JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **12** No 4, 04013(6pp) (2020)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **12** № 4, 04013(6cc) (2020)

Hydrogen Adsorption on Li$^+$ and Na$^+$ Decorated Coronene and Corannulene: DFT, SAPT0, and IGM Study

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(Received 27 April 2020; revised manuscript received 15 August 2020; published online 25 August 2020)

The novel systems for hydrogen storage are of importance for the contemporary energetics. In this paper, we investigate hydrogen adsorption on planar (coronene) and bent (corannulene) adsorbent models by means of DFT-D3 and SAPT0 calculations. We also use the 'decoration' of the adsorbents with M (M = Li, Na) cations to improve H_2 uptake. It was founded that corannulene adsorbs Li and Na cations almost equally compared with coronene. However, hydrogen adsorption is much more pronounced in the case of corannulene. Thus, for instance, adsorption energies (E_a) for the 1st and 4th H_2 molecules adsorbed on Li$^+$@coronene and Li$^+$@corannulene are – 4.387, – 1.336 kcal/mol and – 5.047, – 3.477 kcal/mol, respectively. We also employ the independent gradient model (IGM) method to visualize interacting regions between cations, hydrogen and studied adsorbents. We accurately show the strong interactions between M$^+$ and the adsorbent molecules as well as the weak ones between H_2 and studied cations. The present results should provide in-depth analysis of the fundamentals of hydrogen storage using M$^+$-decorated polyaromatic hydrocarbons.

Keywords: Coronene, Corannulene, Hydrogen, DFT, Adsorption.

DOI: 10.21272/jnep.12(4).04013

PACS numbers: 31.15.E –, 61.46. + w, 79.60.Jv, 68.65. – k, 81.05.ue

1. INTRODUCTION

Hydrogen (H_2) is a gas, which is considered as an alternative source of energy. To make an ultimate transfer to hydrogen economics, one should address the following issues, namely, massive H_2 production, its purification, delivery and storage. Carbon nanostructures (fullerenes, nanotubes, graphene etc.) have been regarded as convenient and effective hydrogen storage media owing to their low weight [1]. However, to store H_2 in an effective way, one should supply high pressures and low temperatures. To overcome disadvantages of pure carbon systems for H_2 storage, researchers involve different techniques, for example, substitute C atoms with B and N atoms to induce dipole moments in the adsorbent, and, thereby enhance H_2/adsorbent interactions [2, 3]. Another strategy to increase the capacity of H_2 storage is to decorate the surface of the adsorbent with alkali metal atoms or cations (Li/Li$^+$, Na/Na$^+$, K/K$^+$ etc.) [4]. It leads to the increase of the subsequent H_2/Me-decorated adsorbent interactions. The strong binding of cations to the surface of the adsorbent is based on the so-called cation-π interactions. It is worth noticing here, that cation-π interactions, strong attractive non-covalent interplay between the positively charged cation and π system, are of importance in many fields of contemporary science, such as physical chemistry, materials science, and related areas [5, 6].

There exist some works in the literature, which report the study of the curvature effect on hydrogen physisorption. Our previous works on carbon and boron-nitride (BN) hollows connected the pore depth with H_2 adsorption energy (E_a) [7, 8]. However, in those works we involved the pristine structures without any decoration. Different scientific groups investigated the curvature effects on adsorption of various molecules. Emampour et al. studied the effects of carbon nanotubes curvature on their interactions with alkanethiols [9]. Klauda et al. reported adsorption of N_2 and O_2 gases on graphite, C60 and C168 nanostructures [10]. Sha and Faller investigated the effect of curvature of BN nanotubes and nanosheets on their adsorption [11]. Bamdad et al. studied H_2O and H_2 adsorption on a graphene sheet and nanotubes of various diameters to figure out the effects of curvature [12].

We study here the coronene ($C_{24}H_{12}$) and corannulene ($C_{20}H_{10}$) molecules as a flat and bent adsorbent structure, respectively. They are in between the small polyaromatic molecules (such as anthracene) and large graphene nanoflakes (or even nanolayers), which have been used as hydrogen storage media [13]. Using dispersion-corrected density functional theory (DFT-D3) and 0th order symmetry-adapted perturbation theory techniques (SAPT0) we unveil the influence of the adsorbate curvature and the nature of decorating ions (Li$^+$ and Na$^+$) on the magnitude of H_2 physical adsorption. Independent gradient model (IGM) method helps to visualize the fields of the non-covalent interactions, and gives an explicit way to obtain clear qualitative knowledge on the adsorbed H_2. The present results are probably to be helpful for further investigations of interactions between hydrogen molecules and cation-decorated carbon nanostructures.

2. COMPUTATIONAL METHODS

Full geometry optimization of all structures has been performed at the BLYP/def2-SVP level of theory, using the Orca 4.0.1 program [14]. The D3 correction for dispersion of Grimme et al. [15] was used in order to properly model the dispersion interactions. BLYP has been shown to be a very reliable density functional that suits well for the adsorption studies [16]. Frequency calculations have been performed to validate equilibrium geometries.

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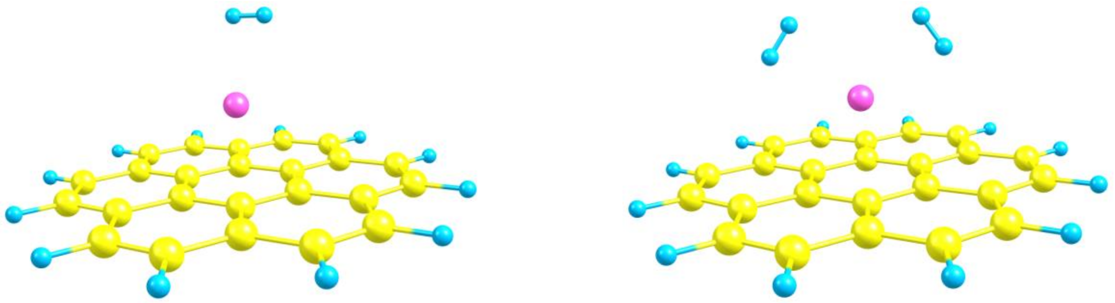
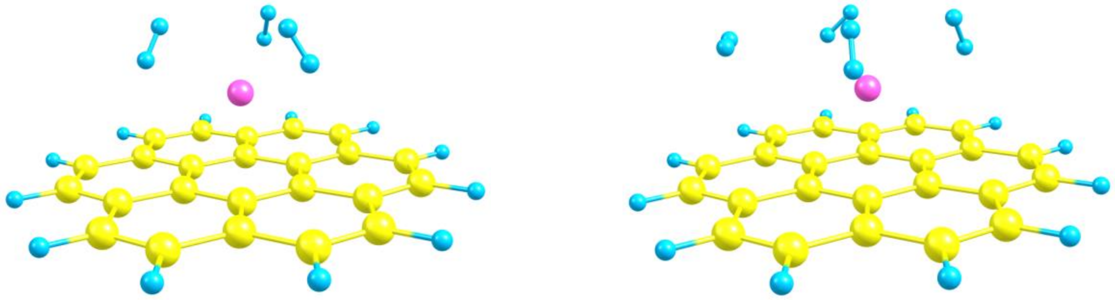
Adsorption energies and energy decomposition analysis has been carried out using the 0th order symmetry-adapted perturbation theory technique (SAPT0) along with the jun-cc-pVDZ basis set [17]. A negative adsorption energy value means that bonding is energetically favorable. SAPT0 calculation results are free from the basis set superposition error (BSSE). The distance (R) between the adsorbents and the metal cation (M^+) is a normal length between them. The distance between H_2 and M^+ ($l_{H2\text{-}M+}$) is defined as the length of a perpendicular line dropped from the hydrogen center-of-mass to the cation.



$1H_2/Li^+$@coronene $2H_2/Li^+$@coronene



$3H_2/Li^+$@coronene $4H_2/Li^+$@coronene

Fig. 1 – 1-4 hydrogen molecules adsorbed on Li^+@coronene structures. Color code: Carbon – yellow, Hydrogen – blue, Lithium cation – magenta

3. RESULTS AND DISCUSSION

3.1 Metal Cations Adsorption on Coronene and Corannulene

First, we study metal cations adsorption on both coronene and corannulene. Using SAPT0 calculations, we performed the expansion of the total interaction energy into meaningful constituents. E_{el}, E_{ex}, E_{ind}, E_{disp} represent electrostatic, exchange, inductive, and dispersion contributions, respectively. E_a is the total adsorption energy. Owing to different ionic radii ($Na^+ > Li^+$), there are two distinct equilibrium distances from these cations to the surface of the adsorbent (Table 1). Besides this, the equal charges and the non-equal radii make their ability to polarize neighboring atoms or molecules various. As the favorable position of Li^+ is substantially closer to the surface than that for Na^+, the E_{disp} term is larger for Li^+ adsorption (Table 1). However, the contribution to the total attraction energy is small in both cases (~ 1-2 %). The curved structure of corannulene gives extra input into E_{disp} term, but it is almost negligible (~ 0.050 kcal/mol). On the contrary, both E_{ind} and E_{el} terms play the major role in stabilizing interactions. The E_{ind} term contributes nearly 4/5 and 2/3 into the attractive interactions for adsorbed Li^+ and Na^+, respectively (Table 1). At the same time, the rest of the attractive energy is the share of the E_{el} term.

To validate the obtained results, we compare the E_a values for both Li^+ and Na^+ adsorption. The work of Adamo et al. has shown that BLYP is a very reliable functional to describe Li^+@benzene interactions [18]. The reference CCSD(T)/CBS method yields E_a of $37.6\ \text{kcal/mol}^{-1}$ at a Li^+@benzene equilibrium distance of 1.88 Å. Our results on coronene adsorption (Table 1) are in very good agreement with the previously obtained ones. The previous work of Tsuzuki et al. [19] showed the following results (at the HF/6-311G* level of theory): $E_a = -39.7$ kcal/mol, $R = 1.869$ Å and $E_a = -24.3$ kcal/mol, $R = 2.425$ Å for Li^+ and Na^+, respectively. The benzene molecule resembles the central ring of coronene, therefore, we can compare the aforementioned results. It can be easily seen that the obtained results and those obtained elsewhere coincide well, therefore we can state that the results seem to be justified.

3.2 Hydrogen Adsorption on M^+@coronene

We, first, study hydrogen adsorption on the M^+-decorated planar structure, namely, coronene. We add one to four hydrogen molecules in the step-by-step regime. For H_2 molecules adsorbed on M^+@coronene, we should note the importance of E_{el} and E_{ind} components of the total adsorption energy, especially in the case of the first adsorbed H_2 molecule. Indeed, the contribution of the E_{ind} term into attractive energy reaches 48 % for Li^+@coronene and 43 % for Na^+@coronene. It witnesses that Li^+ can polarize hydrogen molecules better than the Na cation. It is closely connected with the charge to size ratio of both cations. The dispersion interactions play only a marginal role in the case of one molecule adsorbed, but on going to four molecules, the E_{disp} term becomes more significant. First, the relative contribution of the E_{ind} decreases, and, second, the quantity of the neighboring H_2 molecules increases. Electrostatic interactions play a major, but not prevailing role in non-covalent interactions between H_2 and M$^+$@coronene systems as a hydrogen molecule has zero charge and dipole moment, and, therefore, the interactions are mainly governed by its quadrupole moment.

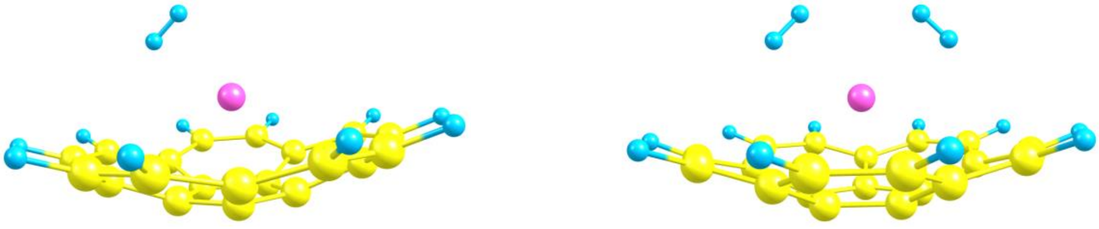
$E_a(H_2)$ for Li$^+$@coronene adsorption is significantly larger (~ 2 kcal/mol) than that for Na$^+$@coronene adsorption. However, the difference becomes smaller in going to three adsorbed molecules (~ 0.7 kcal/mol). Moreover, for the adsorbed four molecules, there arise a substantial drop in E_a for Li$^+$@coronene, and the less significant drop exists in the case of Na$^+$@coronene adsorption (Table 2). The fifth molecule uptake leads to the larger equilibrium distance (3.528 Å for Li$^+$ and 2.615 Å for Na$^+$), hence, we exclude them from the present consideration. The H-H distances (Table 2) at low coverage tend to enlarge, and they become equal to that of the single H_2 molecule at high coverage. It witnesses lower polarization of the molecules in those cases.

Table 1 – SAPT0/jun-cc-pVDZ energies (kcal/mol) as well as M$^+$-adsorbent (M$^+$-ads, M$^+$ = Li$^+$ and Na$^+$) distances (R, Å), and Mulliken charges (Q, e$^-$) for cations adsorbed on coronene and corannulene. The relative contributions into attractive interactions are given in parentheses

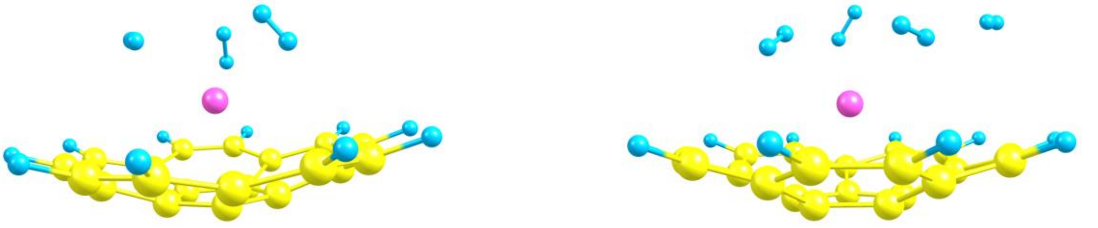
Adsorbent	M$^+$	E_{el}	E_{ex}	E_{ind}	E_{disp}	E_a	R (M$^+$-ads)	Q, e$^-$
Coronene	Li$^+$	– 9.522 (18)	13.604	– 43.962 (81)	– 0.721 (1)	– 40.601	1.80	0.769
	Na$^+$	– 13.532 (36)	9.118	– 23.657 (63)	– 0.529 (1)	– 28.600	2.33	0.788
Corannulene	Li$^+$	– 10.038 (19)	12.189	– 41.421 (79)	– 0.775 (1)	– 40.045	1.92	0.743
	Na$^+$	– 12.234 (35)	6.360	– 22.193 (63)	– 0.582 (2)	– 28.649	2.48	0.713

Table 2 – SAPT0/jun-cc-pVDZ energies (kcal/mol) as well as H_2-M$^+$ (M$^+$ = Li$^+$ and Na$^+$) distances ($l_{H2\text{-}M+}$, Å), H-H bonds ($d_{H\text{-}H}$, Å) for hydrogen molecules adsorbed on M$^+$@coronene. The relative contributions into attractive interactions are given in parentheses

Cation	No.of H_2	E_{el}	E_{ex}	E_{ind}	E_{disp}	E_a	$l_{H2\text{-}Li+}$	$d_{H\text{-}H}$
Li$^+$	1H_2	– 2.847 (37)	3.37	– 3.696 (48)	– 1.214 (15)	– 4.387	1.979	0.769
	2H_2	– 3.452 (37)	5.019	– 3.44 (37)	– 2.427 (26)	– 4.299	2.042	0.769
	3H_2	– 3.663 (37)	5.94	– 3.179 (32)	– 2.994 (31)	– 3.897	2.101	0.767
	4H_2	– 1.815 (35)	3.906	– 0.876 (17)	– 2.551 (48)	– 1.336	3.012	0.766
Na$^+$	1H_2	– 1.823 (48)	1.434	– 1.603 (43)	– 0.343 (9)	– 2.335	2.484	0.769
	2H_2	– 2.62 (40)	3.31	– 1.729 (26)	– 2.189 (34)	– 3.229	2.527	0.769
	3H_2	– 2.502 (40)	2.997	– 1.669 (27)	– 2.061 (33)	– 3.235	2.523	0.769
	4H_2	– 2.305 (41)	3.346	– 1.525 (27)	– 1.799 (32)	– 2.283	2.492	0.767



1H_2/Li$^+$@corannulene 2H_2/Li$^+$@corannulene



3H_2/Li$^+$@corannulene 4H_2/Li$^+$@corannulene

Fig. 2 – Hydrogen molecules adsorbed on Li$^+$@corannulene structures. Color code: Carbon – yellow, Hydrogen – blue, Lithium cation – magenta

3.3 Hydrogen Adsorption on M^+@corannulene

We then investigate H_2 adsorption on Li^+@corannulene (Fig. 2). On going from one to four adsorbed molecules, we can see the increase in E_{disp} and the simultaneous decrease in E_{ind} (Table 3). Dispersion contribution into attraction energy increases owing to additional adsorbed H_2 molecules, and the corresponding decrease is attributed to the smaller ability of a single cation to polarize four molecules rather than one. The relative magnitudes of the E_{el} term show nearly constant trend, and it adds nearly 37-38 % into attractive energy (Table 3).

For hydrogen adsorption on Na^+@corannulene, we can easily see the reverse situation. The E_{el} term decreases (the relative contribution to the attractive energy diminishes from 48 to 41 %), whereas the E_{ind} term undergoes a substantial decrease (from 42 to 25 %) and the E_{disp} contribution increases significantly (from 10 to 34 %). The overall decrease in E_a magnitude is closely connected with reduced effective charge of the cation centre, smaller charge transfer as well as increase in repulsions of H_2 molecules.

Let us compare the cases of H_2 adsorption on Li^+- and Na^+@corannulene. When only one hydrogen molecule is being adsorbed, for the former, the absolute magnitude of E_a is about twice as high as for the latter one. For different number of adsorbed molecules, the ratio changes, but, generally, E_a for adsorption on Li^+@corannulene is substantially higher. The reason of that is the larger charge to size ratio for Li cation. As it was observed earlier, the smaller size of Li^+ renders it a more effective cation for H_2 uptake than the Na one [20].

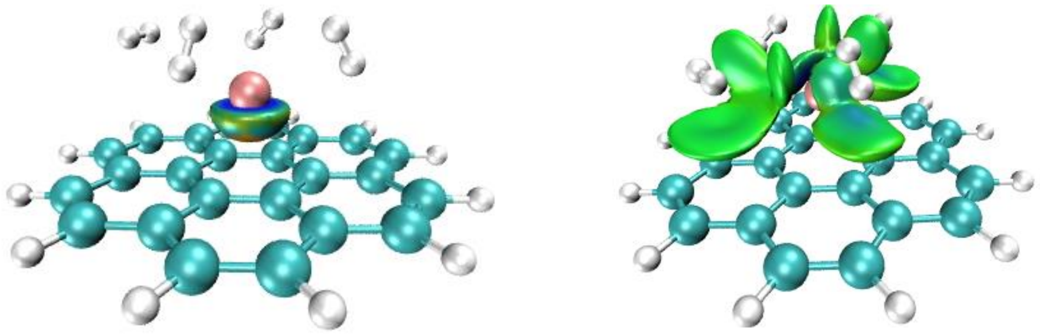
The absolute E_a decrease is higher in the case of Li^+ (> 1.5 kcal/mol) compared with Na^+ (~ 0.6 kcal/mol). However, for the former, the E_a values are in the optimal range of energy values for hydrogen adsorption (> 3.57 kcal/mol [21]), and for the latter, E_a values are beyond that range.

To better understand the interactions between Li^+ and the adsorbent as well as between H_2 molecules and Li^+@adsorbent, we carry out the visual analysis by IGM method, which is described elsewhere [22]. We may separate various types of interactions, namely strong attraction (blue), weak van der Waals forces (green) and repulsive interactions (red) (Fig. 3). For the Li^+ adsorption on corannulene or coronene (Fig. 3, left), the deep-blue lobes prove strong attractive interactions due to electrostatic/polarization forces. On the contrary, for the adsorption of hydrogen molecules on Li^+@corannulene or coronene, the main non-covalent interactions are van der Waals forces. The small admixture of the pale-blue color denotes the polarization induced by Li^+ (Fig. 3, right). A slightly larger size of the lobes reflects the stronger adsorption for corannulene.

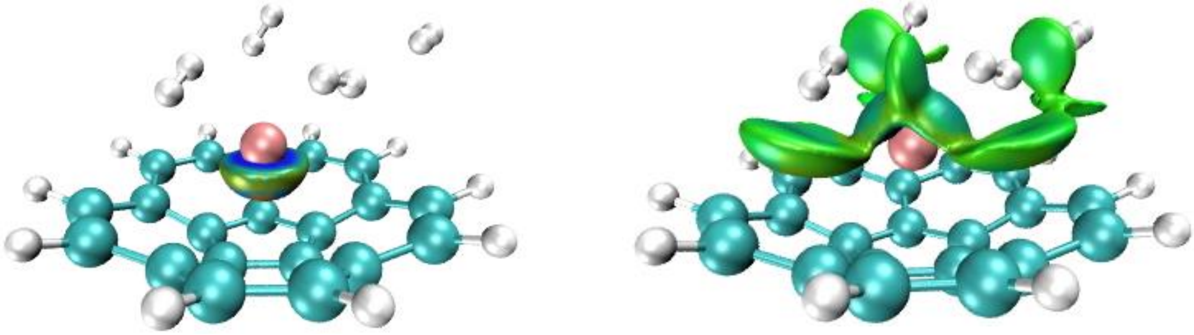
We suppose that the results obtained herein are valuable for the understanding of the physical mechanisms of hydrogen adsorption using cations-decorated polyaromatic hydrocarbons.

Table 3 – SAPT0/jun-cc-pVDZ energies (kcal/mol) as well as H_2-M^+ (M^+ = Li^+ and Na^+) distances ($l_{H2\text{-}M+}$, Å), H-H bonds ($d_{H\text{-}H}$, Å) for hydrogen molecules adsorbed on M^+@corannulene. The relative contributions into attractive interactions are given in parentheses

M^+	No. of H_2	E_{el}	E_{ex}	E_{ind}	E_{disp}	E_a	$l_{H2\text{-}Li+}$	$d_{H\text{-}H}$
Li^+	$1H_2$	– 3.952 (37)	5.657	– 4.165 (39)	– 2.588 (24)	– 5.047	1.971	0.769
	$2H_2$	– 4.431 (37)	7.588	– 4.081 (34)	– 3.373 (29)	– 4.297	2.015	0.768
	$3H_2$	– 4.662 (38)	8.546	– 3.711 (31)	– 3.804 (31)	– 3.631	2.092	0.768
	$4H_2$	– 4.105 (37)	7.642	– 3.55 (32)	– 3.464 (31)	– 3.477	4.096	0.766
Na^+	$1H_2$	– 1.847 (48)	1.45	– 1.626 (42)	– 0.405 (10)	– 2.428	2.481	0.769
	$2H_2$	– 2.600 (44)	3.239	– 1.763 (30)	– 1.567 (26)	– 2.690	2.467	0.769
	$3H_2$	– 2.717 (44)	3.573	– 1.757 (28)	– 1.76 (28)	– 2.661	2.471	0.769
	$4H_2$	– 2.431 (41)	4.084	– 1.499 (25)	– 2.001 (34)	– 1.847	2.566	0.767



$4H_2$/Li+@coronene $4H_2$/Li+@coronene



4H$_2$/Li+@corannulene 4H$_2$/Li+@corannulene

Fig. 3 – IGM graphs for Li$^+$ and four H$_2$ molecules adsorbed on two types of adsorbents. Atomic color code: Carbon – light-blue, Hydrogen – white, Lithium cation – pale red. Color code: green lobes denote weak van der Waals interactions, blue lobes denote strong attraction. Isovalue = 0.005

4. CONCLUSIONS

To sum up, in the present paper, we theoretically study the effects of adsorbents' curvature and different cations as anchoring points on hydrogen adsorption. Using DFT-D3 and SAPT0 methods, we obtain equilibrium geometries as well as adsorption energies (E_a) of hydrogen molecules. Moreover, we decompose E_a into meaningful components (E_{el}, E_{ex}, E_{ind}, E_{disp}) to get deeper insight into H$_2$/adsorbent interactions. For the planar adsorbent, the Li$^+$@coronene model, we note the decreasing trend for H$_2$ adsorption energy (from – 4.387 to – 1.336 kcal/mol). In the case of Na$^+$@coronene adsorbent, the E_a magnitude for 1 to 4 adsorbed H$_2$ molecules changes less significantly (from – 2.335 to – 2.283 kcal/mol). For the bent structures, Li$^+$@ and Na$^+$@corannulene models, we also show the close trends: the significant decrease in E_a for Li$^+$- and the slow decline for Na$^+$-decorated structures. However, E_a values for Li$^+$-decorated models are much higher than those for Na$^+$-decorated models. Taking into consideration the lower weight of Li cations, we may conclude that Li$^+$ is a more promising decorating agent than Na$^+$. Li$^+$@corannulene provides stronger adsorption for 4th hydrogen molecule compared with Li$^+$@coronene. Besides, the Li cation adsorption is more favorable for corannulene. The results witness that corannulene is a more effective hydrogen storage medium compared with coronene.

ACKNOWLEDGEMENTS

This work was partially supported by the IRNITU grant for scientific groups (No. 03-FPK-19).

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Адсорбція водню на іонах Li^+ та Na^+, оздоблених короненом та коранyленом: DFT, SAPT0 та IGM дослідження

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Нові системи для зберігання водню мають велике значення для сучасної енергетики. У роботі ми досліджуємо адсорбцію водню на плоских (коронен) та зігнутих (коранулен) моделях адсорбенту за допомогою обчислень DFT-D3 та SAPT0. Для покращення поглинання водню ми також використовуємо «оздоблення» адсорбентів катіонами M (M = Li, Na). Було встановлено, що коранулен адсорбує катіони Li та Na майже однаково порівняно з короненом. Однак адсорбція водню набагато більш виражена у випадку коранулена. Так, наприклад, енергії адсорбції (E_a) для 1-ї та 4-ї молекул водню, адсорбованих на Li^+@coronene and Li^+@corannulene, складають відповідно – 4.387, – 1.336 ккал/мол та – 5.047, – 3.477 ккал/мол. Ми також використовуємо метод незалежної градієнтної моделі (IGM) для візуалізації взаємодіючих областей між катіонами, воднем та адсорбентами, що вивчаються. Ми ретельно показуємо сильну взаємодію між M^+ та молекулами адсорбенту, а також слабку взаємодію між воднем та досліджуваними катіонами. Отримані результати повинні забезпечити глибокий аналіз основ зберігання водню з використанням поліароматичних вуглеводнів, оздоблених M^+.

Ключові слова: Коронен, Коранулен, Водень, DFT, Адсорбція.