УДК 539.21

ДВЕ СХЕМЫ ПОЛУЧЕНИЯ МОЛЕКУЛЯРНЫХ ИОНОВ НА ИЗОГНУТЫХ ЛИСТАХ ГРАФЕНА

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Приведен краткий обзор методов получения молекулярных ионов, на основе которого предложены две оригинальные схемы генерации потока отрицательно и положительно заряженных ионов из потока электрически нейтральных молекул, рассеивающихся на электропроводящих изогнутых листах графена. При изгибе листов графена происходит перераспределение плотностей π-электронов атомов углерода, и в направлении, перпендикулярном к изогнутой поверхности, появляется индуцированный деформацией электрический дипольный момент. Представленные схемы отличаются взаимным расположением изогнутых листов графена относительно потока молекул. На основе квантово-химических расчетов полуэмпирическим методом PM7 даны оценки сродства к электрону и энергии (потенциала) ионизации ряда молекул (C_{60}, O_2, H_2O, CO_2 и др.), пригодных для получения из них молекулярных ионов по предложенным схемам. Если рассеяние молекулы происходит на отрицательно заряженной стороне графена, то за счет перехода электрона от графена к молекуле она приобретает отрицательный заряд. Если рассеяние молекулы происходит на положительно заряженной стороне графена, то за счет перехода электрона от молекулы к графену молекула приобретает положительный заряд. Для получения молекулярных ионов необходимо выбирать молекулы со значениями сродства к электрону (для получения отрицательных ионов) или энергии ионизации (для получения положительных ионов), близкими к величине работы выхода электрона из графена ($\approx 4{,}3$ эВ).

Ключевые слова: изогнутый лист графена; π-электроны; молекула; молекулярный ион; ионизация; сродство к электрону.

Благодарность. Работа выполнена при поддержке Белорусского республиканского фонда фундаментальных исследований (грант № Ф23РНФ-049).

Образец цитирования:
Поклонский НА, Раткевич СВ, Вырко СА, Власов АТ. Две схемы получения молекулярных ионов на изогнутых листах графена. *Журнал Белорусского государственного университета. Физика.* 2023;3:57–64 (на англ.).
EDN: QHXOWT

For citation:
Poklonski NA, Ratkevich SV, Vyrko SA, Vlassov AT. Two schemes for producing molecular ions on a bent graphene layers. *Journal of the Belarusian State University. Physics.* 2023;3:57–64.
EDN: QHXOWT

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Журнал Белорусского государственного университета. Физика. 2023;3:57–64
Journal of the Belarusian State University. Physics. 2023;3:57–64

TWO SCHEMES FOR PRODUCING MOLECULAR IONS ON A BENT GRAPHENE LAYERS

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A brief review of methods for producing molecular ions is given, on the basis of which two original schemes for generation of a flow of negatively and positively charged ions from a flow of electrically neutral molecules scattered on electrically conductive bent graphene layers are proposed. When graphene layers are bent, the densities of π-electrons of carbon atoms are redistributed, and a deformation-induced electric dipole moment appears in the direction perpendicular to the bent surface. The presented schemes differ in the mutual arrangement of the bent graphene layers relative to the flow of molecules. Quantum chemical calculations using the PM7 semiempirical method provide estimates of the electron affinity and ionisation energy (potential) of a number of molecules (C_{60}, O_2, H_2O, CO_2, etc.) suitable for production of molecular ions from them according to the proposed schemes. If a molecule is scattered on a negatively charged graphene side, then due to the transfer of an electron from graphene to the molecule, the molecule acquires a negative charge. If a molecule is scattered on a positively charged graphene side, then due to the transfer of an electron from the molecule to graphene, the molecule acquires a positive charge. To obtain molecular ions, it is necessary to select molecules with values of electron affinity (to obtain negative ions) or ionisation energy (to obtain positive ions) close to the work function of graphene (≈ 4.3 eV).

Keywords: bent graphene layer; π-electrons; molecule; molecular ion; ionisation; electron affinity.

Acknowledgements. This work was supported by the Belarusian Republican Foundation for Fundamental Research (grant No. F23RNF-049).

Introduction

To solve a number of problems of high-energy ion implantation, mass spectrometry, diagnostics of the composition and topography of the surface of crystals, etc., sources of negative ions are required [1–3]. Let us note the known approaches to obtaining flows of molecular ions and electrically neutral radicals. Thus, a technique was proposed [4] for removing desorbed (from the engineering surfaces of accelerating devices) ions from the general flow using an ion filter, which passes only gas-phase ions from the source to the detector and retains the desorbed ions due to the difference in their kinetic energies. In this case, the interaction of the adsorbate (molecular ion) with the surface of the ion filter (for example, made of a crystalline semiconductor) is important, which leads to bending of single-electron bands of allowed energy values, and further to pinning of the Fermi level at surface energy levels of semiconductor defects [5]. In the case of active semiconductor-adsorbate interfaces, chemical bonds arise between them, which leads to equalisation of the energies of the valence electrons of the adsorbate and semiconductor.

Particles adsorbed on graphene affect the width of the energy band gap induced by them and the position of the Fermi level in graphene. In this case, the adsorbate-graphene binding energy non-linearly depends on the concentration of adsorbed particles [6]. The electric potential of the ion-solid interaction differs distinctly from the potential describing collisions of molecules in the gas phase [7], which is due to an increase in the electron density in the region between the incident particle and the scattering center. In particular, it was shown by calculation [8] that the ionisation energy of the hydrogen atom goes to zero when the distance between the proton and the atomically smooth metal surface becomes slightly less than the Bohr radius. The binding energy between water molecules in a cluster (up to six molecules) is also affected by the presence of a second graphene layer and the distance between the layers [9]. When the distance between the graphene layers becomes less than 0.6–0.8 nm, the intermolecular interaction in the cluster quickly decreases, which leads to a weakening of the adhesion between molecules in the «compressed» cluster.

Dielectric graphene layers and graphene ribbons, as well as soft lipid bilayer membranes, are capable, under certain conditions, of converting the effects of an electric field into mechanical deformation [10]. And vice versa, mechanical deformation can give rise to an electric field. The phenomenon of flexoelectricity is greatly enhanced at the nanoscale, so two-dimensional membranes of atomic thickness exhibit a strong relationship between their curvature (bending) and the external electric field. It has been shown theoretically [11] that the value of the electric polarisation vector normal to the surface of a graphene layer (in the form of an electric double layer) depends on the curvature of the layer, and the electronic charge of the π-bonds of carbon atoms mostly «flows» to the convex side of the layer.

The study of chemical reactions accompanied by the decomposition of water molecules on graphene layers is relevant for applications in biomedicine: the resulting electrically neutral hydroxyl groups OH can be used as a bactericidal agent. Thus, using the flexoelectric properties of graphene, in work [12] a model of an electrical «capacitor» made of graphene was proposed to generate a negatively charged and electrically neutral hydroxyl groups OH from a flow of water molecules. The «capacitor» consists of two graphene layers bent in one direction placed on copper substrate plates bent in the same way (see also [13]). The copper substrates are connected to an external source of electrical voltage: positive potential is applied to the upper concave substrate, negative potential is applied to the lower substrate bent towards the upper substrate. When the water vapor is pumped between the plates of such an electrical «capacitor», the water vapor at the exit from the «capacitor» is enriched with electrically neutral radicals $(OH)^0$ and hydrogen molecules H_2 [12].

Photocatalytic decomposition of water on graphene could be an effective approach to produce hydrogen by converting solar energy into chemical energy [14; 15]. Biophysical methods are being developed for charge separation under the influence of light in the reaction centers of plant photosynthesis [16]. Using quantum chemical methods and thermochemical methods (by the Gibbs energy change), we studied possible chemical reactions involving molecules of water, fullerenes C_{20} and C_{60}, hydrogen and chlorine with the release of atomic or molecular hydrogen at room temperature and atmospheric pressure [17; 18].

The physical processes underlying the generation of ion beams with a high emission current density in electrohydrodynamic emitters operating on liquid metals and alloys, as well as with low-temperature ion liquids, are considered in work [19]. The factors that determine the stability of ion emission and their interaction with engineering surfaces are also analysed there. The results of the one-dimensional theory of a plasma emitter of positive ions are presented in publication [20].

The model of explosive electron emission [21] allows to describe emission processes during discharges at the points of contact of the metal wall with the plasma under magnetic confinement of the plasma. In works [22; 23] a description of models of field (cold) emission from various low-dimensional carbon systems is given.

Another mechanism for the formation of ions is one-electron charge exchange during the collision of fast ions such as H^+ and He^{2+} with a neutral hydrogen molecule. Thus, in paper [24], the cross sections for one-electron charge exchange in collisions of fast ions with an H_2 molecule in the ground state were calculated. Ion-molecular collisions are considered using the relationship between quantum mechanical and quasi-classical charge exchange amplitudes. For the collisions $H^+ + H_2 \to H + H_2^+$, the dependence of the differential charge exchange cross sections on the orientation of the symmetry axis of the H_2 molecule is considered. By numerical modelling the possibility of separating flows of electrically polarised macromolecules in non-uniform electric fields created by charged filaments is demonstrated [25].

The purpose of the work is to propose simple schemes for producing a flow of negatively and positively charged molecular ions from a flow of electrically neutral molecules interacting with two bent layers of electrically conductive graphene.

Schemes for generating molecular ions

In the proposed method, ionisation of molecules is carried out using bent graphene layers. When passing through a non-uniform stationary electric field, the molecules change their configuration and (or) break up into ions. To form a non-uniform electric field, the redistribution of π-electrons (asymmetrically elongated π-bonds) of carbon atoms on the surfaces of a bent graphene layer is used (fig. 1), creating a dipole moment (an electric double layer covering opposite sides of a single graphene layer). The direction of the dipole moment induced by graphene bending is determined by the density of π-electron states, which is greater on the convex side of the graphene layer [11; 26]. The redistribution of charge density that occurs on a graphene layer is determined by its curvature. It is quite natural to use several differently bent graphene layers on metal substrates, to which adjustable electric potentials are applied and between which the movement of ionised molecules and the removal of molecular ions along the surface of an electrically conductive grid are organised.

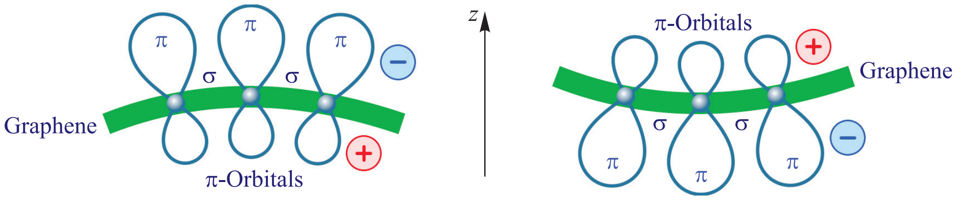

Fig. 1. Schemes of occurrence of a local electric dipole moment in a graphene layer due to the deformation of σ-bonds (determining the mechanical strength of graphene) and the redistribution of electron density for the π-orbitals of carbon atoms along the *z* axis (perpendicular to the graphene layer) when the layer is bent

Due to the bending on the convex side of the bent graphene surface, the electron density increases, and it is chemically reactive to combine with partially positively charged atoms (for example, hydrogen atoms in water molecules [12; 26]). In this case, in molecules, the lowest energy level E_{LUMO} unoccupied by electrons (measured relative to the vacuum level E_{vac}) should be located lower than the highest energy level $(E_{\text{F}} - e\varphi)$ of electron-occupied π-states in bent graphene, which makes it possible for electrons to transfer from graphene to molecules, turning them into negative ions (fig. 2, *a*). Here E_{F} is the Fermi level of graphene in equilibrium, e is the elementary charge, φ is the electric potential of the external voltage source. This corresponds to the fact that the work function of graphene $\text{WF}(\varphi) = E_{\text{vac}} - (E_{\text{F}} - e\varphi)$ should be less than the electron affinity (EA) of the molecule ($\text{EA} \approx -E_{\text{LUMO}}$). The experimentally measured value of the work function of graphene monolayer is $\text{WF}(\varphi = 0) \approx 4.3$ eV [27]. Energy relations for electronic states in macromolecular and metal nanocontacts see in publications [28; 29].

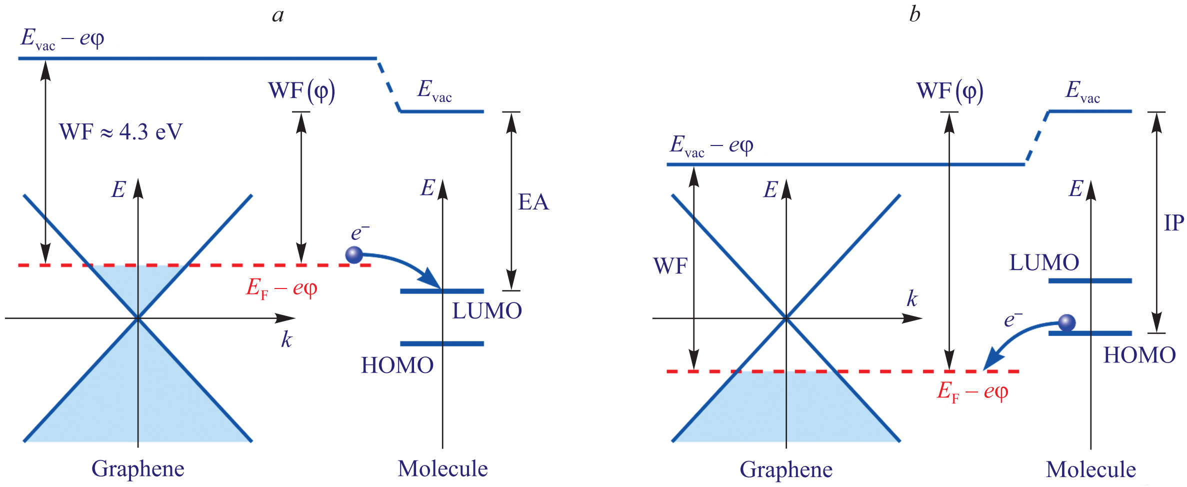

Fig. 2. Schemes of the transition of an electron (e^-) from the Fermi level of graphene ($E_{\text{F}} - e\varphi$) to the lowest unoccupied molecular orbital (LUMO) with the formation of a negative molecular ion (*a*) and the transition of an electron from the highest occupied molecular orbital (HOMO) to the Fermi level of graphene with the formation of a positive molecular ion (*b*). The dependences of the single-electron energy of graphene in one of the six equivalent points of the 1st Brillouin zone on the wave number k of π-electrons when an electric potential $\varphi < 0$ (*a*) or $\varphi > 0$ (*b*) is applied to the graphene are shown; EA is the electron affinity of the molecule, IP is the ionisation energy (potential) of the molecule

Let us consider a scheme for obtaining a flow of negatively charged molecular ions M^- from a flow of electrically neutral molecules M^0 when they interact with two electrically conductive graphene layers bent in opposite directions (fig. 3, *a*). Two bent graphene layers (placed with their convex sides facing each other, which leads to compression and then expansion of the flow, as in a Laval nozzle) are electromechanically attached at the edges to two flat substrates of a chemically inert metal (see also [12]). The substrates are connected to an external source of electrical voltage: a negative potential ($\varphi < 0$) is applied to two substrates (cathodes), and a positive potential is applied to the anode in the form of a metal grid located (perpendicular to the flow of molecular ions) far from the cathodes (see fig. 3, *a*). The intensity of ion formation depends on the flow density, the speed of molecules, the distance from the molecules to the graphene surface and other factors.

The transition of electrons from the convex side of the graphene surface to the lowest unoccupied molecular orbital (LUMO) of a molecule M^0 is initiated by the electric potential φ applied to the substrate from an external source. Potential φ can be either constant or variable. In the case of an alternating potential, the electric field acts on the electron with a certain frequency, this can lead to the coincidence of the electron energy with the energy level E_{LUMO} of the molecule. Varying the frequency of electric field oscillations makes it possible to increase the intensity of ion formation. There is an analogy here with the Sena effect [30; 31], in which, when a negative ion and an atom collide, an electron transfers from the ion to the atom without changing their trajectory (the so-called resonant charge exchange), that is equivalent to the scattering of the ion. The resonant charge exchange cross section replaces the elastic scattering cross section in the phenomena of ion transport in the intrinsic gas of atoms, when the transport of particles is associated with their elastic scattering.

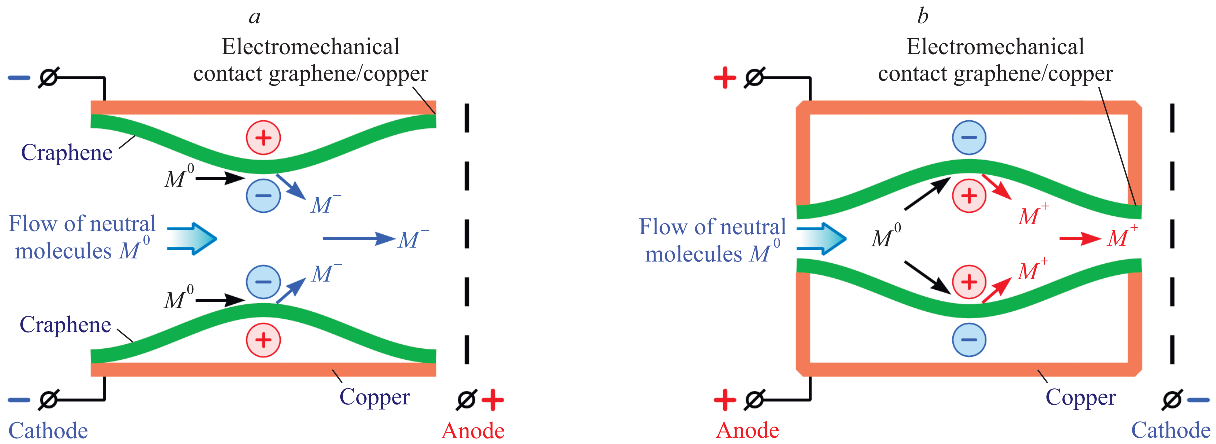

Fig. 3. Schemes for generation of a flow of molecular ions: *a* – scheme for generation of negative ions (M^-) between convex graphene surfaces on a copper substrate (analogy of a Laval nozzle), $\mathrm{WF}(\varphi) < \mathrm{EA}$; *b* – scheme for generation of positive ions (M^+) between concave graphene surfaces, $\mathrm{WF}(\varphi) > \mathrm{IP}$

Similarly, by changing the sign of the electric potential on copper substrates ($\varphi > 0$) (fig. 3, *b*), it is possible to realise transitions of electrons from the highest occupied molecular orbital (HOMO) of molecules to graphene, resulting in the formation of positively charged molecular ions in the flow. In this case, the energy level E_{HOMO} in molecules should be located higher than the energy level ($E_{\mathrm{F}} - e\varphi$) of electron-filled π-states in bent graphene, which makes it possible for electrons to transit from a molecule to graphene, turning molecules into positive ions (see fig. 2, *b*). This corresponds to the fact that the work function of graphene $\mathrm{WF}(\varphi) = E_{\mathrm{vac}} - (E_{\mathrm{F}} - e\varphi)$ should be greater than the ionisation energy of the molecule ($\mathrm{IP} \approx -E_{\mathrm{HOMO}}$).

The table shows the experimental values [32–34] of electron affinity and ionisation energy for molecules that can be used to obtain molecular ions. To compare with experimental values and evaluate data missing from the literature, we have calculated $\mathrm{EA} \approx -E_{\mathrm{LUMO}}$ and $\mathrm{IP} \approx -E_{\mathrm{HOMO}}$ using the PM7 semiempirical method [35], implemented in the *MOPAC2016* package.

Values of electron affinity (EA) and ionisation potential (IP) of neutral molecules and radicals

Molecule	EA, eV	IP, eV	Reference	Molecule	EA, eV	IP, eV	Reference
Hydrogen (H_2)	–0.72 – –7.04	– 15.43 15.02	[32] [33] PM7	Hydroxyl radical ($^{\bullet}OH$)	2.17 1.83 1.63	– 13.02 11.18	[32] [33] PM7
Oxygen (O_2)	0.87 0.45 0.92	– 12.06 9.17	[32] [33] PM7	Nitrogen dioxide ($^{\bullet}NO_2$)	1.62 2.27 1.09	– 9.59 10.56	[32] [33] PM7
Nitrogen (N_2)	– 0.13	15.58 13.66	[33] PM7	Nitrate radical ($^{\bullet}NO_3$)	3.88 3.94 4.95	– 12.57 11.54	[32] [33] PM7
Dicarbon (C_2)	3.27 2.15	11.41 11.74	[33] PM7	Methyl radical ($^{\bullet}CH_3$)	1.08 0.08 –0.54	– 9.84 9.97	[32] [33] PM7
Water (H_2O)	–0.8 – –4.05	– 12.62 12.12	[32] [33] PM7	Ammonia (NH_3)	– –4.57	10.07 10.15	[33] PM7
Carbon dioxide (CO_2)	–0.59 –0.55	13.78 12.76	[33] PM7	Carbon monoxide (CO)	1.33 –1.60	14.01 12.33	[33] PM7
Anthracene ($C_{14}H_{10}$)	1.19 0.53 1.09	– 7.44 8.39	[32] [33] PM7	Adamantane ($C_{10}H_{16}$)	–0.3 – –4.07	– 9.25 10.20	[34] [33] PM7
Fullerene (C_{60})	2.68 2.96	7.6 9.66	[33] PM7	Fullerene (C_{70})	2.77 3.23	8 9.19	[33] PM7
Fullerene + adduct ($C_{60} + [2(COOH)]_3$)	2.88	9.75	PM7	Fullerene + adduct ($C_{70} + [2(COOH)]_2$)	3.54	9.45	PM7

To obtain negative molecular ions, it is necessary to select molecules with electron affinities close to the work function of graphene (WF ≈ 4.3 eV). To obtain positive molecular ions, it is necessary to select molecules with an ionisation energy close to the work function of graphene. When a negative potential ($\varphi < 0$) from the external voltage source is applied to the graphene, the Fermi level in graphene ($E_F - e\varphi$) shifts upward to the vacuum level E_{vac}, this makes it possible to obtain negative ions from molecules with EA < WF ≈ 4.3 eV. When a positive potential ($\varphi > 0$) from the external voltage source is applied to the graphene, the Fermi level in graphene ($E_F - e\varphi$) shifts downward from the vacuum level E_{vac}, this makes it possible to obtain positive ions from molecules with IP > WF ≈ 4.3 eV. From the data presented in the table it can be seen that candidates for obtaining negative and positive ions are molecules of fullerenes and fullerenes with carboxyl adducts, as well as nitrate and hydroxyl radicals and dicarbon. Positively charged ions can also be obtained from oxygen molecules, anthracene, adamantane, methyl radical, nitrogen dioxide and ammonia.

Molecules with negative electron affinity are, as a rule, very stable molecules with fully occupied outer bonding HOMO orbital ($E_{HOMO} < E_{vac}$) and antibonding unoccupied LUMO orbital ($E_{LUMO} > E_{vac}$). This rules out the addition of an extra electron to the molecule and the formation of a stable negative ion. These molecules include: hydrogen, water, carbon dioxide, ammonia, adamantane.

Conclusions

It has been shown that during the charge-exchange interaction of molecules with bent graphene layers, the generation of both negative and positive molecular ions in a flow of electrically neutral molecules is possible. Quantum chemical calculations using the PM7 semiempirical method provided estimates of the electron affinity and ionisation potential of a number of molecules. Based on values of electron affinity and ionisation potential known from the literature, supplemented by our calculated estimates, molecules are identified that are of interest for the production of molecular ions and require electron affinities and ionisation potentials close to the work function of graphene. The energy received by the molecules must be sufficient for their ionisation, which is achieved by changing the electric potential φ by adjusting the circuit to recharge molecules of a certain type.

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Received 12.08.2023 / accepted 22.09.2023.