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H₂, Ne, and N₂ Energies of Encapsulation into C₆₀ Evaluated with the MPWB1K Functional

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Abstract: The recently suggested MPWB1K functional is tested on H₂@C₆₀, Ne@C₆₀, and N₂@C₆₀ as a tool for evaluations of stabilization energies upon encapsulation of nonmetallic species into fullerenes. It is found that the MPWB1K (modified Perdew−Wang and Becke functionals) values can be within a few kilocalories per mole from the MP2 or SCS-MP2 (spin-component scaled MP2) values so that further applications of the functional are clearly encouraged. The best estimates of the encapsulation-energy gains found for H₂@C₆₀, Ne@C₆₀, and N₂@C₆₀ are at least 4 kcal/mol, slightly less than 4 kcal/mol, and about 9 kcal/mol, respectively.

1. Introduction

The suitability of density-functional theory (DFT) for evaluations of weak molecular interactions and especially of dispersion energies has been an important computational issue.[1−10] Very recently, Zhao et al.[11−15] performed a series of test DFT calculations with a conclusion[15] that the MPWB1K functional (the modified Perdew and Wang exchange functional MPW[16] and Becke's meta correlation functional[17] optimized against a kinetics database) is the best combination for evaluations of nonbonded interactions with a relative averaged mean unsigned error of only 11%.

Fullerene encapsulations of nonmetal atoms and small molecules represent an interesting case[18−22] for this type of computation because there are also some related observations. A well-known example is represented by complexes of fullerenes with encapsulated rare gas atoms[23−27] prepared by heating under high pressure. Ion bombardment can produce N@C₆₀[28,29] and P@C₆₀[30] (and also Li@C₆₀[31]), though in very low yields. N@C₆₀ and its derivatives have been studied vigorously,[32−36] inter alia as a candidate for the implementation of qubits in an electron-spin-based quantum computer.[37]

N₂@C₆₀ was prepared by pressure heating[38] and was also reported[39,40] in the chromatographic separation after the nitrogen-ion implantation into C₆₀. Recently, molecular hydrogen[41−43] (and also water molecule[21]) was placed inside an open-cage fullerene, and the cage with H₂ was subsequently closed.[44]

Previous DFT calculations on nonmetallic fullerene encapsulates used mostly[45−52] the B3LYP functional. The present paper reports calculations of H₂@C₆₀, Ne@C₆₀, and N₂@C₆₀ with the newly suggested MPWB1K functional in order to judge its performance for such encapsulation energetics.

2. Calculations

Three systems known from observations were selected for the present calculations: H₂@C₆₀, Ne@C₆₀, and N₂@C₆₀. The computations are carried out at fixed experimental geometries. The C₆₀ geometry is taken from the gas-phase electron diffraction[53] where the 5/6 (i.e., between a pentagon and a hexagon) and 6/6 bonds (between two hexagons) were determined as 1.458 and 1.401 Å, respectively. The bond lengths of H₂ and N₂ are also from observed data.[54,55] The diatomic molecules in the cage are oriented toward a pair of its parallel pentagons so that the complexes exhibit D_{5d} symmetry. This arrangement is known from previous calculations[52] as the lowest energy structure, though energy

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Table 1. Encapsulation Energies Computed in the Observed Geometries (kcal/mol)

level	H$_2$@C$_{60}$	Ne@C$_{60}$	N$_2$@C$_{60}$
B3LYP/6-31G**	1.56	−2.52	7.70
B3LYP/6-311G(2d, 2p)	1.34	−2.95	7.94
MPWB1K/6-31G**	−7.93[a]	−3.08	−14.93
MPWB1K/6-31G** & BSSE	−7.29	−0.22	−11.34
MP2/6-31G**	−3.99	−5.05	−17.05
MP2/6-31G** & BSSE	−2.36	−1.85	−8.90
MPWB1K/6-311G(2d, 2p)	−8.09	−7.20	−13.18
MPWB1K/6-311G(2d, 2p) & BSSE	−7.17	−3.83	−9.54
MP2/6-311G(2d, 2p)	−8.63	−5.39	−23.44
MP2/6-311G(2d, 2p) & BSSE	−6.07		−15.54
SCS-MP2/6-311G(2d, 2p)	−6.71	−4.35	−16.35
SCS-MP2/6-311G(2d, 2p) & BSSE	−4.20		−8.57
MPWB1K/(d, p)−6-311G**	−9.44		
MPWB1K/(d, p)−6-311G** & BSSE	−7.81		
MP2/(d, p)−6-311G**	−10.62		
MP2/(d, p)−6-311G** & BSSE	−6.94		

[a] The value after the full geometry optimization is −8.37 kcal/mol.

differences relative to other orientations are less than 0.1 kcal/mol. In the case of Ne@C$_{60}$, the Ne atom is placed in the cage center so that the system still exhibits icosahedral symmetry.

Single-point energy calculations were carried out with the MPWB1K functional in three well-known basis sets: 6-31G* (6-31G** for H atoms), 6-311G(2d,2p), and the augmented (d,p)-6-311G** basis set.[56] For comparison, some computations were also performed with Becke's[57] three-parameter exchange functional combined with the nonlocal Lee−Yang−Parr[58] correlation functional (B3LYP). The ultrafine grid in numerical integrations of the DFT functional and the tight self-consistent field convergency criterion were used. However, the comparisons are primarily related to the second-order Møller−Plesset (MP2) perturbation treatment[59,60] with the frozen core option carried out in the above three basis sets. Moreover, the conventional MP2 method is also complemented with the spin-component-scaled (SCS) MP2 calculations.[61] Finally, the basis set superposition error (BSSE) was estimated by the Boys−Bernardi counterpoise method.[62] The selected basis sets represent a practical computational limit for calculations of systems comparable to C$_{60}$ at DFT and especially MP2 levels.

The Gaussian[63] and PQS[64] program packages were used for all calculations.

3. Results and Discussion

Table 1 reports the zero-point-exclusive encapsulation energies (also called the energies of interaction or stabilization) corresponding to the change in potential energy for the process:

$$X(g) + C_{60}(g) = X@C_{60}(g) \qquad (1)$$

where X is H$_2$, Ne, or N$_2$. To compare this to an experimental term, one would have to add the changes in zero-point energy and heat content function. Let us note that the quantity computed here is a thermodynamic one, although the kinetics of reaction 1 are also of interest.[65−67]

As already known from previous computations,[21,52] the B3LYP functional does not produce reliable values for nonbonding fullerene encapsulations. In the cases of H$_2$@C$_{60}$ and N$_2$@C$_{60}$, their stabilization energies become positive at the B3LYP/6-31G** and B3LYP/6-311G(2d,2p) levels, which does not agree well with the very fact that the endohedrals can be observed. Only for Ne@C$_{60}$ is the B3LYP/6-31G* encapsulation energy negative (binding), though the stabilization energy is too low compared to other calculations in Table 1 and also to previous evaluations.[20,68]

All of the MPWB1K and MP2 calculations in Table 1 show for H$_2$@C$_{60}$ a substantial stabilization energy. Obviously, the BSSE-corrected energies should be preferred, though it is not necessarily assured[69] that the true energy is closer to the BSSE-corrected term rather than to the uncorrected term. The MPWB1K and MP2 treatments with the 6-31G** basis set differ by some 4 kcal/mol before the BSSE correction. With respect to the remaining computations of H$_2$@C$_{60}$ in Table 1, it seems however likely that the MP2/6-31G** term underestimates the stabilization for the species. Upon moving to the 6-311G(2d,2p) and (d,p)-6-311G** basis sets, the MPWB1K and MP2 values differ only by about 1 kcal/mol. Application of the SCS approach tested for the 6-311G(2d,2p) basis set suggests, however, a reduction of the stabilization by about 2 kcal/mol compared to the conventional MP2 method. Overall, it can be stated that the encapsulation of H$_2$ into C$_{60}$ brings a potential energy gain of at least 4 kcal/mol.

The effect of geometry optimizations was also checked with H$_2$@C$_{60}$. It turns out that, if the full geometry optimization is carried out at the MPWB1K/6-31G** level, the encapsulation energy is changed only by some 0.44 kcal/mol. The perturbation of the cage upon encapsulation changes the C−C bonds only on the fourth digit. The 5/6 C−C bonds in the cage optimized at the MPWB1K/6-31G** level vary between 1.4377 and 1.4388 Å, while for the 6/6 bonds, it is from 1.3792 to 1.3798 Å. It should also be noted that rotating the H$_2$ molecule toward two hexagons (instead of toward two pentagons) changes the energy by less than 0.1 kcal/mol so that the molecule can indeed nearly freely rotate inside the cage.[70]

Let us move now to the Ne@C$_{60}$ system. With the 6-31G** basis set, the MPWB1K and MP2 terms differ by some 2 kcal/mol both before and after the BSSE correction, Ne@C$_{60}$ showing up as more stable in the MP2/6-31G* treatment. However, with the 6-311G(2d,2p) basis set, the MPWB1K functional produces greater stabilization compared to the conventional MP2 value, which is further reduced by about 1 kcal/mol upon application of the SCS approach. Although the BSSE computations could not be finished in this case owing to computational difficulties, Ne@C$_{60}$ is likely stabilized by slightly less than 4 kcal/mol.

The differences between the conventional MP2 and SCS-MP2 treatments are more significant in the N$_2$@C$_{60}$ system, amounting to some 7 kcal/mol. However, if the MPWB1K/6-311G(2d,2p) and SCS-MP2/6-311G(2d,2p) values are compared, they are still within 3 kcal/mol before the BSSE correction and within 1 kcal/mol after correcting for BSSE. The best estimate gives about a 9 kcal/mol gain in the

potential energy upon $N_2@C_{60}$ formation. Interestingly enough, the MP2/6-31G* encapsulation energy without the BSSE correction for $N@C_{60}$ was computed[50] to be -7.3 kcal/mol, that is, roughly one-half of the value found here at the same level for $N_2@C_{60}$.

While the performance of the MPWB1K exchange-correlation potential is reasonably good for the inclusion compounds considered here, it does not perform well for π stacking. For instance, the binding energy predicted for the prototype benzene dimer, in the parallel displaced configuration, is only 0.11 kcal/mol after counterpoise correction, using the 6-311+G(2df,2pd) basis set. The best current estimate is[71,72] 2.78 kcal/mol. For the sandwich conformer, the counterpoise corrected MPWB1K potential is repulsive, although the best estimate of this quantity is 1.81 kcal/mol. Zhao and Truhlar have successfully used[13a] an empirical combination of density-functional and wave-function-based correlation methods to calculate this quantity accurately at a reasonable cost, and they also suggested[13b] an improved version of MPWB1K called PWB6K, with a good performance for stacking interactions. Although the benzene dimer issue is not directly related to the fullerene encapsulation energies, it indicates the fundamental limitations of local or semi-local DFT to describe the dispersion interaction.

It can be concluded that the values for nonmetallic encapsulations into C_{60} evaluated with the MPWB1K functional closely follow the results from the MP2 and SCS-MP2 treatments with the same basis set. This finding suggests the MPWB1K functional as a practical tool for the evaluation of encapsulations of small molecules into fullerenes and model nanotubes, though larger basis sets[73,74] and also other functionals[74,75] are to be still tested, especially for specific cases[76,77] like interactions with metals.

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