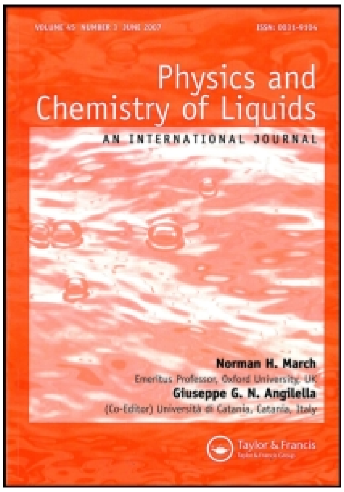

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
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To cite this Article Forte, G. , Grassi, A. , Lombardo, G. M. , Angilella, G. G. N. , March, N. H. and Pucci, R.(2009) 'Quantum-chemical modelling of the structural change of water due to its interaction with nanographene', Physics and Chemistry of Liquids, 47: 6, 599 — 606

To link to this Article: DOI: 10.1080/00319100903045874

URL: http://dx.doi.org/10.1080/00319100903045874

Physics and Chemistry of Liquids
Vol. 47, No. 6, December 2009, 599–606

Quantum-chemical modelling of the structural change of water due to its interaction with nanographene

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(*Received in final form 16 May 2009*)

Motivated by current experimental interest in the interaction of H_2O with nanographene, we have made a start on modelling the above system by reporting a Hartree–Fock calculation of H_2O on coronene. The lowest energy configuration predicted has the H_2O molecule perpendicular to the plane of the coronene molecule, with the oxygen atom away from the plane. The geometry of H_2O in this adsorbed state is reported. The case of two H_2O molecules interacting with anthracene is also considered, and compared with the structure of the free-space H_2O dimer.

Keywords: water; organic molecules; graphene

1. Introduction

Density functional calculations on single H_2O molecule adsorbates on free standing graphene have very recently been reported by Leenaerts *et al.* [1] (see also [2]). What was emphasised [1] was that results thus obtained for physisorption energetics were in accord with previous studies on carbon nanotubes [3].

Here, we have been motivated by experimental results [4] for H_2O on nanographene to attempt a quantum-mechanical modelling of the way the H_2O structure is changed by this interaction by performing Hartree–Fock (HF) calculations for H_2O on the organic molecule coronene. Because of the size of this molecule, we follow with a summary of more precise calculations on a single H_2O molecule interacting with benzene.

Both HF and correlation corrected MP2 calculations were carried out by means of the Berny analytical gradient optimisation method, using the 6-311+G** basis set, consisting of the 6-311G basis set supplemented with polarisation functions, one set of *d* functions on non-hydrogen atoms and one set of *p* functions on hydrogens, adding *s* and *p* diffuse functions on non-hydrogen atoms (6-311+G**).

For H_2O interacting with coronene and coronene, in the MP2 optimisations only valence electrons were included in the correlation calculation while in the other cases here

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ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319100903045874
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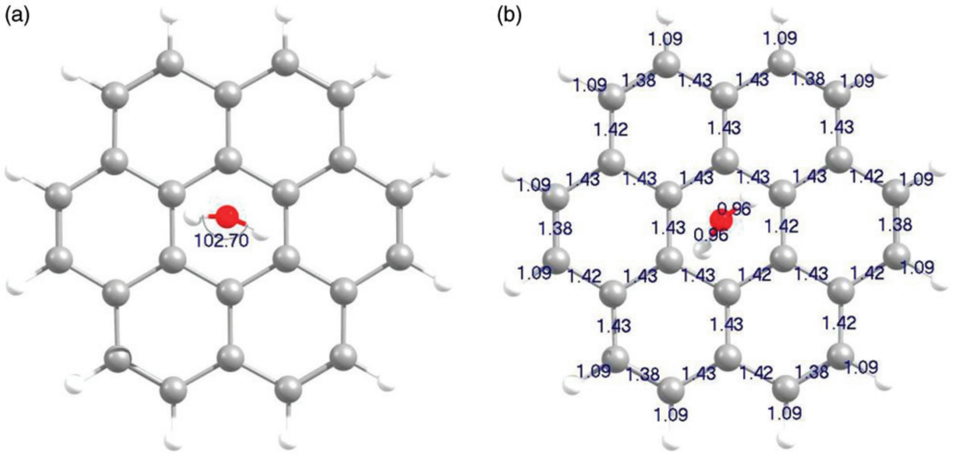

Figure 1. (a) Hartree–Fock ground-state configuration for a single H_2O molecule interacting with coronene. Note that the H_2O molecule has the O atom away from the coronene plane. (b) Depicts bond lengths in ground-state geometry of single H_2O molecule adsorbed on coronene (colour online).

Table 1. MP2 frozen core energies, inner-shell electrons being excluded from the correlation calculation.

	Energy
H_2O	−76.275 Hartree
Coronene	−919.378 Hartree
Coronene + Isolated H_2O	−995.653 Hartree
Coronene + Physisorbed H_2O	−995.670 Hartree
Difference	0.46 eV

considered all the electrons were included. All the computations were performed using the Gaussian 03 package [5].

2. Single H_2O molecule interacting with coronene: Hartree–Fock plus MP2 results

The initial configuration adopted was with a single H_2O molecule having its plane perpendicular to that of coronene with the O atom downwards. The optimised Hartree–Fock geometry is displayed in Figure 1(a) and shows that in this quantum-chemical theory, the O atom is in fact away from the coronene plane. Figure 1(b) shows the bond lengths in the ground state. It is found that: (a) there is no significant change of the O–H bond lengths due to the interaction with coronene; and (b) a decrease in the angle of H_2O by a few degrees occurs.

Table 1 records the ground-state HF + MP2 energy of H_2O interacting with coronene. This lies lower than the sum of the HF energy for isolated H_2O plus coronene by 0.46 eV. This energy is an order of magnitude greater than that reported by Leenaerts *et al.* [1]. Our result is probably due to the inclusion in our calculations of the polarisation functions

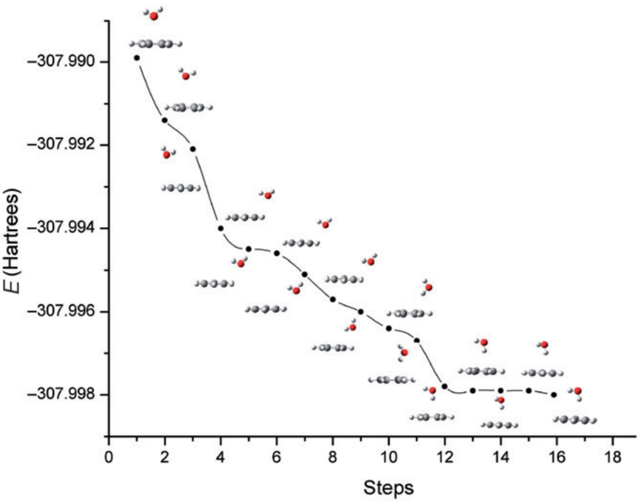

Figure 2. The energy, and the corresponding geometry, of a single molecule of H_2O interacting with benzene, as a function of the optimisation steps (colour online).

because, as stressed by Ribeiro *et al.* [6], polarisation effects greatly enhance the chemisorption energy. In particular, looking at the adsorption data, one may conclude that the adsorption energy for the H_2O–coronene system, calculated at the HF level, is about 20% of the same quantity at MP2 level, thereby implying a remarkable effect of correlations.

At the optimised geometry we have found a distance of the O atom from the coronene plane $d_{\mathrm{O-C}} = 3.61\,\text{Å}$ and a distance of the H atom from the coronene plane $d_{\mathrm{H-C}} = 2.84\,\text{Å}$. For comparison, Leenaerts *et al.* [1] have found a distance of the O atom from the graphene surface $d_{\mathrm{O-C}} = 3.50\,\text{Å}$. Finally, we would like to mention that our calculations show an electron charge transfer from the H_2O molecule to coronene $\Delta Q = -0.016e$. This result is in qualitative agreement with the experimental data of Schedin *et al.* [4] and with the calculations reported in Leenaerts *et al.* [1].

Because of the size of coronene, we have also thought it is important to carry out more precise calculations of a single H_2O molecule interacting next with benzene. However, before reporting these results, we have studied a single free-space H_2O molecule by coupled cluster theory at the singles and doubles level (CCSD).

In Figure 2 the variation is reported, as a function of the optimisation steps, of the orientation of one H_2O molecule interacting with benzene. The initial configuration adopted was that with the H_2O molecule having its plane perpendicular to that of coronene with the O downwards. The final configuration clearly shows that one H is closer to the benzene surface than the O atom.

3. Single H_2O molecule using CCSD

We felt it useful to study the effect of the choice of basis set by carrying out CCSD on a single free-space H_2O molecule. Table 2 shows the results, the first column showing the five basis sets used. The last choice is seen to be giving an accurate H−O−H angle, when compared with the experimental value of 104.5° [7].

Table 2. Free-space H_2O molecule as treated by CCSD using different basis sets.

Basis set	O–H (Å)	$\angle$H–O–H (°)
STO-3G	1.03	96.75
3-21G	0.99	104.74
6-311**	0.96	102.52
6-311+G**	0.96	103.45
aug-cc-pvqz	0.96	104.42
Experiment [7]	0.958	104.50

Table 3. MP2 all electron energies (in Hartrees) and energy differences (in kcal mol^{-1}).

Molecule	Energy (Hartrees)	Molecule + Isolated H_2O	Molecule + Physisorbed H_2O	Difference (eV)
H_2O	−76.29372	–	–	–
Benzene	−231.6973	−307.9910	−307.9979	0.20
Anthracene	−538.2896	−614.5833	614.5928	0.26
Coronene*	−919.8359286	−996.1297	−996.1466	0.46

Note: *This value is obtained by performing a single point MP2 all-electrons calculation on the structure optimised with the frozen core approximation.

4. Interaction of an H_2O molecule with smaller organic molecules: benzene and anthracene

Having obtained information about the choice of basis sets from the above CCSD calculation on H_2O, we felt it of interest to also report results we have obtained on a single H_2O molecule interacting with (a) benzene and (b) anthracene. The results are collected in Table 3, which shows at HF plus MP2 level the energies obtained for the isolated molecules considered, including coronene. When H_2O is adsorbed, the ground-state energies are entered in the penultimate column of Table 3. The adsorption energy lies around 0.2–0.4 eV for the three organic molecules considered in the present study. As to the equilibrium molecular geometries, Figure 3 shows the results of the MP2 calculation of a single H_2O molecule interacting with benzene, while Figure 4 shows corresponding results obtained for the anthracene molecule.

5. Water dimer

We turn next to treat the H_2O dimer. First of all, we report HF and MP2 results with the 6-311+G** basis set. Figure 5 shows the HF potential energy curve as a function of the O–O distance, with a minimum around 2.7 Å. The electrostatics are favourable: the shortest interatomic distances being O–H. More extensive calculations lead to a somewhat larger O–O distance of 2.9 Å in free space [8]. Figure 6 shows the equilibrium geometry predicted for the free-space H_2O dimer, while Figure 7(a) and (b) show respectively the bond lengths and angles of the dimer onto anthracene.

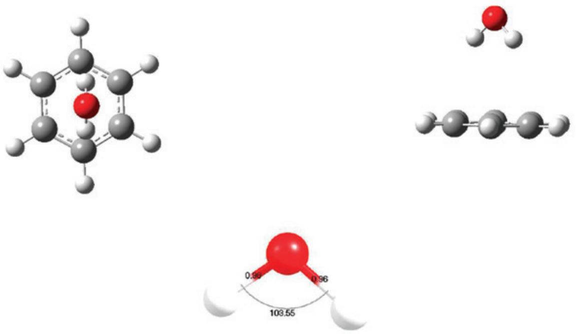

Figure 3. The upper part of the figure depicts the results of the MP2 calculation of H_2O interacting with benzene (benzene: STO-3G, H_2O: 6311+G**). The lower part shows the free-space H_2O geometry using Hartree–Fock plus MP2 6-311+G** (colour online).

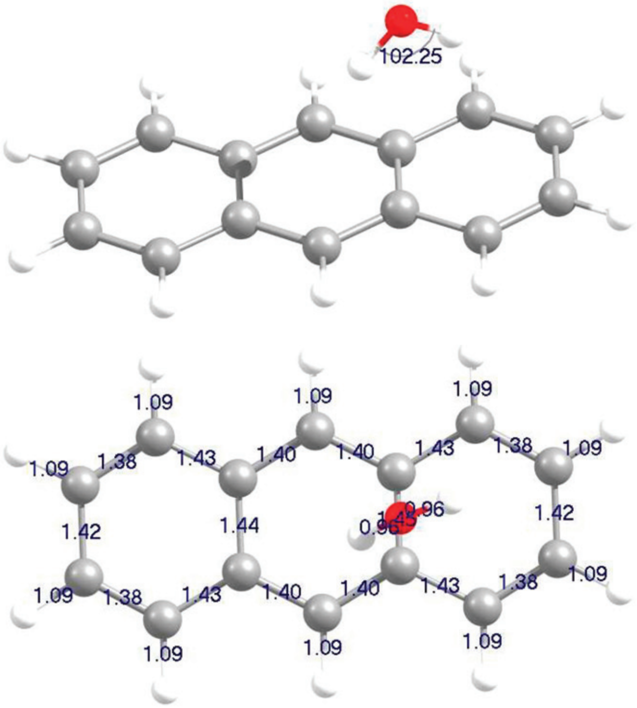

Figure 4. Water molecule interacting with anthracene. Note in the upper part of the figure that the HOH angle is decreased from the free-space angle by some 2° (colour online).

6. Discussion and summary

Because of current interest in the interaction of H_2O with suspended nanographene, we have focused here on the quantum-chemical modelling of the change in the structure of

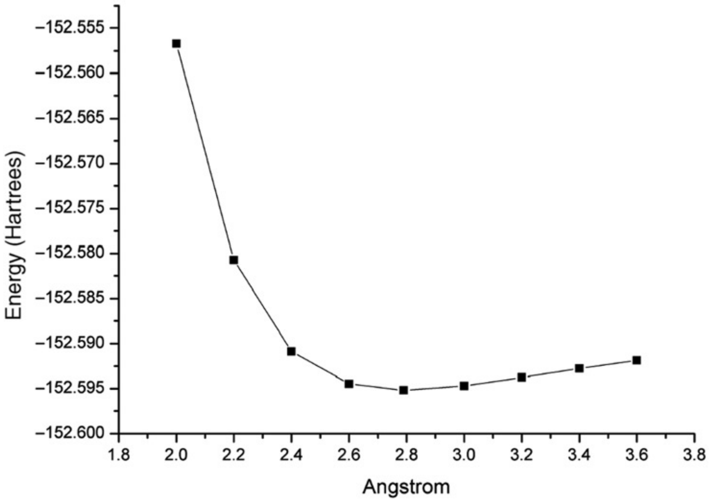

Figure 5. The HF potential energy curve for the H_2O dimer as a function of the O−O distance.

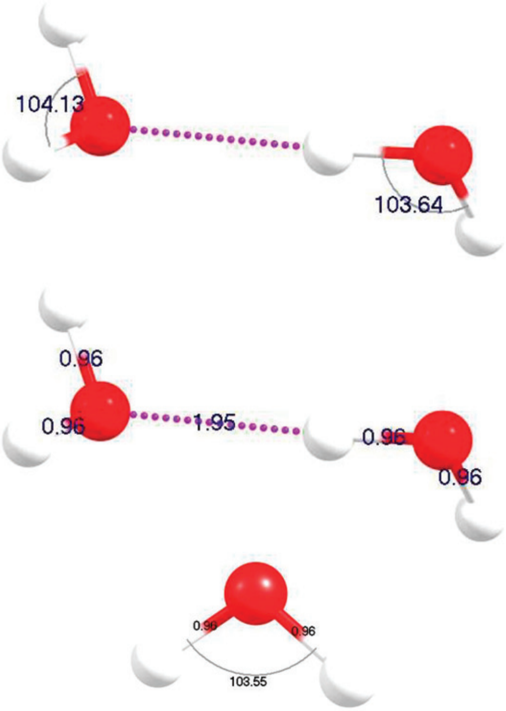

Figure 6. Free-space H_2O dimer. Note that the distance of closest approach is 1.95 Å. The single molecule geometry adopted is reported in the last panel at the bottom (colour online).

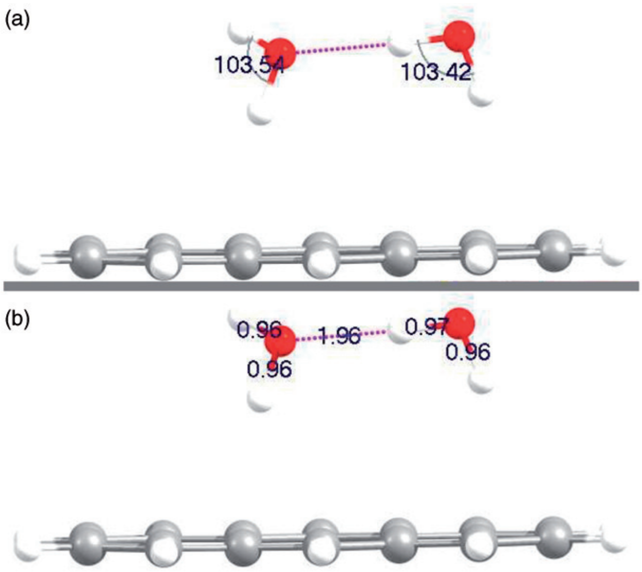

Figure 7. Water dimer interacting with anthracene (colour online).

both H_2O and its dimer by interaction with some organic molecules. The largest of these molecules considered was coronene, but more sophisticated calculations proved possible for H_2O and its dimer in interaction with smaller molecules such as benzene and anthracene. Particular attention has been focused upon the change in the structure of H_2O and its dimer by such interactions.

As this article was nearing completion, we became aware of an earlier related work by Feller and Jordan [9]. However, our emphasis was on the change in the structure of H_2O and its dimer by such interactions with organic molecules.

We also note here a further study to which our attention was drawn during the final stage of our quantum-chemical studies on H_2O and its dimer in interaction with organic molecules of varying sizes. This further study by Wehling *et al.* [2] used the density functional method to study the interaction of H_2O with graphene. Their purpose was again different from ours, in that the influence of a SiO_2 substrate was a major focal point. But their work highlights the potential technological importance of this general area.

Acknowledgements

G. Forte wishes to thank the Consorzio Interuniversitario Cineca for computational support. N.H. March wishes to acknowledge that his contribution to this study was started at the University of Antwerp (UA). He thanks Professors D. Van Dyck and D. Lamoen for partial financial support from UA through the BOF-NOI. N.H. March thanks Professors R. Pucci and G.G.N. Angilella for generous hospitality at the University of Catania, where N.H. March's contribution was brought to fruition.

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