



# Interaction of Fluorine with Vacancy Defects of Graphene

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## Abstract

The results of quantum-chemical modeling of the interaction of F, FHF ions with mono- and divacancy defects in graphene are presented. The energy characteristics of chemisorption of fluorine from associates of ions with water molecules are determined. It is shown that vacancies influence the chemisorption parameters: the activation energy decreases, the heat of adsorption increases in comparison with the ordered graphene sheet. The dependence of the heat of chemisorption on the degree of coverage by fluorine is studied. The characteristics of the reaction of vacancy defects with F, FHF and hydronium ion are compared.

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## Introduction

The synthesis of graphene, the first two-dimensional material, and the study of the remarkable electronic properties of this promising structure, increased attention to carbon nanomaterials. Chemical modification of graphene is a promising method aimed at changing its electronic properties and creating on its basis quantum structures. Fluorine, along with hydrogen, is an element that converts graphene into a semiconductor material. The hydrogen and fluorine atoms adsorbed on graphene form covalent bonds with carbon atoms, and change the hybridization of their orbitals from  $sp^2$  to  $sp^3$ . By varying the shape of graphene sheets and the degree of coverage by fluorine, materials with a tunable non-zero forbidden band can be obtained, which means the possibility of using this material in nanoelectronics. Since the time of synthesis in 2010 [1,2], fluorographene is of great interest. The possibility of the existence of different types of hybridization of carbon atoms and the high value of electronegativity of fluorine, combined with a strong and flexible two-dimensional structure, makes fluorographene a promising interesting material. A unique combination of physical and chemical properties, as well as the possibility of changing them determine the future use of fluorography in various areas of high technology.

Recent studies have shown the possibility of the reaction of fluorination of graphene and low-layer graphene films in a 3-7% aqueous solution of hydrofluoric acid (HF) [3,4,5-7]. However, the atomic mechanism of interaction of particles contained in aqueous solutions of hydrofluoric acid, with point defects of graphene, remains unexplored. Defects such as single vacancies and multivacancies can influence the formation of quantum dots in the fluorination of graphene in aqueous solutions of HF.

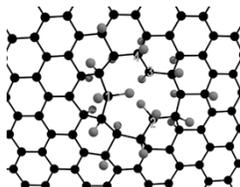
In this work, we investigated the interaction of F, FHF and their associates with water molecules, with mono- and divacancy defects in graphene.

## Method of calculation

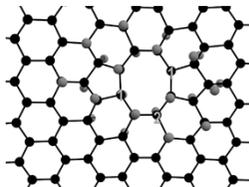
The simulation was carried out using semi-empirical calculation schemes implemented in the software package MOPAC2016 [8], calculations were carried out by the unrestricted Hartree-Fock method. A  $C_{96}H_{24}$  cluster of 96 carbon atoms was used as a model, the broken bonds at the edges of the cluster were passivated by hydrogen atoms. Simulation of point defects (mono- and divacancies) was carried out by removing the carbon atoms of the central part of the cluster. The modeling of the adsorption of particles onto a graphene sheet was carried out by the method of the reaction coordinate. The distance  $r$  between one of the atoms of the ion and the atom-the adsorption center was chosen as the reaction coordinate. The use of the PM3 method for the C96H24 model cluster made it possible to obtain data on the fluorine adsorption energy characteristics closest to the results of similar calculations by the DFT method [9].

## Interaction of fluorine with vacancy defects

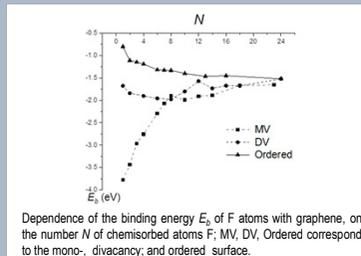
As a result of the study of different vacancy states with attached neutral fluorine atoms, it was found that the configuration with F atoms located along the contour of the vacancy corresponds to a lower energy.



Fragment of cluster  $C_{96}H_{24}F_{23}$ , which simulates a monovacancy defect in graphene with 23 chemisorbed fluorine atoms. The carbon and fluorine atoms are indicated by black and dark gray, respectively.



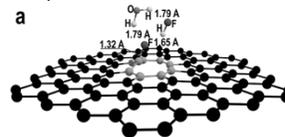
Fragment of cluster  $C_{96}H_{24}F_{24}$ , simulating a divacancy defect in graphene with 24 chemisorbed fluorine atoms. The carbon and fluorine atoms are indicated by black and dark gray, respectively.



Dependence of the binding energy  $E_b$  of F atoms with graphene, on the number  $N$  of chemisorbed atoms F; MV, DV, Ordered correspond to the mono-, divacancy, and ordered surface.

## Interaction of vacancy defects with F, FHF and associates with water molecules

According to [6], at low concentrations of hydrofluoric acid in water the solution contains F and FHF ions. In addition, associates can be formed with water molecules  $H_2O$ ,  $H_2O \cdot HF$ . In the present work, the interactions of ions and associates with the most active adsorption centers of mono- and divacancy defects, corresponding to the initial stage of fluorination (a clean surface) were studied. The most active are atoms with broken bonds in the region of monovacancy, as well as C1 atoms on the boundary of the pentagon, hexagon and heptagon in the divacancy.



Fragment of cluster  $C_{96}H_{24}$ , which simulates the surface of graphene with a monovacancy and associate  $H_2O \cdot F$ . The carbon atoms in the area of defects are marked in gray.

According to our calculations, vacancy defects reduce the activation energy of adsorption of ions and associates in comparison with the ordered surface. In addition, for the bound states of negatively charged particles with the surface, the heat of adsorption decreases. In the case of neutralization of the system (outflow of excess charge to the substrate), the activation energy of desorption of HF and  $H_2O \cdot HF$  fragments from a surface with defects is less than that of an ordered sheet. Thus, at the initial stages of functionalization, point defects are the centers of nucleation of dielectric "islands" of fluorographene (quantum dots) in a graphene matrix.

Defect	Energy parameters of particle interaction with graphene									
	F		FHF		$H_2O \cdot F$		$H_2O \cdot HF$		$H_2O \cdot HF \cdot F$	
	$E_{act}$	$E_b$	$E_{act}$	$E_b$	$E_{act}$	$E_b$	$E_{act}$	$E_b$	$E_{act}$	$E_b$
MV	-0.1	-3.44	0.14	-3.10	-0.16	-3.35	0.02	-3.32	2.80	-0.1
DV	-0.1	-2.88	0.51	-1.73	-0.18	-3.37	0.07	-3.42	1.10	0.14
Ordered	0.50	-1.40	1.61	-0.52	-0.99	-0.27	-0.31	0.01	0.87	-0.98

## Interaction of vacancy defects with the hydronium ion

The adsorption of hydronium on the C1 atom of the monovacancy region requires an activation energy of 0.72 eV. The  $H_3O^+$  bond breaks, the formation of the C1-H covalent bond is accompanied by a decrease in the energy of the "cluster + particle" system by 3.40 eV. Thus, the chemisorption of F is more likely than the addition of H. The adsorption of the hydronium ion onto the C1 divacancy atom requires an activation energy of 0.30 eV. However, the  $H_3O^+$  ion is attached without dissociation and is in a bound state at a distance of 1.66 Å from the surface. Thus, in the considered configuration, the addition of the hydronium ion to the divacancy is determined mainly by physical sorption.

## Conclusion

Analysis of the results of quantum-chemical modeling of the interaction of F, FHF ions and their associates with water molecules, with defects in graphene, makes it possible to draw the following conclusions:

- (1) the most probable process is chemisorption of fluorine on the atoms with broken bonds of the monovacancy region;
- (2) as the degree of coverage is increased, the stability of fluorine atoms on monovacancy decreases monotonically; on divacancy increases, then passes through a maximum and decreases;
- (3) vacancy defects are active centers for the fluorination of graphene in aqueous solutions of hydrofluoric acid.

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