above a metal surface[52] but it has not been reported previously to our knowledge for an ionic adsorbate above semiconductor surfaces.

ACKNOWLEDGMENTS

Financial support from the "Comisión Interministerial de Ciencia y Tecnología" of the Spanish "Ministerio de Educación y Ciencia" under CICyT Projects No. PB92-0766-CO2-01 and No. PB92-0766-CO2-02 and from the "Generalitat de Catalunya" under the CIRIT project No. GRQ93-7003 is fully acknowledged. The authors wish to thank the "Centre de Supercomputació de Catalunya," CESCA, for supporting a part of the calculations.

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