

# Simulation of water adsorption on a diamond (100) surface containing a vacancy defect

N.A. Lvova\*, O.Yu. Ananina\*\*

\*Federal State Budgetary Institution “Technological Institute for Superhard and Novel Carbon Materials”  
Troitsk, Moscow, Russia, nlvova@ntcstm.troitsk.ru

\*\*Zaporizhzhya National University, Physical Faculty, Zaporizhzhya, Ukraine, ananyina@znu.edu.ua

## ABSTRACT

The quantum-chemical calculations of chemisorption characteristics of water adsorption on the diamond C(100)-(2×1) surface with monovacancy are represented. The possible configurations of the surface with H<sub>2</sub>O molecules dissociation fragments are described. It is shown that the presence of monovacancies on the surface reduces the activation energy for water dissociative adsorption.

**Keywords:** the diamond surface, vacancy, water absorption

## 1 WATER MOLECULE ADSORPTION ON THE CLEAN ORDERED (100) SURFACE

In this paper we simulated a dissociative adsorption of a water molecule on a clean diamond surface. Calculations were made by the semiempirical method of modified neglect of differential overlap with a MOPAC2012 software package [1]. In the initial system state, the water molecule was located far from the cluster surface. The modeling of the water molecule adsorption on the C(100)-(2×1) clean surface resulted in a metastable state. In this state, the molecule, without losing its integrity, is chemisorbed on the surface, while the oxygen atom forms a chemical bond to a carbon atom of the surface dimer. The dimer C-C bond becomes single due to the water adsorption. The activation energy of the metastable state formation is 0.92 eV, the system energy in this state is by 0.61 eV higher than in the initial state. Next, from the metastable state we modeled a dissociative adsorption of a water molecule on two C-C carbon atoms belonging to the same dimer; it required the  $E_{ACT} = 0.2$  eV activation energy. With the accession of the -H hydrogen atom and the -OH radical to the surface, the system energy is reduced by 3.12 eV as compared to the initial state. Thus, the dissociative adsorption of water molecules from the initial state to the C(100)-(2×1) surface dimer passing through a metastable state requires a 1.12 eV activation energy. This value, as well as  $E_{ADS} = 3.12$  eV for the heat of the water molecule dissociative adsorption on the isolated dimer, is consistent with those obtained by *ab initio* calculations carried out in [2,3].

We also calculated the  $E_{ACT}^1$  activation energy of dissociative adsorption from the initial state of the system. On the ordered and clean C(100)-(2×1) surface,  $E_{ACT}^1 =$

1.07 eV, and that indicates a possibility of dissociative adsorption of water molecules on a single surface dimer bypassing the metastable state.

## 2 WATER MOLECULE ADSORPTION ON A (100) DIAMOND SURFACE WITH A VACANCY DEFECT

In the C(100)-(2×1) surface vacancy defect simulation in [4], we obtained a steady state of the defect, in which the remaining central dimer atom is located close to the situation on the non-reconstructed C(100)-(1×1) surface. Geometric characteristics of the defect are in qualitative agreement with the data in [5] which were calculated from first principles. Water adsorption on the C1 atom requires a 0.65 eV activation energy and leads to a metastable state formation, as shown in Figure 1a [6]. Addition of a water molecule leads to a change in the hybridization of orbitals localized on the C1 atom: from a close to  $sp^3$ - type (with two bonding orbitals, a filled nonbonding one, and one free orbital) to the type which is close to  $sp^2+p$  - with three bonding  $sp^2$ -orbitals and a high-energy  $p$ -orbital localized on C1. Oxygen in the water molecule exhibits an unusual for oxygen valence of 2.7. A positive charge of +0.166e is localized on it. However, in contrast to an ordered surface, a C1-O covalent bond formation leads to a reduction of the “surface-H<sub>2</sub>O” system total energy by 0.8 eV compared to the initial state.

After adsorption of water molecules on the C1 atom (Figure 1a), a further H<sub>2</sub>O→OH+H dissociation can go in four directions: a hydrogen atom can join one of the atoms of the neighboring C3-C4 (C7-C8) dimer; the second-layer C5 or C6 atoms; move to an atom of the neighboring C10 dimer series; and remain localized on the C1 atom (Figure 1e). Configuration 5 (Figure 1f) was obtained by the calculation of the water dissociative adsorption from the metastable state on the C8 atom. For each of the cases, we calculated the activation energy of adsorption  $E_{ACT}^2$  from the initial system state through a metastable state (Figure 1a), as well as the values of the activation energy of adsorption  $E_{ACT}^1$  from the initial system state bypassing the metastable state (Table 1). Calculations proved that  $E_{ACT}^1$  has similar values in all cases. It should be noted that in all cases, except for the -OH and -H localization on the C1 atom (configuration 4), the dissociative adsorption of water molecules on the cluster surface creates new potential

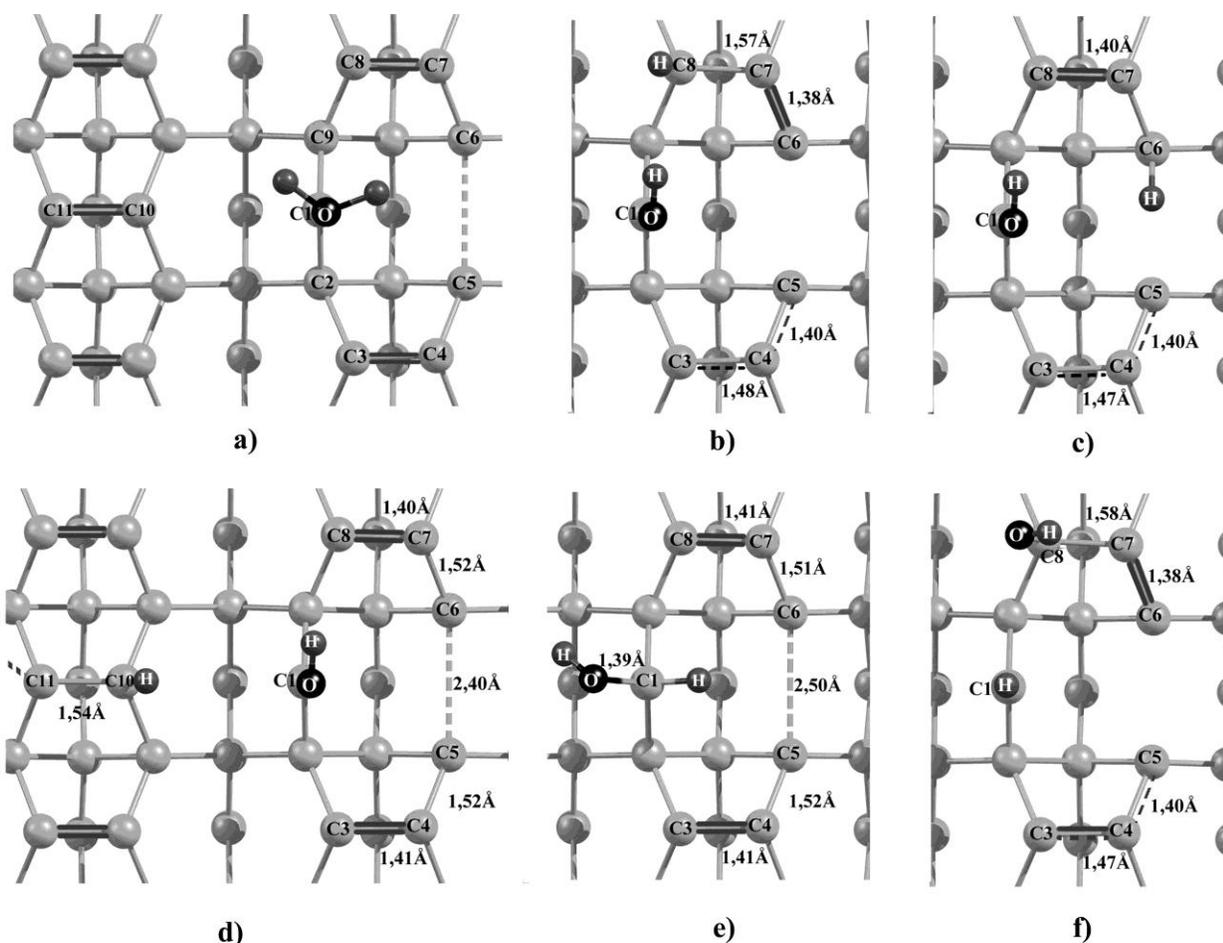


Figure 1. Result of the water molecule adsorption on the C(100)-(2x1) clean surface with vacancy defect. Numbers of atoms are -OH and -H adsorption centers, respectively: a) metastable state, b) C1-C8, configuration 1, c) C1-C6, configuration 2, d) C1-C12, configuration 3, e) C1-C1, configuration 4, f) C8-C1, configuration 5.

adsorption sites of the following molecule (Table 1) in addition to C1 atom which has its high-energy *p*-orbital mainly localized on C1 and slightly overlapped with the orbitals of the second-layer and the vacancy area atoms.

Thus, the presence of monovacancies on the surface reduces the activation energy of water molecules dissociative adsorption as compared to the ordered surface. For all stable configurations 1-5,  $E_{ACT}^1$  value is in the range

	C(100)- (2x1)	Defect, configuration				
		1	2	3	4	5
$E_{ACT}$ metastable state, eV	0.92	0.65				0.75
$E_{TOTAL}$ of configuration (in relation to configuration 1), eV		0	1.26	2.97	2.00	0.88
$E_{ACT}^1$ from initial state, eV	1.07	0.73	0.74	0.95	0.99	0.70
$E_{ACT}^2$ from metastable state, eV	0.20	1.38	1.18	1.26	1.49	0.24
$E_{ADS}$ per molecule, eV	3.12	4.68	3.42	1.70	2.68	3.80
Potential adsorption centers for the second water molecule	Surface dimer atoms	C1, C3, C5	C1, C5, C3	C1, C11	C3, C5, C6	C1, C3, C5

Table 1. Energy characteristics of the first water molecule dissociative adsorption for different carbon atoms of a vacancy area.

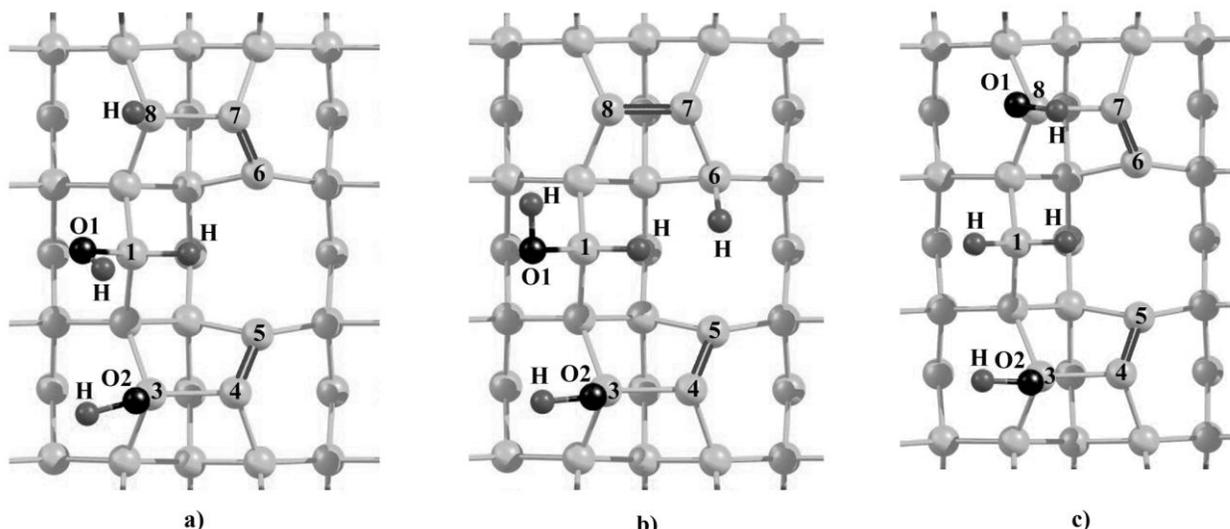


Figure 2. A fragment of a cluster with adsorbed dissociation fragments of the second molecule of water: the -OH group is chemisorbed on the C3 atom, -H – on the C1 surface atom a) in configuration 1; b) in configuration 2, 4, and c) in configuration 5.

of 0.70-0.99 eV, the heat of dissociative adsorption is from 1.70 to 4.68 eV. The lowest activation energy from the initial state is required by configurations 1 and 5 with a minimum total energy. Thus, the adsorption of dissociation fragments of the first water molecule will most likely lead to configurations 1 or 5. Water metastable state formation requires an activation energy  $E_{\text{AKT}}=0.65$  eV, somewhat smaller than in the case of dissociative adsorption from the initial state  $E_{\text{AKT}}^1 \geq 0.70$  eV. Perhaps, the C1 atom of the surface with a defect can be considered as a center of the water molecule “capture” which keeps the water in a molecular form on the surface.

### 3 THE SECOND WATER MOLECULE ADSORPTION ON A (100) DIAMOND SURFACE WITH A VACANCY DEFECT

Total energy analysis of the states of the (100) surface containing a vacancy defect with adsorbed fragments of the first water molecule dissociation, i.e. total energy analysis of the configurations 1-5, shows that the most energetically favorable configuration is 1. All other configurations have a total energy value by 0.88-2.97 eV greater than for configuration 1 (Table 1). In contrast to the (100) clean diamond surface with a vacancy defect

(Figure 1a), adsorption of the second molecule of water does not lead to any metastable states in which the entire molecule would get chemisorbed on the vacancy surface. For a clean surface with a vacancy defect, the adsorption center for a whole water molecule was the C1 atom having two dangling bonds. Adsorption of the whole water molecules to some other dimer atoms neighboring the vacancy led to unbound states. There are no such adsorption centers on the diamond surface in configurations 1-5. Calculation of the whole water molecule adsorption on the C3 - C8 atoms for configurations 1-5 shows the formation of some nonbinding states with a large total energy value for the “N – H<sub>2</sub>O configuration” system. Total energy of clusters in these states is by 0.12-1.52 eV higher than the sum of energy of non-interacting surfaces in the N configuration and a water molecule. However, these states can be considered as transition ones for the further dissociative adsorption of -OH and -H fragments on the adjacent carbon atoms.

Let us consider the second water molecule dissociative adsorption on the C(100) surface with a vacancy defect and adsorbed -OH and -H fragments of the first molecule of water, corresponding to configuration 1 (Figure 1b). Due to the adsorption, the second water molecule dissociation fragments (-OH and -H) can saturate the bonds

State, shown on:	$E_{\text{TOTAL}}$ (in relation to Figure 2c), eV	$E_{\text{ADS}}$ per molecule, eV	$E_{\text{ACT}}^1$ , eV
Figure 2a	0.42	2.92	1.10
Figure 2b	1.56	3.78(for configuration 4) 3.04 (for configuration 2)	1.04 1.09
Figure 2c	0	4.2	0.95

Table 2. Energy characteristics of the second water molecule dissociative adsorption on the C (100) surface with the vacancy defect.

of the surface atoms C1, C2, ... C11. We researched all the options (combinations) of -OH and -H radicals deposition. We calculated the optimal geometry of the obtained states, the surface electronic characteristics, total energies of clusters in the resulting states, the heat of dissociative adsorption for the second water molecule to the surface, and the activation energy of adsorption. The minimum value of the system total energy and the maximum value of the heat of adsorption (per water molecule) correspond to the state shown in Figure 2a.

For configuration 2, the dissociative adsorption of the second molecule of water led to a number of stable states. The lowest energy was found in the state where the -OH group is chemisorbed on the C3 atom, -H – on the C1 atom. The same state is achieved by calculating the adsorption of the second molecule of water on the configuration 4. The heat of adsorption of the second water molecule for the state shown in Figure 2b is 3.78 eV.

For configuration 5, the dissociative adsorption of the second water molecule leads to a state in which the heat of adsorption of a water molecule is maximal, and the total energy is minimal among all the states described above (Figure 2c):  $E_{\text{ADS}} = 4.2$  eV.

For all the options of -OH and -H radicals deposition on the configuration 1-5,  $E_{\text{ACT}}^1$  dissociative adsorption value is in the range of 0.95-1.33 eV. States in Figure 2 are chosen as the most probable after the adsorption of two water molecules. When choosing, we took into account the values of adsorption  $E_{\text{ACT}}^1$ , the total energy of the surface, and the heat of adsorption of the second water molecule to the surface (Table 2). The adsorption activation energy for the state shown in Figure 2c,  $E_{\text{ACT}}^1 = 0.95$  eV is by 0.12 eV lower than the adsorption activation energy on the ordered surface dimer. This suggests that the second water molecule adsorption happens mainly in the vacancy area.

All surface states described in Table 2, are characterized by the absence of dangling bonds (Figure 2). All the carbon atoms of the surface in the defect area have a valence 4, form 4 covalent bonds, resulting in a total surface energy decrease, in contrast to states with dangling bonds.

An increase in the total energy of the system during the -OH fragments adsorption on the C5, C6 second-layer atoms was common for all the initial surface configurations 1-5. Obviously, this led to an increase in the interatomic distances of the neighboring atoms and the emergence of mechanical stress in the lattice.

#### 4 THE THIRD WATER MOLECULE ADSORPTION ON A DIAMOND SURFACE WITH A VACANCY DEFECT

Analysis of potential adsorption centers of the third water molecule on the diamond surface with the vacancy defect (Figure 2) showed that these could be atoms in the vacancy forming a double bond to one another, C4-C5, C6-C7 (Figure 2a, c), C7-C8 (Figure 2b). Water adsorption can as well occur on the carbon atoms of the surface dimers.

We calculated the activation energy of dissociative adsorption for the third water molecule for all supposed adsorption centers.  $E_{\text{ACT}}^1$  adsorption value for the surface dimer remote from the vacancy is 1.07 eV; for C7-C8 atoms of a dimer neighboring the vacancy  $E_{\text{ACT}}^1 = 1.04$  eV (Figure 2b); for C6-C7 atoms (Figure 2a)  $E_{\text{ACT}}^1 = 1.02$  eV; for C6-C7 atoms (Figure 2c)  $E_{\text{ACT}}^1 = 1.00$  eV. In chemisorption of the third water molecules on atoms C6-C7 and C4-C5 the -OH fragments are saturated with atoms C7, C4 of the first surface layer, the H atoms are saturated with atoms C5, C6 of the second surface layer.

Thus, the dissociative chemisorption of the third water molecule will mainly occur on the carbon atoms in the vacancy forming a double bond between them. Only after all the carbon atoms surrounding the vacancy are bonded with the water dissociation fragments, the -OH and -H groups adsorption on the dimers of ordered surface can begin.

Complete saturation of the diamond surface by -OH and -H groups leads to a binding energy reduction in the bonds of adsorbed groups to carbon atoms.

## 5 CONCLUSION

The presence of vacancies on the surface reduces the activation energy of water molecules dissociative adsorption as compared to the ordered surface. When the first H<sub>2</sub>O molecule dissociation fragments add to the surface of the defect, there appear new potential centers for dissociative adsorption of the next water molecules. Thus, vacancies are an additional factor accelerating water molecules precipitation on the surface of the C(100)-(2×1). The C1 atom of the surface with a defect can be considered as a center of the water molecule “capture”, which keeps the water in a molecular form on the surface (Figure 1a). In addition, it can be regarded as a potential center of dihydride states formation on the diamond surface (Figure 2c).

This work was supported by the Ministry of Education and Science of Russian Federation within the framework of state contract No. 12.527.12.5003.

## REFERENCES

- [1] MOPAC2012, James J. P. Stewart, Stewart Computational Chemistry, Version 11.039W, <http://OpenMOPAC.net>.
- [2] Okamoto Y., Phys. Rev. B., V.58, P. 6760, 1998.
- [3] Manelli O., Corni S., Righi M.C. J. Phys. Chem. C., V.114, № 15, P. 7045, 2010.
- [4] Filicheva Yu.A., Lvova N.A., Ananina O.Yu., Fullerenes, Nanotubes, and Carbon Nanostructures. V. 20, № 04-07, P. 616, 2012.
- [5] Long R., Dai Y., Yu L., Jin H., Huang B., Applied Surface Science., V. 254. P. 6478, 2008.
- [6] Lvova N.A., Ananina O.Yu., Russian Journal of Physical Chemistry A, in print.