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Molecular Electrostatic Field as a Reactivity Map for the Si(111) Surface

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We applied the molecular electrostatic field of a cluster model of the Si(111) reconstructed crystal surface as a reactivity map for the prediction of preferred adsorption sites of pointlike dipolar molecules. It was found that experimentally located preferred sites are correctly predicted by both molecular electrostatic field maps, as calculated by the semiempirical NDDO molecular orbital method with the AM1 parametrization, and results obtained by ab initio molecular orbital calculations with a split valence-shell basis set. It is thus probable that electrostatic field maps can be applied to other crystalline surfaces for the pictorial representation of reactivity properties, too.

Introduction

Chemical bonding in the top layers of the reconstructed Si(111) crystal surface considerably differs from the tetrahedral pattern in the bulk.[1] Adatoms in the uppermost layer, protruding from the surface, are centered in a tetrahedron where they have only three neighbors at the corners and an additional Si directly below them providing a fourth bond in a very unconventional direction. Though the average Si−Si distance in these bonds is 239.3 pm, close to the corresponding value in the bulk (235.1 pm) the bonding pattern of adatoms does not fit in the classical picture valid for the majority of small molecules containing silicon. Other types of tricoordinated centers, called rest atoms, are present in the first reconstructed bilayer and possess enhanced affinity toward small molecules.[2−4] The most reactive adatoms stick out of the surface, but a simple "altitude map" is not a perfect guide to reactivity since, in addition to their special position, they attract extra electrons via dangling bonds. Thus, molecular orbital calculations are necessary to shed more light on reactivity that cannot be predicted from classical chemistry. This is especially important since silicon surfaces, having extensive semiconductor applications, attracted great interest in the study of chemical vapor deposition,[5] synthesis of a diamond film from hydrocarbons,[6] and other surface phenomena.

Chemisorption and physisorption on crystal surfaces have been subject of theoretical studies since more than a decade.[7−12] Both ab initio and semiempirical molecular orbital calculations rise technical problems due to the large size of clusters necessary to adequately model the Si(111) 7×7 surface. Thus, it is important to use reactivity maps that can be calculated relatively easily and yet provide valuable information on reactive sites of molecular species.[11] The molecular electrostatic potential (MEP) is widely used as such a reactivity map displaying most probable regions for the electrophilic attack of charged pointlike reagents on organic molecules.[13−15] Its gradient, the molecular electrostatic field (MEF), yields information on the affinity of a system toward small dipolar molecules, such as water or ammonia.[16−18]

In the following we present MEP and MEF maps for the Si(111) 7×7 surface and discuss their use in the interpretation of reactivity. This is one of the most complicated cases in surface modeling; therefore, it is especially important to find adequate simplifications in the description of its reactivity. Recently we published a preliminary study on the topic where we dealt with the adequate modeling of the surface.[19] In this work we present the maps, as calculated with both semiempirical and ab initio methods, and compare our predictions with results of molecular orbital energy calculations and experimental data.

Models and Methods

It is now generally accepted that the geometry of the reconstructed Si(111) 7×7 surface is described by the dimer-adatom-stacking-fault (DAS) model proposed by Takayanagi et al.[20] The unit cell with two triangular subunits, one having a stacking fault and the other unfaulted, is shown in Figure 1. The top layer consists of 12 adatoms, at the corners of the unit cell there are vacancies referred to as corner holes. There are 19 dangling bonds in the 7×7 unit cell; 12 of these are located on adatoms, 6 on rest atoms, and 1 on the atom at the bottom of the corner hole.

We modeled the infinitely large Si(111) surface by an atom cluster in a geometric arrangement obtained from the low-energy electron diffraction experiment by Tong et al.[1] Owing to the large size of the unit cell (242 atoms, cf. Figure 1) we reduced the number of atoms in the models and cut out relevant fractions from the whole entity in order to be able to perform molecular orbital calculations for them. For semiempirical calculations we chose a model (model A) whose constituents are depicted in Figure 2 where each fragment includes the adatom layer extended with four layers beyond which reconstruction is negligible. Since the net charge on silicon atoms in the unreconstructed bulk is just zero, it is not necessary to include further layers in the model because they have no effect on the electrostatics of the surface. We also tried to construct the maps by summing up the contributions calculated for fragments of the unit cell as defined by Tong et al.[1] These fragments, forming model B, can be divided into two groups, corresponding to faulted and unfaulted regions, and related to each other by a 3-fold symmetry. However, due to the presence of hydrogen atoms at the border of the fragments, we obtained artifacts when summing up contributions to provide the whole map. Thus, model B was used only for comparing MEF maps obtained by semiempirical molecular orbital calculations and the monopole approximation. Further reduction was necessary in case of the ab initio calculations. The reduced fragments (model C) contain

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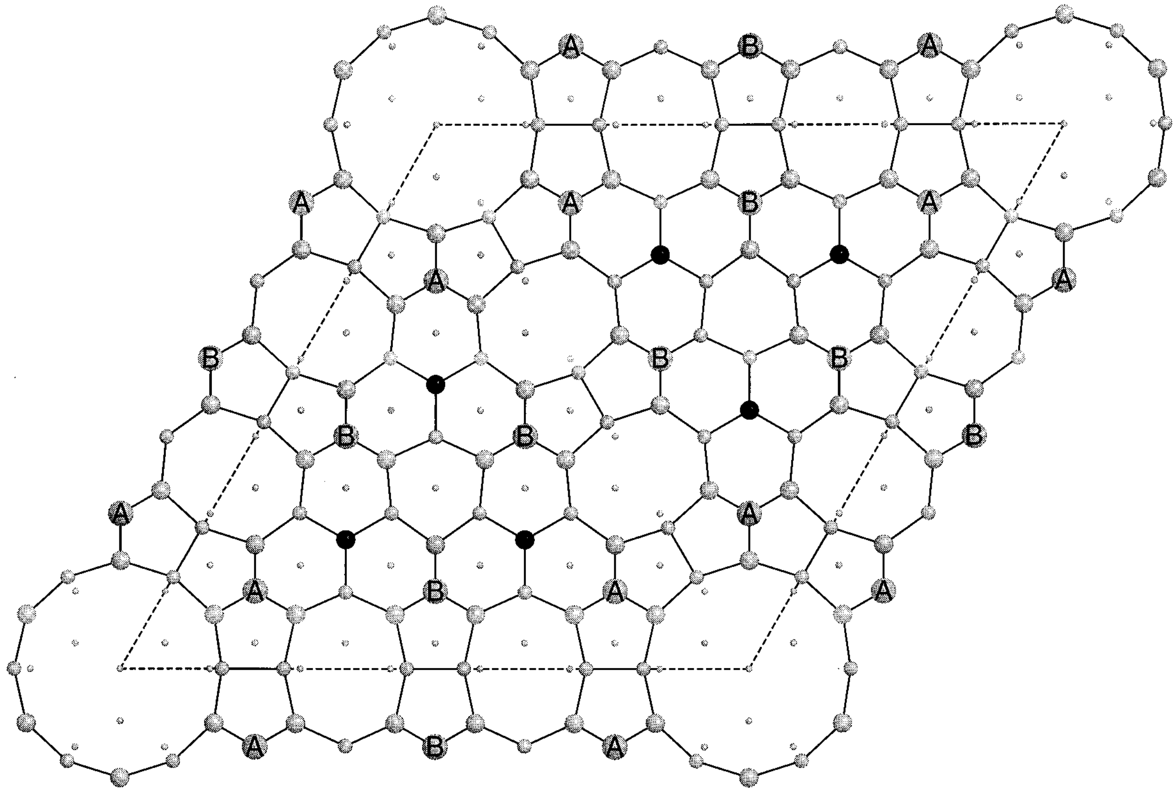

Figure 1. Computer model of the reconstructed Si(111) 7×7 surface. Corner and center adatoms are denoted by A and B, respectively, rest atoms are black, and dimers (connected by full lines) are located on the boundary of the unit cell (dashed line).

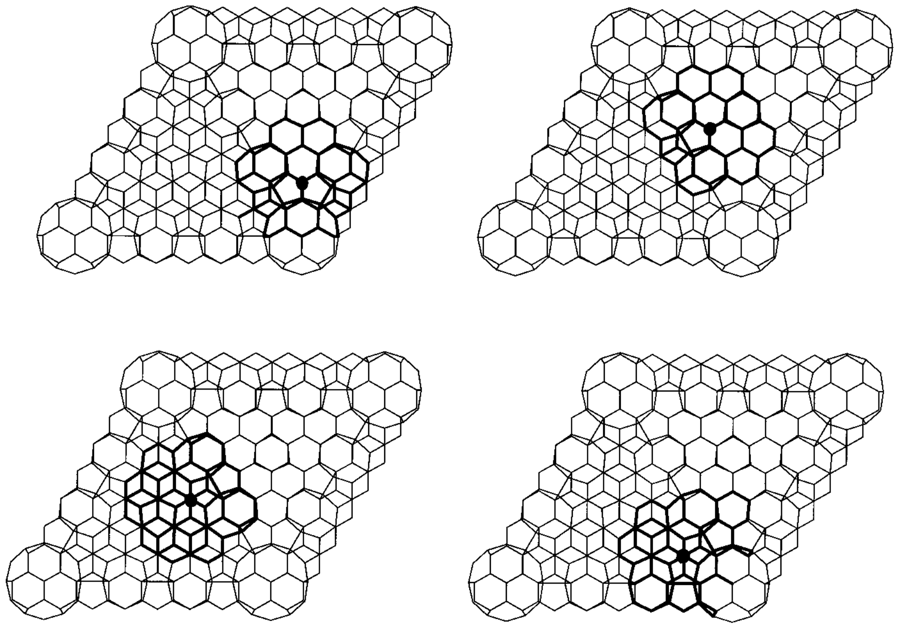

Figure 2. Fragments of the unit cell (heavy lines) of the Si(111) surface (light lines) defining models for semiempirical MNDO/AM1 molecular orbital calculations (Model A, adatoms are indicated by dots). Upper left: corner adatom faulted region; upper right: center adatom faulted region; lower left: center adatom unfaulted region; lower right: corner adatom unfaulted region; rest atoms are included in all models.

16−22 silicon atoms, have adatoms and rest atoms in their center, and include four layers and 16−24 terminating hydrogen atoms. These fragments represent the minimum atomic arrangements that are chemically relevant models of the surface (see Figure 3).

We replaced the bulk around the fragments of Figure 2 by hydrogen atoms, but because the Si−H bond is polar spurious charge transfer may occur from them to the surface. To avoid this effect while doing semiempirical calculations, we elongated the Si−H bond distance as proposed by Tagüena-Martinez et al.[21] According to our previous studies,[19] a bond length of 190 pm, much larger than the experimental one (148 pm), ensured the minimum charge transfer (18 millielectrons) from terminal hydrogen atoms to the surface. To avoid poor convergence in the case of ab initio calculations in Model C, we used experimental Si−H distances. This is acceptable if we are interested in relative values of the MEF.

The MEP and MEF maps were calculated using the MNDO method with the AM1 parametrization[22] and with the ab initio method using a 3-21G basis set[23] in a plane 300 pm above the adatoms. It is known that for classical molecules the AM1 parametrization fairly reproduces the MEP obtained by sophisticated ab initio calculations.[24] Because of its extremely large size we could not consider the full unit cell, neither its faulted

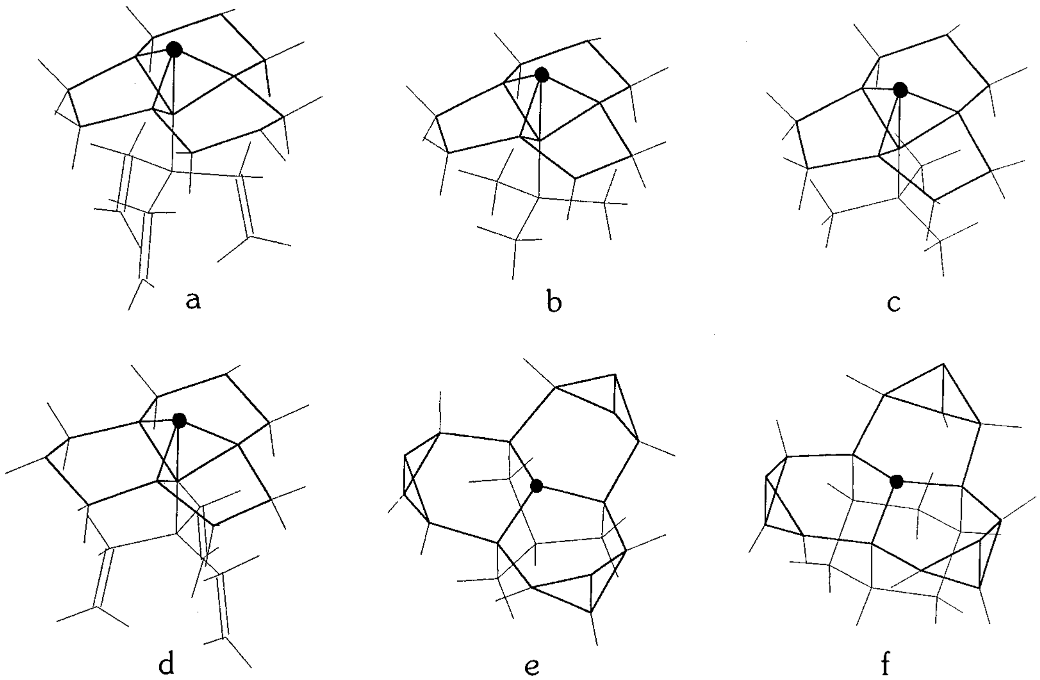

Figure 3. Fragments of the unit cell (heavy lines) of the Si(111) surface (light lines) defining models for ab initio calculations (model C). (a−d) As in Figure 2; (e) rest atom unfaulted region; (f) rest atom faulted region. Adatoms in (a−d) and rest atoms in (e) and (f) are indicated by dots. In fragments (a) and (d) we used >Si=SiH$_2$ groups to mimic the bulk because if using hydrogen atoms an open-shell model is obtained that is inappropriate for calculations.[19]

TABLE 1: Relative Binding Energies, As Obtained by the MNDO/AM1 Method, for Some Configurations of Ammonia Interacting with the Si(111) Surface[a]

position	Si−N distance (pm)	α (deg)	β (deg)	rel BE (kJ/mol)
adatom	300	60	0	0.0
adatom	300	10	30	1.2
adatom	300	0	30	1.4
rest atom	300	0	0	32.7
rest atom	400	0	0	33.1
rest atom	400	30	0	31.5

[a] For the definition of α and β see Figure 4. Total energy for the minimum energy configuration is −622 422.0 kJ/mol.

and unfaulted halves. Though we attempted to do semiempirical molecular orbital calculations for both, considering 866 basis functions, we could not achieve convergence in the self-consistent field procedure even if applying the level-shifting technique[25] (with shift parameters changing between 0.001 and 0.005).

To check the reliability of the MEF maps in predicting adsorption energetics for small dipolar molecules, we calculated the interaction energy between the above fragments of the unrelaxed Si(111) surface and ammonia. We moved the rigid NH$_3$ molecule in the same plane where the MEF was computed and calculated the binding energy (BE) in each point as the difference between the total energy of the cluster−NH$_3$ complex and the sum of total energies of the bare cluster and NH$_3$, BE = E(cluster−NH$_3$) − E(cluster) − E(NH$_3$). Negative BE corresponds to attraction of the ammonia molecule by the surface.

Semiempirical calculations were done with the MOPAC package[26] on IBM RISC/6000 420H and HP 9000/735 workstations. To calculate the MEF, we used the NDDELP subroutine[24,27] attached to the MOPAC program that we modified to some extent in order to be able to generate the MEP in a plane parallel to the Si(111) surface. Ab initio calculations were done with the GAMESS program package[28] on a HP 9000/735 workstation with the direct SCF technique.[29] Some typical running times were as follows: 38 h of CPU time was needed for a single-point ab initio calculation for a model with 20 Si atoms, 16 hydrogens, and the ammonia molecule, geometry optimization with the semiempirical method needed 7.3 h of CPU time for a model with 75 Si atoms, 45 hydrogens, and the ammonia molecule, while the single-point calculation of the wave function and the MEF for the same model took 40 min.

Results and Discussion

To examine the applicability of the MEF map for the prediction of preferred adsorption sites of ammonia, we calculated the binding energy (BE, see above) map for the cluster shown in the upper right segment of Figure 2 with the MNDO/AM1 method. First we roughly optimized the orientation of the ammonia molecule, defined by the parameters given in Figure 4, above the surface. We displayed energies corresponding to various geometries in Table 1 which shows that the energy minimum is in a staggered configuration with the symmetry axis of the molecule perpendicular to the surface and hitting just the adatom or rest atom lying below the ligand. Configurations with the hydrogen atoms pointing towards the surface are strongly repulsive (with BE values around +60 kJ/mol).

The map displaying the surface BE of an ammonia molecule in its optimal configuration (both the surface model and the ammonia molecule unrelaxed), as obtained from the semiempirical calculation, is compared to MEF maps in Figure 5. The z component of the MEF, perpendicular to the surface (Figure 5a), correctly indicates maxima and minima of the interaction energy map (Figure 5c). It is most negative, indicating strongest binding, in the close vicinity of the adatom situated in the center of the model, while it shows maxima near adatoms at the border. We should mention that these maxima do not reflect experimental findings. Owing to the limited size of model A they appear because the adatoms lie at the border with no neighbors present as in the case of the true surface. The map of absolute values of the MEF (Figure 5b) shows three maxima, indicating strongest interaction sites without making a difference between attraction and repulsion. We found a similarly good agreement between the BE and MEF maps for other fragments of Figure 2, as well.

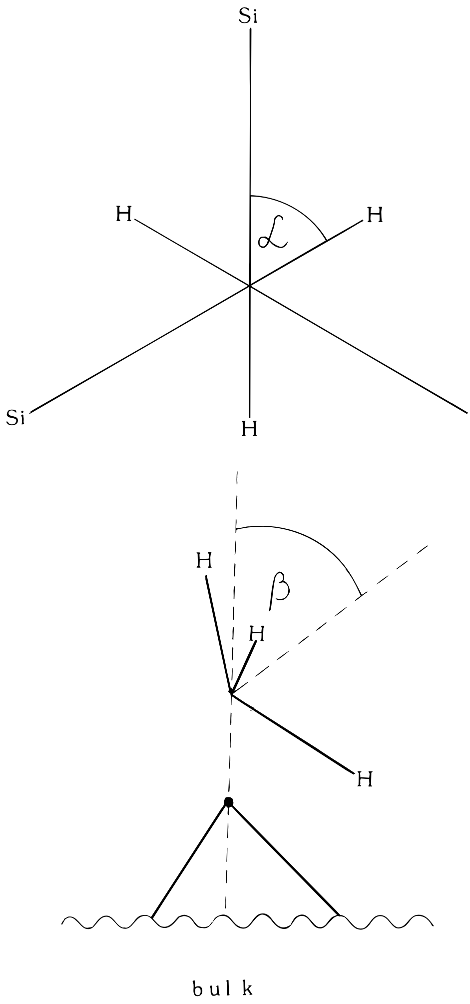

Figure 4. Definition of parameters defining the orientation of the ammonia molecule (indicated by three hydrogen atoms) above the Si(111) surface: (a, top) dihedral angle defining the position relative to Si(adatom)−Si bonds, (b, bottom) tilt angle.

TABLE 2: MEF Values at Various Distances (in pm) above Rest Atoms and Adatoms (V/nm) as Obtained by ab Initio 3-21G Basis Set (Upper Row) and MNDO/AM1 Semiempirical (Lower Row) Molecular Orbital Calculations for Model C[a]

atom type	triangular subunit	distance above atom				
		200	250	300	350	40
rest atom	faulted	41.2	22.1	13.0	9.4	6.5[b]
		31.3	12.4	6.3	3.8	2.5[b]
rest atom	unfaulted	n.c.	n.c.	n.c.	n.c.	n.c.
		24.0	8.3	4.7	3.6	3.0[b]
center adatom	faulted	30.1	14.0	8.4	5.8	4.2
		9.4	2.1	2.7	2.0	1.3
center adatom	unfaulted	28.5	12.7	7.4	4.9	3.5
		10.7[b]	1.2	2.1	1.6	1.1
corner adatom	faulted	30.6[b]	14.4[b]	8.7[b]	6.0[b]	4.4[b]
		12.1	0.2	1.4	1.1	0.8
corner adatom	unfaulted	30.0[b]	14.0[b]	8.5[b]	5.9[b]	4.3[b]
		12.6[b]	0.2	1.2	1.0	0.7

[a] n.c. denotes that the calculation did not converge. Experimental preferences for interaction are rest atom > center adatom > corner adatom, faulted > unfaulted.[2] [b] Incorrect order of adsorption preference.

We examined the relevance of the monopole approximation for the calculation of the MEF. Applying atomic net charges calculated by the semiempirical MNDO/AM1 molecular orbital method for fragments of model B, we constructed the MEF map and compared it to that obtained directly from the wave function determined for the same fragments (cf. Figure 6). The maps are similar, they possess maxima near center adatoms. This is

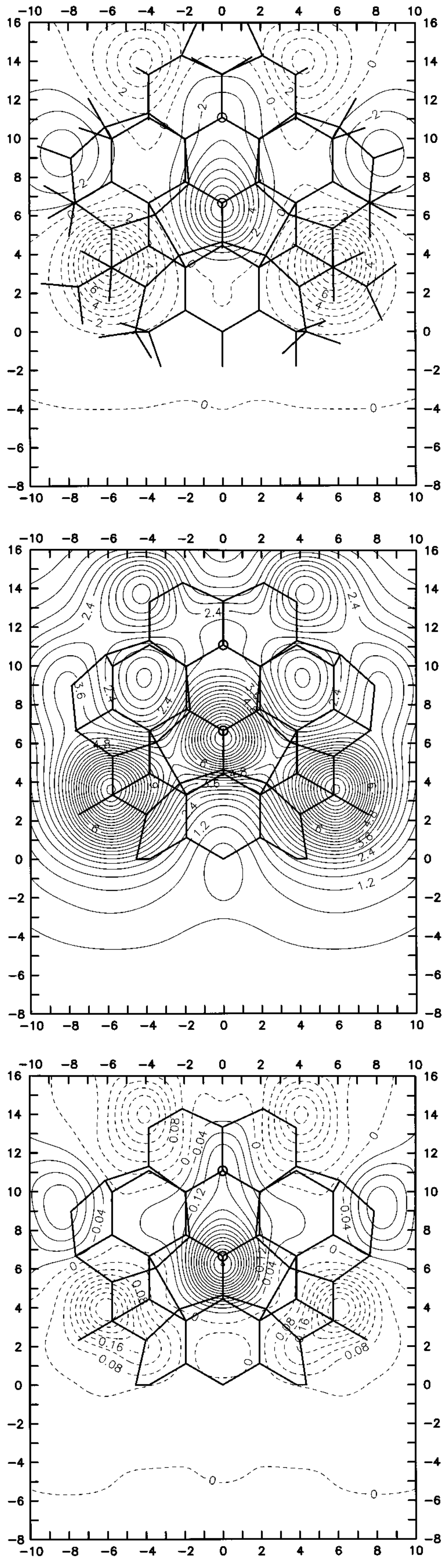

Figure 5. Comparison of reactivity maps for a fragment of the Si(111) surface containing a corner adatom in the faulted region (cf. Figure 2, upper left). (a, top) z component of the MEF (full lines: negative; dashed lines: positive, entries in V/nm), (b, middle) absolute value of the MEF (entries in V/nm), (c, bottom) BE (full lines: negative; dashed lines: positive, entries in V/nm) in a plane parallel to and at a distance of 300 pm from the surface. Adatoms and rest atoms are indicated by circles. Axis units (×100) are in picometers.

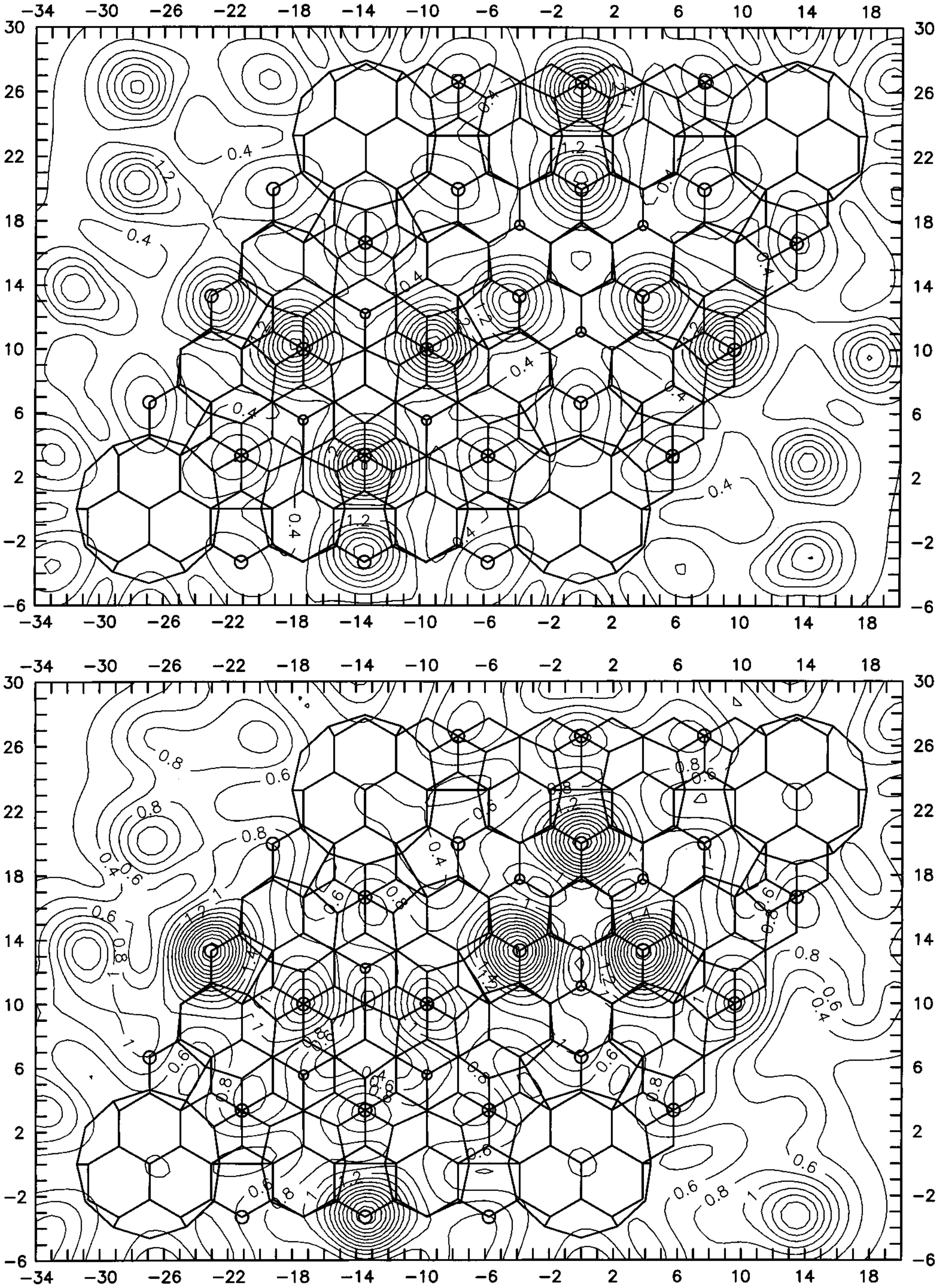

Figure 6. MEF map for the full unit cell of the Si(111) surface as obtained from the summation for the fragments of model B. (a) From semiempirical MNDO/AM1 molecular orbital calculations; (b) from atomic monopoles defined as atomic net charges obtained from the above calculation (entries in V/nm). Adatoms and rest atoms are indicated by circles. Axis units (×100) are in picometers. The small breaking of symmetry is due to interpolation errors; the grid points did not reflect the symmetry of the unit cell.

in agreement with experiments locating preferred adsorption sites for small dipolar molecules (ammonia[2] and water[3]) in these regions; however, finer details differ considerably. While in the MNDO/AM1 map smaller maxima are present near corner adatoms, too (cf. Figure 6a), these are absent from the monopole map in the faulted region (cf. Figure 6b). Furthermore, maxima of the MEF map, obtained by the semiempirical molecular orbital calculations, are higher in the unfaulted than in the faulted region, in contrast to the map calculated by the monopole approximation. Thus, we conclude that MEF maps for the Si(111) surface, as obtained from a monopole approximation, provide only a very rough approximation.

Let us see now, whether finer details of the energetics of surface−ligand interactions are reproduced by the MEF maps. Experimental studies for ammonia[2] indicate an order of adsorption ability as follows: rest atom > center adatom > corner adatom, faulted region > unfaulted region. This is only partly reflected by the MEF map obtained from model B and displayed in Figure 6. Rest atoms lie under the surface determined by adatoms, thus the MEF displayed in a single plane does not allow comparison between rest atoms and adatoms. Thus, we calculated the MEF values at various distances from these atoms in a direction perpendicular to the Si(111) surface (Table 2). As we see, at distances larger than 300 pm the relative magnitude of the calculated electrostatic field correctly reflects the experimentally found adsorption ability in all but one case. Clearly, at smaller distances nonelectrostatic effects play a crucial role, this is why the MEF fails here to predict adsorption energetics.

As a further step, we examined whether more refined calculations reproduce the same trend for adsorption preference. First we allowed to relax atoms of the system composed of one

TABLE 3: Binding Energies of an Ammonia Molecule Lying 300 pm above the Si(111) Surface in a Configuration $\alpha = 60°$, $\beta = 0°$, As Defined in Figure 4 (Unrelaxed) and after Geometry Optimization (Relaxed) As Obtained by Semiempirical MNDO/AM1 and ab Initio Molecular Orbital Calculations (Entries in kJ/mol)[a]

atom type	triangular subunit	AM1 (model A, unrelaxed)	AM1 (model A, relaxed)	ab initio (model C, unrelaxed)	ab initio (model C, AM1 relaxed)
rest atom	faulted	44.4	251.0	108.4	284.2
rest atom	unfaulted	65.6	354.6	n.c.	283.2
center adatom	faulted	61.3	306.7	95.5	181.3
center adatom	unfaulted	64.5	307.6	94.6	178.1
corner adatom	faulted	70.9	n.c.	91.7	179.9
corner adatom	unfaulted	60.5	n.c.	90.8	175.2

[a] n.c. denotes that the calculation did not converge.

of the fragments of model A and the approaching ammonia molecule by performing geometry optimization with the MNDO/AM1 method. We obtained an equilibrium Si−N distance of 180 pm close to the average Si−N bond length (174 pm) found in small molecules.[30] N−H bond lengths in the NH_3 molecule elongated to 101−102 pm, indicating that the reaction is dissociative. Binding energies, given in Table 3, indicate that the sites above adatoms are energetically preferred to those above rest atoms which is in contrast to experiments. Similar results were obtained also for the other models. It may be striking that the direct calculation of the binding energies by the semiempirical molecular orbital method yields wrong results in contrast to the electrostatic approach within the same model. This may be due to the approximations used in deriving the MNDO/AM1 energy formula,[22] while electrostatics is reflected well by the NDDO/AM1method.[31]

We also calculated binding energies of the ammonia molecule for fragments of model C by the ab initio method using a 3-21G basis set. The calculated interaction energies without and with geometry relaxation (optimizing the geometries with the AM1 method) are displayed in Table 3. The results both for the unrelaxed and relaxed models are in a perfect agreement with experiment: the order of binding energies is rest atom > corner adatom > center adatom, and they are larger for the faulted region than for the unfaulted one. In contrast to MNDO/AM1 results, the MEF, as obtained by the ab initio calculations with a 3-21G basis set, does not provide in all cases the correct reactivity order for ammonia (see Table 2). The MEF over center adatoms is smaller than over corner ones for all distances. However, all other adsorption preferences of NH_3 are correctly accounted for by the ab initio energetics. This partial failure may be due to the fact that for molecular electrostatic potentials the AM1 parametrization is a better approximation of the ab initio 6-31G** basis set results than the ones obtained by the smaller 3-21G basis set.[31]

Conclusions

Semiempirical MNDO/AM1 and ab initio 3-21G basis set molecular orbital calculations for various fragments of the unit cell of the Si(111) surface indicate that the molecular electrostatic field is a good descriptor of the adsorption ability of small dipolar ligands, like ammonia. While gross features of adsorption preference are reflected in the case of a variety of surface models, differing in size and geometric arrangement, we could reproduce finer details only with model C possessing the minimum number of silicon atoms around adsorption centers (adatoms and rest atoms). Adequacy of the MEF maps for determining preferred adsorption sites of the very large and complicated Si(111) unit cell allows us to hope that it will be useful for other surfaces, too.

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