

Adsorption of the urea molecule on the B₁₂N₁₂ nanocage

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Abstract: The adsorption of the urea molecule on the external surface of the B₁₂N₁₂ nanocage was investigated using density functional theory (DFT) calculations. Adsorption of urea on the nanocage releases energies of about –23.70 to –29.50 kcal/mol with a significant NBO charge transfer from the urea to the nanocage. It was also found that the urea molecule can be strongly chemisorbed on the surface of the nanocage with Gibbs free energies of –7.91 to –14.81 kcal/mol. The HOMO–LUMO gap of the nanocage does not change significantly upon urea adsorption, while the Fermi level is dramatically changed from –4.27 eV in the pristine nanocage to upper energies upon urea adsorption. The geometric structure, adsorption energy, solvation effect, charge transfer, and frequency analyses of the urea adsorption on the nanocage models showed that the urea molecule could be firmly adsorbed by the nanocage and the nanocage could be a potential efficient adsorbent for the adsorption of urea.

Key words: Boron nitride nanocage, urea, adsorbent, adsorption, electronic properties

1. Introduction

Urea (CO (NH₂)₂) is an organic compound that is synthesized in the body of many organisms, either from the oxidation of amino acids or from ammonia. It is also a major metabolic end product. The removal of urea excess has been an important problem for patients suffering from renal failure. The normal level of urea in human serum is in the range of 15–40 mg/dL. High urea accumulation in serum can cause damage to body organs. Hemodialysis is the conventional treatment for renal insufficiency, but is expensive, time-consuming, and difficult to handle. Therefore, the reduction of urea concentration in serum can potentially delay the onset of hemodialysis therapy in patients.

Recent advances in nanomaterial science open a promising field toward the removal of organic molecules. In our previous study, it was shown that phenol can be absorbed significantly on gallium- and indium-doped boron nitride nanotubes (BNNTs)¹ and this nanotube model can be used for phenol storage. Surface modification of a BNNT by the sulfamide molecule has been investigated by Beheshtian et al.² Their results showed that the sulfamide molecule can be chemically diffused into its wall, accompanied by the release of one NH₃ molecule. Among organic molecules, the proper adsorption of urea is biologically important. The mechanisms of urea decomposition into isocyanic acid (HNCO) and ammonia (NH₃) in the gas phase and on the ZnO (1010) surface have been investigated by Gao et al.³ They showed that urea adsorption on the surface is an exothermic process and the surface can catalyze urea decomposition. In recent decades, active charcoal,⁴ oxystarch,⁵ oxycellulose,⁶ and zirconium phosphate⁷ have been used for the removal of urea. Although there have been

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several experimental papers on the removal of urea using organic and inorganic materials, to the best of our knowledge no theoretical investigations have been reported for the removal of urea using nanomaterials yet. Therefore, further study of urea adsorption on nanomaterials is an important task.

Recently, interactions of different molecules with fullerene-related materials have attracted attention due to their unique physical and chemical properties.^{8–10} Among them, the $B_{12}N_{12}$ fullerene-like cage has attracted considerable attention due to its high-temperature stability, low dielectric constant, large thermal conductivity, and oxidation resistance.^{11,12} Seifert et al.¹³ have investigated structures of $(BN)_n$ fullerene-like cages based on ab initio calculations. They showed that $B_{12}N_{12}$, $B_{16}N_{16}$, and $B_{28}N_{28}$ are “magic” and $B_{12}N_{12}$ appears to be more stable than the others. Moreover, $B_{12}N_{12}$ was synthesized by Oku et al.¹⁴ via laser desorption time-of-flight mass spectrometry. Their results showed that this cluster consists of 8 hexagon and 6 tetragon rings. Therefore, it is important to understand the advantages and disadvantages of the adsorption of urea on the $B_{12}N_{12}$ nanocage. In the present study, the interaction of urea on the pristine $B_{12}N_{12}$ nanocage was investigated using density functional theory (DFT) calculations.

2. Results and discussion

The optimized structure, bond lengths, and calculated density of states of the $B_{12}N_{12}$ nanocage are shown in Figures 1a and b. There are 2 distinct B–N bonds in the nanocage; one is shared between 2 hexagon rings and the other between a tetragon and hexagon ring with bond lengths of 1.44 and 1.49 Å. The calculated NMR spectrum of $B_{12}N_{12}$ consists of 2 single peaks, confirming its T_h symmetry. The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), energy gap (E_g), is about 6.86 eV. This indicates that the nanocage is an insulator. The NBO charges on B and N atoms in the nanocage are 1.17 and $-1.17 |e|$, indicating the strong ionicity nature of B–N bonds. The IR frequencies are in the range of 325.94 to 1447.77 cm^{-1} , showing that the structure is stable.

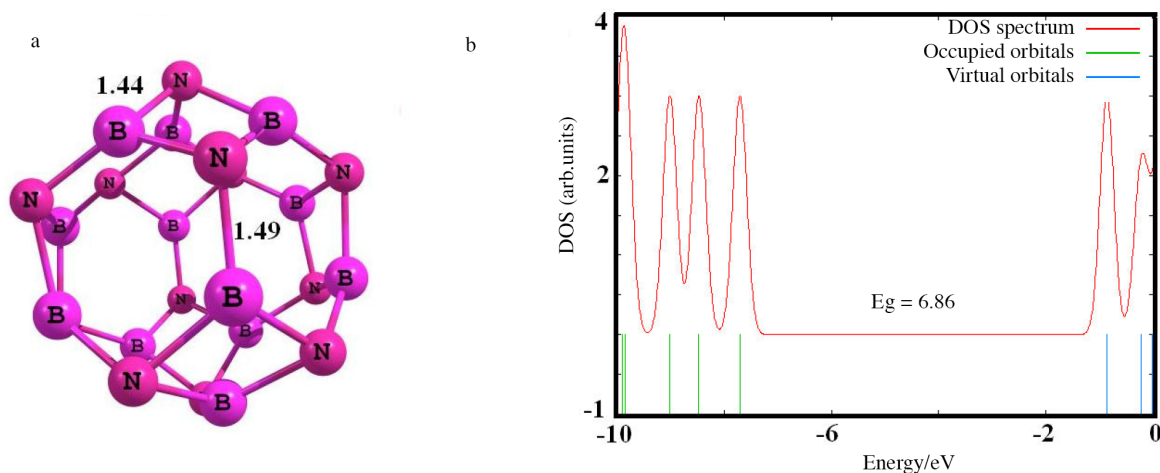


Figure 1. Optimized structure of $B_{12}N_{12}$ nanocage and its density of state (DOS). Distances are in angstroms.

On the basis of NMR spectra, each of the calculated B and N atoms consists of a single peak, indicating that the nanocage must contain one kind of either B or N atom. The results show that there are 2 distinct sites for urea adsorption: the top of the B atom and that of the N one. The MEP and structural parameters of the urea molecule are shown in Figure 2. The partial negative charge on the O atom and slightly negative charge on the N atoms of the urea molecule make it reactive toward the Lewis acid sites of B atoms. On the other hand,

the hydrogen atoms are positively charged (blue colors), making urea reactive toward the Lewis base sites of N atoms. Therefore, the urea molecule can approach the nanocage walls with different orientations.

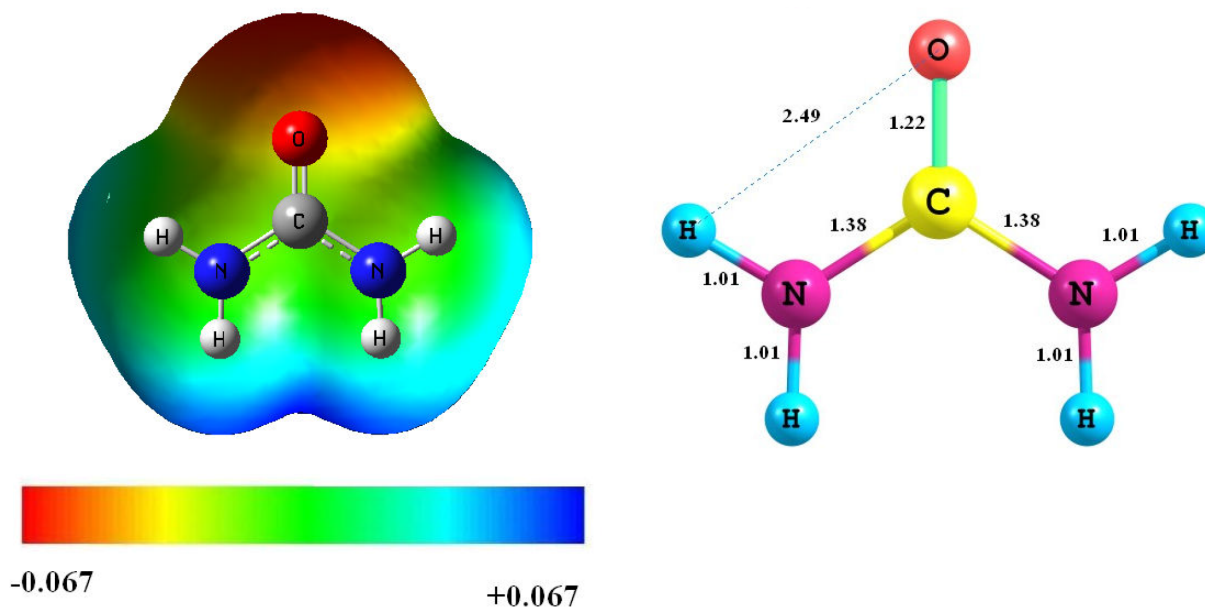


Figure 2. Computed electrostatic potentials on the molecular surfaces of a single urea molecule and its structural parameters. The surfaces are defined by the 0.0004 electrons/b3 contour of the electronic density. Color ranges, in a.u.

For the urea/ $B_{12}N_{12}$ complex, we investigated various possible initial adsorption geometries including the H, N, and O atoms of the urea molecule close to the B and N sites of the $B_{12}N_{12}$ with different orientations. However, only 3 stable structures were obtained upon the relaxation process, which is shown in Figures 3A–C, and their electronic properties are shown in Table 1. E_{ad} values of the configurations are in the range of -23.70 to -29.50 kcal/mol, indicating that the adsorptions are exothermic.

Table 1. Calculated adsorption energy (E_{ad} , kcal/mol), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), Fermi level energy (E_{FL}), and work function (Φ) for the considered systems at B3LYP/6-31G* level of theory. The energies are in eV.

| Structure | E_{ad} | E_{HOMO} | E_{LUMO} | E_g | ${}^a\Delta E_g(\%)$ | ${}^bQ_T e $ | E_{FL} | Φ |
|------------------------------------|----------|------------|------------|-------|----------------------|--------------|----------|--------|
| $B_{12}N_{12}$ | - | -7.70 | -0.84 | 6.86 | - | - | -4.46 | 3.43 |
| $B_{12}N_{12}$ in H_2O | - | -7.65 | -0.73 | 6.92 | - | - | -4.19 | 3.46 |
| (A) urea/ $B_{12}N_{12}$ | -20.95 | -7.05 | -0.45 | 6.60 | 3.79 | 0.38 | -3.75 | 3.30 |
| (B) urea/ $B_{12}N_{12}$ | -21.44 | -7.02 | -0.49 | 6.53 | 4.81 | 0.34 | -3.76 | 3.26 |
| (C) urea/ $B_{12}N_{12}$ | -24.85 | -6.53 | -0.35 | 6.18 | 9.91 | 0.31 | -3.44 | 3.09 |
| (C) urea/ $B_{12}N_{12}$ in H_2O | -29.83 | -6.91 | -0.22 | 6.69 | 3.32 | 0.34 | -3.56 | 3.34 |

^aThe change in HOMO–LUMO gap of $B_{12}N_{12}$ nanocage after urea adsorption.

^b Q_T is defined as the total natural bond orbital charges on the urea molecule (positive values show charge transfer from the urea to $B_{12}N_{12}$ nanocage).

In Figure 3, configurations A and B show the interaction between N and H atoms of the urea molecule with the B and N sites of the nanocage, so that the N atom of urea molecule is bonded to the B atom of the

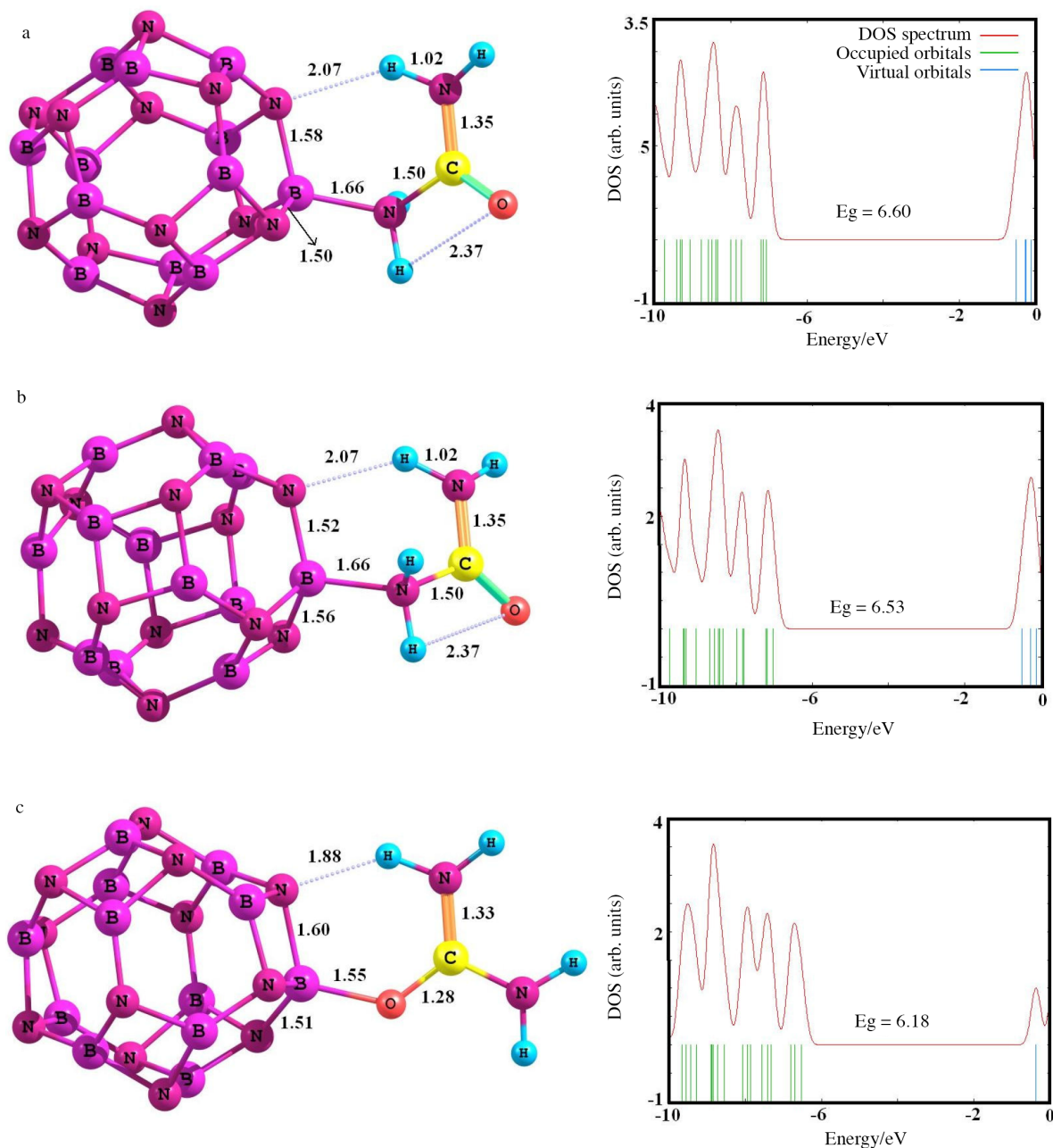


Figure 3. Models for 3 stable configurations of urea/ $B_{12}N_{12}$ complex and their density of state (DOS) plots. Distances are in angstroms.

nanocage. Based on the NBO results and structural analysis after the adsorption process of the configurations, the new bond of B–N is formed with length 1.66 Å. Moreover, the interaction distance between the H atom of the urea molecule with the N site of the nanocage in the configurations A and B is about 2.07 Å (Figure 3). The E_{ad} in these configurations is about –23.70 and –23.74 kcal/mol and a significant NBO charge of 0.38 and 0.34 |e| is transferred from the urea molecule to the nanocage, respectively. In the configurations, the adsorption of urea shows a local structural deformation on both the urea and the $B_{12}N_{12}$ nanocage. The bond length of

C–N of the urea molecule is increased from 1.38 Å in free urea to 1.50 Å in the configurations. In addition, the length of B–N bonds in the adsorbed ring increased from 1.44 and 1.49 Å in the pristine to 1.50 and 1.58 Å in configuration A and 1.52 and 1.56 Å in configuration B. The above results indicate that the adsorption process of the configurations is strong and should be considered chemisorption.

The most stable case, however, is the adsorption of the urea molecule on the B₁₂N₁₂ nanocage through configuration C. In this configuration, the O atom of the urea molecule is bonded to the B atom of the nanocage. For the configuration, the calculated value of E_{ad} is –29.50 kcal/mol and a notable charge of about 0.31 |e| is transferred from the molecule to the nanocage. Moreover, the length of the newly formed B–O bond is about 1.55 Å. As can be seen in Figure 3, in configurations A and B, the interaction distance of H–N is 2.07 Å, whereas in configuration C it is 1.88 Å, resulting in more stability compared to configurations A and B. The bond length of C–O of the urea molecule is increased from 1.22 Å in free urea to 1.28 Å in the configuration. The above results indicate that the urea molecule has chemisorbed on the B₁₂N₁₂ nanocage and the nanocage can be a promising candidate for the reduction of urea concentration. For further investigation of the adsorption of urea, the solvation effect, electronic properties, and frequency analyses of the configurations are studied.

Solvation effects in water are investigated in adsorption of urea on the B₁₂N₁₂ nanocage. Solvation energies (E_{solv}) for the pristine nanocage and configuration C (the most stable configuration) were obtained by optimizing the structures in the gas and water. The difference between these optimization energies is defined as E_{solv} . The E_{solv} for the pristine nanocage and configuration C is –6.32 and –25.02 kcal/mol, respectively. The results show that configuration C is more soluble in water than the pristine nanocage. For the configuration, the calculated value of E_{ad} is increased from –29.50 kcal/mol with charge transfer of about 0.31 |e| in the gas phase to –32.89 kcal/mol with charge transfer of about 0.34 |e| in the solvent phase (see Table 1). Therefore, presence of polar solvent increases the adsorption and electron donor of the urea molecule on the nanocage.

The influence of urea adsorption on the electronic properties of the B₁₂N₁₂ nanocage was also investigated. Comparing the density of states of the pristine B₁₂N₁₂ nanocage (Figure 1) and configurations A, B, and C, it was found that their E_g values changed about 3.79%–9.91% after the adsorption of urea. The results show that the adsorption of urea cannot significantly influence the E_g or conductivity of the nanocage. As shown in Table 1, although the change in E_g is not significant in the configurations, the Fermi level energy (E_{FL}) of the configurations is increased from –4.27 eV in the pristine B₁₂N₁₂ nanocage to –3.75, –3.76, and –3.44 eV in configurations A, B, and C, respectively. This increasing of E_{FL} with urea adsorption leads to a decrement in the work function (Φ), which is important in field emission applications. The work function is defined as the energy difference between the Fermi level energy and the LUMO.¹⁵ For the configurations, work function is decreased from 3.43 eV in the pristine B₁₂N₁₂ nanocage to 3.30, 3.26, and 3.09 eV in configurations A, B, and C, respectively (Table 1). The results show that the field emission properties of the configurations are facilitated upon urea adsorption.

The dispersion corrected functional M06 was used to calculate the mentioned parameters. The results are shown in Table 2. The results show that the calculated values for the parameters from this method are slightly greater than those of the B3LYP in all cases due to adding an empirical dispersion correction to the complex systems in calculating the parameters. Furthermore, the results indicate that the urea molecule has chemisorbed on the B₁₂N₁₂ nanocage and the nanocage can be a promising candidate for the adsorption of the urea molecule.

Table 2. Calculated adsorption energy (E_{ad} , kcal/mol), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), Fermi level energy (E_{FL}), and work function (Φ) for the considered systems at M06/6-31G* level of theory. The energies are in eV.

| Structure | E_{ad} | E_{HOMO} | E_{LUMO} | E_g | ${}^a\Delta E_g(\%)$ | ${}^bQ_T e $ | E_{FL} | Φ |
|--|----------|------------|------------|-------|----------------------|--------------|----------|--------|
| B ₁₂ N ₁₂ | - | -8.28 | -0.66 | 7.62 | - | - | -4.47 | 3.81 |
| B ₁₂ N ₁₂ in H ₂ O | - | -8.27 | -0.60 | 7.67 | - | - | -4.44 | 3.84 |
| (A) urea/B ₁₂ N ₁₂ | -22.26 | -7.53 | -0.35 | 7.18 | 5.77 | 0.33 | -3.94 | 3.59 |
| (B) urea/B ₁₂ N ₁₂ | -22.10 | -7.50 | -0.33 | 7.17 | 5.90 | 0.33 | -3.92 | 3.58 |
| (C) urea/B ₁₂ N ₁₂ | -26.62 | -7.00 | -0.21 | 6.79 | 10.89 | 0.31 | -3.60 | 3.96 |
| (C) urea/B ₁₂ N ₁₂ in H ₂ O | -30.89 | -7.53 | -0.19 | 7.34 | 4.30 | 0.32 | -3.86 | 3.67 |

However, in order to investigate the stability of configurations, it is necessary to calculate the harmonic frequencies for the structures. The calculated harmonic frequencies for the configurations are positive (Table 3), confirming that the configurations are stable. In configurations A and B, the stretching mode of the B–N (the distance between the urea molecule and the nanocage) is approximately 763.7 and 765.2 cm⁻¹, respectively, confirming the formation of the new B–N bond and the strong interaction of the urea molecule with the nanocage. Moreover, in configuration C, the stretching mode of the B–O (the distance between the urea molecule and the nanocage) is approximately 775.8 cm⁻¹, demonstrating that the B–O interaction is stronger than the B–N interactions. Values of ΔE , ΔH , ΔG , and ΔS of these configurations are shown in Table 3. The values show that ΔE , ΔH , and ΔG of this configuration are more negative than those of configurations A and B. We think that this is due to the fact that upon urea adsorption on the B₁₂N₁₂ nanocage, the entropy of the system (ΔS) is much more increased compared to the other cases. Briefly, study of the adsorption, solvation effect, structural parameters, charge transfer, and frequency analyses of the configurations shows that the urea molecule has chemisorbed on the nanocage and the B₁₂N₁₂ nanocage can be used for the adsorption and reduction of urea concentration.

Table 3. Calculated thermodynamic properties [ΔH , ΔG (kcal/mol), and ΔS (kcal/mol-K)], minimum and maximum vibrational frequencies (cm⁻¹) for the considered systems at B3LYP/6-31G* level of theory.

| Structure | ΔE | ΔH | ΔG | ΔS | ν_{min} | ν_{max} |
|--|------------|------------|------------|------------|-------------|-------------|
| B ₁₂ N ₁₂ | - | - | - | - | 325.94 | 1447.77 |
| (A) urea/B ₁₂ N ₁₂ | -19.63 | -20.22 | -7.91 | -0.04 | 39.02 | 3665.81 |
| (B) urea/B ₁₂ N ₁₂ | -19.65 | -20.24 | -7.91 | -0.04 | 41.05 | 3664.07 |
| (C) urea/B ₁₂ N ₁₂ | -26.26 | -26.85 | -14.81 | -0.02 | 40.13 | 3721.07 |

In summary, by performing density functional calculations we found that the pristine B₁₂N₁₂ nanocage showed a strong interaction towards the urea molecule. The geometric structure, adsorption energy, solvation effect, charge transfer, and frequency analyses of the configurations presented dramatic changes after the adsorption of the urea molecule. All these results show that the urea molecule could be firmly adsorbed by the nanocage and the nanocage could be a potential efficient adsorbent for adsorption of urea.

3. Computational methods

The spin-unrestricted B3LYP hybrid DFT method within 6-31 G* all electron basis sets was performed for the geometry optimizations, natural bond orbital (NBO), molecular electrostatic potential (MEP), density of states analyses, frontier molecular orbital (FMO) analyses, and energy calculations on the B₁₂N₁₂ nanocage with and

without a urea molecule. The B3LYP is one of the most popular hybrid density functional methods for the study of different nanostructures.^{1,2,8–12} Frequency analyses of the optimized structures were also computed at the same level of theory to confirm that all the stationary points correspond to true minima on the potential energy surface. Solvation effects (water) were investigated on the urea/B₁₂N₁₂ complexes by using a polarized continuum model (PCM). We also calculated the urea/B₁₂N₁₂ complexes using the newly developed M06 functional¹⁶ with 6-31 G* basis set to reoptimize the structures. When a urea molecule is adsorbed on the B₁₂N₁₂ nanocage surface, the adsorption energy (E_{ad}) of urea on the nanocage is obtained using the following equation:

$$E_{ad} = E_{urea/B_{12}N_{12}} [E_{B_{12}N_{12}} + E_{urea}] + E_{BSSE},$$

where $E_{urea/B_{12}N_{12}}$ is the total energy of the adsorbed urea molecule on the B₁₂N₁₂ nanocage. $E_{B_{12}N_{12}}$ and E_{urea} are the total energy of the pristine B₁₂N₁₂ and single urea molecule, and E_{BSSE} is the basis set superposition errors corrected for all E_{ad} values. The negative value of E_{ad} shows that the adsorption is exothermic. All the calculations were carried out by using the GAMESS suite of programs.¹⁷

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