

## SINDO1 Study of Water Dissociation at the Clean and Stepped MgO(100) Surface

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The adsorption of water at the clean and stepped MgO(100) surface was studied with the semiempirical molecular orbital method SINDO1. A cluster simulation was used for the MgO surface. Molecular and dissociative adsorption structures and their relative energies were calculated. Transition structures for dissociation and migration were determined. Pathways from the molecular adsorption structure on the clean surface to the dissociated structure at a step are presented.

## 1. Introduction

The adsorption and dissociation of water on MgO crystals has been the subject of experimental and theoretical investigations. But a detailed mechanism of the dissociation is not known. In particular, experimental results disagree on the question whether water is dissociated on a clean MgO(100) surface. For example, there is no evidence of hydroxylation on the MgO(100) surface by IR spectroscopy studying MgO smoke<sup>1</sup> and FTIR spectroscopy on a clean MgO(100) surface.<sup>2</sup> Quite differently, ultraviolet photoemission spectroscopy and X-ray photoemission spectroscopy of single-crystal MgO<sup>3</sup> and high-resolution electron energy-loss spectroscopy studies<sup>4</sup> show that water undergoes heterolytic dissociation on highly ordered ultrathin MgO films with properties essentially identical with single-crystal MgO and nearly free from pointlike defects.<sup>4</sup> Also, dissociative adsorption of water was discovered on MgO powder by an IR study.<sup>5</sup> Results of theoretical investigations are more straightforward. According to them, water can dissociate on defects of a crystal, but not on a clean surface. Enthalpies of adsorption of H<sup>+</sup> and OH<sup>−</sup> were calculated,<sup>6,7</sup> and chemisorption on the clean surface was rejected due to the large endothermicity of the dissociation. The role of defects was studied also in other work.<sup>8–10</sup> With *ab initio* periodic Hartree–Fock (HF) calculations<sup>9</sup> it was found that dissociation on the clean MgO surface is endothermic by about 30 kcal/mol. Energies of physisorption and chemisorption at a step are about equal. Only at a corner is the dissociation extremely exothermic, by about 50 kcal/mol. The same qualitative result was obtained in *ab initio* molecular dynamics calculations of water on a cluster modeling the MgO crystal.<sup>10</sup>

Our work was aimed at the calculation of a potential energy surface (PES) for possible motions of a water molecule on a clean surface obtained by cleavage of the MgO crystal, which may contain steps as defects. This includes adsorption energies of molecular and dissociated water and the barriers to dissociation and migration processes.

## 2. Method of Calculation

The semiempirical quantum-chemical method SINDO1 was used as the method of calculation.<sup>11–13</sup> This method was previously successfully used for calculations of adsorption processes on NaCl, MgO, and TiO<sub>2</sub>.<sup>14</sup> More recently H<sub>2</sub>O adsorption was studied on NaCl<sup>15,16</sup> and MgO.<sup>16</sup> The reaction profile for dissociation of water on rutile was calculated.<sup>17</sup> Since

all proposed processes are on the ground-state surface of the water molecule and the bond cleavage during dissociation is a heterolytic process, the HF level of approximation is sufficient. In accordance with the previous investigations of the MgO crystal only s and p atomic orbitals (AOs) formed the basis set, but p AOs on the atom H were included in order to account for hydrogen bonds.<sup>18</sup> Different values for the parameter  $\alpha$  in the core matrix elements for Mg–O pairs had to be chosen for the molecule and the bulk: 0.375 inside the cluster and 0.18 between Mg of the cluster and O of adsorbed water.<sup>19</sup> Similarly, the parameter  $\alpha$  for O–H pairs is different for the water oxygen (0.333) and for the cluster oxygen (0.100). The energetics of processes was evaluated as differences of the calculated binding energies. The sum of binding energies of the pure model clusters (see below) and the isolated water molecule was taken as the zero point of energy. Transition states for dissociation processes were identified as saddle points with only one negative eigenvalue of the Hessian matrix.

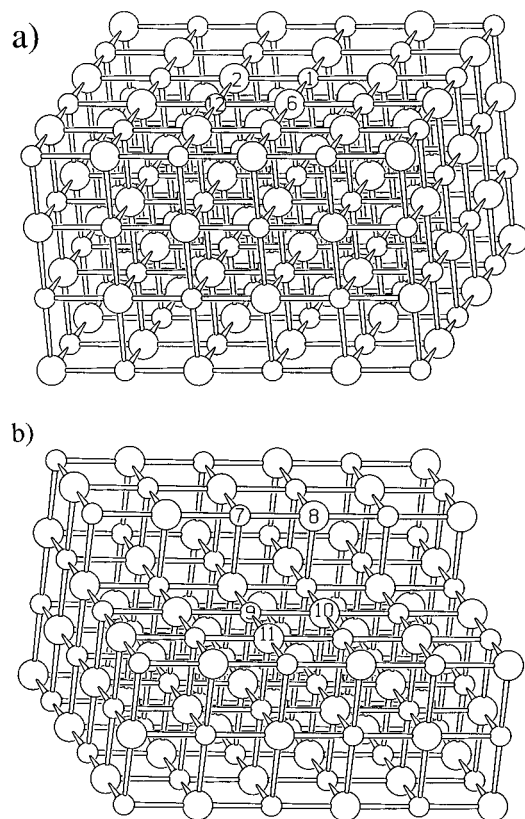
## 3. Cluster Model

Potential energy surfaces (PESs) for all processes were calculated using a regular Mg<sub>72</sub>O<sub>72</sub> cluster of 6 × 6 × 4 shape and a stepped Mg<sub>63</sub>O<sub>63</sub> cluster of 6 × 6 × 4 shape in which a slice of size 6 × 3 × 1 was cut out. The regular cluster was used for the simulation of a clean surface. The stepped cluster modeled a crystal with a defect in the form of a step. Both clusters are shown in Figure 1. Their size is sufficient for the study of adsorption of a single water molecule. Both clusters are stoichiometric and neutral. All Mg–O distances were set equal, and the optimized value of the distance is 2.032 Å for the regular cluster and 2.025 Å for the stepped cluster.

A cluster as a model of a crystal has at least two drawbacks. First, the optimized Mg–O distances in the cluster are shorter than in a real crystal. The experimental value of the Mg–O distance in the crystal MgO is 2.104 Å.<sup>20</sup> Other authors have concluded that dissociation becomes energetically more favorable with increasing lattice constant.<sup>9</sup> Their conclusion is based on a nonequilibrium situation of the bulk. In general we would expect the bonding between surface atoms to decrease for increasing Mg–O distances, which therefore allows for stronger adsorption.<sup>21</sup> Second, the smaller the cluster, the more the net charges on the atoms differ from each other, in particular for surface atoms. This leads to a dependence of calculated adsorption energies on nearest neighbors, because a calculated adsorption energy depends on the coordination number of the adsorption center and on the net charge of the center, which is different for different sites on a cluster surface. For a smaller cluster of size 6 × 5 × 3 the variation of net charge on the 6

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**Figure 1.** (a)  $\text{Mg}_{72}\text{O}_{72}$  cluster as a model for the clean surface. (b)  $\text{Mg}_{63}\text{O}_{63}$  cluster as a model for the stepped surface.

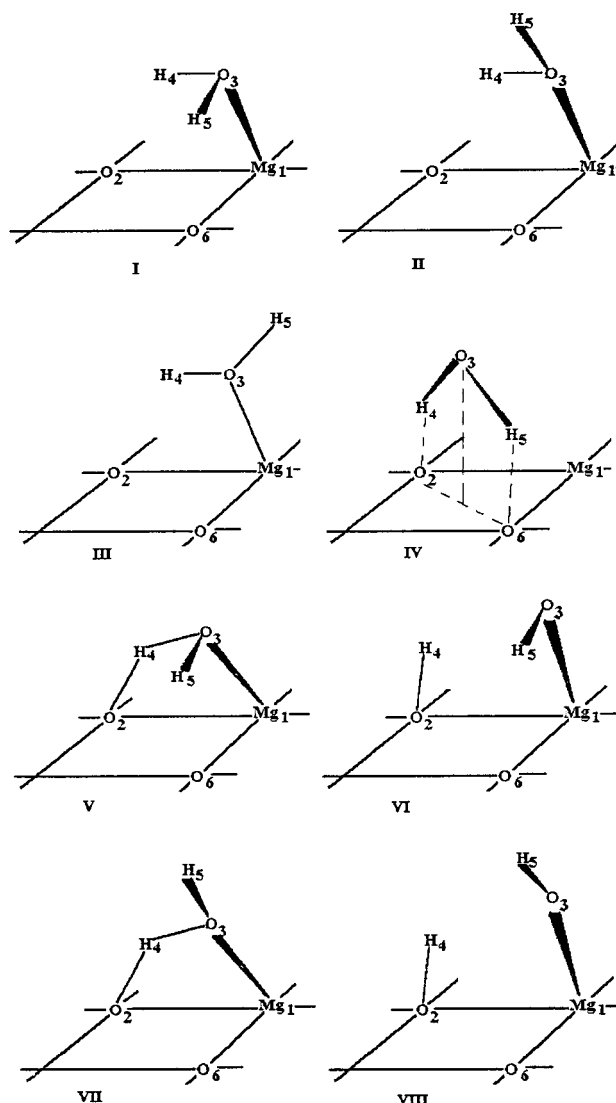
$\times 5$  surface is in the range of 0.021, compared with only 0.013 for the chosen  $6 \times 6 \times 4$  cluster. This leads to a variation of adsorption energy of 5 kcal/mol for the smaller cluster, compared with 1 kcal/mol for the chosen cluster. This latter value seemed a good criterion for the choice of the  $6 \times 6 \times 4$  cluster.

To evaluate the possible influence of a relaxation of atoms of the reaction center on the dissociation process, corresponding calculations were performed for systems where the geometry of the reaction center of the cluster was optimized. For this purpose the following clusters were optimized: the regular  $6 \times 6 \times 4$  cluster with four relaxed atoms,  $\text{Mg}_1$ ,  $\text{Mg}_{12}$ ,  $\text{O}_2$ , and  $\text{O}_6$  (Figure 1a), for the calculation of the process on the clean surface; the stepped cluster with four relaxed atoms,  $\text{Mg}_7$ ,  $\text{O}_8$ ,  $\text{Mg}_9$ , and  $\text{O}_{10}$  (Figure 1b), for the calculation of the process in a region of the edge. These surface atoms were optimized separately from the rest of the atoms for the relaxed structures.

#### 4. Results

**4.1. Clean Surface.** Three conformational minima were found depending on the angle between the planes of the water molecule and the surface (structures I–III in Figure 2). The lowest in energy is planar (I) with the plane of the water molecule nearly parallel to the surface. Orientation and distance to the surface of our calculated adsorbate structure I are close to the structure found in a recent force field calculation.<sup>22</sup> Higher in energy is the conformation II, where one O–H bond is directed almost parallel to the surface and the second O–H bond is directed up to the surface under an acute angle. For the third structure (III) the plane of the water molecule is perpendicular to the surface. Structure III is separated from structure II by a very small barrier. The former minimum disappears if the surface is relaxed.

The geometrical parameters for all structures are given in Table 1.



**Figure 2.** Relevant portion of  $\text{Mg}_{72}\text{O}_{72}$  cluster for clean surface adsorption of water: (a) molecular adsorption (I–III), (b) transition structures (IV, V, VII), (c) dissociative adsorption (VI, VIII).

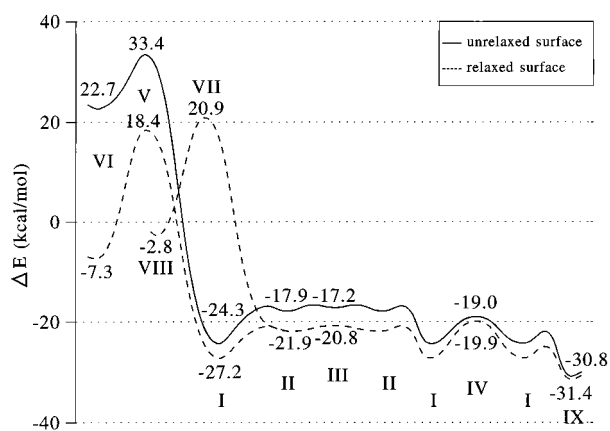
**TABLE 1: Calculated Geometry (Å, deg) and Adsorption Energy  $\Delta E$  (kcal/mol) of the Water Molecule on the Clean Surface of  $\text{Mg}_{72}\text{O}_{72}$ ; For Labels See Figure 2**

scheme	I	II	III	IV	V	VI
1–3	2.162	2.249	2.301	2.474	2.022	1.963
3–4	0.994	0.993	0.991	0.994	1.407	1.846
3–5	0.994	0.978	0.976	0.994	0.973	0.970
4–2	2.015	1.988	1.989	1.990	1.172	1.015
5–6	2.015	3.348		1.990	2.064	2.053
2–1–3	78.4	75.3	73.4		73.0	78.4
1–3–4	89.4	89.7	91.4			
1–3–5	89.4	129.7	161.0		94.1	95.6
$\Delta E$	–24.3	–17.9	–17.2	–19.0	33.4	22.7

Molecular dynamics calculations of the adsorption energy yield a value of about 5 kcal/mol.<sup>10</sup> Three minima were found using periodic HF calculations<sup>23</sup> with binding energies ranging from 4.1 to 5.6 kcal/mol (8.2 to 11.1 kcal/mol with correlation correction) and another one<sup>24</sup> with a parallel orientation of the water molecule to the surface with a binding energy 9.7 kcal/mol (17 kcal/mol with correlation correction). Experimental estimates of the adsorption energy range from 10 to 19 kcal/mol.<sup>25,26</sup> From the latest low-energy electron diffraction (LEED) and helium atom scattering (HAS) experiments an adsorption energy of 20.4 kcal/mol for molecular adsorption on a clean surface is obtained.<sup>27,28</sup>

**TABLE 2: Calculated Geometry (Å, deg) and Adsorption Energy  $\Delta E$  (kcal/mol) of the Water Molecule on the Stepped Surface of  $\text{Mg}_3\text{O}_3$ ; For Labels See Figure 4**

scheme	IX	X	XI	XII	XIII	XIV	XV
7-3	2.071	2.265	2.086	1.878	2.086	1.947	1.886
3-4	0.996	1.014	1.318	2.175	0.998	1.256	1.922
3-5	0.995	0.994	0.978	0.981	0.976	0.962	0.963
3-9		2.155	2.090	2.012	3.796	3.547	3.387
4-8	1.995	1.979	1.289	1.017	1.937	1.259	0.963
4-10		2.005	2.106	2.169			
5-11		2.098	2.171	3.094			
8-7-3	78.9	76.6	73.0	93.0	77.5	72.3	82.3
7-3-4	86.6	85.7	72.2		91.4	76.7	
7-3-5	91.3	156.8	160.0	93.0	123.6	117.6	104.8
$\Delta E$	-30.8	-45.3	-8.9	-49.6	-33.3	1.2	-27.6

**Figure 3.** Reaction pathway from molecular adsorption on the clean surface (I) to dissociative adsorption on the clean surface (VI) without and with relaxation.

Possible transformations of the water molecule adsorbed on the surface are desorption, migration on the surface, and dissociation. Desorption will not be discussed here. For migration from one center to another the water molecule has four nearest Mg centers, but they are not equivalent. The truly nearest of those is the Mg atom with the shortest distance to the O of water (structure I). Migration to this center is easy, because it requires only 5.3 kcal/mol. The corresponding transition state (structure IV) is shown in Figure 2. In recent work<sup>22</sup> with a classical force field, parametrized from periodic Hartree-Fock calculations, the flipping motion was calculated as 5.7 kcal/mol, which compares favorably with our value. Migration to the last three centers needs much more energy. But there is a way not to confine the water molecule to migrate inside only one square of two Mg and two O atoms. Rotation about an O-H bond allows it to transfer to a neighbor square. This requires about 7 kcal/mol. Thus, migration followed by rotation or vice versa is part of a directed motion of the water molecule along the surface. It lasts until it reaches a defect, i.e., an atom with a coordination number less than five. The adsorption of water at an edge in the conformation of structure I is stronger than on the clean surface by 6.5 kcal/mol, as can be seen from the comparison of structure I in Table 1 and structure IX in Table 2. The energetics of the motion toward the edge is presented in Figure 3. In this figure we have optimized all stationary points and connected them by smooth curves. So the reaction pathway is loosely defined as the easiest way to get from a stationary point to the next when moving from the clean surface to the edge and into the step. The further fate of the water molecule which reaches a step is presented in the following subsection.

The dissociation process is characterized by structures I, V, and VI, and its energetics is shown in Figure 3. According to our calculations, its barrier is about 58 kcal/mol, and this reaction

is predicted to be highly endothermic. In any case, the dissociation on the clean surface is energetically a highly unfavorable process.

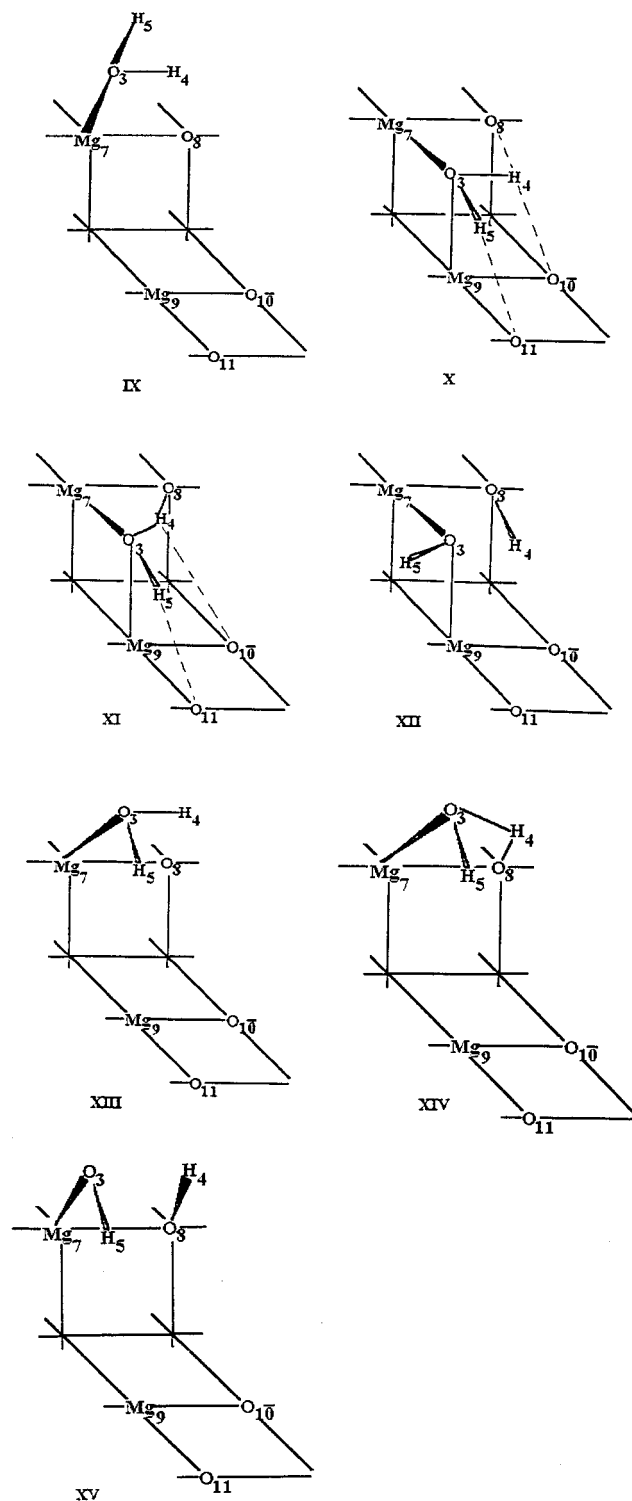
**4.2. Stepped Surface.** Three minima were found for the adsorption of the water molecule on the edge of the stepped cluster. Their geometries and energies are presented (structures IX, X, XIII, Figure 4) in Table 2. The minima differ by their orientation of the water molecule to the step. The structure of the lowest in energy (X) has a bridged form for the adsorption of the water oxygen. Energies of adsorption are much lower than on a clean surface. The lowest calculated energy is -45.3 kcal/mol. So defects, in particular a step, are traps for water wandering around the clean surface. The water molecule, reaching an edge (structure IX) very easily through the barrier of about 2.5 kcal/mol, falls down to structure X. Exothermicity of these motions is 14.5 kcal/mol. The whole process is illustrated by the potential curve in Figure 5. Again all stationary points were determined and connected by smooth curves. The obtained results do not agree quantitatively with those of Langel and Parrinello,<sup>10</sup> where the calculated energies of physisorption on a terrace and chemisorption in a step are about equal, -4.1 to -5.6 and -7.3 kcal/mol, respectively. Here it is implied that the adsorption is stronger if the adsorption energy is more negative.

The further reaction process of the water molecule is mainly determined by the large depth of the potential well (X). The reverse pathway to the clean surface requires about 20 kcal/mol. An alternative process is the dissociation on the step. The structures and energetics of the transition structure (XI) and product of reactions (XII) are represented by Figures 4 and 5, and numerical data are contained in Table 2. The calculated barrier is 36.4 kcal/mol, and the exothermicity equals 4.3 kcal/mol.

There exists in this case an alternative pathway for the dissociation process, beginning from the local minimum XIII. This pathway leads to a local minimum for the dissociated product (XV). The latter lies 22 kcal/mol higher than the global minimum (XII) and can fall down to it through an insignificant barrier which is not shown in Figure 5. The calculated barrier (XIV) of 34.5 kcal/mol for the alternative pathway is a few kcal/mol lower than for the main dissociation via structure XI. This is caused by the fact that the main reaction pathway takes place via structures that have two O-Mg bonds (XI) compared to one O-Mg bond (XIV) for the alternative pathway. The process from structure XIII to XV via XIV is a secondary process at the one-layer step. For the multilayer step, where the influence of the inner part of the step is removed, the process becomes more unfavorable.

We do not discuss here adsorption at corners, because they occur frequently only in powders.

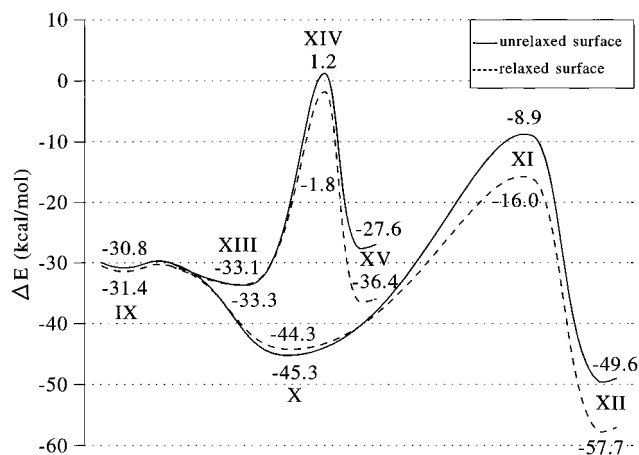
**4.3. Influence of Relaxation.** As was pointed out earlier,<sup>10</sup> relaxation is an important effect for adsorption studies at



**Figure 4.** Relevant portion of  $\text{Mg}_{63}\text{O}_{63}$  cluster for stepped surface adsorption of water: (a) molecular adsorption (IX, X, XIII), (b) transition structures (XI, XIV), (c) dissociative adsorption (XII, XV).

defective surfaces. Our calculation supports its significance. For all relaxed structures the adsorption of the O atom of water to an Mg atom pulls this Mg atom out of the surface plane. Binding of the H atoms to surface O atoms moves these less out of the surface plane. We have relaxed those surface atoms involved in binding.

The effect of local relaxation has been studied for the process of dissociation both on a perfect surface and for reaction on the edge. Corresponding potential curves are represented in Figure 3 and in Figure 5; numerical data are in Tables 3 and 4. The values  $\Delta E$  in these tables are obtained under the condition



**Figure 5.** Reaction pathway from molecular adsorption on the stepped surface (IX) to dissociative adsorption on the stepped surface (XII) without and with relaxation.

**TABLE 3: Calculated Geometry (Å, deg) and Adsorption Energy  $\Delta E$  (kcal/mol) of the Water Molecule on the Relaxed Clean Surface of  $\text{Mg}_{72}\text{O}_{72}$ ; For Labels See Figure 2**

scheme	I	II	IV	V	VI	VII	VIII
1-2	2.076	2.085	2.048	2.208	2.247	2.219	2.342
1-3	2.101	2.154	2.790	1.974	1.905	1.969	1.891
3-4	0.996	0.996	0.995	1.303	1.921	1.294	1.916
3-5	0.996	0.977	0.995	0.977	0.972	0.961	0.960
4-2	2.011	1.978	1.983	1.245	1.001	1.228	1.002
5-6	2.011	3.404	1.983	2.081	2.058	3.211	3.201
2-1-3	79.2	76.5		70.1	75.5	69.2	77.2
1-3-4	89.7	90.9					
1-3-5	89.7	125.1		93.0	95.0	116.8	107.6
$\Delta E$	-27.2	-21.9	-19.9	18.4	-7.3	20.9	-2.8

**TABLE 4: Calculated Geometry (Å, deg) and Adsorption Energy  $\Delta E$  (kcal/mol) of the Water Molecule on the Relaxed Stepped Surface of  $\text{Mg}_{63}\text{O}_{63}$ ; For Labels See Figure 4**

scheme	IX	X	XI	XII	XIII	XIV	XV
7-8	2.072	2.006	2.113	2.115	2.013	2.161	2.207
9-10		2.029	2.043	2.034	1.983	1.987	2.002
7-3	2.062	2.112	1.967	1.889	2.060	1.923	1.855
3-4	0.995	1.018	1.265	2.182	0.999	1.230	1.950
3-5	0.998	0.974	0.960	0.982	0.976	0.962	0.962
3-9		2.216	2.061	1.959	4.001	3.820	3.675
4-8	1.996	1.961	1.370	1.008	1.945	1.295	0.992
4-10		1.997	2.073	2.094			
5-11		3.446	3.353	3.194			
8-7-3	78.4	76.1	71.9	89.2	78.5	70.8	81.4
7-3-4	86.8	94.1	81.8		90.6		
7-3-5	91.5	127.9	126.1	93.6	121.8	116.6	103.9
$\Delta E$	-31.4	-44.3	-16.0	-57.7	-33.1	-1.8	-36.4

that the zero point of the energy scale is the sum of the energy of the corresponding cluster and the energy of the water molecule. This means that the unrelaxed cluster is the reference in Tables 1 and 2 and the relaxed cluster in Tables 3 and 4.

The main effect of relaxation is due to the fact that relaxation correction is different for the molecular adsorption, the transition structure, and the dissociated product. Therefore shapes of the potential curves differ in these cases from the unrelaxed cluster described above. One can see that relaxation has the greatest influence on the energy of the product, whereas the influence on the energy of the transition structure is less.

The most significant influence of relaxation is found on the clean surface. Here structure VI is lower in energy than for the separated cluster-water system. Two new structures, VII as a transition structure and VIII as a minimum for dissociation on the clean surface, appear. However, they do not change the picture, which declared dissociation on the clean surface as very unlikely. For the rest of the structures the effect of relaxation

is less pronounced, except that dissociation in the step is more favored over molecular adsorption with a lowering of the barrier (XI) and the dissociated product (XII). This trend is much less pronounced for the dissociation at the edge.

## 5. Conclusion

We conclude that a dissociation of a water molecule adsorbed on a clean surface is very unlikely. It can desorb or wander around the surface until it reaches some defect. In particular, a step is a trap for the water molecule. The adsorption energy in this region is much larger, and the possibility for dissociation is increased. This is qualitatively consistent with other theoretical investigations.

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