

Comparative studies on the adsorption of small molecules at NaCl and MgO surfaces

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Abstract

The adsorption of CO₂, CO and H₂O at NaCl and MgO surfaces is studied with the SINDO1 method. The bulk is simulated by clusters of cuboid shape with appropriate surface and layer size. The suitability of the clusters was tested with respect to binding energy and bond length. Submonolayer and monolayer coverage of the adsorbate molecules were investigated, and adsorbate structure and energy were calculated. Various overlayer structures are studied and their relative stability is determined. The results are compared with experimental findings.

Keywords: Adsorption; Magnesium oxide; Sodium chloride

1. Introduction

The study of adsorption of small molecules at ion crystal surfaces is a challenging subject for theoreticians. In the last decade experimental techniques have been improved and have made a wealth of information on adsorbate structures at low temperatures available. Among the substrates NaCl and MgO have been a favored subject as can be seen from the proceedings of a recent conference [1]. It is now the task of the theoretician to substantiate these studies by theoretical investigations. We have chosen NaCl and MgO not only because of the available experimental data, but also because they offer a

good basis for a comparative study. The standard surface is the (100) surface and the structure of the surface is the same for both NaCl and MgO bulk. Both solids have a cubic structure and can be well represented by cluster simulation, because the cluster structure is very similar to the bulk structure [2–7]. The formal charge on the atoms of the ideal ionic solid is ± 1 for NaCl and ± 2 for MgO. This should have an influence on the adsorption. Also the experimental lattice distance in NaCl is much larger than in MgO, because two atoms of the second row are involved in the first case compared to one in the second case. This means that the available space for adsorption of molecules on the surface is much larger in the first case, which again influences the lateral interaction of adsorbed molecules. We have chosen CO₂, CO

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and H₂O as adsorbate molecules, because they offer a variety of possibilities for adsorption structures and have been of experimental interest.

For the study of adsorption phenomena we have chosen the semiempirical molecular orbital method SINDO1 which was initially designed for the study of first-row [8], second-row [9] and third-row [10] molecules and has been recently extended to the study of clusters and surfaces [11]. A comprehensive review of the method has just been published [12]. The suitability and accuracy of SINDO1 has been documented in numerous publications and will not be discussed here in detail. The cluster approach for NaCl and MgO surface studies has been used in SINDO1 before [13] and an important relation between binding energy, bond distance and average coordination number was found and explained [14]. An average coordination number of atoms in a cluster was defined and normalized by dividing it by the bulk value of 6. This so-called relative average coordination number k equals 1 for the bulk and 0.9 for a $(10 \times 10 \times 10)$ cube of 1000 Na, Cl or Mg, O atoms. For a cubic structure of Na₄Cl₄ or Mg₄O₄ the average coordination number of the atoms is 3 and $k = 3/6 = 0.5$. It was found that the binding energy per molecular unit, NaCl or MgO, shows a quasi linear dependence on k if the shape of the clusters is close to a cube. The same holds for the bond distance between two adjacent atoms in the cluster in dependence of k . This allows a Taylor-made design of suitable clusters for the study of adsorption.

In the following sections we present calculations of submonolayer and monolayer adsorption of CO₂, CO and H₂O on NaCl(100) and MgO(100) surfaces. All clusters used are neutral closed-shell systems which were optimized as bulk structures. Subsequently the adsorbate structures were optimized on the cluster surfaces. We explain the similarities and differences of the two surfaces for adsorption of these molecules. We also discuss agreement and disagreement with experimental data.

2. CO₂ adsorption

2.1. CO₂/NaCl(100)

The study of adsorption of CO₂ on the NaCl(100) surface was among the first adsorption studies with SINDO1 [13]. We present here only the essential findings together with some new results. The submonolayer was simulated by a single CO₂ molecule adsorbed on a $(4 \times 4 \times 3)$ Na₂₄Cl₂₄ cluster. The orientation of the CO₂ was parallel to the surface with the O atoms oriented towards the Na atoms (Fig. 1) at a distance of 2.82 Å about the surface. The uniform Na–Cl distance was calculated as 2.778 Å with SINDO1 compared to 2.814 Å from experiment [15]. The calculated binding energy per NaCl unit of the cluster was 6.38 eV compared with the experimental value of 6.62 eV from heats of formation [16,17]. The adsorption of a CO₂ submonolayer has been studied with Fourier-transform infrared (FTIR) spectroscopy at clean NaCl surfaces cleaved in ultra high vacuum (UHV). The adsorption energy was determined at 6.8 kcal/mol [18]. Our calculated adsorption energy of 6.5 kcal/mol [13] for the $(4 \times 4 \times 3)$ cluster was very close.

We have now studied the dependence of the adsorption energy E_{ad} on the relative average coordination number k . The results are in Fig. 2. This figure shows a similar quasilinear dependence of E_{ad} on k as the binding energy E_{bu} per NaCl unit. Our initial reference cluster of shape $(4 \times 4 \times 3)$ refers to a k value of about

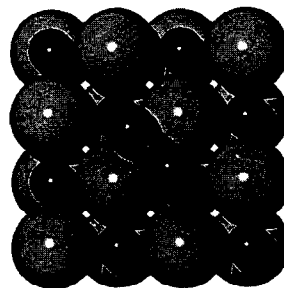


Fig. 1. Structure of submonolayer of CO₂ on NaCl(100) simulated by a single CO₂ on a $(4 \times 4 \times 3)$ Na₂₄Cl₂₄ cluster.

0.72. For a larger cluster of shape $(6 \times 6 \times 6)$ the k value increases to 0.83 and the binding energy correspondingly to 7.2 kcal/mol. The explanation for the increase is similar to the one previously given for E_{bu} [19]. Here we explained k as a truncated Madelung sum. Since the Coulomb interactions, which have a determining influence on the adsorption energy, depend linearly on the Madelung sum, a linear dependence of E_{ad} on k is the consequence. The extrapolated value for the bulk would be 8.3 kcal/mol.

Another interesting problem is the migration of CO_2 molecules on the surface. We determined the most favorable transition structure for migration of a CO_2 molecule from one adsorption site to another adjacent adsorption site. Here a $(5 \times 4 \times 3)$ $\text{Na}_{30}\text{Cl}_{30}$ cluster was used. In the transition structure the CO_2 molecule is found exactly over a Na–Cl bond. One O atom is above the Na atom and the molecule is tilted up in the direction from Na to Cl. The Na–O distance for the closer O atom is 2.552 Å, slightly less than for the minimum, and the tilt angle is 41.1° . The barrier for migration is only 0.8 kcal/mol, which is in the range of the experimental estimate of 0.7–1.0 kcal/mol. The potential curve for the migration of CO_2 is presented in Fig. 3.

Here the relative energy change ΔE_{ad} is shown in dependence of the rotation angle φ .

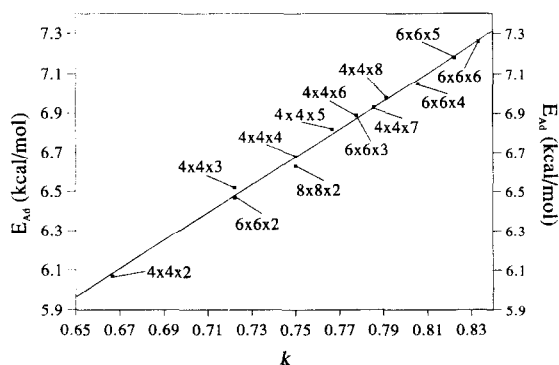


Fig. 2. Dependence of adsorption energy (kcal/mol) on the relative average coordination number k for submonolayer adsorption of CO_2 on $\text{NaCl}(100)$.

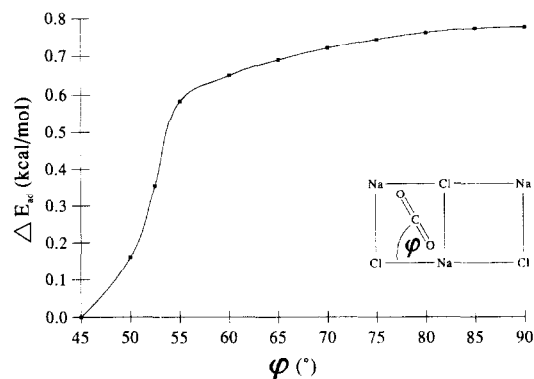


Fig. 3. Potential curve for migration of CO_2 on the $\text{NaCl}(100)$ surface.

This angle is the angle between atoms Cl, Na and the projection of the atom C on the surface. We see that there is a pronounced increase for the first 10° from 45 to 55° . Here one of the O–Na physisorption bonds is broken. This bond breaking constitutes the main portion of the activation energy.

The monolayer coverage of CO_2 on NaCl has been studied experimentally with FTIR [18,20–22], with low energy electron diffraction (LEED) [23], and helium atom scattering (HAS) [24]. From some of these experiments [21–23] a monolayer adsorption with a (2×1) overlayer structure could be deduced. We first calculated the adsorption of 7 CO_2 molecules on a $(7 \times 6 \times 2)$ $\text{Na}_{42}\text{Cl}_{42}$ cluster. We studied both the (1×1) and (2×1) overlayer structures [13]. We obtained a slightly more stable (2×1) overlayer structure with an adsorption energy of 5.3 kcal/mol compared to 5.0 kcal/mol for the (1×1) overlayer structure. This relative stability was in good agreement with experiments. The experimental adsorption energy was determined at 5.8 kcal/mol [18,20]. We also studied the dependence of the adsorption energy on cluster size by increasing the cluster surface to the (9×8) shape keeping 2 layers. This $\text{Na}_{72}\text{Cl}_{72}$ cluster was covered with 17 CO_2 molecules (Fig. 4). The adsorption energy increased slightly to 5.5 kcal/mol. We explain the slight decrease of adsorption energy from 6.5 kcal/mol for the submonolayer to 5.5

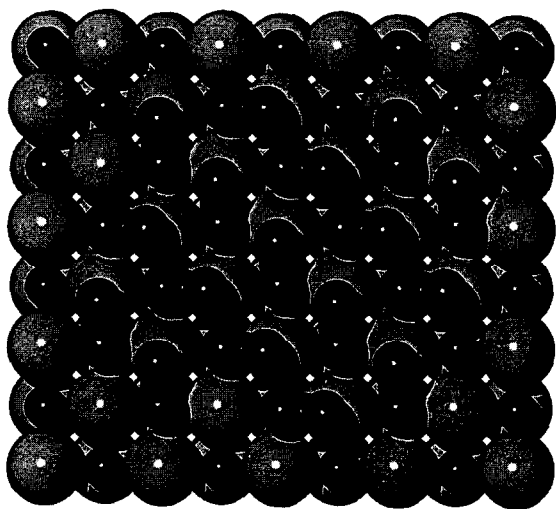


Fig. 4. Structure of monolayer of CO_2 on $\text{NaCl}(100)$ simulated by 17 CO_2 on a $(9 \times 8 \times 2)$ $\text{Na}_{72}\text{Cl}_{72}$ cluster.

kcal/mol for the monolayer with the tilting of the CO_2 molecules from the surface. The calculated tilt angle is 23° compared to 34° from experiments [18,20]. The tilting causes a partial removal of one of the atoms from the adjacent Na atoms which reduces the electrostatic attraction [25]. This lowering of the adsorption energy is partially compensated by an attraction between the CO_2 in the so-called herringbone structure due to lateral interaction.

2.2. $\text{CO}_2/\text{MgO}(100)$

The adsorption of CO_2 on the $\text{MgO}(100)$ should have similar features as the adsorption on $\text{NaCl}(100)$. The difference is that MgO is an ionic crystal with formal charges of ± 2 instead of ± 1 . Since one of the atoms is from the first row the $\text{Mg}-\text{O}$ bond distance of 2.105 \AA in the bulk is substantially smaller than the 2.814 \AA in NaCl . The submonolayer was simulated with a single CO_2 molecule on a $(4 \times 4 \times 3)$ $\text{Mg}_{24}\text{O}_{24}$ cluster. This cluster has again a k value of 0.72 and is sufficient for this purpose. From the previously established linear relationships between k and E_{bu} as well as k and bond distance R for MgO [14] it is not surprising that the binding energy of 8.54 eV for the $\text{Mg}_{24}\text{O}_{24}$

cluster calculated with SINDO1 is much smaller than the experimental value of 10.26 eV [17,26], because the $\text{Mg}-\text{O}$ distance of this cluster is more underestimated than for the corresponding NaCl cluster. However, the extrapolated bulk value of 10.21 eV from SINDO1 is very close. The R_{MgO} value of 1.994 \AA for this cluster is 0.11 \AA smaller than the experimental value. Again the extrapolated bulk value of 2.122 \AA is close to the experimental value of 2.105 \AA . The adsorbate structure for the CO_2 submonolayer is presented in Fig. 5. It is not surprising that the structure is similar to the one on NaCl . The CO_2 is parallel to the surface with the two O atoms oriented towards Mg atoms and with a distance of 2.54 \AA from the surface.

Due to the smaller $\text{Mg}-\text{O}$ distance compared to the $\text{Na}-\text{Cl}$ distance the oxygen atoms of CO_2 are closer to the adsorbing cations. This may explain the larger adsorption energy of 7.3 kcal/mol compared to the 6.8 kcal/mol for NaCl . However, this increase is slight because the repulsion from the bulk oxygens is also increased due to the reduced distance. We expect that the difference between the adsorption energies on MgO and NaCl will increase if we extrapolate to the bulk, because the $\text{Mg}-\text{O}$ distance is more underestimated than the $\text{Na}-\text{Cl}$ distance. No experimental value for this adsorption energy is available.

The monolayer adsorption has been experimentally studied by different groups [27,28]. A $(2\sqrt{2} \times \sqrt{2})R$ 45° overlayer structure was found with 2 CO_2 molecules per unit cell which are energetically, but not translationally equivalent. We considered a $(\sqrt{2} \times \sqrt{2})R$ 45° structure in

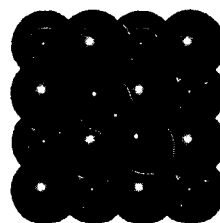


Fig. 5. Structure of submonolayer of CO_2 on $\text{MgO}(100)$ simulated by a single CO_2 on a $(4 \times 4 \times 3)$ $\text{Mg}_{24}\text{O}_{24}$ cluster.

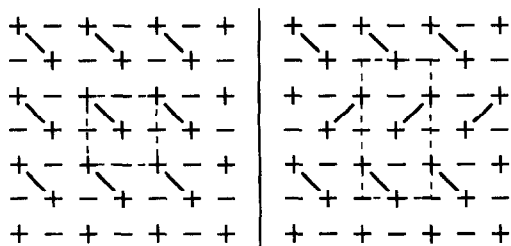


Fig. 6. Scheme for overlayer structures of CO_2 on $\text{MgO}(100)$, left: $(\sqrt{2} \times \sqrt{2})R 45^\circ$, right: $(2\sqrt{2} \times \sqrt{2})R 45^\circ$.

addition to the experimentally predicted structure. In both cases the coverage of the surface is 0.5. The scheme for these overlayer structures is shown in Fig. 6. We used a $(10 \times 10 \times 3)$ cluster for adsorption. 14 CO_2 were placed in the $(2\sqrt{2} \times \sqrt{2})R 45^\circ$ structure (Fig. 7). The adsorption energy per molecule turned out to be almost the same from the submonolayer adsorption energy. In the first case we found 7.3 kcal/mol, and in the second case 7.4 kcal/mol. The molecules are again parallel to the surface as in the submonolayer case. The lateral interaction between them is quite small. However, from IR experiments [27] a tilt angle of about 20° to the surface is deduced. Also a rotation angle of 66° out of the diagonal between two Mg atoms which corresponds to 45° was predicted. LEED experiments [28] indicate a nearly parallel orientation to the surface.

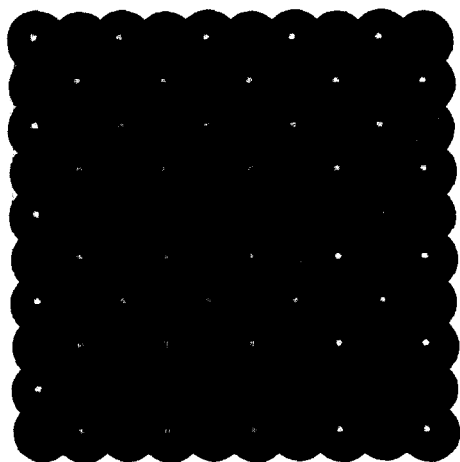


Fig. 7. Structure of monolayer of CO_2 on $\text{MgO}(100)$ simulated by 14 CO_2 on a $(10 \times 10 \times 3)$ $\text{Mg}_{150}\text{O}_{150}$ cluster.

3. CO adsorption

3.1. $\text{CO}/\text{NaCl}(100)$

The CO adsorption on NaCl has been the subject of intensive experimental studies. From HAS [29] and FTIR [30] investigations two overlayer structures were deduced for the monolayer coverage, a (2×1) structure below 35 K and a (1×1) structure above 35 K. We started again with the study of the submonolayer simulated by a single CO molecule on a $(5 \times 5 \times 4)$ $\text{Na}_{50}\text{Cl}_{50}$ (Fig. 8). This cluster was chosen for an appropriate adsorption at a central Na surface atom. An even number of layers was necessary for a neutral closed-shell system. There are two possibilities for adsorption, C adsorption or O adsorption. The SINDO1 calculation clearly favors the C adsorption with E_{ad} 6.6 kcal/mol over the O adsorption with E_{ad} 5.3 kcal/mol. For C adsorption CO appears perpendicular to the surface; whereas the O adsorption shows a tilt angle of 49° with respect to the surface. In the first case a blue shift of 10 cm^{-1} for the IR frequency is observed compared with the red shift of 20 cm^{-1} for the second case. Such a shift was already described in previous work [31]. The same scaling procedure was used here for CO. Since no experimental data on the submonolayer adsorption are available, we performed an additional ab initio calculation with a 6-31G basis for a single CO on a $(3 \times 3 \times 2)$

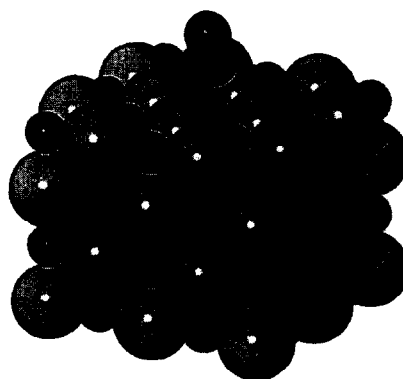


Fig. 8. Structure of submonolayer of CO on $\text{NaCl}(100)$ simulated by a single CO on a $(5 \times 5 \times 4)$ $\text{Na}_{50}\text{Cl}_{50}$ cluster.

Na_9Cl_9 cluster. Here the adsorption energy is 3.8 kcal/mol for C adsorption and 3.3 kcal/mol for O adsorption.

Different from the SINDO1 calculation the CO molecule is found tilted with a tilt angle of 83.8° to the surface for C adsorption and perpendicular for O adsorption. However, the perpendicular arrangement for C adsorption increases the energy by less than 0.01 kcal/mol. We have recently shown with a physisorption model analysis based on ab initio wavefunctions for CO on Na_9Cl_9 and CO on $\text{Na}_{25}\text{Cl}_{25}$ [25] that the binding of CO at NaCl surfaces is dominantly electrostatic by nature and that the tilting is related to the shape of the isodensity surfaces of molecule and cluster. It is therefore difficult to predict the exact arrangement for such small energy changes. The tilting in SINDO1 for O adsorption seems to be caused by interactions between the C atom and Na cluster atoms. In comparison the ab initio calculation suffers from basis set dependence and lack of a proper CI for the CO molecule.

FTIR studies for the monolayer adsorption [32,33] found a (2×1) overlayer structure which cannot be explained with a perpendicular arrangement of CO molecules on all Na atoms. We studied this problem with 8 CO on a $(6 \times 6 \times 3)$ $\text{Na}_{54}\text{Cl}_{54}$ cluster and 18 CO on a $(8 \times 8 \times 3)$ $\text{Na}_{96}\text{Cl}_{96}$ cluster with SINDO1. Two overlayer structures were considered, a (1×1) structure with the CO molecules on top of all Na surface atoms, i.e. except the Na edge and corner atoms (Fig. 9), and a (2×1) structure where there are two alternating rows of CO molecules tilted in opposite direction. Only the (1×1) structure was found stable, the optimization of the (2×1) structure ended up with the same geometry as the (1×1) structure. To explain the discrepancy compared with the experiments, it must be considered that there are two opposing effects. The single molecule adsorption favors the perpendicular arrangement for C adsorption, whereas the lateral interaction between the vertical CO molecules is repulsive and favors a tilting. Since the Na–Na distance is

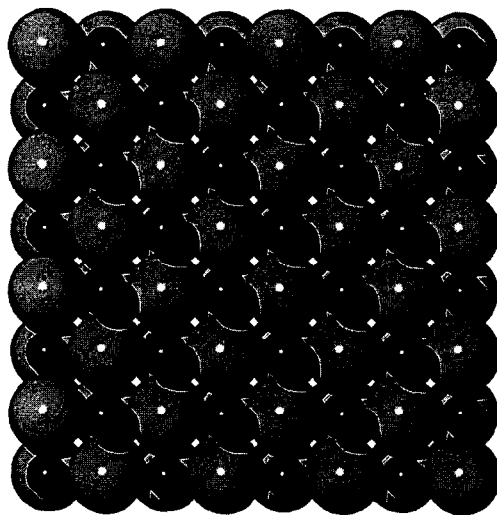


Fig. 9. Structure of monolayer of CO on NaCl(100) simulated by 18 CO on a $(8 \times 8 \times 3)$ $\text{Na}_{96}\text{Cl}_{96}$ cluster.

quite large with 3.98 \AA , this lateral interaction is quite small. One explanation is therefore that the relative magnitudes of the attraction at an Na site on the one hand and the lateral repulsion on the other hand are not correctly reproduced by the SINDO1 method. Another explanation is also that the island of 18 CO molecules (Fig. 9) has 10 outer molecules which have a larger tendency for vertical orientation due to incomplete environment.

The calculated adsorption energy was 6.3 kcal/mol compared to 4.4 kcal/mol from experiments [32,33]. The reduction of the adsorption energy of 6.6 kcal/mol from the submonolayer to 6.3 kcal/mol for the monolayer can be explained mainly by the different adsorption sites, to a lesser extent by lateral repulsion. The latter agrees with the experimental finding that the growth of the monolayer is not by islands, but statistically [34].

3.2. CO / $\text{MgO}(100)$

The submonolayer adsorption was again studied with a single molecule on a $(5 \times 5 \times 4)$ $\text{Mg}_{50}\text{O}_{50}$ cluster (Fig. 10). The optimized Mg–O distance was 2.021 Å. The CO molecule was placed on top of the central Mg atom and

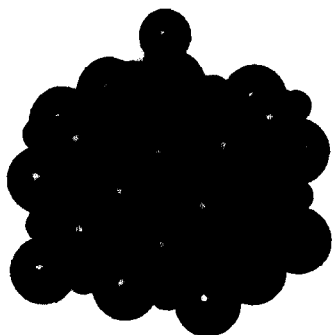


Fig. 10. Structure of submonolayer of CO on MgO(100) simulated by a single CO on a $(5 \times 5 \times 4)$ $\text{Mg}_{50}\text{O}_{50}$ cluster.

optimized for the two ways of adsorption. Again the C adsorption is favored with $E_{\text{ad}} = 8.1$ kcal/mol compared to $E_{\text{ad}} = 5.2$ kcal/mol. In both cases the CO is found perpendicular to the surface. We have used the previously described scaling procedure [31] for the calculation of the frequency shift. We find blue shift of 11 cm^{-1} for C adsorption and a red shift of 26 cm^{-1} for O adsorption. Such a shift was observed before with a DFT $X\alpha$ calculation [35]. It corresponds to the shift for adsorption on NaCl. An explanation can be given on the basis of electrostatic effects [36,37]. It is simply the interaction of the positive charge of the Mg or Na atom with the dipole of the CO molecule which causes the shift, blue or red depending on the orientation of the dipole. A more detailed comparison with ab initio and density functional calculations can be found elsewhere [38].

Monolayer adsorption was studied extensively. A (4×2) overlayer structure was found with LEED at 39 K and a (3×2) structure at 45 K [28]. FTIR [39] and HAS [40] experiments deduce a $c(4 \times 2)$ structure with 6 CO molecules which have three different orientations. The most recently determined experimental adsorption energy is about 10 kcal/mol [41]. We tried several arrangements of overlayer structures: a $(\sqrt{2} \times \sqrt{2})R 45^\circ$ structure with coverage 0.5, a (4×2) structure with coverage 0.75, and a (1×1) and (2×1) structure with coverage 1. In the first case only half of Mg sites are adsorption places for CO molecules, in the second case

three quarters and only in the third and fourth case each Mg was used for adsorption. The simulation was done with a $(10 \times 10 \times 3)$ $\text{Mg}_{150}\text{O}_{150}$ cluster which was covered with 16, 24, 32 and 32 CO molecules, respectively. In the first case the distances between the CO molecules are quite large and the lateral interaction is negligible. Due to the increased cluster size as mentioned in Section 2.1 and noncentral adsorption sites, there is a slight increase in adsorption energy per molecule to 8.6 kcal/mol compared to the 8.1 kcal/mol for a single CO on the $(5 \times 5 \times 4)$ $\text{Mg}_{50}\text{O}_{50}$ cluster. In the second case (Fig. 11) the adsorption energy is 7.3 kcal/mol which drops to 4.9 and 5.0 kcal/mol in the third and fourth case, respectively. It is now important to realize that these numbers have to be scaled with the coverage, since the gain in energy for the stabilization of a whole layer depends on the number of molecules per unit area. Here the (4×2) structure is favored with 5.5 kcal/mol over the $(\sqrt{2} \times \sqrt{2})R 45^\circ$ structure with 4.3 kcal/mol. Since the coverage for the other two cases is 1, the numbers remain 4.9 and 5.0 kcal/mol. The most stable arrangement is therefore the (4×2) structure in agreement with experiments. After completion of this work we became aware of periodic Hartree–Fock calculation [42] where an overlayer struc-

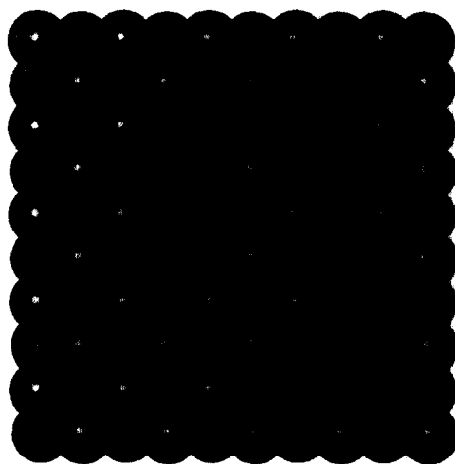


Fig. 11. Structure of monolayer of CO on MgO(100) simulated by 24 CO on a $(10 \times 10 \times 3)$ $\text{Mg}_{150}\text{O}_{150}$ cluster.

ture with two different CO orientations, a perpendicular and a bridging orientation, was presented. The adsorption energy was found to be in the order of 1–2 kcal/mol. A similarly low adsorption energy was predicted with ab initio calculations for embedded cluster model of MgO_5^{3-} [43].

4. H_2O adsorption

4.1. $\text{H}_2\text{O} / \text{NaCl}$

The H_2O adsorption on NaCl is more complicated than the previous cases, because the bent structure of H_2O allows more possibilities for binding. We have optimized a single H_2O molecule again on a $(9 \times 9 \times 2)$ $\text{Na}_{81}\text{Cl}_{81}$ cluster. The optimized structure is given in Fig. 12. The O–Na distance is 2.39 Å and the angle ϑ between the H_2O and the surface is 38° . The adsorption energy is 8.3 kcal/mol. The adsorption takes place mainly through the electrostatic interaction between the O atom of H_2O and a surface Na atom.

The monolayer coverage was experimentally studied by FTIR [44], LEED [45,46] and HAS

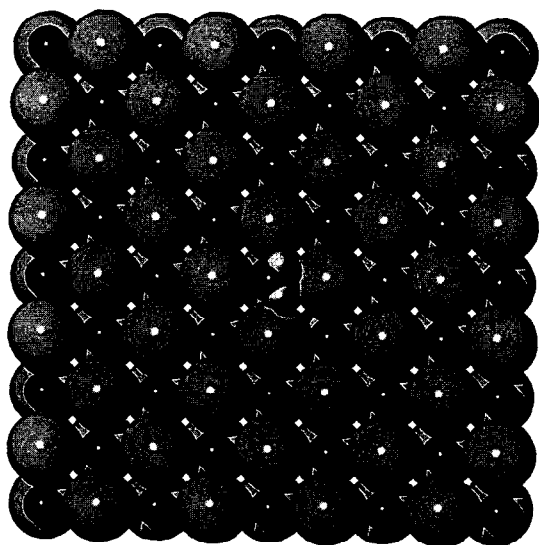


Fig. 12. Structure of submonolayer of H_2O on NaCl(100) simulated by a single H_2O on a $(9 \times 9 \times 2)$ $\text{Na}_{81}\text{Cl}_{81}$ cluster.

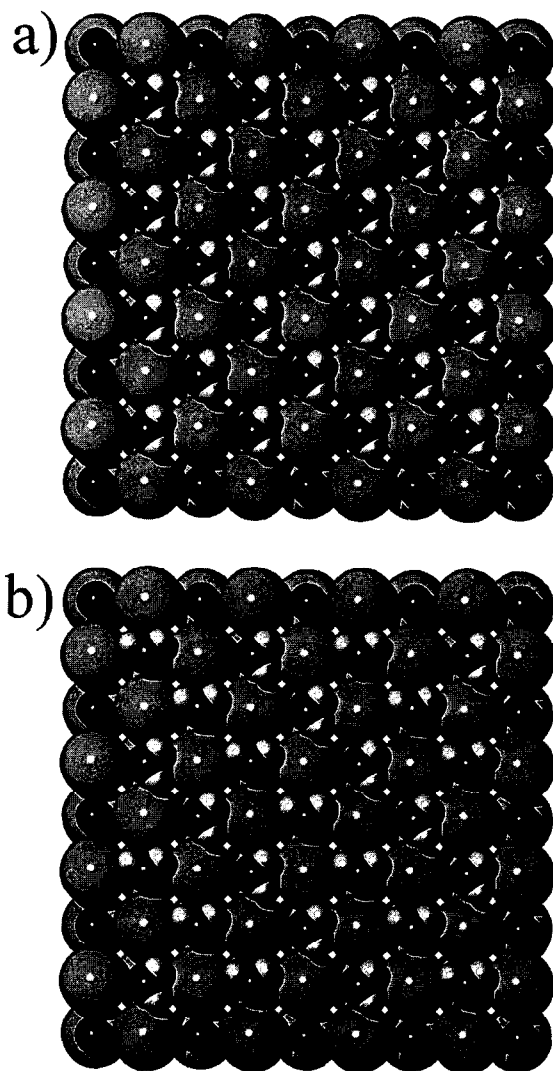


Fig. 13. Structure of monolayer of H_2O on NaCl(100) simulated by 25 H_2O on a $(9 \times 9 \times 2)$ $\text{Na}_{81}\text{Cl}_{81}$ cluster, (a) (1×1) , (b) (2×1) overlayer structure.

[47]. Whereas the LEED experiments predict a $c(4 \times 2)$ overlayer structure, the HAS experiments show a (1×1) structure. The isosteric heat of adsorption was 15.6 kcal/mol in the first case and 13.9–15.1 kcal/mol in the second case. We used again the $(9 \times 9 \times 2)$ $\text{Na}_{81}\text{Cl}_{81}$ cluster and covered it with 25 H_2O in (1×1) and (2×1) overlayer structures. The adsorbate structures are shown in Fig. 13. We can include hydrogen bonding by a special feature [48] incorporated into SINDO1. Hydrogen bonding has

some influence on the orientation, but its effect is again negligible for the adsorption energy which is 7.3 kcal/mol for both overlayer structures. The reduced adsorption is due partially to outer adsorption sites and partially to lateral interaction between the H_2O molecules. A more detailed analysis of structural and energetic data can be found elsewhere [49].

4.2. $\text{H}_2\text{O}/\text{MgO}$

For the submonolayer adsorption of H_2O on MgO we used the $(9 \times 9 \times 2)$ $\text{Mg}_{81}\text{O}_{81}$ cluster. The optimized system from SINDO1 calculations under inclusion of hydrogen bonding is shown in Fig. 14. Here hydrogen bonding from one H atom of H_2O to an O atom of the surface is substantial. This can be explained with the highly negative charge on the O atom of the surface. For the OH^- bound to H_2O the hydrogen bonding was estimated at about 28.5 kcal/mol [50]. The adsorption energy is 25.0 kcal/mol. The O atom of H_2O binds as expected to an Mg atom of the surface. The O–Mg distance is 2.08 Å and the angle ϑ between H_2O and the surface is -20° . This means that the hydrogens are closer to the surface than the oxygen.

For the monolayer experimental data from FTIR are again available [51]. A (4×2) overlayer structure is predicted. We investigated a (1×1) , a (2×1) and the (4×2) overlayer

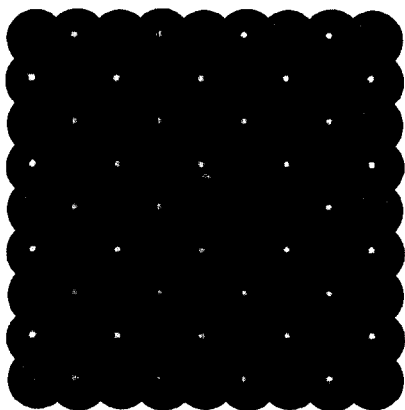


Fig. 14. Structure of submonolayer of H_2O on $\text{MgO}(100)$ simulated by a single H_2O on a $(9 \times 9 \times 2)$ $\text{Mg}_{81}\text{O}_{81}$ cluster.

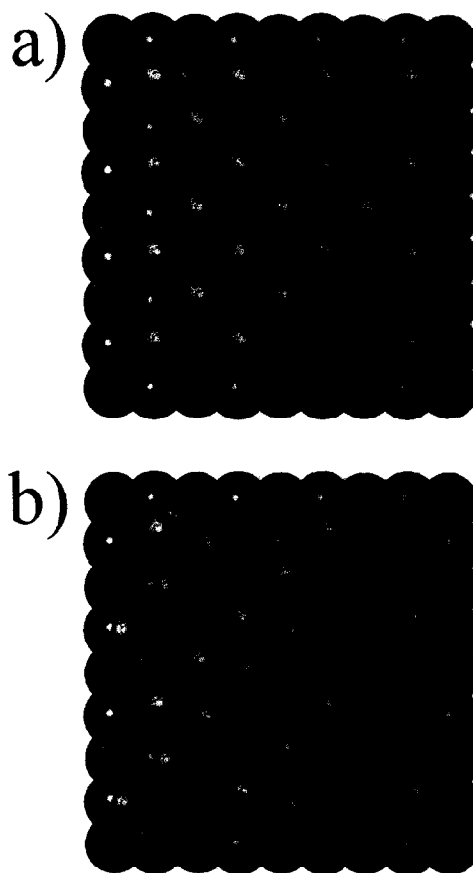


Fig. 15. Structure of monolayer of H_2O on $\text{MgO}(100)$ simulated by 25 H_2O on a $(9 \times 9 \times 2)$ $\text{Mg}_{81}\text{O}_{81}$ cluster. (a) (1×1) , (b) (2×1) overlayer structure.

structure with SINDO1. In all three cases the calculated adsorption energy was almost the same with 18.7, 18.5, and 18.5 kcal/mol, respectively. We show the most stable structures in Fig. 15. There are two kinds of adsorbed water molecules. In the first case one hydrogen is closer to the surface than the oxygen, in the other case both hydrogens are closer to the surface than the oxygen. Different from the situation of H_2O on NaCl where some rotational motion of the H_2O molecules about a vertical axis is possible, the H_2O molecules are well ordered on the surface. Rotation faces a substantial barrier. Again there is hydrogen bonding to the surface. The border effects of the cluster atoms at edges and corners must be removed before a final assessment.

5. Conclusion

We have shown that the SINDO1 method provides a suitable approach to adsorption studies at ion crystal surfaces. Clusters of sufficient surface and layer size can be conveniently used for surface and bulk simulation. It was found that the adsorption of single atoms representing the submonolayer situation is similar for NaCl and MgO except when hydrogen bonding is important as in H₂O on MgO. It could be seen that the larger lattice distance in NaCl compared to MgO is the major reason for the differences in monolayer coverage. The coverage with CO₂ is lower for MgO compared to NaCl in order to avoid sterical hindrance. This leads to reduced lateral interaction and in consequence to a different orientation of the CO₂ molecules on the surface. A similar consideration holds for CO adsorption. The preferred adsorption structure for MgO has a lesser coverage than for NaCl in order to avoid lateral repulsion. For NaCl the lateral interaction is so small that the tilting of molecules predicted from experiment could not be reproduced with SINDO1 calculations. For H₂O adsorption there is no hydrogen bonding, but free rotation on NaCl, whereas this is not the case on MgO.

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