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Calculation of adsorption and interaction mechanisms of O_2 and CO_2 molecules on $BaTiO_3$ surface

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The paper presents the results of quantum chemical calculations using the extended Huckel method for adsorption of O_2 and CO molecules on $BaTiO_3$ surface. It is shown that on (001) surface, the physical adsorption is dominant, whereas on (002) surface the chemical adsorption prevails, the Ti ions being the most active adsorption centres. The possible dissociation mechanisms of the adsorbed oxygen molecule and a heterogeneous oxidation reaction of CO in CO_2 are considered.

Key words: *surface, electron density, semiempirical quantum chemical methods and calculations, adatoms, clusters, barium titanate $BaTiO_3$*

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1. Introduction

We have carried out the calculations for interaction of the adsorbate molecules with every surface point of clusters simulating the surface of $BaTiO_3$ crystal; and have built the energy surfaces corresponding to potential energy minimum of a complex “adsorbed molecule+cluster” ($E_{\mathrm{ads}} = E_{\mathrm{min}} - E_{\infty}$).

The calculations were carried out using the Extended Huckel method (EHM) which takes into account only the electronic interaction energy. Here, a base program “Paramol-1” updated by us was used [1]. Earlier we had used this method to calculate the adsorption of oxygen O_2 and hydrogen H_2 on small clusters of $BaTiO_3$. We have also accounted for the interaction of thermal sputtering vapour components with the substrate surface in deposition and formation process of compound films [2–4]. The modified EHM was used in [5] to calculate the geometry of polyatomic molecules. The use of large clusters resulted in a considerable decrease of the “edge” effects on the character of interaction of an adsorbed molecule with the adsorption centre. When choosing the clusters of $BaTiO_3$ single crystal surface, the shifts of ferroelectric and surface atoms were taken into account [6,7]. While calculating the adsorption, the orientation of the adsorbate molecules relative to the adsorbent surface is to be taken into account. In case of adsorption of a two-atomic molecule O_2 and CO we have considered two basic orientations: a) a molecule axis is parallel to the adsorbent surface plane (s-type orientation adsorption); b) a molecule axis is normal to the adsorbent surface (c-type orientation adsorption). There are two possible orientations for CO molecule: by oxygen or carbon atoms towards the surface (the adsorption centre). The similar calculations for MgO and SnO_2 surfaces, accomplished *ab initio* like in the Hartree-Fock approximation, are presented in papers [8,9].

The "TiO_2" surface layer of $BaTiO_3$ single crystal with TiO_2 adsorbing plane (a crystallographic plane $(00\frac{1}{2})$ was modelled by a cluster of 32 atoms: 16 atoms of TiO_2 plane, 13 atoms of an underlying BaO plane, two O atoms and Ba atom of still more underlying planes for symmetry and electroneutrality of the cluster (106 valence electronic orbitals). The second cluster with BaO adsorbing plane consisted of 48 atoms: 18 Ba atoms, 26 O atoms and 4 Ti atoms (146 valence electronic orbitals). The coordinate axes X and Y are in the plane of the cluster surface and Z axis is normal to it coinciding with C axis of the crystal.

The calculations have shown the "BaO" cluster surface to be poorly active for adsorption; here the physical adsorption of O_2 and CO molecules dominates, which weakly influences the electric and physical properties of $BaTiO_3$ single crystal and the strongest electronic density redistribution takes place at adsorption on "TiO_2" surface. Therefore, we present the results of the calculations of the interaction of the adsorbed molecules with various points of "TiO_2" plane of $BaTiO_3$ adsorber as well as the possibility of O_2 dissociation and a heterogeneous oxidation reaction of CO in CO_2.

2. Theoretical analysis

2.1. Adsorption of O_2 and CO on the atomically pure surface

Figure 1 shows the minimum interaction energy surface of O_2 adsorbed molecule (c-type) with the "TiO_2" cluster surface and the surface of the corresponding minimum distances $R_{\min}$. It is obvious that $E_{\min}$ and $R_{\min}$ sharply decrease in the vicinity of Ti atoms, changing slightly above the interstitial sites and oxygen atoms of the cluster. The potential wells in the vicinity of Ti are practically of a conic form. The potential energy $E_{\min}$ sharply increases moving away for over 0.05 nm from Ti atom along X and Y axes that testifies to a distinct direction of binding O_2 absorbed molecule and Ti atom of the cluster.

We have also carried out similar calculations for O_2 s-type adsorption and CO adsorption on the atomically pure plane of the "TiO_2" cluster. The values of binding energies of the adsorbed molecules with the cluster ($E_{\text{bind}}s = |E_{\text{ads}}|$) and their corresponding equilibrium distances from the surface adsorption centre are given in table 1.

The comparison of the data in figure 1 and in table 1 shows that the most energetically favourable adsorption centres for O_2 and CO molecules on the "TiO_2"

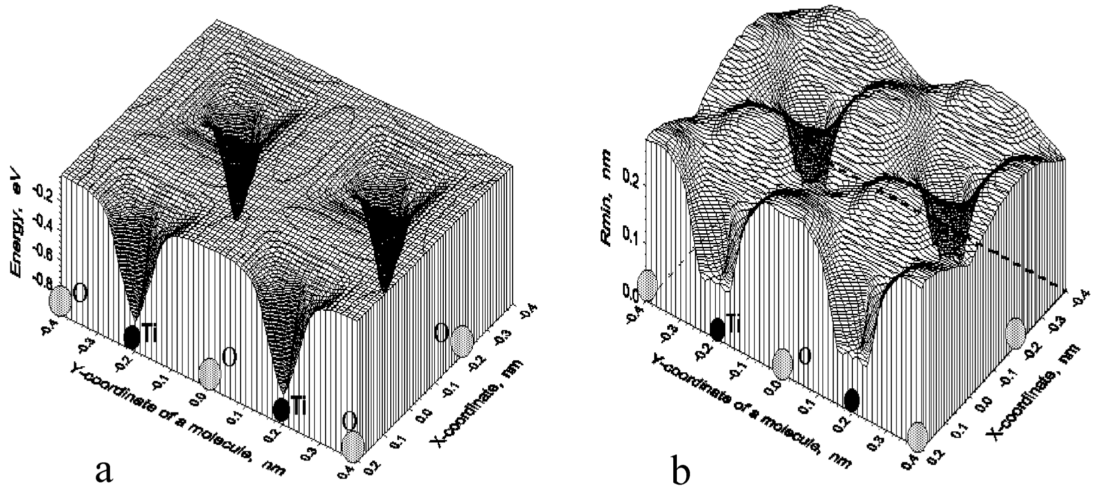

Figure 1. The minimum potential energy surfaces and the corresponding minimum distances ($R_{\min}$) at the interaction of O_2 molecule (c-type orientation) with the atomic pure surface of the "TiO_2" cluster of $BaTiO_3$ single crystal. (In figure the coordinates of Ti atoms are $X, Y = \pm 0.2$ nm).

cluster surface are Ti atoms with c-type adsorption geometry and for CO molecules – by the oxygen downward (closer to Ti atom). The most pronounced redistribution of the electron density both inside adsorbate molecules and between the adsorbed ones takes place and the surface also corresponds to this localization geometry (table 2) [10]. Below, a possibility of dissociation of O_2 molecule bound with Ti atom is considered.

The dissociation of O_2 molecule along Z-coordinate after a c-type adsorption on Ti ($R_{\text{ads}} = 0.1$ nm) has been considered: one of the molecule atoms (O2) moves away from the other (O1, localized above Ti) in the direction normal to the surface; O1 in its turn changes the position above the surface reaching the potential energy mini-

Table 1. The energy (in eV) and length (in nm) of the adsorbed molecules bond on the most energetically favourable localization centres of "TiO_2" surface for $BaTiO_3$ single crystal.

Locali-zation centre	O_2 molecule adsorption				CO molecule adsorption					
	s-type		c-type		s-type		c-type O downward		c-type C-downward	
	E_{ads}	R_{ads}	E_{ads}	R_{ads}	E_{ads}	R_{ads}	E_{ads}	R_{ads}	E_{ads}	R_{ads}
Ti	–0.25	0.21	–0.77	0.10	–0.29	0.22	–0.65	0.14	–0.28	0.16
O	–0.09	0.26	–0.03	0.28	–0.12	0.25	–0.04	0.29	–0.02	0.32
M	–0.06	0.24	–0.04	0.24	–0.06	0.25	–0.05	0.23	–0.04	0.29

Table 2. Charges Q (in electron charge units, e) of localization centres and the atoms of molecules adsorbed on a "pure" "TiO_2" surface of $BaTiO_3$ crystal.

O_2 adsorption			CO adsorption, c-type				CO adsorption, s-type		
Atom	c-type	s-type	Atom	O-downward	C-downward	C-downward	Charge	Atom	Charge
Ti	+3.61	+3.880	Ti	+3.75	+3.74	interstitial site	+3.86	O_{lat}	–1.93
O1	+0.27	–0.014	C	+0.43	+0.56	+0.448	+0.45	C	+0.46
O2	–0.15	–0.014	O	–0.30	–0.49	–0.441	–0.45	O	–0.46
O_2	+0.12	–0.028	CO	+0.13	+0.07	+0.007	–0.04	CO	0.006
Charges before the adsorption: $Q(O_{\mathrm{lat}}) = -1.943$, $Q(CO) = 0(\pm 0.441)$									

mum of the adsorption complex. The surface of minimum energies in Z-coordinates of O1 and O2 atoms was calculated. It was obtained that if O2 atom moves away from the surface, O1 atom approaches the surface, the depth of a dissociation potential well decreases approximately from 2.4 eV (note that the dissociation energy of O_2 isolated molecule is equal to 4 eV) to ≈ 1.6 eV, and $R_{\mathrm{bond}}(\mathrm{O1}) = 0.05$–$0.06$ nm (above Ti). If we take into account the energy equal to about 1 eV that can be liberated during adsorption and given to the molecule, then the additional dissociation energy becomes equal to 0.6–0.7 eV. This is much less compared to the isolated molecule dissociation, but total energy of the adsorption complex after desorption of O2 becomes larger (+0.3 eV) than before the interaction of O_2 with the surface.

According to EHM evaluations, the O1 atom becomes almost neutral (its charge is +0.2e and just −0.2e goes to Ti), and the desorbed O2 becomes doubly charged (it is given −0.5e from each of the four nearest O^{2-} ions of the TiO_2 surface) due to the closeness to Ti and due to strong overlap of the electron orbitals. The formation and desorption of such an ion are hardly possible. Therefore, we have also studied some other possible ways of O_2 dissociation.

At the O_2 absorption of s-type above Ti atom or above O_{lat} oxygen atom of the cluster by O1 and O2 orientation in the direction of Ti atoms, the O_2 dissociation also becomes possible without the desorption of oxygen atom but with the localization of O1 and O2 atoms in a form of O^- ions in the vicinity of O_{lat} (the free migration radius of O_{ad} above the atoms along the surface equals about 0.1 nm, $R_{\mathrm{ads}} \approx 0.16$ nm, $E_{\mathrm{bond}} = 0.4$ eV, $Q = -1$e – figure 2) or, in the second case, approximately above the centre of the O–Ti bonds along the O–Ti–O line (see Y-coordinate in figure 2) at the height $R_{\mathrm{ads}} \approx 0.1$ nm ($E_{\mathrm{bond}} = 1.1$ eV, $Q = -0.85$e). In both cases the energy barrier height equals $\approx$1 eV and with the account of the adsorption energy (see table 1) for the O_2 dissociation, an energy of $E_{\mathrm{dis}} \approx 0.7$–$0.8$ eV is needed. The O_{ad} atom is charged by O_{lat} electrons. In the first case O_{ad}–O_{lat} bond is like O_2 with −2e charge, and in the second case a complex O1–O_{lat}–O2 (or O1–Ti–O2) is formed with a geometry similar to the water molecule H_2O (H–O–H). After dissociation, the energy E_{min} of "O–O-cluster" adsorption complex decreases to −0.4 eV (after O1 and O2 bond formation with O_{lat}) or before dissociation -1.1 eV (after localization of O1 and O2 between Ti and O_{lat}).

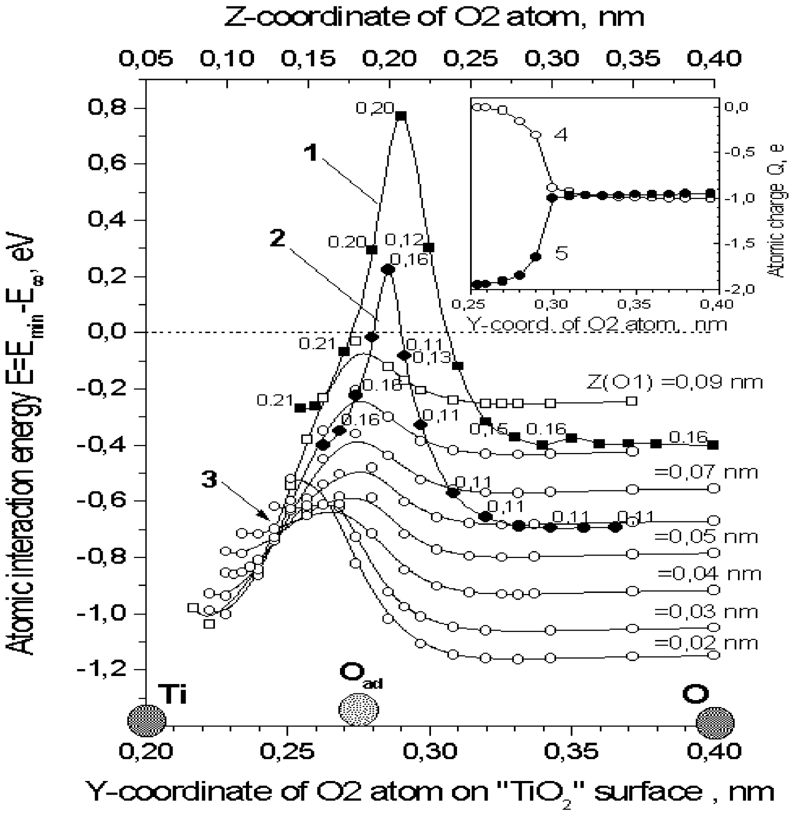

Figure 2. Potential curves of the interaction of O1 and O2 atoms of O_2 oxygen molecule with the cluster of "TiO_2" surface: 1) at O1–O2 molecule dissociation along the surface on Y coordinate after its s-type localization above Ti (the numbers near points show the height (z) of O1 and O2 atoms above the surface plane; 2) at O2 atom desorption (the upper axis of Z-coordinates, the numbers near • points show the height z above O of atom O1 that remained; 3) at O_2 desorption after the two atoms localization (O1 and O2) in O_{ad} position on both sides of Ti (curves series, Z-coordinates axis). 4,5) the behavior of oxygen atoms charge of O_2 molecule (4) and the oxygen atom of the O_{lat} lattice (5) which is approached by the molecule O2 atom in the process of its dissociation (see "1").

After O_2 dissociation of s-type the activation desorption of one of the two oxygen ions can take place. Consequently, a free O^{2-} ion is formed and bound with the nearly neutral surface oxygen atom O_{ad}. If O1 and O2 ions were situated in the vicinity of their neighbouring O_{lat}, then one of them, getting about 0.65 eV, would be desorbed and the other one as a result of a charge loss, would be bound to the surface atom O^{2-} ($R_{ads} = 0.11$ nm, total energy drop of "molecule-cluster" system $E_{min} = -0.7$ eV). If O1 and O2 ions are definitely localized on Ti–O bond, then for desorption of O_2, for example, 0.4–0.5 eV are needed with the simultaneous shift of O1 closer to Ti–O bond centre and decrease in height to $R_{ads} \approx 0.01$ nm, and the system energy decreases to $E_{min} = -1.5$ eV. Thus, we see that if in the first

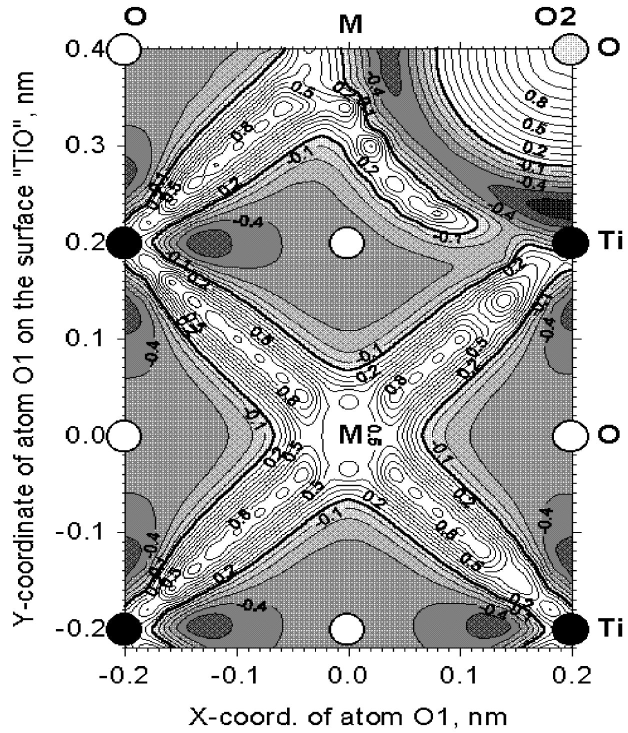

Figure 3. The chart of isoenergies migration levels of a dissociated oxygen atom (O1) along the "TiO_2" cluster of $BaTiO_3$ surface. The second atom (O2) of O_2 molecule after its dissociation is localized above the O_{lat} atom of the surface. The region of negative energies are shadowed. M – interstitial site.

case the desorption barrier exceeds "zero" energy E_∞ by $\approx +0.3$ eV, then in the second case it does not. So, the desorption here is energetically more favourable. Both after the dissociation and the desorption of one of O_2 molecules for the atoms which remained O_{ad}, it becomes energetically favourable to localize above Ti–O_{lat} surface bond (figure 3, dark regions between Ti and O).

2.2. Adsorption of CO molecules at the presence of a chemosorbed oxygen on the surface

In practice, CO adsorption takes place on the surface that is already partially filled with molecules of other gases, in particular, oxygen molecules which have a large binding energy of *c*-type on Ti atoms (see figure 1 and table 1). Thus, we have calculated the potential interaction energy curves of CO molecules with adsorption centres O, Ti and M (interstitial site) of the "TiO_2" surface cluster of $BaTiO_3$ single crystal in the presence of O_2 *c*-type localized molecule on the neighbouring titanium atom at a distance of $R_{\min} = 0.11$ nm, showing the possibility of a direct localization of CO on the adsorbed molecule O_2.

For CO adsorption by *s*-type orientation on the partially oxidated TiO_2 plane, the potential energy minimum for the system "adsorbed molecule-cluster" is not reached. This energy minimum is attained only in case of *c*-type orientation – at CO

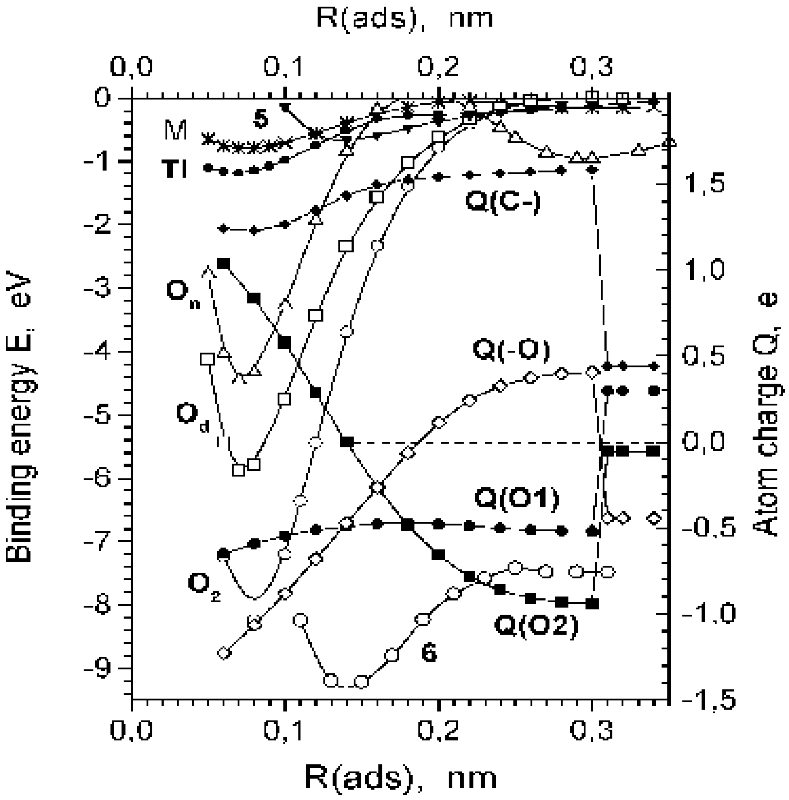

Figure 4. *c*-type adsorption of CO molecule by C atom to the surface on the adsorption centres (M, Ti, O_n, O_d) of "TiO_2" cluster of $BaTiO_3$ surface and on the oxygen (O_2) adsorbed on the surface, which is also *c*-type localized above the titanium atom (by O1 atom to Ti, $R_{\min}(O_2 - Ti) = 0.11$ nm); on the right ordinate the change in the charges of CO molecule atoms (Q(C−) and Q(−O)) and O_2 (Q(O1) and Q(O2) at CO approaching O_2 is shown; curve 5 – CO adsorption on Ti by O atom to titanium; curve 6 – CO_2 desorption (i.e. O2–CO) from the surface after the interaction of CO with O_2 (O1 oxygen atom remains bound with Ti).

localization on Ti the minimum is observed for both orientations of the adsorbed molecule, while for the rest of adsorption centres – only at CO orientation with carbon nearer to the surface. Thus, in the presence of an adsorbed oxygen on the surface, the energetically favourable is *c*-type adsorption of CO, which, however, has the opposite orientation in comparison with the adsorption on "TiO_2" "pure" surface. The results of these evaluations are given in figure 4. The curve of O_d is calculated for the case of CO localization on the surface oxygen atom distant from Ti atom with which O_2 molecule is *c*-type bound; the curve of O_n is calculated for the interaction of CO with the oxygen atom of lattice nearest to Ti atom. It is seen that the binding energy of CO with such an "unclean" surface increases almost 10 times. The strongest decrease in the potential energy of the "adsorbed molecule-cluster" system is observed at the interaction of CO with O_2 *c*-type molecule localized on Ti. Possible mechanisms of the oxidation of CO into CO_2 are presented below.

2.3. Low degree of the surface covering with the adsorbate molecules (O_2 and CO); a non-dissociative form of oxygen adsorption

Let CO molecule on Ti2 atom be adsorbed, then on the nearest neighbouring Ti1 atom O_2 molecule of c-type is localized. For such a succession, the energetically favourable is c-type of CO orientation with O atom to Ti ($E_{\mathrm{ads}} = -0.65$ eV, see table 1). In the opposite case more probable is CO localization with carbon atom to titanium (see figure 4, $E_{\mathrm{ads}} = -1.2$ eV), although the binding energy of opposite orientation is also large, approximately 0.7 eV (curve 5, figure 4). The oxygen atom of CO molecule is 0.14 nm away from Ti2 atom, R(C–O) = 0.11 nm, and O1 atom of O_2 adsorbed molecule is at a distance of 0.10 nm from Ti1. An equilibrium distance between O1–O2 of O_2 adsorbed molecule is equal to 0.16 nm (whereas far from the surface it is 0.12 nm). Thus, the O2 atom is 0.26 nm away from Ti1. The "extension" of O_2 molecule favours its dissociation. Along the coordinate Z, this leads to desorption of O2 atom with the activation energy of 0.7 eV. Along the coordinate Y (or X), the O2 atom migrates along the surface (figure 5) to CO molecule adsorbed on titanium with the formation along the axis Z (normal to the adsorbing plane) of Ti–O–C–O complex, i.e. CO_2 adsorbed molecule. It is seen that the system energy remains practically unchanged with quite large (± 0.11 nm) distances of O2 atom from a geometric centre above Ti1 atom, and permits it to approach CO "without difficulty". To form CO_2 adsorbed molecule (Ti2–O–C–O2) O2 atom needs to overcome a potential barrier about 0.6 eV high which is followed by an energy well, 8 eV deep (i.e. the reaction of oxidation of CO into CO_2). However, the bond of CO_2 with Ti is comparatively weak, $E_{\mathrm{bond}} \approx 0.4$ eV.

2.4. Adsorption of CO with dissociative adsorption of oxygen on the "TiO_2" cluster surface

As stated above, O_2 adsorbed molecule after having received additional energy of 0.6–0.8 eV in the process of adsorption, can dissociate with localization of O_{ad} on Ti or approximately above the binding line centre of the surface atoms Ti and O at a distance of 0.09 nm from the surface. The second case of dissociation process is energetically more probable. For this geometry of O_{ad}, the calculations of CO interaction with the surface show that the potential energy minimum is observed neither at CO localization in the interstitial sites nor at s-type orientation on titanium or oxygen atoms. The energy minimum is attained only for c-type CO localization on O and Ti atoms of the surface, CO adsorption being of an activation character: at the adsorption on the lattice oxygen, the barrier height is the largest (≈ 1.8 eV), and on Ti atom it is the smallest (≈ 1 eV). In the latter case, an interesting effect was found: after c-type CO localization on Ti at a distance $R_{\mathrm{bond}} = 0.17$ nm, corresponding to $E_{\mathrm{min}} \approx -1.8$ eV, the movement of the adsorbed molecule becomes energetically favourable. It is almost parallel to the Ti–O_{lat} surface in the direction towards the atomically adsorbed ion of O_{ad} oxygen at the height $R_{\mathrm{ads}} = 0.09$ nm above the "TiO_2" surface and thus forms CO_2. The total energy drop of the system is 3.7 eV. After having overcome a somewhat higher barrier (≈ 1.5 eV) CO molecule

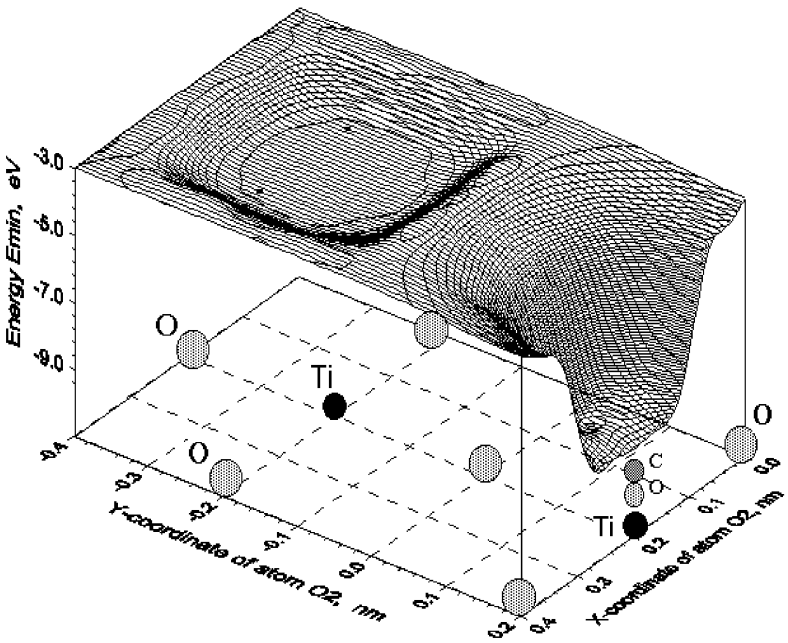

Figure 5. The minimum energy surface at dissociative movement above the "TiO_2" surface of $BaTiO_3$ crystal of O2 atom of O_2 oxygen molecule *c*-type localized above the Ti atom to CO molecule which is also *c*-type bound with the neighboring Ti atom (with O atom to Ti).

can also be localized directly above O_{ad} with $R_{bond} \approx 0.08$ nm ($E_{min} \approx -3.7$ eV). In both cases, the desorption of CO_2 molecule being formed is energetically favourable.

2.5. CO adsorption at a high coverage of the "TiO_2" surface with oxygen molecules

In such a case, a molecular form of *c*-type oxygen absorption on Ti atoms prevails (Ti–O1–O2). Energetically more favourable localization centre of CO is the O2 atom of *c*-type adsorbed oxygen (i.e. O_2 adsorbed molecule) with CO_2 molecule formation (O2–C–O, curve "O_2" in figure 4). As it is seen from the curve 6 of the same figure, the simulation of a detachment of O–C–O2 molecule (i.e. CO_2) from Ti–O1 bond is accompanied by a further energy decrease of the system, and CO_2 molecule can either stay on the surface being localized above Ti–O1 bond with $R_{ads} = 0.14$ nm and the energy decreases in the system additionally by 1 eV (total energy drop is 9.1 eV), or desorbs having overcome the potential barrier of 2 eV, which is considerably less than total energy drop due to CO molecule adsorption and its subsequent oxidation to CO_2.

3. Conclusion

To explain the experimental data concerning the effect of the adsorption on electrical and physical properties of the solid states, it is important to know the charge

Table 3. The charges (in e units) of atoms O_2 and CO molecules in the process of CO_2 desorption (figure 4, curve 6) from the surface of "TiO_2" cluster of $BaTiO_3$ crystal.

R, nm	Ti	O1	O_{lat}	O2	C	O	CO_2
0.110	3.457	–0.592	–1.950	0.834	1.228	–1.064	0.998
0.130	3.507	–0.662	–1.951	0.691	1.306	–0.979	1.018
0.150	3.526	–0.669	–1.951	0.531	1.360	–0.884	1.007
0.170	3.534	–0.661	–1.949	0.346	1.400	–0.761	0.985
0.190	3.539	–0.686	–1.941	0.149	1.429	–0.603	0.975
0.210	3.545	–0.742	–1.910	–0.060	1.446	–0.446	0.941
0.230	3.552	–0.826	–1.841	–0.176	1.448	–0.399	0.873
0.250	3.606	–0.854	–1.670	–0.650	1.402	–0.666	0.086
0.270	3.611	–0.847	–1.686	–0.697	1.397	–0.698	0.002
0.310	3.611	–0.846	–1.685	–0.698	1.398	–0.699	0.001

distribution in the system "adsorbed molecule-adsorbent". For the atomically pure "TiO_2" surface of $BaTiO_3$ crystal, c-type geometry adsorption on Ti atoms is the most energetically favourable for O_2 and CO molecules. A more obvious redistribution of the charges also corresponds to this geometry of adsorption (table 2).

1. It was obtained for a c-type absorption of O_2 in the interstitial site, that approaching $E_{\min}$ ($R_{\min} = 0.24$ nm), the charge of a molecule is practically unchanged, and only a slight charge redistribution between the atoms of the molecule itself takes place. If an oxygen is c-type localized on Ti ($R_{\min} = 0.1$ nm), then the charges of all the nearest neighbours in the cluster change evidently as well as does the electronic charge density on the atoms of the adsorbed molecules. However, the lack of free electrons in a cluster predetermines a weakly pronounced donor mechanism of O_2 adsorption on a "pure" "TiO_2" surface: the charge of -0.12 eV goes from O_2 on Ti, where the redistribution of electron density from the neighbouring oxygen atoms also takes place (-0.14e, i.e. approximately -0.035e from each of the four nearest surface atoms), decreasing titanium charge by 0.26e. The similar situation also takes place at CO absorption. Probably this explains a weak effect of O2 and CO adsorption on the electrical conductivity value of $BaTiO_3$ monocrystalline samples and their substantial effect on the spontaneous polarization value of the ferroelectric due to the appearance of the induced dipole moments of the adsorbed molecules [11].

2. Quite a different picture is obtained at CO adsorption on a "real" surface, when there is already an oxygen on it bound according to c-type on Ti atoms (see figure 4 and table 3, table 4). From the analysis of the calculation data it follows that: a) the charge of adsorbed molecules and surface atoms substantially changes in the process of adsorption and in many cases it does not

change monotonously (see, e.g., curves Q in figure 4); b) CO molecule changes its charge state depending on the localization centre; c) if on a pure ideal surface the molecular adsorption of CO and O_2 follows a weak donor mechanism separately, then at CO, appearing on the surface, a charge of ≈ -1.5 eV is localized on O_2 adsorbed molecule, i.e. an acceptor mechanism of molecular adsorption of O_2 appears.

3. It is possible to predict the change in the charge state of a "weakly oxidated" surface on the whole depending on its occupation with CO molecules. Initially, i.e. at a small surface occupation, the most probable is localization of CO on O_{lat} (figure 4). This causes a relocalization of the electron density from these atoms to O_2, forming a surface negatively charged layer, and O_{lat} and CO create, on the whole, a practically neutral adsorption pair O–CO, an external atom O of the adsorbed molecule CO having also the charge -1.1e (table 4). The occupation of the surface with the adsorption atoms will lead to the interaction of CO with O_2 and to the formation of CO_2. This causes the disappearance of a negative charge on O_2 and the appearance of a positive charge +1e on CO_2 (the total value with the centre O1 charge equals +0.34e). In case of its desorption, there remains an oxygen ion localized on Ti with a charge equal to -0.85e. As it is seen from the calculations, this charge passes to it from O_{lat} atoms surrounding the Ti. This should substantially effect the electrical conductivity of a crystal.

4. The calculations were carried out for a dielectric. Free electrons will be easily caught by the adsorbed molecules, – this should substantially effect the electrical conductivity of a crystal.

Table 4. The distribution of charges Q (in e units) between the atoms of adsorbed molecules O_2, CO, CO_2 and the TiO_2 layer atoms of the surface cluster of $BaTiO_3$ crystal after adsorption of CO on a surface "contaminated" with O_2 molecules.

CO ads. centre charge	R_{ads}, nm	C–	–O	CO	Ti_{lat}	O_{lat}	Ti below O_2	O1	O2	O_2
Ti: 3.94	0.07	+1.54	–0.22	+1.32	+3.87	–1.81	+3.33	–0.52	–0.95	–1.47
O: –0.23	0.07	+1.28	–1.10	+0.18	+3.92	–1.94	+3.33	–0.52	–0.95	–1.47
M	0.08	+1.56	–0.18	+1.38	+3.88	–1.80	+3.35	–0.52	–0.95	–1.47
O_2	0.08	+1.23	–1.06	+0.17	+3.87	–1.94	+3.46	–0.59	+0.83	+0.24
–	∞	+0.44	–0.44	0.00	+3.87	–1.94	+3.56	0.30	–0.06	+0.24
CO_2 on O1:	0.14	+1.36	–0.88	CO_2 +1.01	+3.87	–1.94	+3.53	–0.67	+0.53	–
CO_2 on ∞		+1.40	–0.70	0.00	+3.87	–1.94	+3.61	–0.85	–0.70	

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Розрахунок механізму адсорбції і взаємодії молекул O_2 і CO_2 на поверхні $BaTiO_3$

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У роботі наведено результати квантово-хімічних розрахунків розширеним методом Хюккеля адсорбції молекул O_2, CO_2, CO та атомів O і C на поверхні $BaTiO_3$. Показано, що на поверхні (001) переважає фізична адсорбція, а на поверхні (002) – хімічна, причому найбільш активними центрами адсорбції є іони Ti. Розглянуті можливі механізми дисоціації адсорбованих молекул кисню і гетерогенної реакції окислення CO в CO_2.

Ключові слова: *поверхня, електронна густина, напівемпіричні квантово-хімічні методи та розрахунки, кластери, титанат барію $BaTiO_3$*

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