Molecular-orbital study of Li and LiOH adsorption on a Cu(001) surface. II. Cluster-model calculations with image charges

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Hartree-Fock and configuration-interaction calculations were performed for Cu_4Li and Cu_4LiOH, as models of Li/Cu(001) and LiOH/Cu(001), respectively. To take into account the dielectric-response effect of the metal surface to external point charges, we used cluster models with image charges. For Cu_4Li, the calculated vibrational frequency was almost the same as that given by a cluster model without image charges, and both values agreed well with the experimental value. Image charges improved the Li-OH vibrational frequency for Cu_4LiOH. On the other hand, simple cluster calculations without image charges gave poor results for work-function changes upon Li and LiOH adsorption; however, by considering image charges, we obtained excellent results, were comparable to the observed values. [S0163-1829(97)01208-3]

I. INTRODUCTION

Since Langmuir's experiment[1] for alkali-metal adsorption on a metal surface in the 1920s, many experimental and theoretical studies of adsorption have been performed. Alkali-metal adsorption is particularly important because of its practical use in relation to heterogeneous catalysis and fundamental interest as a simple-adsorption system. An early treatment of quantum mechanics was given by Gurney[2] in 1935. In the latter half of the 1960s, the dielectric response of a metal surface to an external point charge was investigated by Newns[3,4] using the linear Fermi-Thomas approximation and by Lang and Kohn[5] using the local-density functional theory with a jellium surface. In the 1970s, Newns and co-workers used the Anderson model[6] to investigate the mechanism of chemisorption[7] and to perform qualitative analyses of the change in work function versus the coverage of the alkali-metal adatom.[8–11] Lang and Williams[12] performed first-principles calculations within the local-density functional theory by replacing the substrate with a jellium to describe chemical adsorption.

In the 1980s, with the rapid development of computer hardware and software, first-principles calculations could be applied to large systems. Tatewaki and co-workers[13,14] performed molecular-orbital calculations for Cu_nNa clusters ($n=1\sim4$) to examine the electronic structure of Na adsorption on the Cu surface. They were the first to show the essential features of alkali-metal atom adsorption on a metal surface from the perspective of molecular-orbital calculations. The ground state of the system is a charge-transfer state, where there is also a large amount of back donation. Ishida[15–18] studied the electronic structures of alkali-metal adlayers on metal surfaces in a variety of coverages by the local-density-functional theory using a jellium surface. He successfully explained the characteristic dependence of the work function and dipole moment on adatom coverage and claimed that the alkali-metal bond is covalent at all coverages.

In the 1990s, Pacchioni and Bagus[19,20] performed Hartree-Fock (HF) calculations on Cu_5K and $Cu_{25}K$ clusters to clarify the bonding nature of alkali-surface bonds at a low coverage limit and concluded that at a low coverage limit the K-surface bond is predominantly ionic. We[21] recently performed HF and configuration-interaction (CI) calculations on Cu_4Li, $Cu_{13}Li$, and Cu_4LiOH clusters to investigate the mechanism of Li adsorption and linear LiOH formation on Cu(001) using the model potential method.[22–24] That study was inspired by a series of works on Li/Cu(001) performed by Tochihara and co-workers.[25–33] The charge-transfer-type ^2E state was the ground state for Cu_4Li. The calculated Li-surface distance of 2.01 Å and vibrational frequency of 309 cm^{-1} agreed well with the experimental values. The results for $Cu_{13}Li$ were similar to those for Cu_4Li. Cu_4LiOH showed a stable state in which a linear LiOH is weakly bound to Cu_4. The calculations supported the experimental finding of Tochihara and co-workers that a linear LiOH is formed on the surface when H_2O interacts with the Li adatom on Cu(001) at low coverage.[25] However, the calculated Li-O vibrational frequency of 895 cm^{-1} did not agree with the observed strong peak (600 cm^{-1}) assigned to Li-OH.

The dielectric response of a semi-infinite metal surface to external fields is generally ignored in cluster model calculations. In this paper, to obtain a better Li-O vibrational frequency, we try to better describe the substrate by taking into account the dielectric response in cluster model calculations. In this regard, Nakatsuji and co-workers[34,35] have proposed a dipped adcluster model for chemisorption on a metal surface, where the adcluster (admolecule+cluster) is dipped toward the electron bath of a solid metal and electrons are transferred between them until the chemical potential of the adcluster is equal to that of the solid metal. In this study, we used classical image theory in cluster model calculations to account for the effect of the dielectric response of the metal surface.

Our justification for using classical image theory in

quantum-mechanical cluster calculations, and the computational details, are explained in Sec. II. In Sec. III, we summarize the calculated results, including the vibrational frequencies and equilibrium distances. Cluster calculations with image charges were also used to calculate the work-function changes upon Li adsorption and LiOH formation on Cu(001), and the results are discussed in Sec. IV. Concluding remarks are given in Sec. V.

II. COMPUTATIONAL DETAILS

It has been well established that cluster-model calculations using molecular-orbital theory are useful because they can take into account chemical bonding effects and final-state relaxation effects. However, it is difficult to consider the effects of the dielectric response of semi-infinite metal surfaces to external fields in these calculations because of the finite size of the clusters. Thus, cluster-model calculations may not be suitable for describing the adsorption of charged particles to metal surfaces, where the effects of the dielectric response play an important role. The adsorption of the LiOH molecule, which includes a ionic bond between Li^+ and OH^-, to a Cu(001) surface is such a system. Therefore, it is desirable to take into account the effects of the dielectric response in cluster calculations to treat the adsorption of LiOH on Cu(001).

The dielectric response of semi-infinite metal surface to an external field has received considerable attention.[3–5,36,37] In alkali-metal adsorption systems, a theoretical study using image charges to consider the dielectric response of a metal surface was presented by Gadzuk, Hartman, and Rhodin.[38] The dielectric response effects can be represented by images charges on the condition that the charge distribution of the metal surface changes instantly following changes in the adsorbate charge distribution. The change in the surface charge distribution is delayed by the inverse of the surface plasmon frequency ($1/\omega_s$). Thus, the condition can be expressed as

$$\tau > 1/\omega_s, \tag{1}$$

where τ is the time scale in which the charge distribution of the adsorbate changes. Remy[39] studied Li atom adsorption on metal surfaces by using a perturbation theory and showed that the time scale is longer than 10^{-15} sec. Since the plasmon frequency of the Cu(001) surface was estimated to be 3.3×10^{16} sec^{-1},[40,41] condition (1) is satisfied for Li adsorption on a Cu(001) surface. Thus, we used image charges in cluster-model calculations to represent the dielectric response of the metal surface.

Newns[3] examined the dielectric response of a semi-infinite metal to a point charge q by using the linear Fermi-Thomas approximation and found that the Fermi-Thomas solution for the energy of the point charge agrees well with the approximate expression $-q^2/4(z + \lambda^{-1})$ given by Gomer and Swanson,[42] where z is the distance from the surface to the charge q and λ^{-1} is the Fermi-Thomas screening length. This indicated that the classical image theorem is valid if the effective surface is recessed by λ^{-1}. For a Cu surface λ^{-1} is 1.04 a.u. (0.55 Å) and the linear Fermi-Thomas approximation is valid if the following condition is satisfied:[43]

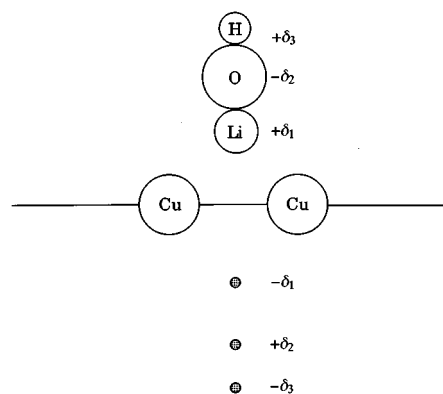$$z \gg 2.2 \text{ a.u.} \quad (1.2 \text{ Å}), \tag{2}$$

FIG. 1. A view of the cluster model with image charges for Cu_4LiOH.

where the classical image potential $-q^2/4z$ is a good approximation of the Fermi-Thomas energy. Moreover, relation (2) is satisfied for Li adsorption on a Cu(001) surface.

Thus, to take into account the effect of the dielectric response of the Cu surface we used the classical image theory in cluster calculations. It is to be noted that image charges should not interact with real charges inside the bulk. However, since there are only surface atoms in the present cluster models, Cu_4Li and Cu_4LiOH, which are the same as in our previous paper,[21] image charges interact with all real charges in the present model clusters. In this connection, it is important to note that the above relation (2) is satisfied in the present calculations. Of course, we ignored interactions between the image charges. Image charges were determined self-consistently to be the inverse of the sign of the calculated gross charges of adsorbate atoms given by the Mulliken population analysis. It is well known that the Mulliken population analysis often gives nonphysical charges as the size of a basis set is increased. Therefore, it is desirable to use the method which is basis-set independent to determine image charges. A method proposed by Huzinaga et al.[44] can be one of such a method. However, we used here the Mulliken population analysis because Mulliken charges were reasonable values in the present calculations. A cluster model with image charges for Cu_4LiOH is schematically shown in Fig. 1.

We performed HF and CI calculations for clusters with and without image charges by using a model potential (sp-MP) for Cu,[23] where $3d$ and $4s$ electrons were treated explicitly and the other electrons were replaced by a model potential. The basis sets for Li, O, and H were taken from Huzinaga's works.[45,46] The contraction schemes of Gaussian-type functions (GTFs) for basis sets were as follows: Cu, (41/1*/41); Li, (421/1*1*); O, (421/311*); and H, (41), where 1* denotes an additional GTF.

All single and double excitations from the HF configuration were considered by maintaining that the Cu $3d$, Li $1s$, and O $1s$ and $2s$ orbitals were always doubly occupied in CI calculations, which were referred to as CI1. We also performed more advanced CI calculations (C12) in which the excitations from the Cu $3d$ orbitals were considered. The HF and CI calculations were performed using the JAMOL4,[47] MICA3,[48] and ALCHEMY2 (Ref. 49) software packages.

TABLE I. Surface Li distances (d_e's) and stretching frequencies (ω_e's) for the Cu$_4$Li cluster with and without image changes (IC).

Method	HF	CI1	CI2
	ω_e (cm^{-1})		
NCT ($^4A_2$) without IC[a]	171 (168)	205 (209)	
NCT ($^4A_2$) with IC	171	203	
CT (^2E) without IC[a]	312 (312)	309 (305)	
CT (^2E) with IC	330	321	316
	d_e (Å)		
NCT ($^4A_2$) without IC[a]	2.61 (2.54)	2.47 (2.44)	
NCT ($^4A_2$) with IC	2.61	2.47	
CT (^2E) without IC[a]	1.98 (1.99)	2.02 (2.01)	
CT (^2E) with IC	1.84	1.86	1.68

[a]Values in parentheses have been previously reported (Ref. 21).

III. VIBRATIONAL FREQUENCIES

A. Cu$_4$Li

The HF and both CI calculations were performed for the $^4A_2$ and ^2E states of the Cu$_4$Li cluster with and without an image charge: $^4A_2$, (42 electrons) $5a_1^2 6a_1^1 6e^2$; ^2E, (42 electrons) $5a_1^2 6e^3$. $^4A_2$ is a non-charge-transfer (NCT) state, in which the $6a_1$ orbital consists mainly of the Li 2s orbital, while the $5a_1$ and $6e$ orbitals consist of Cu 4s orbitals. ^2E is a charge-transfer (CT) state, in which the 2s electrons of Li transfer to the half-occupied e_u orbitals of Cu$_4$. The calculated results for equilibrium surface Li distances, d_e's, and vibrational frequencies of Li normal to the surface, ω_e's, are listed in Table I. The image charge determined self-consistently was nearly zero and -0.4 for the NCT and CT states, respectively. For the NCT state, the image charge did not change d_e or ω_e, while slight changes were seen for the CT state. The d_e of the CT state given by cluster calculations was closer to the observed value of 1.96 ± 0.08 Å[30] than that given by calculations with the image charge. It should be noted that the observed value was at a coverage of 0.5, and the distance is expected to decrease at lower coverage. The cluster with the image charge in the present study is considered to be a model of a lower coverage (0.25) of Li adsorption. The image charge decreases the equilibrium surface-Li distance by 0.15 Å for the CT state. The calcu-

lated ω_e's (310~320 cm^{-1}) at the CI levels agree with the observed value of 316 cm^{-1} for Li/Cu(001) at low coverage.[50] This observation implies that Li adsorption on a metal surface can be adequately described even by a simple cluster model calculation that includes a substrate composed of several atoms.

Contour maps of the electron-density difference for the CT state given by CI2 calculations with and without image charges are depicted in Figs. 2(a) and 2(b), respectively. The plane depicted is normal to the surface and contains a Li and two Cu's. The density difference was obtained by subtracting the densities of noninteracting component systems, $\rho(\text{Cu}_4) + \rho(\text{Li})$, from the density of the cluster, $\rho(\text{Cu}_4\text{Li})$, while retaining the positions of the component systems at the same location as Cu$_4$Li. The solid and broken lines denote an increase and decrease, respectively, in electron density upon Li adsorption onto the surface. Figure 2(a) is almost identical to Fig. 2(b), which also supports the observation mentioned above that simple cluster model calculations work well for these systems. One small difference between the figures is that a high density of electrons is observed between Li and the surface in Fig. 2(a). Thus, the dielectric response effect makes the surface Li bond stronger. The stabilization energy due to this effect was calculated to be 0.16 eV in the CI1 calculation.

B. Cu$_4$LiOH

In our previous study,[21] Cu$_4$LiOH showed a stable state in which a linear LiOH is weakly bound to Cu$_4$. These calculations supported the experimental finding by Tochihara and co-workers that a linear LiOH is formed on the surface when H$_2$O interacts with the Li adatom on Cu(001) at low coverage.[25] However, the calculated Li-O vibrational frequency of 895 cm^{-1} was quite different than the observed strong peak (600 cm^{-1}) assigned to Li-OH stretching. To eliminate this discrepancy, we performed a preliminary calculation using a larger cluster, Cu$_{13}$LiOH, to represent the substrate. These calculations were not successful, and the discrepancy actually increased, contrary to our expectation. We considered that this failure was due to the positive charge of the central Cu atom in Cu$_{13}$, which is close to the image position of a positively charged Li atom. In classical image
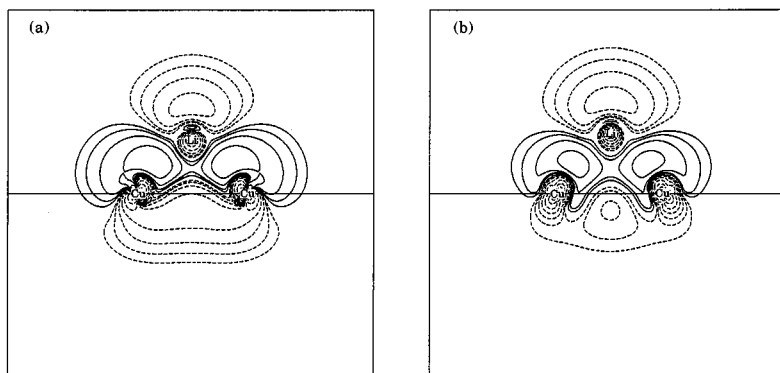

FIG. 2. Contour map of the electron-density difference, $\rho(\text{Cu}_4\text{Li}) - \rho(\text{Cu}_4) - \rho(\text{Li})$, for the CT ($^2E$) state (a) with and (b) without image charges. Solid and broken lines denote positive and negative contours, respectively. Values of the contour lines are ± 0.04, ± 0.02, ± 0.01, ± 0.005, ± 0.0025, $\pm 0.001\,25$, $0.000\,625$, and $\pm 0.000\,313$, respectively.

TABLE II. Equilibrium bond distances (d_e's) and stretching frequencies (ω_e's) for the Cu$_4$LiOH cluster with and without image charges (IC).

Method	Cu-Li	Li-O	O-H
	ω_e (cm^{-1})		
HF without IC	78	912	4057
HF with IC	116	792	4056
CI1 without IC[a]	85	895	3702
CI2 without IC	113	937	3850
CI2 with IC	107	796	3849
Experiment	<200	600	3600
	d_e (Å)		
HF without IC	2.63	1.63	0.968
HF with IC	2.01	1.70	0.954
CI1 without IC[a]	2.55	1.65	0.995
CI2 without IC	2.23	1.63	0.969
CI2 with IC	1.70	1.69	0.968

[a]Ref. 21.

theory, this position should be occupied by a negative image charge. Thus, we used Cu$_4$ clusters with classical image charges for the adsorbate in place of a semi-infinite metal surface. The calculated equilibrium bond distances and vibrational frequencies for the ground state of Cu$_4$LiOH with and without image charges are summarized in Table II. The vibrational frequencies were obtained by a normal mode analysis normal to the surface for the Cu$_4$-Li-O-H system by assuming that Cu$_4$ has an infinite mass. Contour maps of the electron-density difference, $\rho(\text{Cu}_4\text{LiOH}) - \rho(\text{Cu}_4) - \rho(\text{LiOH})$, for the ground state of clusters with and without image charges are shown in Figs. 3(a) and 3(b), respectively. The plane depicted is normal to the surface and contains an LiOH molecule and two Cu's.

The equilibrium surface-Li distance calculated with image charges is 0.5~0.6 Å shorter than without image charges, indicating that the dielectric response of the metal surface strengthens the bond between LiOH and the metal surface. This is also seen in Figs. 3(a) and 3(b); the charge density between Li and the metal increases when image charges are considered. This is the result of a polarization effect at the surface due to image charges. The stretching frequency of

Cu-Li calculated at CI2 with image charges is 107 cm^{-1}, which is almost the same as that without image charges. On the other hand, the frequency of the Li-O stretching mode decreases by more than 100 cm^{-1}. The discrepancy observed in the previous study has been reduced, but the difference between the calculated and experimental values is still about 200 cm^{-1}, which may reflect a limitation of the present method. The frequency of the O-H stretching mode and the equilibrium O-H bond distance are scarcely affected by considering image charges.

IV. WORK-FUNCTION CHANGES

Mizuno et al.[25] measured work-function changes (WFCs) with increasing H$_2$O exposure at a Li coverage of 0.25. The work-function reduction due to Li adsorption was 2.0 eV before H$_2$O exposure. This reduction decreased with increasing H$_2$O exposure and seemed to be saturated at 0.7 eV, which was attributed to the formation of LiOH on the Cu(001) surface.

In our cluster calculations, we calculated the work functions (WFs) of Cu(001), Li/Cu(001), and H$_2$O/Li/Cu(001) as the first ionization potentials (IPs) of Cu$_4$, Cu$_4$Li, and Cu$_4$LiOH, respectively. The calculations were performed for clusters with and without image charges in the HF and CI2 calculations. The results are listed in Table III together with the experimental values.

The calculated IPs of Cu$_4$ were greater than the WF of the Cu(001) surface by about 0.5 eV. This difference is due to the size of the cluster considered in this study. Tatewaki et al.[51] showed that larger Cu clusters have lower IPs. In HF calculations without image charges, the IPs of Cu$_4$Li and Cu$_4$LiOH were greater than the experimental values by about 2 eV. The calculated WFC (-0.90 eV) for Li adsorption was less than the observed changes by 1.6 eV, and the WFC for LiOH adsorption was qualitatively incorrect, indicating that simple cluster-model calculations are not suitable for describing work-function changes.

On the other hand, HF and CI2 calculations with image charges gave IPs about 2 eV lower than those without image charges, which are reasonably comparable to the experimental WFs. The calculated WFCs were -2.4 and -1.1 eV for
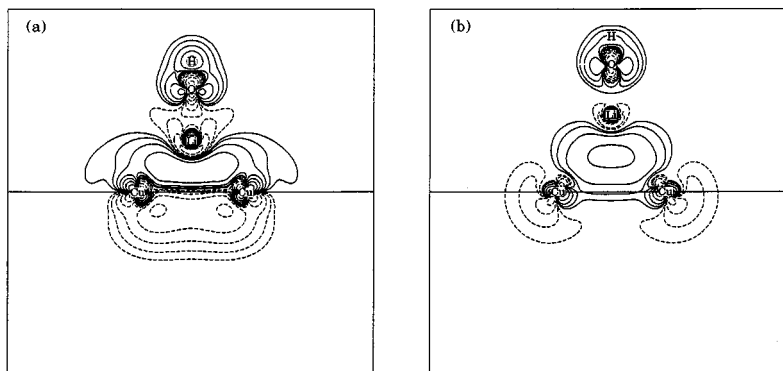

FIG. 3. Contour map of the electron-density difference, $\rho(\text{Cu}_4\text{LiOH}) - \rho(\text{Cu}_4) - \rho(\text{LiOH})$, for the ground state (a) with and (b) without image charges. Solid and broken lines denote positive and negative contours, respectively. Values of the contour lines are ± 0.04, ± 0.02, ± 0.01, ± 0.005, ± 0.0025, $\pm 0.001\,25$, $0.000\,625$, and $\pm 0.000\,313$, respectively.

TABLE III. Work functions (WF) and work-function changes (WFC) (eV).

Method (system)	WF	WFC
Experiment		
Cu(001)	4.6	0.0
Li/Cu(001)	2.1	−2.5
H_2O/Li/Cu(001)	3.9	−0.7
HF calculation without IC		
Cu_4	5.10	0.0
Cu_4Li	4.20	−0.90
Cu_4LiOH	5.83	+0.73
HF calculation with IC		
Cu_4	5.10	0.0
Cu_4Li	2.16	−2.94
Cu_4LiOH	3.73	−1.37
CI2 calculation with IC		
Cu_4	5.16	0.0
Cu_4Li	2.77	−2.39
Cu_4LiOH	4.07	−1.09

Cu_4Li and Cu_4LiOH at the CI2 level, which agreed well with the experimental values (−2.5 and −0.7 eV) for Li/Cu(001) and H_2O/Li/Cu(001). This observation indicates that cluster-model calculations with image charges properly describe the work-function changes upon the adsorption of such alkali-metal atoms and an ionic LiOH compound.

V. CONCLUDING REMARKS

To take into account the dielectric response effect of a metal surface to an external charge distribution, we performed Hartree-Fock and configuration-interaction calculations for the cluster models Cu_4Li and Cu_4LiOH with image charges, which were models of Li/Cu(001) and LiO/HCu(001), respectively.

For Cu_4Li, in which the bond between Li and the substrate is covalent and donation-backdonation plays an important role, the calculated vibrational frequency was almost the same as that given by a simple cluster model without image charges. Both of the calculated results agreed excellently with the observed value of 316 cm^{-1} for Li/Cu(001) at low coverage.[50] This observation implies that Li adsorption on a metal surface can be adequately described even by a simple cluster model calculation which includes a substrate composed of several atoms.

On the other hand, considering image charges improved the Li-OH vibrational frequency for Cu_4LiOH, in which ionic LiOH is weakly bound to the Cu substrate. The dielectric response of the metal surface also strengthens the bond between LiOH and the metal surface.

Simple cluster calculations without image charges gave poor results for work-function changes on Li and LiOH adsorption. However, by considering image charges, we obtained excellent results which were comparable to the observed values. Thus, cluster-model calculations that incorporate the classical image-charge theory can be a useful tool for estimating work-function changes in adsorption systems.

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