

Supporting Information

Role of Graphene Edges in the Electron Transfer Kinetics: Insight from Theory and Molecular Modeling

Sergey V. Pavlov,^{†,§} Renat R. Nazmutdinov,[‡] Maxim V. Fedorov,[§] Sergey A. Kislenko^{*,†,||}

[†]Joint Institute for High Temperatures of RAS, Izhorskaya 13/2, 125412 Moscow, Russian Federation

[‡]Kazan National Research Technological University, K. Marx Str. 68, Kazan, 420015 Republic of Tatarstan, Russian Federation

[§]Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, 143026 Moscow, Russian Federation

^{||}Moscow Institute of Physics and Technology, 9 Institutskiy per., 141701 Dolgoprudny, Russian Federation

1. Structures of graphene clusters

We used two graphene clusters with different edges (zigzag for $C_{150}H_{30}$ and armchair for $C_{114}H_{30}$). All carbon atoms at edges were terminated with hydrogen atoms. Structures of these clusters are shown in Figure S1

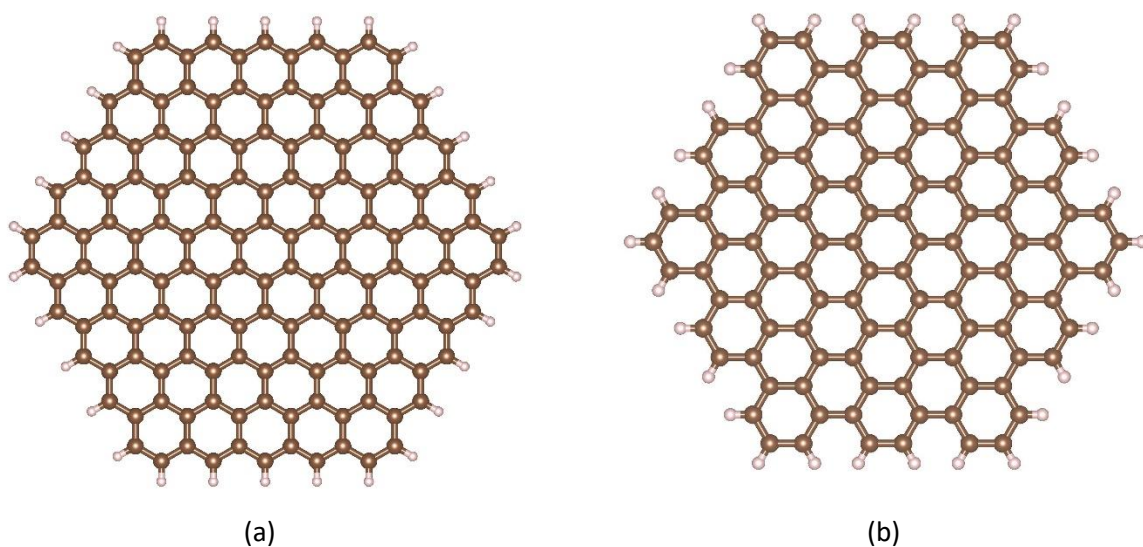


Fig. S1 The graphene clusters (a) – $C_{150}H_{30}$ with zigzag graphene edges and (b) – $C_{114}H_{30}$ – with armchair graphene edges

2. Calculation of electronic transmission coefficient

We calculated the ET rate constant following the approach developed in ref. (1) for adiabatic limit,

$$k(x) = \frac{\omega_{eff}}{2\pi} \sum_{j=1}^N \kappa_e^{(j)}(x) \exp(-\Delta E_a^{(j)} / k_B T), \quad (S1)$$

where j numerates the occupied energy levels of an electrode; $\kappa_e^{(j)}$ and $\Delta E_a^{(j)}$ are partial electronic transmission coefficients and activation barriers defined by eqs. S2 and S3,

$$\kappa_e^{(j)}(x) = 1 - \exp\left(-2\pi \frac{H_{if}^2(\varepsilon_j, x)}{\hbar \omega_{eff}} \sqrt{\frac{\pi}{\lambda k_B T}}\right), \quad (S2)$$

$$\Delta E_a^{(j)} = \frac{(\lambda + \varepsilon_F - \varepsilon_j - e_0 \eta)^2}{4\lambda}, \quad (S3)$$

where ω_{eff} is the effective polarization frequency ($3 \times 10^{13} \text{ s}^{-1}$ (2) for acetonitrile), λ is the total reorganization energy, ε_F is the electrode Fermi level (i.e. the energy of the highest occupied molecular orbital (HOMO) of the graphene cluster), η is the electrode overpotential, H_{if} is the electronic coupling matrix element. If a number of electronic energy levels are addressed, resulting values of the transmission coefficient and activation barrier can be estimated from the temperature dependence of the rate constant defined by eq S1 (see (1) for details).

In our calculations we multiplied the argument of exponential function in eq 1 by a factor of $\frac{1}{4}$ which originates from the two degenerated acceptor π - orbitals of O_2 , (which gives the probability $\frac{1}{2}$) and their half-occupied character (which yields in turn spin factor $\frac{1}{2}$).

We obtained that for weak coupling and for zero (or small) values of the electrode overpotential eq S1 can be recast as follows,

$$k(x) \approx \frac{\omega_{eff}}{2\pi} \kappa_e(x) \exp\left(-\frac{\lambda}{4k_B T}\right), \quad (S4)$$

where only the HOMO is used to calculate the matrix element H_{if} , and therefore, only the corresponding energy level of a graphene cluster is considered.

In the regime of strong coupling (adiabatic limit) we used Newns-Anderson formalism (3, 4) (a spinless version in the narrow band approximation) to calculate the reaction free energy surface along the solvent coordinate, $E(q)$,

$$E(q) = \lambda q^2 + \frac{1}{\pi} \int_{-\infty}^0 \frac{\varepsilon \Delta(\varepsilon) d\varepsilon}{\Delta^2(\varepsilon) + (\varepsilon - \varepsilon_f(q) - \Lambda(\varepsilon))^2}, \quad (S5)$$

where q is dimensionless solvent coordinate, $\varepsilon_f(q)$ is the fluctuating acceptor energy level of reactant ($\varepsilon_f(q) = \varepsilon_0 - 2\lambda q$, where ε_0 is an equalizing parameter which depends on η) and $\Delta(\varepsilon)$ describes its broadening ($\Delta(\varepsilon) = \pi H_{if} \rho(\varepsilon)$, $\rho(\varepsilon)$ is the electrode DOS).

The Hilbert transform $\Lambda(\varepsilon)$ in eq S5 takes the form,

$$\Lambda(\varepsilon) = \frac{1}{\pi} \int_{-\infty}^0 \frac{\Delta(\varepsilon') d\varepsilon'}{(\varepsilon - \varepsilon')} \quad (S6)$$

The free energy surface $E(q)$ looks as a two-well function; then the activation barrier can be readily estimated. We used an analytical expression of the perfect graphene DOS (5). A piecewise

continuous approximation (similar to that in ref. (6)) was employed in numerical calculations of the integral in eq S5.

3. Densities of States for graphene clusters

We calculated Densities of States (DOS) for both clusters in order to make sure that our model clusters imitate graphene surfaces well. As can be seen from Figure S2, DOS of graphene clusters qualitatively corresponds to the DOS of pure graphene (7).

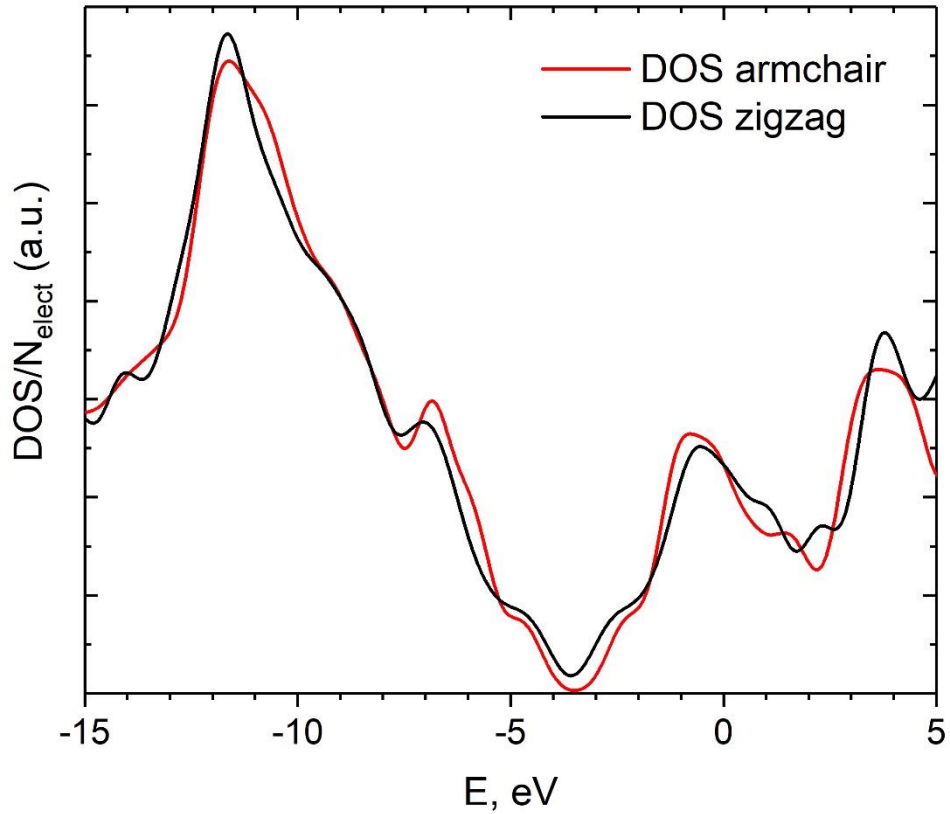
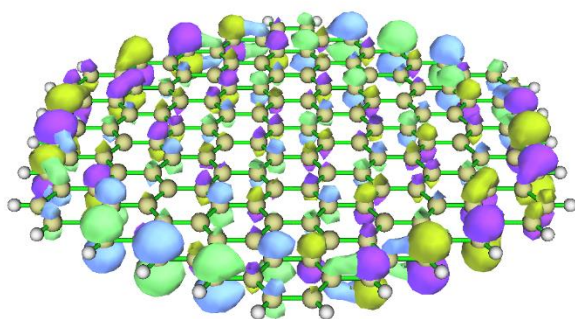
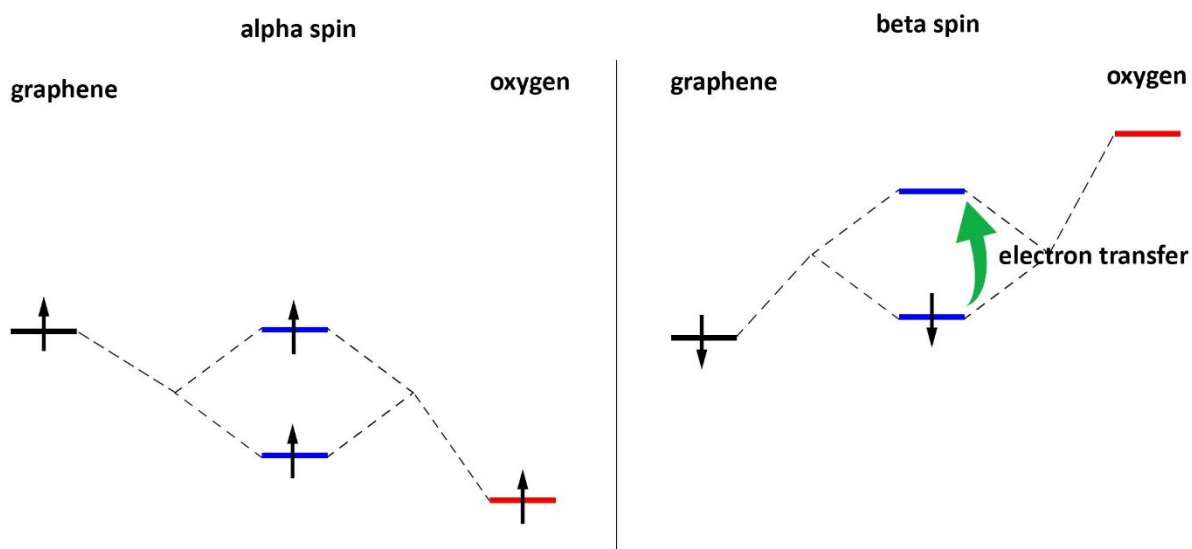


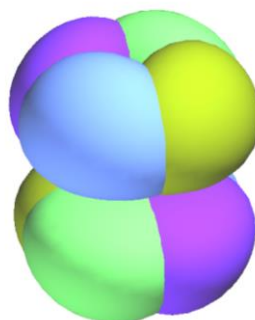
Fig. S2 Densities of states of two graphene clusters with zigzag and armchair edges. The values are normalized to the number of electrons of correspondent cluster.

4. Scheme of orbitals of graphene – oxygen complex

Scheme. S1 Black states correspond to graphene HOMO, red states – to LUMO of oxygen, blue – to mixed bonding and antibonding orbitals of graphene –oxygen cluster.

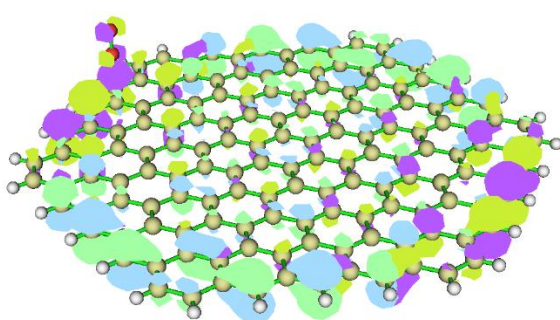


(a)

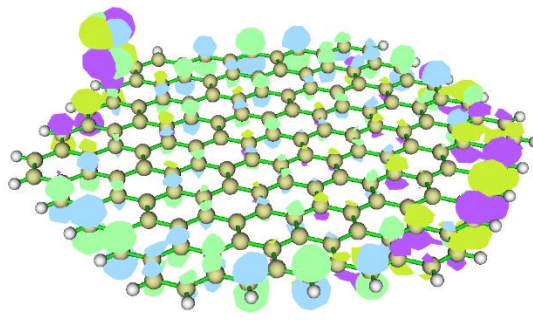


(b)

Fig. S3 “Pure” Molecular orbitals of separated graphene cluster and oxygen molecule



(a)



(b)

Fig. S4 Example of molecular orbitals chosen as bonding and antibonding for GMH method

5. HOMO-1 of the $C_{150}H_{30}$

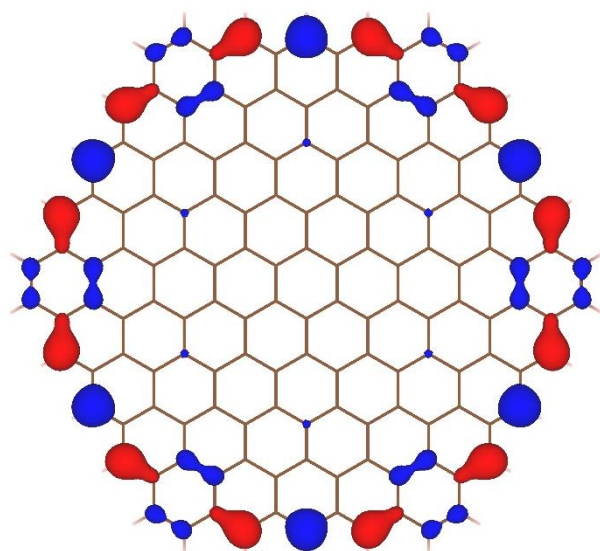


Fig. S5 HOMO-1 of the graphene cluster with zigzag edges

6. Electronic densities

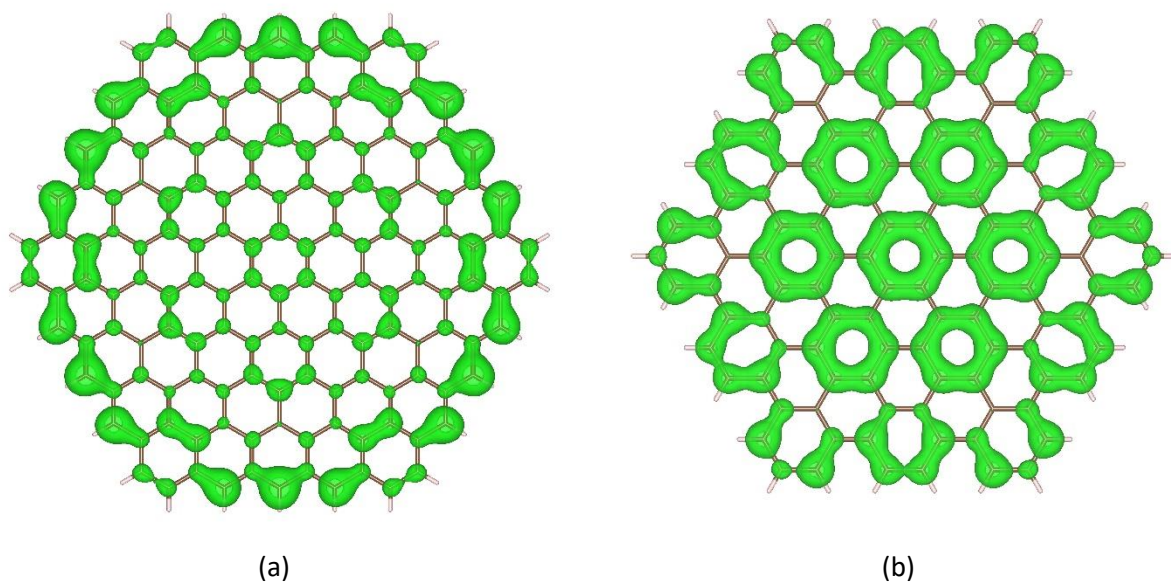


Fig. S6 Electronic density from the doubly degenerated highest occupied molecular orbital of: (a) the graphene cluster $C_{150}H_{30}$ with zig-zag edges, (b) the graphene cluster $C_{114}H_{30}$ with armchair edges

7. Electronic transmission coefficient

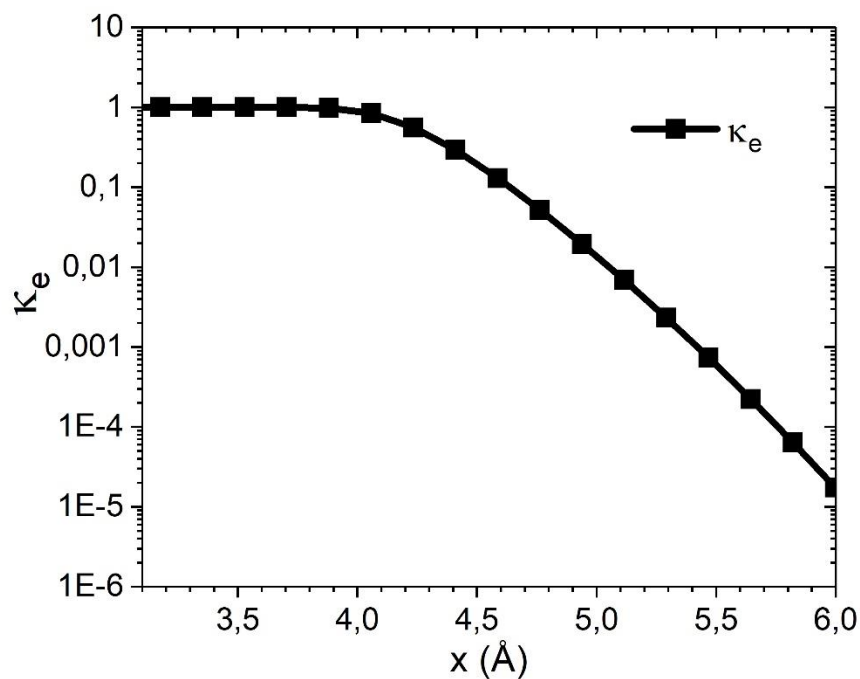


Fig. S7 Electronic transmission coefficient as a function of the distance between oxygen molecule and the surface of graphene cluster over the hollow position of basal plane region

8. Averaging of results

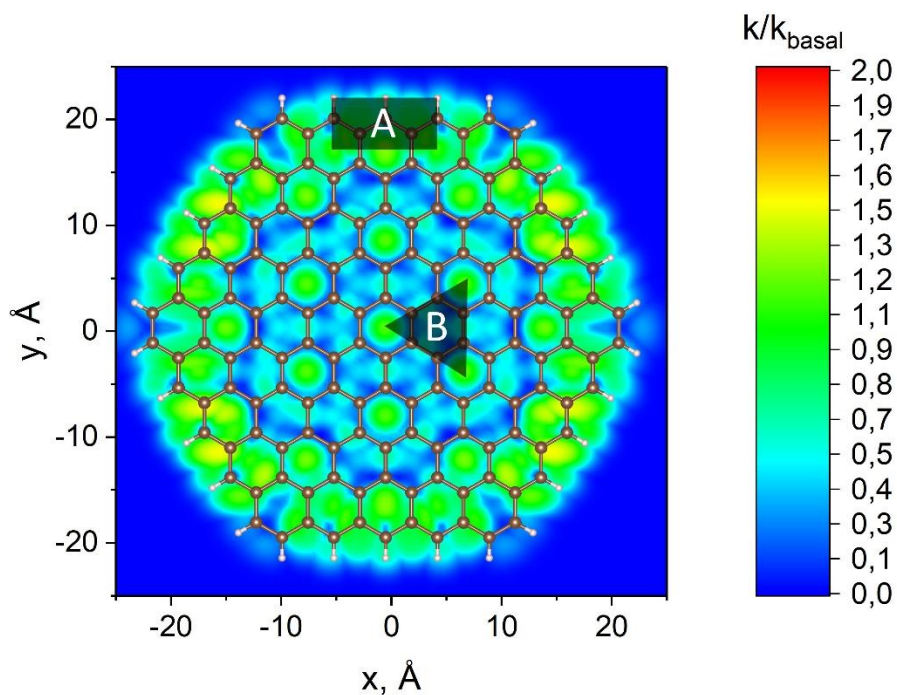


Fig. S8 Schematic representation of averaging areas. A – area of zig-zag edge, B – are of basal plane

9. Comparison of zigzag edge and basal plane

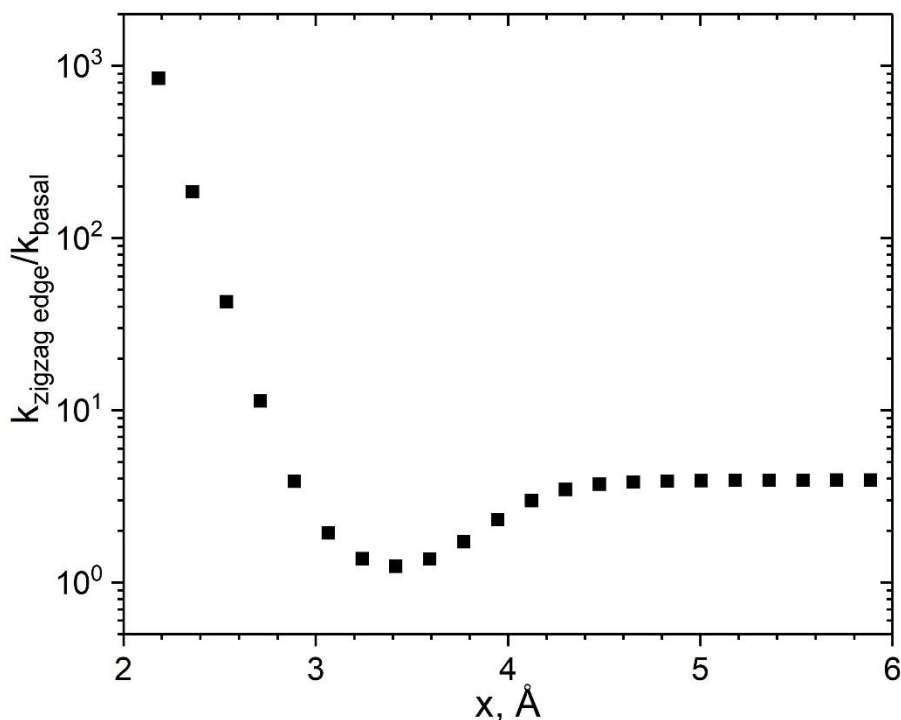


Fig. S9 The ratio of rate constants at zigzag edge basal plane regions as a function of distance between reactants

10. Activation energy as a function of electronic coupling matrix element H_{if} in the frameworks of Newns-Anderson formalism.

The Anderson-Newns formalism (3, 4) in the narrow band approximation was employed; a value of 1.7 eV was taken for the solvent reorganization energy. The results are shown in Table S1.

Table S1. Resonance integral (H_{if}) and activation barrier (ΔE_a) describing the first electron transfer to molecular oxygen calculated at several distances to graphene electrode.

$x, \text{\AA}$	basal plane		zigzag edge	
	H_{if}, eV	$\Delta E_a, \text{eV}$	H_{if}, eV	$\Delta E_a, \text{eV}$
2.18	0.24	0.4	0.62	0.32
2.35	0.196	0.41	0.513	0.34
2.53	0.153	0.41	0.408	0.37
2.89	0.087	0.42	0.24	0.4
3.06	0.064	0.425	0.173	0.41

References

1. Nazmutdinov, R. R.; Bronshtein, M. D.; Zinkicheva, T. T.; Glukhov, D. V., Modeling of electron transfer across electrochemical interfaces: State-of-the art and challenges for quantum and computational chemistry. *International Journal of Quantum Chemistry* **2016**, *116* (3), 189-201.
2. Nikitina, V. A.; Kislenko, S. A.; Nazmutdinov, R. R.; Bronshtein, M. D.; Tsirlina, G. A., Ferrocene/Ferrocenium Redox Couple at Au(111)/Ionic Liquid and Au(111)/Acetonitrile Interfaces: A Molecular-Level View at the Elementary Act. *The Journal of Physical Chemistry C* **2014**, *118* (12), 6151-6164.
3. Newns, D., Self-consistent model of hydrogen chemisorption. *Physical Review* **1969**, *178* (3), 1123.
4. Lebedeva, M. V.; Pierron-Bohnes, V.; Goyhenex, C.; Papaefthimiou, V.; Zafeiratos, S.; Nazmutdinov, R. R.; Da Costa, V.; Acosta, M.; Zosiak, L.; Kozubski, R., Effect of the chemical order on the electrocatalytic activity of model PtCo electrodes in the oxygen reduction reaction. *Electrochimica Acta* **2013**, *108*, 605-616.
5. Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K., The electronic properties of graphene. *Reviews of Modern Physics* **2009**, *81* (1), 109-162.
6. Davydov, S.Y.; Sabirova, G.I., Adsorption of hydrogen atom on graphene. *Technical Physics Letters* **2010** *36* (12), 1154-1157.
7. Heller, I.; Kong, J.; Williams, K. A.; Dekker, C.; Lemay, S. G., Electrochemistry at single-walled carbon nanotubes: the role of band structure and quantum capacitance. *Journal of the American Chemical Society* **2006**, *128* (22), 7353-7359.