A theoretical approach for modeling reactivity at solid–liquid interfaces

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We present a new general methodology capable of modeling chemical reactions at solid–liquid interfaces called CECILIA (combined embedded cluster at the interface with liquid approach). The main idea is to combine the embedded cluster molecular orbital or density functional methods for describing interactions at the surface of a solid with the dielectric continuum approach for modeling a liquid. More details are given on how to apply this methodology to model processes at the ionic solid–water interface. Geometries and adsorption binding energies of H_2O, NaCl, Na^+, and Cl^- at the NaCl(001)–water interface are calculated using this approach and compared with those at the NaCl(001)–vacuum interface. © *1997 American Institute of Physics.* [S0021-9606(97)50818-X]

I. INTRODUCTION

Molecular processes at the solid–liquid interface play important roles in environmental chemistry, biochemistry, electrochemistry, corrosion, and other fields. Understanding reaction mechanisms at such interfaces is important for industry and environmental protection.[1] For example, the interface between titanium dioxide (TiO_2) and water has shown very promising applications in the photochemical splitting of water and photocatalytic water purification.[2] Sodium chloride crystals apart from being a useful model system for theoretical developments, participate in atmospheric processes. Sea salt aerosoles react with various gases, such as NO_2, in the earth's troposphere.[3] As the aerosole surface is normally covered by several layers of water, these reactions occur at the solid–liquid interface.

Despite much experimental progress, very little is known for certain regarding the mechanisms of interfacial processes. One of the reasons is that many experimental surface sensitive techniques, such as thermodesorption, scanning tunneling, and photoelectron spectroscopies require low coverage, ultrahigh vacuum or high–low temperature conditions, thus may be not directly relevant to the solid–liquid interface situation in Nature. Theory can play a crucial role here. Classical molecular dynamics (MD) or Monte Carlo (MC) simulations can provide valuable information about solvent structure at interfaces.[4–7] However, these approaches depend on the accurate description of solvent–solid interactions by molecular mechanics (MM) force fields. Development of such force fields is a difficult and time-consuming task.[8] Furthermore, the MM methods are not particularly suitable for describing chemical reactions. Any theory for realistic modeling of chemical reactions at solid–liquid interfaces should provide an accurate description of bond-forming and bond-breaking processes and interactions of adsorption complexes and surface defects with the crystal lattice and solvent (water). This implies that *ab initio* molecular orbital or density functional (DFT) theory with appropriate treatment of elec-

tron correlation is required. Full *ab initio* quantum mechanical calculations of solid–liquid interfaces to date are limited to studies of monolayer or bilayer adsorption of water molecules using small surface unit cells.[9–11] Often these methods are not practical for modeling low-symmetry defect sites and exploring potential energy surfaces.

Embedded cluster models, well known in the quantum chemistry of condensed matter, seem to be the most suitable for such studies. In these models, the central part of the chemical system is treated by accurate *ab initio* or DFT methods and the rest is described by various classical approximations. These approximations can be divided into methods using either an atomistic or a continuum representation for the remainder of the chemical system. The atomistic approach may represent atoms as point charges, pseudopotentials, pseudoatoms, etc. A great deal of experience is accumulated in quantum chemical studies of point defects in the bulk and on the surface of crystals by using different atomistic embedding techniques (see, for example, books[12,13] and references therein). Practically the same method is known in solvation studies under the name QM/MM approach.[14] Atomistic methods are most important when the structure of the solvent is of interest. However, for comparison with many experiments only average properties of the solute are important. Thus, solvent structures should be averaged over a long period of time using MD or MC techniques. Such methods are still too expensive for use with nonempirical electronic structure theories for large realistic solutes. *Ab initio* calculations are usually performed by representing the solvent as a structureless polarizable medium. This is the central approximation in various dielectric continuum solvation models.[15]

Atomistic and continuum methods were found very useful in their areas of applicability, e.g., point defects in the bulk and on the surface of crystals and chemical processes in the bulk and on the surface of a liquid.[16–19] However, describing localized chemical processes at the solid–liquid interface requires a more elaborate theory because in addition to including an embedding potential from the rest of crystal and nearest solvation shells, one should also take into account self-consistently the long-range polarization of the solvent. To the best of our knowledge, no such method exists to
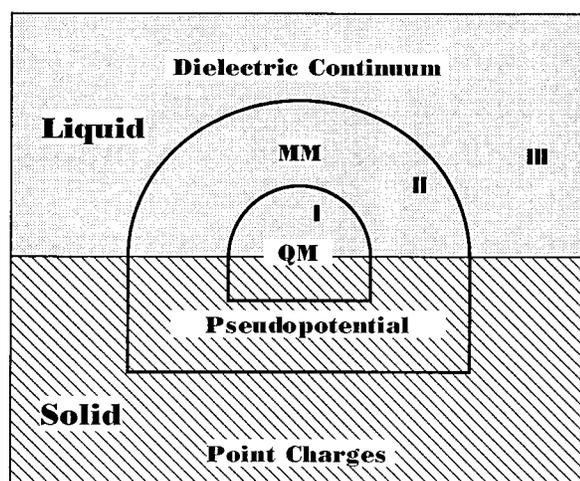
FIG. 1. The CECILIA model.

date. The main idea of the present work is to combine atomistic and continuum models into one computational approach capable of studying reactive processes at the solid–liquid interface. For brevity, we call this model CECILIA: Combined embedded cluster at the interface with liquid approach. We describe general features of the CECILIA model in Sec. II, and computational details in Sec. III. To illustrate the applicability of the CECILIA model, we studied adsorption of Na^+, Cl^-, NaCl, and H_2O at both the NaCl(100)–water and the NaCl(100)–vacuum interfaces, and our results are discussed in Sec. IV.

II. METHODOLOGY

In the CECILIA approach, the whole system ''surface defect+crystal+solvent'' is divided into three main regions as illustrated in Fig. 1.

I. The innermost QM (quantum mechanics) region, where chemistry occurs, is treated by accurate *ab initio* approaches such as HF, MP2, CIS, or DFT. Normally, the QM cluster may consist of several lattice atoms near the defect site, the adsorbate and a couple of water molecules making strong hydrogen bonds with the surface complex. The size of this region, level of theory, basis set, and use of effective core pseudopotentials are dictated by the specific problem and available computational resources.

II. The buffer or MM region normally includes several dozen atoms in the crystal lattice surrounding the QM cluster and several solvent molecules. This region is designed to describe short-range forces between nuclei and electrons in the QM cluster and surrounding medium. There are several methodologies with different levels of accuracy and complexity that can be used to represent the buffer region. The simplest way is to treat atoms in this region as point charges.[14,20] Such treatment is not accurate for ions close to the QM cluster, especially for cations, and cannot prevent unphysical delocalization of the cluster wave function due to neglect of Pauli repulsion effects. For highly ionic crystals this difficulty can be overcome by using effective core

pseudopotentials to describe interaction of ions in the buffer zone with cluster electrons.[21,22] For semiconductors and zeolites, one may use pseudoatoms to cap bonds at the boundary of the QM cluster.[20] Classical particles in the buffer zone can interact with each other and with cluster nuclei by means of force fields. For example, solvent water molecules can be approximated by the TIP3P potentials,[23] and interactions between lattice ions can be taken from pair potentials existing in the literature.[24,25]

III. The peripheral zone containing point charges and a dielectric continuum ensures correct Madelung and long-range solvent polarization potentials in the quantum cluster region. This is important for an accurate representation of the cluster electron density, correct positions of the crystal electronic band edges with respect to vacuum, and redox potentials of molecular solutes. As described below and in our previous study,[26] several hundred point charges are often sufficient to approximate the Madelung potential in the cluster with an accuracy of about 1%. A self-consistent treatment of the solvent polarization can be achieved by using dielectric continuum solvation methods.[15] In this study, we adopt the GCOSMO method documented in the literature.[27–29] In this approach, the crystal surface and adsorbate are surrounded by a boundary constructed as a set of interlocking spheres centered on nuclei and having fixed radii. This is shown schematically in Fig. 2. In contrast to homogeneous solvation studies, the surface of the dielectric cavity is not closed. Only the QM cluster and its nearest neighbors on the surface need to be solvated in order to obtain relative energies of surface configurations. As discussed below, our test studies show that extension of the cavity beyond these limits does not change the energetics and electronic structure of the QM cluster.

In the boundary element method, the cavity boundary is divided into M surface elements with areas $\{S_u\}$. The solvent polarization field is approximated by a set of M point charges $\{q_u\}$, located at the centers of surface elements, $\{t_u\}$. These charges are determined self-consistently with the electronic and atomic structure of the adsorption complex through the matrix equation

$$\mathbf{q} = -\frac{\epsilon - 1}{\epsilon} \mathbf{A}^{-1} \mathbf{f}, \tag{1}$$

where ϵ is the dielectric constant of the liquid, $\mathbf{A}$ is the $M \times M$ matrix with matrix elements[30]

$$A_{uv} = \frac{1}{|\mathbf{t}_u - \mathbf{t}_v|} \quad \text{for } u \neq v, \quad \text{and } A_{uu} = 1.07 \sqrt{\frac{4\pi}{S_u}}, \tag{2}$$

and vector $\mathbf{f}$ contains electrostatic potentials produced by the charge density of the crystal at points $\{\mathbf{t}_u\}$. This potential can be conveniently separated into contributions from classical particles (atomic nuclei, whole-ion pseudopotentials surrounding the cluster, and point charges representing the rest of the lattice) with charges z_i and positions $\mathbf{R}_i$ and from the electron density $\rho(\mathbf{r})$ in the QM cluster

$$f_u = f_u^{\text{class}} + f_u^{\text{el}} = \sum_i \frac{Z_i}{|\mathbf{t}_u - \mathbf{R}_i|} - \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{t}_u|} d^3 r, \tag{3}$$
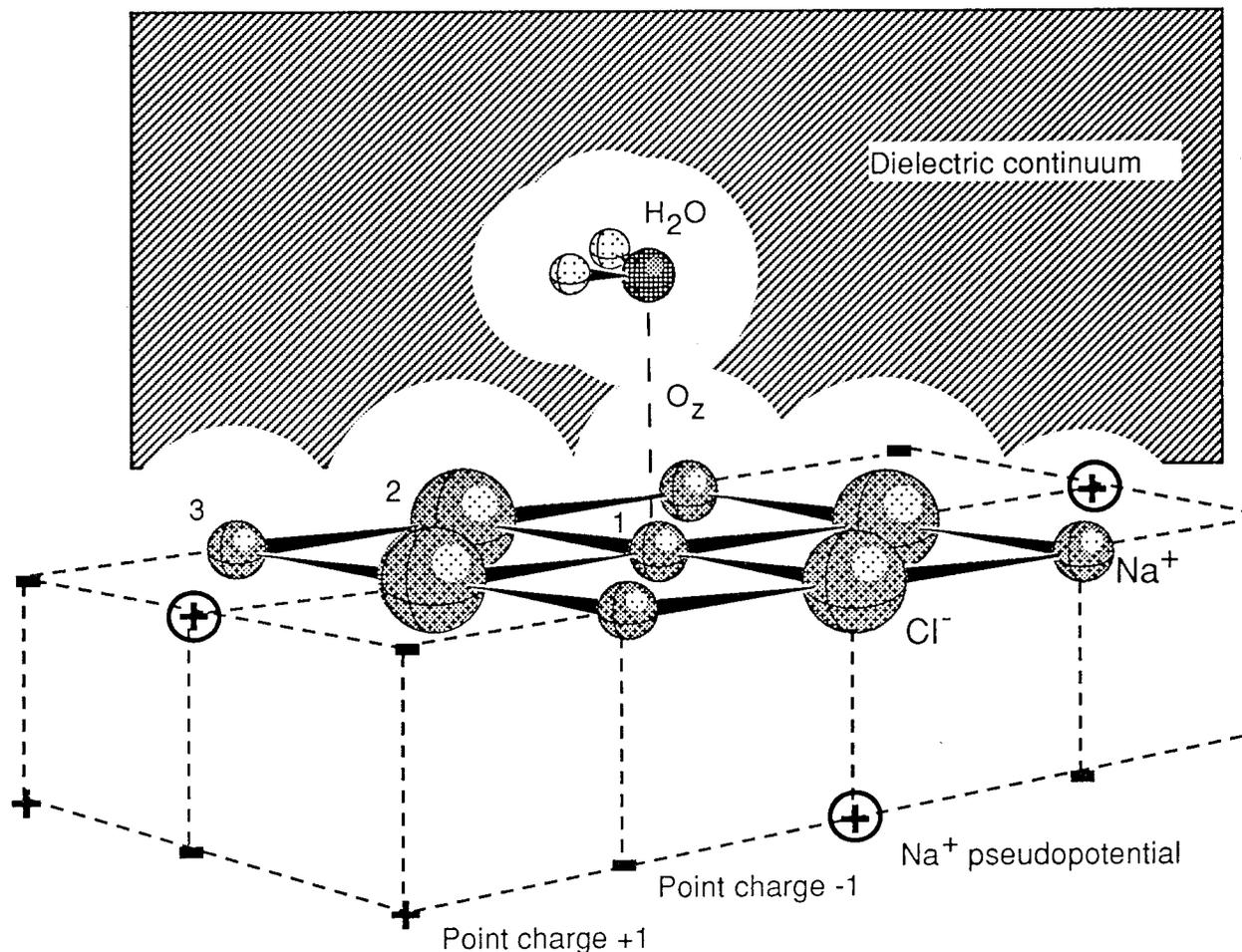
FIG. 2. Sketch of the CECILIA model used for studies of H_2O adsorption. The equilibrium geometry for the H_2O molecule at the NaCl(001)–water interface is shown.

Note that in the traditional GCOSMO approach the first sum in Eq. (3) runs only over atomic nuclei of the solvated molecule. Correspondingly, surface charges in Eq. (1) can be separated into ''classical'' $\mathbf{q}^{class}$ and ''electronic'' $\mathbf{q}^{el}$ components. The classical surface charges are taken into account by adding the term

$$H_{\mu\nu}^{s} = \mathbf{q}^{class}\mathbf{L}_{\mu\nu}, \tag{4}$$

to the one-electron part of the Fock matrix ($H_{\mu\nu}^{0}$). Here $\{L_{\mu\nu}^{u}\}$ are matrix elements of the potential generated by a unit point charge at the point $\{\mathbf{t}_u\}$. The contribution of electronic surface charges $\mathbf{q}^{el}$ to the two-electron part of the Fock matrix is given by

$$G_{\mu\nu}^{s} = \mathbf{q}^{el}\mathbf{L}_{\mu\nu}. \tag{5}$$

Then, the self-consistency between the electron density and solvent polarization field is achieved in a single SCF procedure by calculating $\mathbf{q}^{el}$ from Eqs. (1) and (3) at each iteration.

Finally, the total energy of the system in HF and DFT methods is expressed as

$$E_{tot} = \sum_{\mu\nu} [P_{\mu\nu}(H_{\mu\nu}^{0} + H_{\mu\nu}^{s} + V_{\mu\nu}) + \tfrac{1}{2}P_{\mu\nu}(G_{\mu\nu}^{0} + G_{\mu\nu}^{s})]$$
$$+ \tfrac{1}{2}\mathbf{q}^{class}\mathbf{f}^{class} + E_{nn} + E_{nonels}, \tag{6}$$

where $P_{\mu\nu}$ is the converged density matrix of the QM cluster, $V_{\mu\nu}$ are matrix elements of the potential from the buffer and point charge zones. E_{nn} is the energy of interaction between classical particles, i.e., nuclei in the QM cluster and ions in the buffer and point charge zones. Apart from simple Coulomb interactions, this term may include short-range potentials taken from various force-fields. E_{nonels} contains nonelectrostatic dispersion–repulsion and cavity formation contributions to the solvation free energy. These terms are calculated using methods described in Refs. 31 and 32 with the optimized solvent water radius of 1.29 Å.[28] We used the OPLS force field parameters[33] for calculating dispersion–repulsion interactions in this work. For fast geometry optimization of structures at solid–liquid interfaces we derived first derivatives of the total energy (6) with respect to the coordinates of atoms in the cluster and buffer zone.[29] The

CECILIA model described above was implemented in our local version of the GAUSSIAN92/DFT computer code.[34]

It is important to point out that the methodology of the CECILIA model is suitable for incorporation of various new theoretical developments. For example, to be consistent with the treatment of the solvent polarization, one needs (in particular for charged surface complexes) to take into account polarization of the semi-infinite substrate. This can be achieved by using an atomistic surface polarization approach.[35] A recently developed pseudopotential model of solvent water molecules[36] and embedded density functional theory (EDFT) cluster model[37] can further improve the accuracy of the embedding potential. For metals, one possibility is to use the embedded cluster molecular orbital approach proposed by Whitten and co-workers.[38] Applications of these theoretical developments are beyond the scope of the present study.

III. CALCULATION DETAILS FOR THE NaCl(001)–WATER INTERFACE

For the CECILIA model, the QM region consisted of a $[Na_5Cl_4]^+$ cluster containing nine atoms that form a 3×3 square on the NaCl(001) surface and the atoms of an adsorbate (see Fig. 2). The structure of the NaCl(001) surface was assumed fixed as bulk lattice termination. Geometries of all molecular species studied in this work (gas phase, liquid phase, adsorbed on the clean surface, and adsorbed at the interface) were fully optimized at the pseudopotential Hartree–Fock level. Na and Cl ions were described by Hay–Wadt effective core pseudopotentials (ECP) and standard valence double-zeta basis sets.[39] The oxygen atom was described by the SBK ECP and CEP-31+G* basis set.[40] The 311+G** basis set was used for hydrogens. Electron correlation was included at the MP2 level as single point calculations at HF optimized geometries. Dissociation and adsorption energies were calculated as total energy differences between the compound system and its separated fragments. For energy calculations of Na^+, Cl^-, and NaCl species, their basis sets were augmented by standard polarization and diffuse functions, and an additional diffuse function with the exponent of 0.015 was added to the basis set of chlorine.

The buffer region included Na^+ cations that are nearest neighbors to the QM cluster in the crystal lattice. They were represented by the Hay–Wadt ECP (a frozen $1s^2 2s^2 2p^6$ core) without basis functions attached. More distant Na^+ ions can be rather accurately represented as point charges ($q = +1$). Actually, when they were treated as pseudopotentials, cluster energies changed by less than 0.1 kcal/mol. We are not aware of any accurate whole-ion pseudopotential representation of lattice Cl^-. However, as indicated in Refs. 21 and 22, the ground-state electron density in the quantum cluster only slightly penetrates surrounding anions, therefore they can be described rather accurately in the point charge ($q = -1$) approximation. The point charge region of the crystal lattice was selected in such a way that the whole surface was represented by an $8 \times 8 \times 4$ block of the NaCl lattice (four layers deep). This size of the lattice was spe-
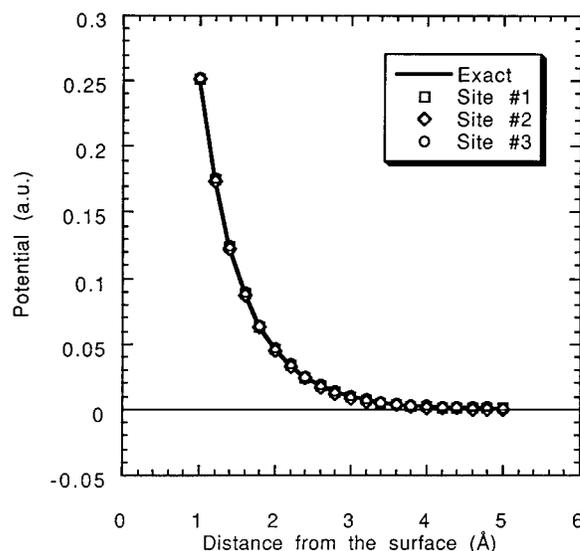

FIG. 3. Absolute values of the electrostatic potential above three sites (for numbering of sites, see Fig. 2) on the NaCl(001) surface modeled as an $8 \times 8 \times 4$ point charge lattice compared to the exact potential from the infinite lattice of point charges.

cially chosen to provide a rather accurate approximation of the Madelung potential inside the QM cluster and above the surface. Electrostatic potentials above three sites on the surface of the $8 \times 8 \times 4$ block are compared with the "exact" potential above the infinite lattice of point charges in Fig. 3. The latter values were calculated using the Ewald summation procedure. One can see that differences are almost negligible.

The dielectric cavity was constructed using the gepol93 algorithm[41] as a set of interlocking spheres centered on atoms. The cavity boundary adjusted automatically when atoms in the QM region moved during the geometry optimization. Each complete atomic sphere contained 60 surface charges. Atomic radii were taken from our previous work:[28] 1.172 Å for H, 1.576 Å for O, and 1.75 Å for Cl. For the Na^+ cation, an atomic radius of 1.61 Å was fitted to the experimental hydration energy of 98 kcal/mol. With these radii, the hydration free energy of the NaCl molecule is 46.1 kcal/mol as compared to the experimental value of 47.0 kcal/mol.[42] The cavity boundary was truncated so that only QM atoms and nearest neighbors to the QM region on the surface were solvated. The effect of such truncation was found to be very small. For example, when the boundary was truncated so that only QM atoms were solvated, the adsorption energies changed by less than 0.1 kcal/mol. The value of 78.3 was used for the dielectric constant of water. This value for bulk water may not be accurate for the interfacial region due to the specific ordering of water layers near the surface of polar crystals.[7] The effect of such ordering on dielectric properties of water is not well understood yet. In principle, this difficulty may be alleviated in the CECILIA approach by including explicit first-solvation-shell water molecules in the QM or buffer zones. However, statistical average over configurations of these solvent molecules is required in this case.

TABLE I. Structure (distances in Å, angles in degrees) of adsorbates at the NaCl(001)–water interface and on the clean NaCl(001) surface.

Parameter[a]	Aqueous interface	Clean surface
Water adsorption		
O–H	0.952 (0.951[b])	0.949 (0.947[c])
H–O–H	104.5 (104.6[b])	98.3 (105.8[c])
O_z	2.60	2.40 (2.14[d])
$O_x = O_y$	0.06	0.41 (0.55[d])
tilt angle[e]	11.9	0.3 (1.0[d])
Na^+ adsorption		
$Na^+ z$	2.84	2.77
Cl^- adsorption		
$Cl^- z$	3.08	2.92
NaCl adsorption		
$Na^+ x$	2.71	2.41
$Na^+ z$	2.85	2.74
$Cl^- x$	0.03	−0.01
$Cl^- z$	3.57	3.12

[a]The origin is placed on the central Na^+ ion (see Fig. 2), x and y axes are directed toward nearest Cl^- ions, z axis is perpendicular to the surface plane.
[b]Calculated for hydrated molecule.
[c]Calculated for free molecule.
[d]From pair potential calculations in Ref. 5.
[e]The angle between the bisector of H_2O and the (001) surface plane.

IV. RESULTS AND DISCUSSION

Table I shows geometry data for four studied adsorbates at both NaCl–water and NaCl–vacuum interfaces. In Table II we present adsorption energies calculated at the HF and MP2 levels. The electron correlation effects generally increase adsorption energy by 1–3 kcal/mol. In the last column of Table II, the nonelectrostatic solvation effects were added to the MP2 adsorption energy. These effects result from competition of two main contributions. Since a molecule adsorbed at the interface is less solvated than in bulk water, the dispersion attraction to the solvent decreases. On the other hand, the cavity formation term also decreases. In all studied cases the latter term prevails to the favor of stronger adsorption at the interface. In Table III we list bond distances and dissociation energies (including nonelectrostatic solvation effects) for the NaCl molecule in different environments.

A. Adsorption at the clean NaCl(001) surface

The equilibrium structure for H_2O adsorption at the NaCl(001)–vacuum interface (see Fig. 2) is qualitatively

TABLE II. Adsorption energies (kcal/mol) at the clean NaCl(001) surface and NaCl(001)–water interface.

	Adsorption energy (kcal/mol)				
	NaCl(001) surface		NaCl(001)–water interface		
Species	HF	MP2	HF	MP2	MP2 + Enonels
Na^+	12.3	14.7	2.2	3.4	3.6
Cl^-	1.5	3.0	−1.2	0.7	1.0
NaCl	9.3	12.5	2.0	4.6	4.7
H_2O	6.7	8.1	1.0	2.9	5.5

TABLE III. Na–Cl equilibrium distances and dissociation energies $(NaCl \rightarrow Na^+ + Cl^-)$ in different environments.

	Na–Cl distance (Å)	Dissociation energy (kcal/mol)		
Medium	HF	HF	MP2	Expt.[a]
Gas phase	2.43	126.4	128.6	130.1
NaCl(001) surface	2.45	122.0	123.5	n/a
Aqueous solution	2.75	3.0	4.8	0.0
NaCl(001)/water	2.78	3.5	4.9	n/a

[a]$\Delta \Delta H^f$ (298.15 K) from Ref. 42.

similar to that obtained in *ab initio* periodic calculations of H_2O–MgO(001) adsorption.[7–9] The water oxygen atom binds to the surface Na^+ ion. Water hydrogen atoms are attracted to Cl^- ions so that the molecular plane is almost parallel to the surface. To facilitate this interaction, the O atom shifts by 0.58 Å in the $\langle 110 \rangle$ direction, and HOH angle decreases by 7.5°. Earlier experimental measurements[43] yielded the value of about 10.5 kcal/mol for isosteric heat of the H_2O–NaCl(001) adsorption at zero coverage. More recent results indicate that this value is about 15.1 kcal/mol.[5] Assuming that water molecules on the surface are immobile, the zero temperature potential energy of adsorption should be about 2 kcal/mol lower than the isosteric heat of adsorption,[43] that is 8.5–13.1 kcal/mol. Due to the presence of surface defects, these experimental values may overestimate the actual interaction energy of a single water molecule with the flat NaCl(001) surface.[5] Thus our calculated value of 8.1 kcal/mol (see Table II) is in a reasonable agreement with experimental data.

The dissociation reaction $NaCl \rightarrow Na^+ + Cl^-$ is highly unfavorable in the gas phase with a calculated D_e of 128.6 kcal/mol (see Table III). The dissociation energy is still quite large for NaCl adsorbed on the clean NaCl surface, even though dissociation products Na^+ and Cl^- lower their energy due to adsorption. The energy required to desorb molecular NaCl from an NaCl(001) surface is 12.5 kcal/mol in our calculations. This is much larger than the value of 1.5 kcal/mol obtained in simple classical pair potential calculations.[44]

B. Adsorption at the NaCl(001)/water interface

Interesting conclusions can be drawn from comparison of adsorptions at the clean NaCl surface and its interface with water. The screening effect of the solvent reduces attraction of the H_2O molecule to surface ions (see Table I). The distance of the oxygen atom from the surface increases by 0.2 Å. H atoms no longer feel a strong attraction to Cl^- lattice anions, therefore, the tilt angle between the molecular axis and surface plane increases from 0.3° to 11.9°, the lateral shift of the molecule along $\langle 110 \rangle$ axis decreases from 0.58 to 0.08 Å, and the HOH angle increases to the value of 104.5 characteristic for the hydrated water molecule. In general, the internal structure of the H_2O molecule adsorbed at the interface is much closer to the geometry of hydrated H_2O than to the geometry of water adsorbed at the clean NaCl(001) surface. In agreement with these results, dielectric

screening by the solvent reduces the interaction energy between H_2O and the solid surface by about 2.6 kcal/mol (see Table II). However, there is still a noticeable attraction (5.5 kcal/mol) which immobilizes the H_2O molecule near the NaCl surface in agreement with previous molecular dynamics simulations[4,6] and a helium atom scattering study.[5] About half of this adsorption energy (2.6 kcal/mol) is due to non-electrostatic solvation effects.

Similar effects can be seen from calculations of Na^+, Cl^-, and NaCl adsorption at the interface. Adsorption distances increase and adsorption energies decrease with respect to those on the free NaCl(001) surface (see Tables I and II). Nonelectrostatic solvation effects facilitate adsorption at the interface, however much less than in the case of H_2O. As seen from data in Table III, the presence of the aqueous solvent leads to Na–Cl bond elongation by about 0.32–0.33 Å. On the other hand, when a free or solvated molecule binds to the NaCl(001) surface the Na–Cl bond distance increases by only 0.02–0.03 Å.

As expected, the polar solvent facilitates dissociation of NaCl into the ion pair (see Table III). Our calculations yield a dissociation energy of NaCl in water that is too large, mainly due to an underestimation of Cl^- hydration energy (72.0 kcal/mol instead of the experimental value of 76 kcal/mol). The agreement can be easily improved by adjusting the radius of the Cl^- solvation sphere. However even uncorrected results show a clear qualitative tendency. The NaCl dissociation energy at the NaCl(001)–water interface is almost the same as in bulk water, while the dissociation energy on the clean NaCl surface is close to that for the free molecule. This indicates that the aqueous solvent has much stronger influence on the geometry and energetics of the NaCl molecule than the NaCl substrate.

V. CONCLUSION

We presented a general methodology for *ab initio* electronic structure calculations of reactivity at the solid–liquid interface (CECILIA model). Initial applications of this model to adsorptions at the NaCl(001)–water interface were carried out. These results indicate that the presence of water significantly changes the geometries and energetics of adsorbed species. In fact, NaCl and H_2O molecules adsorbed at the interface are more similar to hydrated molecules slightly perturbed by the presence of the substrate than to molecules adsorbed on the surface and perturbed by the aqueous solvent. As results, the crystal growth, sublimation–dissolution mechanisms, and chemical reactivity at solid–vacuum and solid–liquid interfaces may be completely different.

ACKNOWLEDGMENTS

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