Cluster Study of the Interaction of a Water Molecule with an Aluminum Surface

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(Received 10 September 1984)

The Kohn-Sham scheme is used to calculate the interaction energy of an H_2O monomer with clusters simulating different adsorption sites on an Al(100) surface. A well-defined on-top ground state with the molecular plane tilted away from the normal is found. The adsorption is accompanied by a substantial donation of charge to the metal. The electron energy-loss spectrum is dominated by a frustrated rotation of the molecule.

PACS numbers: 68.30.+z, 82.20.Kh, 82.30.Fi

The behavior of water layers in intimate contact with metal surfaces has been the subject of many recent experimental studies.[1-16] These have demonstrated that H_2O monomers remain intact on most metal surfaces held at low temperatures but show a strong tendency to cluster and form hydrogen-bonded networks. Because of this tendency it is difficult to gain information concerning the interaction of a monomer with the bare surface. This interaction, of great importance in electrochemistry,[17] is sometimes thought of in terms of a competition between dipole-image attraction and Pauli repulsion,[18] which gives a binding energy in the millivolt range. In fact, the H_2O-surface interaction, like the bond between the molecule and a single metal atom,[19] involves a dominant chemical component and is sufficiently strong (a few tenths of an electronvolt) to compete on equal terms with hydrogen bonding between water molecules.

We have performed a detailed investigation of the bonding between an H_2O monomer and clusters which simulate the local environment of the Al(100) on-top, bridge, and hollow adsorption sites. In contrast to earlier cluster studies,[19-22] a full variation of the internal H_2O coordinates as well as the location and orientation of the molecule with respect to the surface has been carried out.[23] We use the Kohn-Sham scheme for energy calculation[24] with the local density approximation for exchange and correlation. The cluster method has been described[25] and further details will be published elsewhere.

Though absolute binding energies tended to be sensitive to cluster composition, particularly at bridge sites, the main features of the interaction were similar for all clusters. These features are as follows:

(i) Though dissociation to chemisorbed $O+H_2$ is thermodynamically favorable, spontaneous dissociation of a single monomer is a highly activated process. The same is true for Na clusters[26] and we expect the isolated monomer to be stable on all metal surfaces. The fact that dissociation is apparently spontaneous on many metals at room temperature probably indicates a complex reaction path involving more than one H_2O molecule.

(ii) On Al(100) there is a well-defined ground-state geometry (Fig. 1). The O atom lies 3.9 bohrs above an Al surface atom and the HOH plane is tilted about 55° from the normal to the surface. A substantial zero-point motion is associated with the tilt and rotation about the Al-O axis is practially unhindered. The binding energy is 0.53 eV and the tilt is stable by about 0.1 eV.

(iii) The variation of the energy as the molecule moves along the surface is not trivial. At bridge and hollow sites, the binding energy decreases to about 0.25 and 0.15 eV, respectively. Orientational energies are relatively weak at hollow sites but stronger at bridge sites, where the favored configuration has the protons directed upwards and the HOH plane perpendicular to the bridge direction. These variations may play an important role in determining the kinds of hydrogen-bonded networks that are energetically favorable.

(iv) In all cases investigated, the bonding is accompanied by a net donation of charge ($\simeq 0.1$ electron for the ground state) to unoccupied cluster lev-

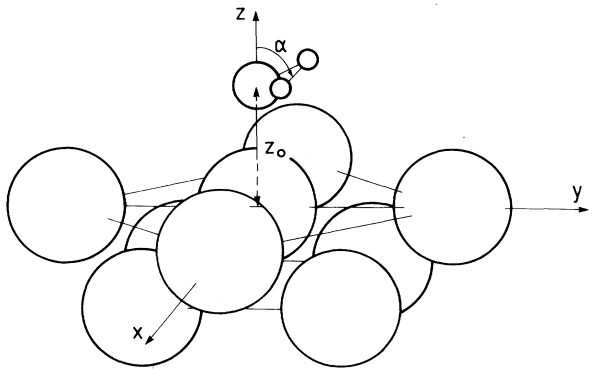

FIG. 1. Equilibrium geometry for an H_2O molecule on a nine-atom cluster simulating the local environment of an Al(100) on-top site.

els. This donation leads to a strong reduction of the work function even when the intrinsic dipole of H_2O is oriented parallel to the surface.

(v) Consistent with the charge donation, we find a slight expansion of the O-H bond length ($\simeq 0.03$ bohr) and the HOH bond angle ($\simeq 5°$ at equilibrium) and a marginal softening of the internal vibrations of the molecule. This is true even when the molecule bonds via the H atoms, i.e, observation of the HOH bend mode in electron energy-loss (EEL) spectroscopy does not necessarily imply an upright configuration of the molecule on the surface.

The behavior of the energy as a function of O-Al distance, z_0, and tilt angle, α, for the surface cluster of Fig. 1 is illustrated in Fig. 2. For fixed z_0, the energy as a function of α shows a broad, shallow well with a steep wall as the HOH plane crosses the horizontal. The z_0 variation is much less anharmonic and confines the coordinate to values around 3.9 bohrs. Over most of the α range the coupling between the two coordinates is very weak, i.e., the curve marked $E_B(\alpha=0°)$ in Fig. 2(b) moves more or less rigidly. Towards $\alpha=90°$ the minimum begins to shift outwards (for $\alpha=180°$ it is at 6 bohrs) and the curvature at minimum diminishes. Variation with respect to the azimuth, ϕ, about the O-Al axis is extremely weak and can be neglected. Under these conditions we can write approximate wave functions for low-lying vibrational states in the form

$$\psi_{vlm}(z_0,\alpha,\phi)=\mu_v(z_0)\chi_{lm}(\alpha)e^{im\phi},$$

where $\mu_v(z_0)$ is a solution of the Schrödinger equation for the potential $V(z_0)=E_b(z_0,\alpha=60°)$ and $\chi_{lm}(\alpha)$ the wave function of a rigid rotator in the potential $V(\alpha)=E_B(z_0=3.9,\alpha)$, shown in Fig. 2(a). The two low-lying states of interest, χ_{00} and χ_{10}, are shown in the figure to illustrate the large zero-point motion in the ground state and that the excited state is practically delocalized over a half space. Excited states corresponding to the normal frustrated translation ($v=1$, $l=0$, $m=0$) and to the wag of the HOH plane ($v=0$, $l=1$, $m=0$) are found to have energies of 36 and 51 meV, respectively. Coupling between the two coordinates has been estimated to give perturbations of the order of 1 meV.

The origin of the H_2O-surface bond can be understood in terms of a simple model that is most easily illustrated for bonding to a single atom. The Al($3s$) function and a water lone pair, denoted $|L\rangle$, make bonding and antibonding combinations which are fully occupied, giving a net bond order of zero. The binding arises because of an admixture of Al($3p$) functions by amounts

$$\beta[L]\simeq\langle 3p|V|L\rangle/(\epsilon_{3p}-\epsilon_L), \quad (1)$$

and

$$\beta[3s]\simeq\langle 3p|V|3s\rangle/(\epsilon_{3p}-\epsilon_{3s}), \quad (2)$$

corresponding, respectively, to charge donation and s-p promotion and giving rise to energy lowerings $\Delta E_L\simeq\beta^2[L](\epsilon_{3p}-\epsilon_L)$ and $\Delta E_{3s}\simeq\beta^2[3s](\epsilon_{3s}-\epsilon_{3p})$. The amount of donated charge is roughly $\Delta Q=\beta^2[L]$. In general, it is not possible to say *a priori* whether these polarization effects will lead

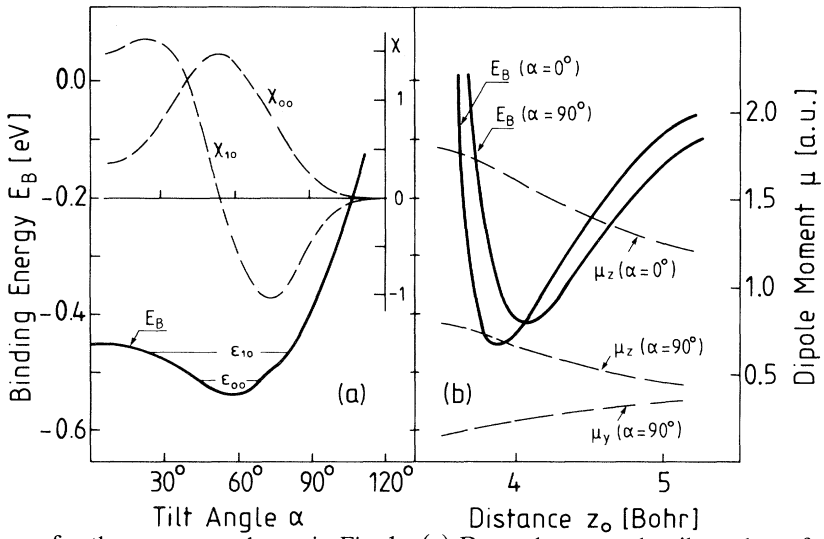

FIG. 2. Energy curves for the geometry shown in Fig. 1. (a) Dependence on the tilt angle α, for $z_0=3.9$ bohrs. The two lowest-lying wave functions describing the angular motion and the corresponding energies are shown. (b) Dependence on z_0 for $\alpha=0°$ and $\alpha=90°$. Also shown are components of the cluster dipole moment $\mu_{z,y}(\alpha,z_0)$, where z,y refer to the coordinate axes in Fig. 1.

to a substantial bonding because the energy lowerings are superimposed on the closed-shell repulsion. For rare-gas atoms on metal surfaces, for example, where charge transfer of similar origin occurs,[27] the closed-shell repulsion dominates. We expect a substantial charge transfer to the metal whenever the adparticle has occupied levels $|L\rangle$ that lie within the metal conduction band and no unoccupied levels below the vacuum. This is the case for H_2O and also for NH_3, where a donation has been postulated in order to explain the anomalous decrease of the Pt(111) work function following adsorption.[28] For CO, on the other hand, bonding takes place with essentially no net donation because the molecule as well as the metal has unfilled levels below the vacuum.

Many features of the energy surface for H_2O on a metal surface can be understood *a posteriori* in terms of the factors β in (1) and (2) that lower the energy. The overall stability of on-top sites reflects the larger values of the matrix elements for this configuration, while the weak dependence on tilt angle is due to a competition between the σ-like $3a_1$ and the π-like $1b_1$ lone pairs of H_2O. These orbitals lie approximately 5 eV and 3 eV, respectively, below the Fermi level. For an on-top site the factor $\beta[3a_1]$ is largest (smallest) and $\beta[1b_1]$ smallest (largest) when $\alpha=0°$ ($\alpha=90°$). The tilt geometry results from an optimization of these two sources of polarization energy. For the bridge site, on the other hand, $\beta[1b_1]$ is large when the $1b_1$ orbital points along the bridge, which implies an upright geometry with the HOH plane normal to the bridge direction. These properties have to do with the lone-pair structure of the H_2O monomer and should not be metal specific.

The charge donation is reflected in the behavior of the cluster dipole moment defined by

$$\vec{\mu}(\alpha,z_0)=\int d^3r\,\vec{r}\rho_{\alpha,z_0}(\vec{r}), \tag{3}$$

where $\rho_{\alpha,z_0}(\vec{r})$ is the cluster charge density (nuclei plus electrons). Roughly, $\vec{\mu}(\alpha,z_0)$ comprises two independent contributions arising from the charge transfer and from the permanent dipole of H_2O together with its induced "image" in the metal cluster. For a fixed position of the oxygen nucleus, calculated values of $\vec{\mu}$ for $0<\alpha\lesssim 70°$ behaved approximately like

$$\mu_z(\alpha,z_0)=\mu_w[1+a(z_0)]\cos\alpha+\mu_{ct}(z_0), \tag{4a}$$

$$\mu_y(\alpha,z_0)=\mu_w[1-a(z_0)]\sin\alpha, \tag{4b}$$

where μ_z,μ_y are the projections of $\vec{\mu}$ along the coordinate axes shown in Fig. 1, $\mu_w\simeq 0.7$ a.u. is the permanent dipole of H_2O (1 a.u. = 2.54 D) and $\mu_{ct}(z_0)=\mu_z(90°,z_0)$ is the charge-transfer contribution, which depends on the distance z_0 as shown in Fig. 2(b). The factors $1\pm a(z_0)$ are due to the partial formation of an image dipole in the cluster, with $a\simeq 0.4$ for the equilibrium distance $z_0=3.9a_0$.

Though the electrostatic balance is important in other contexts, it has a relatively weak direct influence on the energetics. For example, at equilibrium the dipole-image attraction is only $\simeq 20$ meV, while the direct electrostatic attraction between surface and molecule arising from the charge transfer is at most 50 meV. Both contributions are small compared with the binding energy.

Most experimental studies of water layers on metal surfaces refer to hydrogen-bonded networks. The hydrogen bonding interaction (in the range 0.2–0.3 eV), although weaker than the surface-monomer bonding, is stronger than the orientational energy of the molecule, and comparable with the activation energy for monomer transport along the surface. Binding energies for Pt(100) and Ru(100) of 0.7 eV[3] and 0.6 eV,[5] respectively, have been reported. Although a binding energy for Al surfaces has not been quoted, a detailed study of H_2O-Al(111) showed that the absorption is molecular at 80 K with bonding through the O atom. Angular distributions of electron-desorbed H^+ were interpreted to imply a tilt of the HOH plane.[13] Significant dissociation accompanied by H_2 evolution was observed during thermal desorption.[13] As remarked above, direct dissociation of the monomer, though energetically favorable, is strongly activated and we conclude that the observed dissociation can take place only within H_2O clusters on the surface.

Since electrostatic forces are long range one can give only rough values for work-function changes on the basis of cluster calculations. If we interpret the cluster dipole as giving the correct far-field on the vacuum side, we find a work-function change $\Delta\phi=-5$ eV for a surface density of 10^{15} molecules cm^{-2} (roughly one H_2O per surface Al atom). Obviously, this value can refer only to the derivative at zero coverage for adsorption at low surface temperatures where network formation is prevented. A typical value of $\Delta\phi$ for a monolayer of hydrogen-bonded H_2O is $\simeq -1$ eV,[5,16] implying a strong cancellation of the intrinsic dipoles and substantial frustration of the layer with respect to the monomer-surface interaction.

Because H_2O has strongly dipole-active modes, EEL spectroscopy is a particularly powerful probe. According to the energy curves shown in Fig. 2, we expect two distinct low-energy modes associated, respectively, with a frustrated translation of the en-

tire molecule normal to the surface, and a frustrated rotation of the HOH plane. For Al(100), the calculated energies of these modes are 36 and 51 meV, respectively. The strength of the corresponding EEL lines, determined by the squares of the matrix elements of the normal dipole moment,

$$\mu_{tr} = \langle \nu = 1, l = 0 | \hat{z} \cdot \vec{\mu}(\alpha, z_0) | \nu = 0, l = 0 \rangle = 0.02 \text{ a.u.},$$

and

$$\mu_r = \langle \nu = 0, l = 1 | \hat{z} \cdot \vec{\mu}(\alpha, z_0) | \nu = 0, l = 0 \rangle = 0.16 \text{ a.u.},$$

differ by two orders of magnitude so that the rotational mode should dominate the low-energy spectrum. Frustrated translations parallel to the surface and rotations about the normal direction couple far too weakly to be observed in dipole scattering, the latter being at very low energies. The intramolecular modes of H_2O should lie within a few millielectronvolts of the free-molecule energies. The associated matrix elements are $\mu_b \simeq 0.10$ a.u. for the HOH-bend and $\mu_s \simeq 0.05$ a.u. for the OH-stretch modes.

Most EEL studies for H_2O on metals, including one for Al(100),[12] show complex spectra that indicate formation of clusters. Since the structure of such clusters is unknown, definitive assignments of the peaks cannot be made. A study of Ru(001) showed a single dominant loss peak at the very lowest coverages with energy 50 meV, which could be a rotation of the kind we propose. Recently, EEL spectra for Cu(100) and Pd(100) have been reported, with sufficiently low coverage and low temperature to prevent clustering.[15] Both spectra exhibit two lines: a weak one at the HOH-bend frequency and a strong one at 28.5 and 41.5 meV for Cu and Pd, respectively. These energies are in reasonable correspondence with our calculated energy of 51 meV for the frustrated rotation on Al(100). The intensities of the peaks are in semiquantitative agreement with our calculations of the dynamic dipole moments and the nonobservation of frustrated translations and OH-stretch modes is consistent with the small cross sections for these modes. The EEL intensity analysis predicted an equilibrium geometry with the HOH plane tilted 60° from the surface normal, again in good agreement with our findings.

In conclusion, we remark that our calculations refer to clusters and that binding energies and vibration frequencies are not converged with respect to cluster size. While we expect the H_2O-surface interaction to have the general features noted above, we also warn against a too literal interpretation of the results.

We gratefully acknowledge helpful discussions with S. Andersson, A. Bringer, G. B. Fisher, H. Ibach, N. D. Lang, A. Liebsch, B. N. J. Persson, and J. K. Sass.

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