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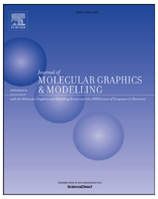

An accurate empirical method to predict the adsorption strength for π-orbital contained molecules on two dimensional materials

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ABSTRACT

To obtain the adsorption strength is the key point for materials design and parameters optimization in chemical engineering. Here we report a simple but accuracy method to estimate the adsorptive energies by counting the number of π-orbital involved atoms based on theoretical computations for hexagonal boron nitride (h-BN) and graphene. Computational results by density function theory (DFT) as well as spin-component scaled second-order Møller-Plesset perturbation theory (SCS-MP2) both confirm that the adsorptive energies correlate well with the number of π-orbital involved atoms for π-orbital contained molecules. The selected molecules (adsorbates) are commonly used in chemical industry, which contains C, N, S, O atoms. The predicted results for the proposed formulas agree well with the current and previous DFT calculated values both on h-BN and graphene surfaces. Further, it can be also used to predict the adsorptive energies for small π-orbital contained molecules on BN and carbon nanotubes. The interaction type for these adsorptions is typical π-π interaction. Further investigations show that the physical origin of these interactions source from the polar interactions between the adsorbents and adsorbates. Hence, for separation or removal of aromatic molecules, how to modify the aromaticity and polarity of both adsorbents and adsorbates will be the key points for experiments.

1. Introduction

Adsorption is very important for chemical separation, molecular recognition, self-organization or other application aspects [1–7]. To obtain the adsorption strength is the key point for materials design and parameters optimization in chemical engineering. Commonly used methodology is based on experimental characterization as well as theoretical computation. Especially, theoretical computation and its derived empirical methods become more and more importantly and efficiently techniques to deep understanding of the adsorption process in nowadays [8–12]. Recent years, two-dimensional nanomaterials attract tremendous researchers to study their structures, physiochemical properties, and potential applications. Among which, graphene as well as the hexagonal boron nitride (h-BN) are undergoing continuous interests. The applications of these two dimensional (2D) materials mainly focus on piezoelectricity, field emission, catalysis, adsorption, and so on [13–16]. Especially, h-BN and graphene were used as adsorbents to separation of diverse chemicals, such as aromatic sulfur compounds in diesel, benzene, 9,10-anthraquinone as electrode materials, methylene blue, which shows remarkable adsorptive activity and selectivity to aromatic compounds [7,10,17–20]. The driven force for adsorption of aromatic compounds on h-BN is qualitatively proposed to be π-π interaction according to previous works. However, it is still lack of deep investigation on this type of interaction for two dimensional materials, e.g. what's the physical origin of π-π interaction? Moreover, based on previous findings, if the adsorption strengths for various adsorbates can be quantitatively predicted that may be very valuable for rational design highly

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efficient adsorbents, chemical separations, or other aspects (e.g. kinetic and thermodynamic parameters) of chemical engineering. For the purpose of deep understanding of the interaction between adsorbents and adsorbates, here we report a simple but accuracy method to estimate the adsorptive energies by counting the number of π-orbital involved atoms based on theoretical computations for graphene and h-BN. This formula can be also generally expanded to other similar systems. Besides, the physical origin of the π-π interaction in the current systems is ascribed to the polar interaction between the adsorbents and adsorbates. It hopes the present work can afford some new insights into the adsorptive interaction on two dimensional materials and designing highly efficient adsorbents for different purposes.

2. Computational details

The π-π interaction plays an important role in the adsorptive reaction for two dimensional materials [21]. Theoretical calculations show that π-π interaction is known due to a special electron correlation (dispersion) effect [22–24]. It was found that the dispersion corrected density functional can give good results as compared to the results of perturbation theory [21]. Hence, the dispersion corrected B3LYP functional at 6-31 + G(d) level was chosen as the routine method in the current work. The validation of this model chemistry was further confirmed by a larger basis set (B3LYP + D3/6-311 + G(2d,p), Table S1). Results show that the adsorptive energies predicted by 6-31 + G(d) basis set are very close to the results predicted by the larger basis set. Combined consideration of the accuracy and computational time, it is proper to employ B3LYP + D3/6-31 + G(d) model chemistry to study the current systems. Moreover, in order to avoid computational artifact by DFT method, the geometrical structures of two smallest and most representable complexes (thiophene … borazine and thiophene … benzene) were fully optimized using the SCS-MP2 at cc-pVTZ level of theory which has been wildly adopted in the investigation of non-covalent interactions (Supporting Information Fig. S1 and Table S2) [25]. The block-localized wavefunction (BLW-ED) calculations were also carried out aiming at further examining the DFT conclusions [26]. Results show that the preferred configurations of two parallel molecules predicted at both theoretical levels are qualitatively identical for each complex, which represents the character of π-stacking interactions. Furthermore, the binding energy calculated at B3LYP-D3/6-31 + G(d) level is very close to the result of SCS-MP2/cc-pVTZ, while strength of the interaction between thiophene and benzene is underestimated at B3LYP-D3/6-31 + G(d) level. However, the overall tendency of relative bonding strength predicted by DFT-D3 and SCSMP2 is the same. At last, the importance of each energy component of BLW-ED approach calculated at both levels is consistent. The bonding energy between parallel molecules in each complex is dominated by dispersion interaction and enhanced by both polarization and charge transfer interactions for both complexes. Overall, the DFT calculations reproduce the conclusions obtained from the SCS-MP2 theory which show the current DFT method is accurate.

In addition, cluster models were widely used in studying the properties and interaction reactions for h-BN and graphene systems [21,27,28]. Furthermore, it has been used to explore the physisorption of ionic liquids on boron nitride sheets [29]. Recently, this model was also used to study the adsorption of explosive molecules on boron nitride and graphene nano flakes. The current cluster model (e.g. C_{353}-h-BN, Fig. 1) contains 19 rings (5 rings in the middle row), which is proper to simulate the adsorption of the π-orbital contained molecules because the largest adsorbate contains 4 rings. The adsorptive energy is obtained according following equation:

$$E_{ads} = E_{com} - (E_{mol} + E_{sub}) + E_{BSSE} \qquad (1)$$

Where E_{ads} denotes the adsorptive energy, E_{com}, E_{mol} and E_{sub} are the electronic energies for the complex, adsorbates, and adsorbents, respectively. E_{BSSE} stands for the basis set superposition error (BSSE) generated in the current level of model chemistry. In order to reach deep understanding of this kind of adsorptive interaction, the reduced density gradient (RDG) analysis was implemented, which is a powerful method to investigate the interaction strength, types for non-covalent systems [30]. All the calculations were used the Gaussian 09 suite of programs [31].

3. Results and discussion

3.1. Structures and adsorptive energies

Cluster Models used to simulate the h-BN and graphene materials (C_{353}-h-BN and C_{353}-Graphene) were plotted in Fig. 1. The adsorbates, which are all planar, π-orbital contained molecules, were also illustrated in Fig. 1. They are named as, BTD (butadiene), OA (oxylic acid), FD (formaldehyde), BF (benzofuran), FR (furan), BQ (benzoquinone), BZ (benzene), IM (imidazole), Py (pyridine), BP (benzpyrrole), TH (thiophene), BT (benzothiophene), DBT (dibenzothiophene), and BNT (benzo[*b*]naphtho[*2,3-d*]thiophene). The reason for the selection of these molecules is that their adsorption behaviors are very important for separation science in chemical engineering, molecular recognition or other applications, for example, the adsorption of FD in environmental science, as well as the separation of BZ and the sulfur removal of DBT in petrochemical industry. These molecules consist of different type of elements, such as C, H, O, N, S. Some of typical adsorptive configurations were plotted in Fig. 2 while others could be found in Fig. S2. The selected configurations are the complexes formed by the adsorption of PY, BT, OA and DBT on h-BN and graphene. It can be seen from Fig. 2 (and Fig. S2) that all the adsorbates are paralleled with the plane of adsorbents from both top view and side view. The vertical distances between them (from Fig. 2a–d) are 3.210 Å, 3.247 Å, 3.200 Å, and 3.373 Å, respectively. These values are typical distances for π-π interaction [10]. Previous studies also show that the optimal configurations for π-orbital contained molecules are paralleled [10,27,28,32,33]. Besides, heavy atoms from π-orbital contained molecules tend to locate on either top of substrate atom or the center of rings for both h-BN and graphene, which is also similar to those works. The planarity of the h-BN and graphene surfaces are almost unchanged after adsorption because the physical adsorption nature, which is similar with previous works [10,12]. All of the adsorptive energies were listed in Table 1. The adsorptive energies range from −4.4 to −25.3 kcal/mol on h-BN, −3.9 to −24.3 kcal/mol on graphene, respectively. For both adsorbents, the smallest adsorptive energy is formed by the adsorption of FD while the largest adsorptive energy is formed by the adsorption of BNT. It was interesting to find that similar adsorptive energies were obtained for a specific molecule on different sites or on different materials (graphene and h-BN nanosheet) [10]. Besides, most of the adsorptive energies are larger on h-BN for a given molecule. Similar phenomenon has been also reported by previous works and the reason is ascribed to the higher charge transfer in the complexes formed by h-BN [27]. In the current work, the calculated results will show the reason correlates with the stronger polar interaction between adsorbates and h-BN in the following section.