Investigation of the electronic structures and associated properties including hyperfine interactions for halogen-adsorbed silicon surfaces: Fluorine through iodine

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First-principles self-consistent-field Hartree-Fock cluster investigations have been carried out for the halogen atoms, fluorine through iodine, adsorbed on Si(111) surface. Clusters involving 5, 14, and 27 atoms were employed, where for the first two clusters both all-electron and pseudopotential procedures and for the third cluster pseudopotential procedure alone have been used. The Si—X bond distances for these clusters have been obtained from the minimization of the total energy as a function of adatom position and have been found to compare very well with the available experimental results by surface extended x-ray-absorption fine-structure (SEXAFS) and x-ray standing-wave techniques and with earlier theoretical results. The five-atom cluster corresponds to the SiH$_3X$ molecule for which the calculated Si—X bond distance and the nuclear quadrupole hyperfine coupling constants (e^2qQ) are in good agreement with the experimental values obtained from microwave measurements. For the surface-adsorbed systems, the location of the adatom, the local density of states (LDOS), the frequencies and the amplitudes associated with the Si—X vibrations, and the quadrupole coupling constants for ^{19}F* $(I = \frac{5}{2})$, ^{20}F, ^{35}Cl, ^{79}Br, and ^{127}I nuclei have been studied for the various adsorbed systems. Satisfactory agreement is found between available ultraviolet photoemission spectroscopy (UPS) data for the Cl-adsorbed system and the predictions from our calculated LDOS. Our calculated vibrational amplitude for Br on Si compares well with the available data for Br on Ge surface. It will be very helpful to have experimental data in the future to test our predictions for a number of properties not currently available, especially for the LDOS through UPS measurements and for the e^2qQ by the beam-foil and radiative techniques to verify the interesting trends in both these properties in going from F through I and also the significant decrease in e^2qQ in going from the SiH$_3X$ molecules to the surface-adsorbed systems.

I. INTRODUCTION

During the past few years, a number of interesting experimental investigations[1-22] on the geometry and electronic structures of pure and adsorbate-covered semiconductor surfaces have been reported in the literature. Experimental techniques that have led to valuable information on the structure of surfaces include some recently developed methods such as x-ray standing wave (XSW),[1-5] scanning tunneling microscopy (STM),[6] surface extended x-ray-absorption fine structure (SEXAFS),[7-10] and kinematical total reflection Bragg diffraction (TRBD).[11] Other well-known methods, such as, Auger-electron spectroscopy (AES),[12,13] ultraviolet photoemission spectroscopy (UPS),[14-17] and x-ray photoemission spectroscopy[18] (XPS) have also been employed for the study of surfaces. Techniques such as XSW (Refs. 3–5) and SEXAFS (Refs. 7–10) lead to information on the arrangement of adatoms on the surfaces, whereas UPS and XPS provide information about the nature of electronic distributions on the surfaces. Very recently, there have been efforts to probe surfaces with nuclear radiative techniques such as Mössbauer spectroscopy,[19] perturbed angular-correlation[20,21] methods, and beam-foil techniques[22] to obtain finer details of the electronic distribution through the measurements of quantities like the nuclear quadrupole hyperfine coupling constants and as-

sociated asymmetry parameters. A quantitative understanding of these results is necessary to gain a clear understanding of the physics of surfaces.

The problem of chemisorption of halogens on (111) surfaces of homopolar semiconductors, silicon and germanium, has also received substantial attention from theoretical[17,23-28] points of view. The main interest in the (111) surface of the diamond structure lies in its presumed simplicity. Each atom on the surface has only one unsaturated bond projected along the [111] direction into the vacuum, while the other three bonds, in the sp^3 hybridization picture for silicon and germanium, are saturated by the atoms in the second layer of the bulk crystal. From simplified ideas about chemical bonding, the monovalent halogen atoms by attaching themselves with the dangling bonds are expected to saturate them leading to a stable surface with minimal distortions of the surface layer. This binding site of the monovalent atoms on (111) surfaces is known as atop or on-top position in the literature. Here we limit our discussions to silicon surfaces only, where the binding site happens to be the atop position. Of all the halogens, chlorine on silicon and germanium has been studied in greatest detail through various theoretical approaches.[17,24,26-28] In a previous article in this journal[24] we had presented some of our results on the location and the associated properties of chlorine adsorbed on silicon. In the present paper it is intended to

provide a detailed analysis of the results of our calculations on the electronic structures and associated properties for all four halogens (fluorine through iodine) adsorbed on silicon (111) surfaces for comparison with results from other theoretical[17,26−28] investigations and experimental results that are currently available. Further, a critical evaluation of the Hartree-Fock cluster procedure[23−25,27−31] as a viable alternative to understand local properties of the surfaces has been attempted, based on its ability to explain and predict experimental observables associated with a surface. We have tried to provide an explanation of a variety of available properties like the bond length Si—X, where X is the adatom, the local density of states, and the amplitude and frequency of thermal vibrations associated with the adatom. We have predicted the nuclear quadrupole coupling constants for the halogen nuclei with the hope that they will be studied experimentally in the near future. We have also examined how the Si—X bond changes, especially the bond length and the halogen quadrupole coupling constant, as one moves from the SiH$_3X$ molecule to more complicated clusters used to describe the adsorbate-covered surface and the trends in various properties as one goes from fluorine through iodine.

Section II will discuss the procedure for the determination of the energy levels and wave functions for the adsorbed system including the clusters chosen for this investigation. Section III presents the results for the various properties that have been investigated here. In the Conclusion section we summarize the main features of our results and suggest the experimental measurements that are needed to verify a number of our predictions.

II. PROCEDURE

In the present work, the Hartree-Fock (HF) cluster procedure[23−25,27−33] has been utilized to obtain the electronic wave functions and total energies of the clusters. Before we proceed to discuss the procedure used in this calculation, it is pertinent to examine critically this cluster procedure and its relevance in studying the electronic structures of adsorbed surface. Ideally, a surface is a two-dimensional system defining the boundaries of solid crystals and is infinite. For a quantitative description of the interaction between an atom and a solid surface by the cluster procedure, a reasonable number of atoms representing the surface plus an adsorbed atom are considered as a giant molecule (cluster) with appropriate symmetry. To be confident that the infiniteness of the solid surface is taken care of reasonably well, one has to perform calculations self-consistently with clusters of different sizes and examine the nature of the convergence obtained. Second, the boundaries of the cluster have to be chosen in such a way as to reflect the effect of the rest of the system on the cluster. This is usually known as the embedding procedure in literature and has received a lot of attention in cluster studies. A commonly used procedure[23−25,27−34] in this respect is to use hydrogens as terminal atoms at the surface of the cluster, which is the choice we have used.

In our work here, to test convergence with respect to cluster size, we have used three different clusters, SiH$_3X$,

Si$_4$H$_9X$ and Si$_9$H$_{15}X_3$, consisting of 5, 14, and 27 atoms, respectively, to represent the (111) adsorbed surface, where X represents the adatoms which could be F, Cl, Br, or I in our case. The first cluster is useful as a check on the accuracy of our calculations since it represents a free and stable molecule for which experimental results[35] on structural and electronic properties are available in the literature. The other two clusters are shown in Figs. 1(a) and 1(b). In the 14-atom system, the surface Si atom A, directly below the halogen atom is bonded to three Si atoms on the next layer below the surface. These latter atoms are terminated by the hydrogen saturators. Thus, the environment of the halogen atom and the Si atom A is closer to the real solid than SiH$_3X$. The 27-atom cluster is expected to be an even better representation than the other two, since this cluster has a substantially larger number of atoms, composed of three surface Si A atoms with adsorbed halogen atoms in atop positions and six Si B atoms terminated by hydrogen atoms. The surfaces are all assumed to be planar because of the experimental evidence[4,5] that there is no relaxation and reconstruction of the surface in these surface-adsorbed systems. In going from the 5-atom to the 27-atom cluster, we have in stages incorporated the effects of bulk and surface atoms by expanding the cluster vertically as well as horizontally. In another investigation[27] in the literature, the convergence has been tested more in a vertical sense by going down to more layers of the bulk system below the surface but with less atoms on the surface. The two calculations thus
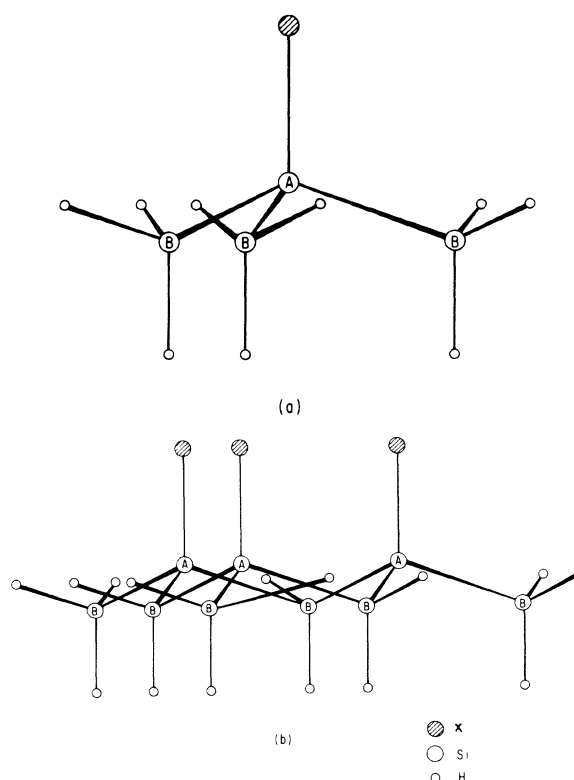

FIG. 1. Atomic arrangements for (a) 14- and (b) 27-atom clusters used in the present investigations, with A and B atoms representing the silicon atoms on the surface and second layers.

complement each other in terms of the convergence test with respect to the sizes of the clusters used. It should also be pointed out that in our present work, all the dangling bonds which are terminated by hydrogen atoms are kept at Si—H covalent bond lengths. This choice for the termination of the dangling bonds has been found to be quite satisfactory in previous surface-cluster[23−25,27−29,32] calculations. It has also been observed in the present calculation that local properties associated with the adsorbed atom are not very sensitive to the variation in the Si—H bond length. For example, the results of calculations for local properties performed with the Si—H covalent bond length were quite close to those obtained when the Si—H bond distance was replaced by the Si—Si covalent bond length.

As mentioned before, we have utilized the HF cluster procedure.[23−25,27−33] For the two smaller clusters, both all-electron and pseudopotential[36] versions of the HF procedure were utilized. In the largest cluster of 27 atoms, the total number of electrons for $X = $ F, Cl, Br, and I are respectively 168, 192, 246, and 300, the total numbers of atomic orbitals involved being 111, 123, 150, and 177. Except for F, all-electron calculations would be prohibitively difficult to perform in attaining convergence in using the HF procedure. The use of the pseudopotential form of the Hartree-Fock procedure, on the other hand, allows one to work within the framework of valence electrons only, involving the relatively smaller numbers of 72 electrons and 63 orbitals.

In the valence-electron calculation, the contributions of core electrons to the potential experienced by the valence electrons are taken care of by an appropriate pseudopotential. The accuracy[23] and reliability of the pseudopotential procedure was tested for an intermediately heavy atom like Br by performing both all-electron and pseudopotential valence calculations for the 14-atom cluster and pseudopotential calculations for the 27-atom cluster alone. Pseudopotentials for Si and halogen atoms are taken from the literature.[36] We have utilized STO-3G–type basis functions,[37] where each Slater type of atomic orbital is expressed as a linear combination of three normalized Gaussian functions

$$\psi = \sum_{l,m,n} C_G \psi_G \tag{1}$$

with

$$\psi_G = N_G x^l y^m z^n e^{-\xi r^2} \tag{2}$$

centered about the different atoms with $l + m + n = L$, corresponding to the angular momentum quantum number associated with the atomic orbital. N_G is the normalization constant, and C_G are parameters obtained through the least-squares-fitting procedure to reproduce Slater functions. The choice of Gaussian basis functions enables one to calculate analytically all the one- and two-electron integrals that occur in the HF procedure. The choice of STO-3G–type basis functions has been found[37] to be adequate in studies related to the determination of structural parameters in molecules and is expected to be satisfactory for our surface calculations.

III. RESULTS AND DISCUSSION

A. Geometry of the host-adatom system

In order to obtain the equilibrium bond length, variations in the total energies of the clusters were plotted against the Si—X bond distances, and the minima from these curves allow us to predict the Si—X bond lengths in the molecule SiH_3X and the adsorbed systems. As mentioned before, the total energy curves for the cluster Si_4H_9Br from both all-electron and pseudopotential valence-electron calculations[23] and for $Si_9H_{15}Br_3$ from valence calculation alone have been compared in Fig. 2. To draw these curves on a common scale, we have taken zero for the total energy in each case at the minimum. The excellent agreement between the first and second energy curves indicates that valence-electron calculations can be used with confidence for analyzing the variation of total energy with geometry, whereas the close agreement between the second and third indicates satisfactory convergence with respect to cluster size.

In Table I, Si—X equilibrium bond lengths are reported for the SiH_3X molecules for X going from F to I and for the two larger clusters from both all-electron and valence calculations. Available results from recent experimental measurements[3,4,9,10,35] have been listed for ready comparison. It is observed that there is a very good agreement between the valence and all-electron calculations for both SiH_3X molecules as well as from the Si_4H_9X clusters. The Si—X bond distances in all the SiH_3X molecules are in excellent agreement with the experimental[35] bond distances from microwave and infrared data which demonstrates the accuracy of the HF cluster procedure that is used in this investigation. The Si—X distance for Si_4H_9X is almost exactly the same as that for the larger $Si_9H_{15}X_3$ cluster, which is expected to be close to the distance for the infinite cluster representative of the real adsorbed system. This distance agrees very well with the experimental distances measured by XSW (Refs. 3 and 4) (for Br) and SEXAFS (Refs. 9 and 10) (for Cl and I) techniques. But so far no experimental value for the F-adsorbed system is available to compare with theoretical predictions. Though there are three symmetric sites for adsorption on Si(111) surfaces, we studied only the atop position, where the adatom is directly over a surface Si atom. As a test, in case of Cl,[24] besides varying the Si—Cl distance in the normal direction, we have calculated the total energy as a function of Si—Cl distance when the Si—Cl bond was 5° off the atop position towards the centroid of the equilateral triangle (threefold open posi-
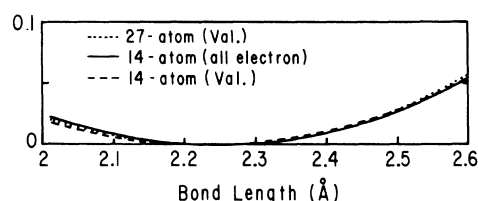

FIG. 2. Variation of total energy with bromine position in the [111] direction for 14- and 27-atom clusters.

TABLE I. Si—X distances (in Å) for different clusters for adsorbed halogen atoms on Si(111) surface.

Clusters	All-electron	Valence only	Experiment
SiH_3F	1.565	1.540	1.595 ± 0.012[a]
Si_4H_9F	1.643	1.558	
$Si_9H_{15}F_3$	1.556		
SiH_3Cl	2.084	2.060	
	2.146[b]	2.118[b]	2.0479 ± 0.007[d]
	2.086[c]	2.069[c]	
Si_4H_9Cl	2.111	2.085	
	2.108[c]	2.082[c]	
$Si_9H_{15}Cl_3$		2.072	2.03 ± 0.03[e]
SiH_3Br	2.199	2.209	2.21[d]
Si_4H_9Br	2.218	2.234	
$Si_9H_{15}Br_3$		2.230	2.17 ± 0.04[f]
			2.22 ± 0.01[g]
SiH_3I	2.450	2.453	2.45 ± 0.09[h]
Si_4H_9I	2.470	2.471	
$Si_9H_{15}I_3$		2.470	2.44 ± 0.03[i]

[a] *Chemical Physics Handbook,* Ref. 35.
[b] 3-21G basis set, an extended basis set with two basis functions per valence atomic orbital used.
[c] Si—H distance has been taken to be equal to the covalent Si—Si distance.
[d] C. Newman *et al.* in Ref. 35.
[e] Reference 10.
[f] Reference 4.
[g] Reference 3.
[h] R. N. Dixon *et al.* in Ref. 35.
[i] Reference 9.

tion) formed by the three A atoms. The minimum total energy in this case was found to be 0.02 eV higher as compared to the atop position, indicating that there is a local minimum with respect to bending of the Si—X bond from the atop position. Seel and Bagus[27] in their investigations for F and Cl have shown that the order of the binding energy (D_e) for the atop and the two other sites referred to as open and eclipsed follow the sequence

$$D_e(\text{eclipsed}) < D_e(\text{open}) < D_e(\text{atop}) ,$$

demonstrating that the atop position is the most stable binding position. Regarding this site, our investigations[24] and those of Seel and Bagus[27] are complementary to each other in terms of study of convergence with respect to cluster size. In our investigations, starting with the 14-atom cluster, we expand the cluster laterally and add more than one adatom to the host surface and find that both the lateral extension of the cluster including more host atoms and the adatom-adatom interactions do not have much influence on the host-adatom bond length and bond character. In their work, Seel and Bagus,[27] starting with the 14-atom cluster, keep the number of adatoms unchanged, expanding the cluster vertically to incorporate more substrate layers, and reach the same conclusion regarding the adequacy of the 14-atom cluster. These results show that the adsorbate-substrate interaction is located at the nearest-neighbor environment, with little perturbation by the more distant neighbors.

B. Ultraviolet photoelectron spectra

The accuracy of the energy levels obtained from our cluster investigations can be tested by comparing our calculated local density of states (LDOS) curve with UPS measurements.[14-17] Historically,[14-17] UPS is one of the first techniques used to probe the nature of surface states, and was also used in conjunction with theoretical[14,17] analysis to predict qualitatively the bonding sites. In the present work, we have obtained the LDOS from the molecular orbital energies that we get from the cluster calculations for the geometry corresponding to the minimum in the total energy and made comparisons with the UPS spectrum where available. In an infinite system like a surface, one expects continuous bands of energy eigenvalues. The clusters used being finite systems, however, lead to discrete molecular orbital energies. In order to obtain a continuous density of states, for visual considerations, the discrete grouping of the one-electron energy levels has to be adjusted to appear continuous. For this purpose, we have utilized a broadening procedure used earlier in the literature[38] involving the application of a Lorentzian function

$$D(E) = \sum_n \frac{\lambda/\pi}{(E - E_n)^2 + \lambda^2} , \qquad (3)$$

λ being an adjustable parameter which was chosen to be 0.8 in our calculations. It has been observed[23,24] that the positions of the predicted peaks are insensitive to the

choice of the parameter λ. The positions of the peaks that we have obtained for the four halogen-adsorbate systems are given in Table II. The LDOS curves presented in Fig. 3 have been obtained from molecular orbital energies for the largest clusters $(SI_9H_{15}X_3)$ in each case. In this cluster, there are 27 atoms with 72 electrons occupying the 36 lowest energy levels. The zero in the energy scale in Fig. 3 refers to the energy of the highest occupied level, the Fermi energy. The peak positions obtained in this work together with those from other theoretical investigations[17,26] and experimental measurements[14–17] are listed in Table II for the chlorine-adsorbed silicon surface. Table III presents the peak positions we have obtained for the other three halogen-adsorbed surfaces. There are no experimental data or theoretical results available for these systems. In the case of Cl,[24] from Table II it can be seen that the positions of the three peaks B, C, and D agree very well with experiment[14,15,17] and earlier theoretical results[14,17,26] obtained by band calculations involving slabs of planar arrangements of surface-adsorbed and substrate atoms. Peak A is found to be somewhat displaced to the left as compared to experiment, a feature shared with the results from some of the other theoretical investigations.[14,17,26] The compositions of the various peaks in terms of the atomic orbital characters of surface Si and halogen atoms have been obtained from the molecular orbitals from our HF cluster investigations. The compositions of the peaks (A –D) in terms of states of surface Si and Cl atoms agree with earlier work,[14–17,26] the peaks A and B involving σ bonding of surface Si and Cl atoms, C primarily the π orbitals of Cl and D involving π bonding between surface Si atoms with significant interaction with Cl π orbitals. The peak E at much lower energy, close to 20 eV below the valence-band maximum, corresponds to the 3s state of Cl and the peak F, about 1.2 eV below the valence-band maximum, involves π bonding, similar to D. Peaks similar to E and F have also been observed in another recent theoretical investigation.[26] For F-, Br-, and I-adsorbed systems, as mentioned earlier, there are no experimental data or results from other theoretical work to compare with. It is interesting, however, to compare the LDOS

curves for the F-, Cl-, Br-, and I-adsorbed systems among themselves to attempt to observe trends. From analysis of the molecular orbitals corresponding to the peaks in the LDOS curves for the other halogen-adsorbed systems besides chlorine, it was found that the constituents of the various peaks in their LDOS curves are very similar to those for the Cl system, with the valence orbitals now being 2s and 2p for F, 4s and 4p for Br, and 5s and 5p for I as compared to 3s and 3p of Cl. The peaks A and B in Fig. 3 involve σ bonding of surface Si and halogen atoms, while the peaks C, D, and F involve π bonding between halogen and Si atoms. The degree of π bonding is different for the two peaks of the doublet C in the Br and I systems, and the one close to the Fermi energy involves substantially more halogen character than the other. The peak E involves predominantly the s valence orbital, 2s of F, 3s of Cl, 4s of Br, and 5s of I. For all of these peaks there are significant contributions from orbitals of the first-layer Si atoms below the surface Si layer. Considering next the trends in the positions of the LDOS peaks in going through the halogen series F to I from Table III, one observes that the peak E shifts toward the right with respect to the Fermi energy in going from F to I. This is expected since the one-electron energy of the 5s state of I is larger than that for the 4s state of Br, which again is larger than 3s state energy of Cl, the latter in turn being higher than the 2s state energy for F. The separation between the peaks in the C doublet is observed to increase continuously and the separation between D and F is found to decrease in going from F to I. These trends are expected to be associated with the variations in the strength of the bonding between the host-Si atoms and the adsorbed halogen atoms at the surface. An examination of the energy levels[39] of the halogen atoms indicates that the difference in energies between the valence 3p states of the Si atom and valence p states of the halogen atoms decreases continuously[39] in going from F (0.43 a.u.) to Cl (0.21 a.u.) to Br (0.16 a.u.) to I (0.11 a.u.). Since this difference can influence the π bonding between the surface silicon and halogen atoms, it is a likely factor that is responsible for the trends observed for the C doublet and the separation between the D and F peaks.

TABLE II. Positions of peaks in the UPS spectra for Cl atoms adsorbed on Si(111) surface obtained from $Si_9H_{15}Cl_3$ cluster.

Cluster		Theory[a]	Energy (eV) Theory[b]		Theory[c]	Experiment[d]
$Si_9H_{15}Cl_3$	A	12.2	10.25	9.3	10.0	9.4
	B	9.1	9.0	6.6	7.1	7.5
	C	5.4	5.9	4.3	5.4	5.4
	D	2.9	2.5	2.9	2.7	2.7
	E	20.2		15.6		
	F	1.2		1.6		

[a]Present work.
[b]References 14 and 26. (Slab procedure using a pseoudopotential approach allowing for infinite extension in two dimensions.)
[c]Reference 17. (Slab procedure using a semiempirical tight-binding approach allowing for infinite extension in two dimensions.)
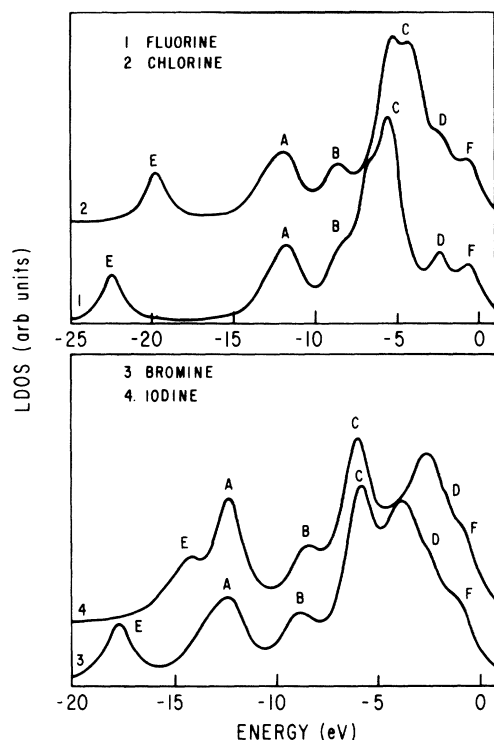[d]References 14–17.

FIG. 3. Local density of states (LDOS) curves for all halogens calculated for the 27-atom cluster. The peaks A to F are discussed in the text.

TABLE III. Positions of expected peaks for F, Br, and I atoms adsorbed on Si(111) surface obtained from $Si_9H_{15}X_3$ clusters.

Peaks	Energy (eV)		
	$Si_9H_{15}F_3$	$Si_9H_{15}Br_3$	$Si_9H_{15}I_3$
A	12.2	12.1	12.1
B	8.7	8.8	8.3
C	6.0	5.5	5.8
		3.5	2.8
D	2.5	2.2	2.0
E	23.2	17.5	14.1
F	0.6	1.2	1.2

C. Vibrational frequency and thermal vibrational amplitude

The vibrational frequencies and thermal vibrational amplitudes associated with the adsorbed halogen atoms were calculated by the following procedure. The force constant $k = (d^2V/dZ^2)_{Z=Z_0}$, a measure of the curvature of the total energy curve at equilibrium distance Z_0 of

the adatom above the surface, can be obtained from our calculated total energy curves. In the approximation assuming the substrate to be rigid, the frequency of vibration perpendicular to the surface is given by $\omega = (k/m)^{1/2}$, where m is the mass of the halogen atom. One, however, expects that there would be some motion of the substrate Si atoms which would lead to a reduction in m and therefore an increase in ω from that obtained using the free mass of the halogen atom. The calculated values of the vibrational frequencies of three different clusters for all halogen systems and the available experimental[35] values for the SiH_3X molecules have been listed in Table IV. The agreement between experiment and theory is reasonably good for SiH_3F but the agreement gets progressively worse as one goes to the molecules involving the heavier halogens. This is to be expected since the rigid substrate approximation becomes less valid as the halogen atom mass gets larger. The assumption of a stationary silicon substrate is expected to be more satisfactory for the surface-adsorbed system than for the molecules, since only a single Si atom is involved in the latter case. It would be beneficial to have experimental data for ω for the surface-adsorbed system to compare with our

TABLE IV. Vibrational frequencies (ω) and thermal vibrational amplitudes $(\langle u^2 \rangle_{eff})^{1/2}$ for SiH_3X molecules and halogen-adsorbed silicon systems.

Clusters	ω (cm^{-1}) (theor.)	ω (cm sup $^{-1}$) (expt.)	$(\langle u^2 \rangle_{eff})^{1/2}$ (Å) (theor.)	$(\langle u^2 \rangle_{eff})^{1/2}$ (Å) (expt.)
SiH_3F	809	872[a,b]	0.13	
Si_4H_9F	842		0.13	
$Si_9H_{15}F_3$	823		0.13	
SiH_3Cl	428	551[a,b]	0.12	
Si_4H_9Cl	427		0.12	
$Si_9H_{15}Cl_3$	429		0.12	
SiH_3Br	288	430[a]	0.11	
Si_4H_9Br	272		0.11	
$Si_9H_{15}Br_3$	284		0.11	0.067 ± 0.053[c]
SiH_3I	199		0.11	
Si_4H_9I	188		0.11	
$Si_9H_{15}I_3$	196		0.11	

[a]C. Newman *et al.* in Ref. 35.
[b]ω (cm^{-1}) for diatomic molecules: Si—F = 857.19; Si—Cl = 535.6.
[c]References 3 and 4 [bromine on germanium (111) surface].

predictions in Table IV for the largest clusters utilized. It is satisfying that the agreement between the predicted values for the largest clusters with 27 atoms are quite close to those from the smaller 14-atom clusters.

To calculate the vibrational amplitude associated with the adatom, the theoretical procedure employed is as follows.[40] In a harmonic oscillator approximation, the extension ΔZ in the Si—X bond length is given by

$$\langle n \mid (\Delta Z)^2 \mid n \rangle = \langle n \mid Z^2 \mid n \rangle = (n + \tfrac{1}{2}) \frac{\hbar}{m\omega} . \quad (4)$$

At a temperature of 0 K this reduces to $(\hbar/2m\omega)$ because only the lowest vibrational level is occupied. At a finite temperature of T K, however, one has to carry out a Boltzmann averaging, leading to

$$\langle u^2 \rangle = \sum_{n=0}^{\infty} (n + \tfrac{1}{2}) \frac{\hbar}{m\omega} \exp(-Kn) \bigg/ \sum_{n=0}^{\infty} \exp(-Kn) , \quad (5)$$

where $K = (\hbar\omega/k_B T)$. Carrying out the summations in (5) one gets

$$\langle u^2 \rangle = \left[\frac{\hbar}{m\omega} \left\{ \tfrac{1}{2} + 1 \bigg/ \left[\exp\left[\frac{\hbar\omega}{k_B T} \right] - 1 \right] \right\} \right] , \quad (6)$$

using the results

$$\sum_{n} e^{-Kn} = (1 - e^{-K})^{-1} , \quad (7)$$

$$\sum_{n} n e^{-Kn} = e^{-K} (1 - e^{-K})^{-2} . \quad (8)$$

Since the values of ω are already available, one can obtain the root-mean-square amplitude $(\langle u^2 \rangle)^{1/2}$ from Eq. (6). To compare with experiment, one has to include the effect of the vibration of the surface atoms on the substrate. Since the vibration of the adatoms and the substrate atoms are incoherent, the effective rms vibrational amplitude is

$$(\langle u^2 \rangle_{\text{eff}})^{1/2} = (\langle u^2 \rangle + \langle u^2 \rangle_s)^{1/2} , \quad (9)$$

where the subscript s refers to surface host atoms. The quantity $\langle u^2 \rangle_s$ is not directly available but is considered in the literature[41] to be related to the bulk vibrational amplitude $\langle u^2 \rangle_b$ by a multiplying factor ranging from 1.0 to 3.5 with the most likely value being 2. With this choice, our theoretical values of $(\langle u^2 \rangle_{\text{eff}})^{1/2}$ for the three different clusters used for all four halogen-adsorbed systems are listed in column 4 of Table IV. Recently, the vibrational amplitude for Br on the germanium[3,4] (111) surface has been measured by the XSW technique using synchrotron radiation. While this value is for a different substrate than silicon, one does not expect it to be too different from the result expected for bromine on silicon because of the similarity in the bonding expected for bromine on silicon and germanium and the closeness[41] of the bulk vibrational amplitudes for the two materials. It is hoped that experimental results for all the halogen atoms adsorbed on Si surfaces will be available in the near future to compare with the theoretical predictions in Table IV.

D. Quadrupole interaction

Recently there have been several attempts to probe the surface electronic structures through hyperfine interaction studies.[19-22] Among such efforts are the measurements of quadrupole interactions associated with adsorbates on copper metal surfaces through the perturbed angular correlation technique,[20,21] with the surface of Fe_2O_3 crystal by the Mössbauer technique,[19] and with alkali atoms on tungsten surface by beam-foil spectroscopy.[22] It is hoped that in the near future there will be further significant developments in this direction to include surface-adsorbed semiconductor systems. Keeping this in mind, we have predicted the quadrupole coupling constants (e^2qQ) for the halogen nuclei for both the SiH_3X molecules and the cluster of 14 atoms for all the halogens. These systems were chosen for the evaluation of the field gradients at the host nuclei because they involve all-electron calculations. As mentioned in Sec. II, our 27-atom-cluster work involved a pseudopotential valence investigation, and the question of the accuracy of electron density near the nucleus derived from pseudopotential calculation has not yet been settled.[36,42] However, since it has been observed from our results earlier in this section that properties like Si—X bond length, vibrational frequency, and vibrational amplitude did not change significantly in going from the 14- to 27-atom cluster, it is reasonable to expect the quadrupole coupling constant for the 14-atom cluster to be representative of the real surface as well.

For both the SiH_3X molecule and the surface-adsorbed system, there is axial symmetry in the charge distribution about the Si—X bond direction. As a result, the field gradient tensor at the halogen nuclear site is also axially symmetric with respect to the Si—X bond direction and the asymmetry parameter[43] η vanishes. Thus the only parameter that characterizes the field gradient tensor is the component q along the Si—X direction [111]. The expression for q at the halogen nucleus in a cluster is given[43] by

$$q = \sum_{n} \xi_N \frac{3\cos^2\theta_N - 1}{r_N^3} - \sum_{\mu} \left\langle \psi_\mu \left| \frac{3\cos^2\theta - 1}{r^3} \right| \psi_\mu \right\rangle , \quad (10)$$

ξ_N being the nuclear charges on the various nuclei in the cluster, θ_N the angle between the line joining X to the nucleus N, and the [111] direction and r_N the distance between the two nuclei. The sum over μ refers to the contribution from all the occupied electron states (with both spins) in the cluster. It is not necessary to include summations of the type in Eq. (10) because the atoms outside of the cluster are neutral and therefore make little net contribution to the field gradient at the halogen nucleus. Additionally, Sternheimer antishielding effects are implicitly incorporated in the HF calculation since both core- and valence-electron states are included, and thus the distortion of the core-electron states is explicitly considered, obviating the need for introduction of any factors for including these effects. We have calculated the field gradient q for both SiH_3X and the Si_4H_9X clusters using Eq. (10) and our HF electronic wave functions. These results have been combined with the quadrupole moment[44] Q to

obtain the quadrupole coupling constants e^2qQ for the molecules SiH_3X as well as surface-adsorbed systems which are listed in Table V. In the case of molecules, there is good overall agreement between theory and available experimental data,[45] the quantitative nature of the agreement being apparently somewhat better for the $SiH_3{}^{79}Br$ molecule than for $SiH_3{}^{35}Cl$, where the experimental result is a little smaller than the theoretical value in Table V. In analyzing the nature of the agreement between theory and experiment, it should be noted that the bromine atom being heavier, the field gradient at its nucleus due to the electrons would be subject to some relativistic enhancement which would make the difference between theory and experiment somewhat more than one sees in Table V. Relativistic effects are expected to be unimportant for the lighter atom Cl. Thus, it appears from Table V that for both chloride and bromide, the theoretical quadrupole coupling constants are somewhat larger than the experimental results. It is possible that the influence of many-body effects may be responsible for the small but significant difference between theory and experiment for the molecules involving chlorine and bromine. It would be helpful in the future to carry out the difficult task of treating many-body effects perhaps by the configuration-interaction procedure.[46] However, for the present, the reasonable agreement between experiment and the results of the Hartree-Fock procedure for the molecular systems suggests that one can rely on the predictions by this procedure for the surface-adsorbed systems. From Table V, it appears that except for F, the coupling constants decrease in going from the surface-adsorbed systems to the corresponding molecules. This decrease in going to the surface-adsorbed systems could be a consequence of the π bonding between halogen and surface Si atoms. In the case of F, there may be changes in other factors which characterize the bonding with the surface besides the π character. It would be interesting and very helpful to have experimental data both to verify our theoretical results, in Table V and also the observed trend in the coupling constants e^2qQ in going from molecule to surface.

As regards possible techniques for measurement of e^2qQ, the $^{19}F^*$ ($I = \frac{5}{2}$) and ^{20}F ($I = 2$) could perhaps be studied by the radiative techniques, TDPAD (Ref. 47)

and β-decay NMR.[47] For ^{127}I, one could use Mössbauer technique. For the $^{35,37}Cl$ and $^{79,81}Br$ nuclei there are no suitable nuclear levels for applying one of the radiative techniques. One could apply conventional resonance techniques like nuclear magnetic or quadrupole resonance, but because of the low frequencies involved, there would be problems connected with the intensities involved. However, the beam-foil technique[22] recently used for studying nuclear quadrupole interaction effects for nuclei at metallic surfaces has the potential for studying these effects for the halogen nuclei. It should be pointed out that recent TDPAD measurements on $^{19}F^*$ implanted in Si have provided two quadrupole coupling constants, (34.9 ± 0.3) and (23.0 ± 0.03) MHz. If one assumed that the calculated $^{19}F^*$ quadrupole coupling constant at the surface is significantly overestimated as in the case of the ^{35}Cl coupling constant in SiH_3Cl, one could ascribe the larger $^{19}F^*$ coupling constant in implanted silicon to be associated with surface-adsorbed fluorine and the smaller one perhaps with a center in the bulk.

E. Core-level energies

Photoemission from core levels at surfaces[48−50] have been observed for a variety of semiconductor and metal surfaces by the ESCA (also referred to as XPS) technique in different x-ray energy regions. Structural and chemical information is obtained[48] from the intensity ratio of the surface emission relative to the bulk and from the core energies. Recently the ESCA intensity and surface core-level shifts for clean and halogen- (Cl,Br) covered Ge(100) and Ge(111) surfaces[48] and (F,Cl) covered Si(111) surfaces[49,50] have been determined with the use of synchrotron radiation. We have used Koopmans's theorem[51] to equate the core orbital energies to the expected ionization potentials (IP). In Tables VI and VII, we have listed the orbital energies of core states of Si and halogen atoms. The results for the F-adsorbed system are listed separately in Table VI because there are results available from an earlier calculation and from XPS measurements which are listed along with our results. Table VII lists our results for the core-level energies for the other halogens for

TABLE V. Nuclear quadrupole coupling constants for SiH_3X molecules and halogen nuclei adsorbed on Si(111) surface.

Molecule	e^2qQ (MHz) Theor.	e^2qQ (MHz) Expt.	Cluster	e^2qQ (MHz) Theor.	Q (b)
$SiH_3{}^{19}F^*$	41.49		$Si_4H_9{}^{19}F^*$	45.23	0.072[b]
$SiH_3{}^{20}F$	22.57		$Si_4H_9{}^{10}F$	27.01	0.043[b]
$SiH_3{}^{35}Cl$	49.14	40.0[a]	$Si_4H_9{}^{35}Cl$	46.77	0.0789[c]
$SiH_3{}^{79}Br$	355.4	336[a]	$Si_4H_9{}^{79}Br$	286.8	0.32±0.02[c]
$SiH_3{}^{127}I$	1439.01		$Si_4H_9{}^{127}I$	1020.05	0.79[c]

[a]J. M. Mays and B. P. Dailey in Ref. 35.
[b]K. C. Mishra, K. J. Duff, and T. P. Das, Phys. Rev. B 25, 3389 (1982).
[c]G. H. Fuller and V. W. Cohen in Ref. 44.

TABLE VI. Core-level energies for F/Si(111). Si^1 and Si^2 represent the first- and the second-Si layer, respectively. The energies are in eV.

Core levels	Present work		Seel et al.[c]	Expt. (XPS)
	SiH_3F	Si_4H_9F		
$F(1s)$	702.9	702.4	714.7	685.5, 687.2[a]
$Si^1(2s)$	163.9	161.9	168.7	151[a]
$Si^1(2p)$	109.6	108.2	117.5	100,[a] 105[b]
$Si^2(2s)$		161.6	167.5	
$Si^2(2p)$		107.8	116.3	
$F(2s)$	39.4	38.5		36[b]

[a]Reference 52.
[b]F. R. McFeely et al. in Ref. 50.
[c]Reference 27.

which no experimental data are available with the exception of the Cl-adsorbed Si(111) surface, for which the Si(2p) core-level shift between Si atoms on the bare surface and Cl-adsorbed surface is available.[49]

In comparing core-level shifts for surface-adsorbed atoms with experiment for the halogens, one can consider the free-atom core levels as a reference. For the Si atoms at the surface in the halogen-adsorbed systems, one has a choice of either using the core levels in the free Si atom, bulk Si, or Si at the bare surface as reference. In using the atomic core levels as reference, one has the problem that experimentally one measures the difference in ionization energies from the core states in the two systems, requiring one to include the influence of orbital relaxation effects[53] not considered when Koopmans's theorem is used, as well as differences in many-body effects[54] in the two systems. Additionally in cluster calculations like ours aimed at studying surface properties depending primarily on valence electrons, the orbital basis set chosen is aimed at providing a good description of the valence-electron properties and is not flexible enough to accurately describe core-electron properties. For the halogen atoms, therefore, it is not possible in the present work to attempt an accurate comparison with the core-level shifts. We have therefore only compared the absolute core-level energies with experiment. For the Si core levels, on the other hand, one can attempt a comparison between calculated and experimental shifts[50] between Si atoms next to the adsorbed halogen atoms and Si atoms on the bare surface, with the expectation that orbital relaxation and many-body effects in both cases could be quite similar, leading to substantial cancellations in the

influence of these effects on taking differences. We shall, therefore, discuss these shifts for Si atoms in analyzing the results as was done in earlier theoretical work.[27]

Considering first the results for the F-adsorbed system, the IP for F(1s) from our calculation is 702.4 eV as compared to the earlier theoretical result[27] of 714.7 eV for the atop site. Experimental[52] XPS measurements in this energy range show a broad peak with half-width of 4.3 eV which contains two maxima at 685.5 and 687.2 eV which could arise from adsorption of F at two different sites since one of them (at 687.2 eV) vanishes at 550 °C. Seel and Bagus[27] have suggested the possibility of surface penetration of the F atom at the open site for the second IP from XPS measurements because of a relatively small barrier height (~ 1 eV for F and ~ 13 eV for Cl) and the formation of intermediate-surface species during the reaction of F with the Si surface. The large differences between the positions of the XPS peaks[52] and both our IP and that from the earlier calculation[27] can arise from orbital relaxation effects as well as many-body effects. The former has been ascribed in earlier work[27] as the major source of the difference. As regards the F(2s) IP, a peak has been found in the XPS measurements[50] at 36 eV which agrees quite well with our results of 38.5 eV for the F(2s)-like level in Table VI for the larger cluster Si_4H_9F.

Considering next the XPS peaks associated with the Si atoms, two peaks have been found from XPS measurements at ~ 151 eV and ~ 100 eV (105 eV) which have been associated with surface Si atom 2s and 2p states. Also recent high-resolution synchrotron soft-x-ray photoemission spectroscopy[50] measurements have provided information regarding the chemical shifts of Si(2p) levels

TABLE VII. Core-level energies (eV) for Cl, Br, and I adsorbed in Si(111) surface.

	Cl/Si(111)			Br/Si(111)			I/Si(111)	
Core levels	SiH_3Cl	Si_4H_9Cl	Core levels	SiH_3Br	Si_4H_9Br	Core levels	SiH_3I	Si_4H_9I
$Cl(2s)$	280.9	280.3	$Br(3s)$	249.5	249.0	$I(4s)$	189.0	188.6
$Cl(2p)$	211.3	210.7	$Br(3p)$	186.8	186.3	$I(4p)$	147.2	146.8
$Si^1(2s)$	164.3	162.6	$Si^1(2s)$	163.6	162.1	$Si^1(2s)$	163.8	162.2
$Si^1(2p)$	110.6	108.8	$Si^1(2p)$	109.9	108.3	$Si^1(2p)$	110.0	108.3
$Si^2(2s)$		162.1	$Si^2(2s)$		162.0	$Si^2(2s)$		162.1
$Si^2(2p)$		108.4	$Si^2(2p)$		108.2	$Si^2(2p)$		108.4

for Si atoms bonded to one, two, and three F atoms at the surface as compared to bulk Si. Since our investigation is confined to a single F ligand at the atop position, we can make comparisons only with the data for the SiF_1 case. Thus, in the real F-chemisorbed surface the surface $Si(2p)$ levels will undergo a chemical shift while the Si atoms in the layers underneath having Si neighbors should have their $2p$ levels remain unshifted. However, in our 14-atom cluster the Si atoms in the second layer have only single Si atoms (surface atom) as nearest neighbors with the other three ligands being terminator hydrogens. This could partly be the reason why our computed value (0.43 eV) for the difference in the IP for surface and next layer Si atoms (Table VI) is less than the experimental value of 1 eV. On the other hand, in the cluster used by Seel and Bagus,[27] each of the second-layer Si atoms has two Si neighbors, which is a better representation of the bulk Si. They obtain 1.2 eV for this shift. An all-electron calculation on our 27-atom cluster is expected to yield a better result than the 0.43 eV we have currently obtained, since it would allow for the second-layer Si atoms to have two Si ligands and two hydrogens. This expectation is based on the observation from our results that there is always some electron transfer ($\sim 0.15e$) from the Si to a terminator hydrogen. The replacement of one of the terminator hydrogens by Si is expected to reduce this electron transfer and thus increase the screening of the nuclear charge, thus reducing the IP for the second-layer Si atoms from the value of 107.8 eV in Table VI. Unfortunately our available computing facilities do not allow us to carry out a 27-atom cluster all-electron calculation at the present time.

It should be pointed out that no special significance should be attached to the fact that the core-level energies from our calculation agree better with experiment than those from the earlier work[27] listed in Table VI. This is because, in addition to the contributions from orbital relaxation and many-body effects which could be different for the clusters and orbital basis sets used in the two theoretical calculations, the basis sets used in our calculations are minimal ones for analysis of properties associated with the valence electrons and are not as suitable for core-electron properties. The basis set used[55] in the earlier calculation[27] is more extensive than the STO-3G basis set that we have used and is, therefore, expected to be more suited for core-electron properties. It leads[55] to core-energy levels in free atoms closer to the Hartree-Fock values from numerical differential equation calculations[56] than with the basis set we have used.

In Table VII we have presented for the rest of halogen-adsorbed systems the IP for the $2s$ and $2p$ levels of the surface and second-layer Si atoms and for the (ns) and (np) levels of Cl, Br, and I, n being one smaller than the valence-electron principal quantum number. As mentioned earlier, there are no available XPS data on these systems to compare with our results except for the $Si(2p)$ level in the Cl-adsorbed system. The shift between the $2p$ levels for the surface and next layer atoms is seen from Table VI to be 0.4 eV as compared to 0.93 eV from experiment.[49] As in the case of F-adsorbed system, a part of the reason for this difference could be the factor that we have used the theoretical result from our 14-atom cluster calculation instead of the 27-atom cluster for which an all-electron calculation was not possible with our computing facilities.

IV. CONCLUSION

The HF cluster method utilized for electronic structure calculations has successfully explained the observed experimental data like Si—X bond distance[3,4,9,10] ($X = $Cl,Br,I) for adsorbed halogens on Si(111) surface, local density of states[14−17] for Cl (the only system for which data is available from UPS measurements so far), and the vibrational amplitude[3,4] for Br. It is also demonstrated that the agreement between the results of the all-electron calculation and pseudopotential calculation for these properties is satisfactory. We have also made predictions for the local density of states for (F,Br,I), vibrational frequencies, amplitudes associated with vibrational motions and nuclear quadrupole coupling constants for ^{19}F, ^{35}Cl, ^{79}Br, and ^{127}I nuclei. It is expected that experimental results on these properties will become available in the future to verify our results, especially the interesting trend observed for the local density of states in going from F through I and in the nuclear quadrupole coupling constant in going from the molecule to the surface-adsorbed system.

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