Theoretical Study of the Adsorption of Water on a Model Soot Surface: I. Quantum Chemical Calculations

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In this work, we study the interaction between water molecules and a soot surface by means of quantum calculations. The partially oxidized soot is modeled by the anchoring of COOH groups on the face side of a graphite surface. The quantum chemical calculations aim at providing the local structure of such a COOH site as well as the surface rearrangements around it. They also provide values of the interaction energies and spectroscopic properties of a hydrogen-bonded water molecule that could be used for comparison with experimental data. Additionally, the calculations supply values of point charges at the COOH site that can be used to derive a pair potential for the water-active site interaction.

1. Introduction

Adsorption properties of soot particles have recently attracted some attention because of their implications in atmospheric processes. It has been shown that soot particles emitted into the troposphere are partially responsible for the nucleation of cirrus cloud ice particles.[1,2] These particles or even the initial condensation nuclei may have a large impact on the chemistry of the upper troposphere in a fashion similar to that of polar stratospheric clouds.[3,4] Such an influence may arise through chlorine activation via heterogeneous reactions of $ClONO_2$ and HCl. Furthermore, the reactions of HNO_3 in water−soot particles have been proposed to convert HNO_3 to NO_x.[5,6] An understanding of the condensation mechanism of cirrus clouds is critical to the quantification of future climate changes caused by greenhouse gases and airplane condensation trails.[7] This interest has motivated the characterization of aircraft combustion soot by means of different spectroscopic techniques.[8] It has been found that this soot is made of spherical-like particles with diameters in the 20- to 50-nm range. These particles are composed of microcrystallites made of graphite-type layers concentrically arranged in an onionlike structure. The graphitic layers are found to contain surface OH and C=O groups. Unlike pure graphite, the soot particles can acquire a substantial water monolayer, even under young plume conditions.[9] This provides a mechanism for the reduction of supersaturation as required by a heterogeneous water-nucleation process.

Despite the likely importance of atmospheric soot particles, very few studies on this topic have been reported so far, and a detailed understanding at the molecular level of the water adsorption ability and nucleation dynamics remains a challenge. From the works mentioned above, it seems most likely that soot consists of graphitelike layers plus groups containing oxygen such as carboxyls, hydroxyls, and aldehydes. Experimental or simulation works on the interaction of water with this type of surface are scarce. The adsorption of water on bare graphite has been studied by means of thermal desorption spectroscopy and high-resolution electron energy loss spectroscopy.[10] It has been suggested that water adsorbs nondissociatively, forming hydrogen-bonded aggregates that undergo a phase transition from a 2D to a 3D structure as the coverage is increased from 0.5 to 1.0 monolayer. A more recent study of water droplets and films on graphite by means of noncontact scanning force microscopy shows that water adsorbs on the surface, forming flat, rounded islands of 5-nm thickness that transform into 2-nm-thick islands as the relative humidity drops slightly.[11] Recent molecular dynamics simulations of a water layer on graphite show icelike structure below 298 K and restricted diffusion in the direction perpendicular to the surface, as compared to the surface plane.[12]

A more complex problem is the interaction of water with a graphitelike surface containing oxygenated hydrophilic groups such as those mentioned above. That topic has attracted some attention because of its implications in the technology of activated carbons. Adsorption equilibrium has been studied by means of grand canonical Monte Carlo simulations. In some of these works, the hydrophilic group is modeled as a single site, and no detailed description of the structure of that site is assumed.[13−15] In other works, the hydrophilic surface site has been modeled as a carboxylic group that interacts with water through the OPLS potential fitted for water−acetic acid interactions.[16] These works have shown that the adsorption is strongly dependent on the presence and arrangement of the hydrophilic groups. In a very recent paper, Tarasevich et al.[17] used the semiempirical PM3 method to study the interaction of very few water molecules with a partially oxidized graphite surface modeled by the anchoring of a carboxyl center at the edge of a small graphite sheet. The main conclusion of this work is that the water molecules are adsorbed at the hydrophilic center (i.e., the carboxyl) with the formation of microclusters consisting (at initial coverages) of 2 to 3 molecules.

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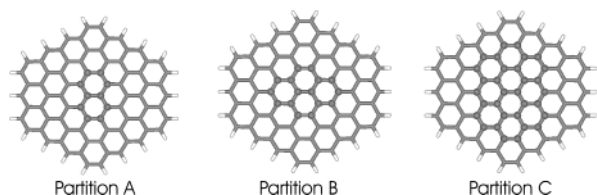
Figure 1. Basic cluster used in the quantum calculations to model the graphite surface. This cluster contains 80 carbon atoms plus 22 additional hydrogen atoms that are used to saturate the edge of the cluster. The carbon atoms pertaining to the three different partitions chosen as the DFT shell in the ONIOM calculations are represented by small circles. These partitions contain 2 (partition A), 4 (partition B), and 10 (partition C) fused benzene rings. (See the text.)

Although these previous simulation works have taken into account the influence of active sites with hydrogen-bonding ability, there are two important issues that remain to be studied. First, no full quantum chemical study has been done on the structure and adsorption ability of the active sites on the side faces of a graphitic surface. Second, there are no molecular simulations on the dynamics of the adsorbed water. This might be an important piece of information because the transport properties of the adsorbed water will affect the nucleation mechanism as well as the uptake or release of air pollutants.

In this work, we report a combined quantum chemical (this paper) plus molecular dynamics simulation study[18] that will provide information on these two issues. For the hydrophilic site, we focus on a carboxyl group attached to one of the carbon atoms in the graphite layer. The quantum chemical calculations aim at providing the local structure of such a site as well as the surface rearrangements around it. Furthermore, these calculations provide values of the interaction energies and spectroscopic properties of a hydrogen-bonded water molecule that could be used for comparison with experimental data. Additionally, the calculations supply values of point charges at the COOH site. These have been used to derive a pair potential for the water–active site interaction. The molecular dynamics simulations presented in the companion paper[18] provide a view of the dynamics and the structure of a water adlayer on the model soot surface that consists of a planar graphitic layer plus different numbers of active carboxylic sites.

The paper is organized as follows. In section 2, we briefly describe the methods and summarize the computational details. In section 3, we report the quantum chemical study of the surface COOH active group and discuss the implications of our results. The main conclusions are summarized in section 4.

2. Method and Computational Details

The graphitelike surface has been modeled by means of a cluster that consists of a set of 30 fused benzene rings, $C_{80}H_{22}$, as shown in Figure 1. The edge of the cluster has been saturated with hydrogen atoms. This cluster has planar geometry, with all of the carbons having sp^2 hybridization characteristic of an aromatic system. To calculate the structure of the COOH site on this surface, we place this group on one of the two carbons that are located at the center of the cluster. This breaks a double bond of the conjugate system and leaves the neighboring central atom with an unpaired electron. This free valence is saturated with an additional hydrogen. Thus, the formation of the COOH site can be described as the addition of H–COOH to the central conjugated double bond. This results in a $C_{81}O_2H_{24}$ cluster. The carbon atoms to which this HCOOH unit is added will adopt sp^3 hybridization. That leads to a surface rearrangement that will be included in our model by means of a full geometry relaxation. To perform geometry optimizations and energy calculations of such a large cluster, we make use of the two-layer ONIOM method,[19] in which the central part of the system, containing the carboxyl group and the closest neighboring atoms, is treated with an accurate quantum chemical method. For that first shell, we use density functional theory[20] (DFT) with a mixed exchange functional that combines 50% Becke's functional[21] and 50% Hartree–Fock exchange. For the correlation potential, we make use of the Lee–Yang–Parr potential.[22] For the second shell, containing C and H only, we make use of the semiempirical PM3 method.[23] Currently, PM3 is one of the most reliable methods among those available for the prediction of the structure of this type of system. The calculations have been made with the use of the Gaussian 98 quantum chemistry package.[24] For the description of the first layer by means of DFT, we need to use a basis set that provides accurate geometries and vibrational frequencies with affordable computing resources. For these calculations, we use the cc-pVDZ basis set that includes polarization functions on all atoms.[25] However, for the calculation of the energy of the hydrogen bonds between water and the active site, it is necessary to use a larger basis to avoid the basis set superposition error (BSSE) and to describe accurately the charge distribution of the interacting fragments. Thus, once the geometry of the active site on the surface and its complex with water is optimized with the cc-pVDZ basis set, the final energy is calculated with the 6-311++G(2d,2p) basis set.[26] We have also calculated the final energy by using the B3LYP[27] exchange-correlation functional plus the 6-311++G(2d,2p) basis set for the DFT layer. To assess the accuracy of the procedure, we have studied the interaction between formic acid and a water molecule with these different methods. We have also compared the results from the mixed basis set (MBS) approach (geometries and frequencies from cc-pVDZ and final energy from 6-311++G(2d,2p)) to the results from optimizing the structures and calculating the vibrational frequencies with the 6-311++G(2d,2p) basis set. The results are compared in Table 1, to which we have added the results from using the cc-pVDZ basis set only as well as the counterpoise correction to the basis set superposition error for all basis sets. It is clearly seen that the use of the cc-pVDZ basis set for both the geometry and the final energy leads to an overestimation of the binding energy, enthalpy, and free energy as compared to the use of

TABLE 1: Energy (ΔE), Enthalpy (ΔH), and Gibbs Free Energy (ΔG) of Formation of the Hydrogen-Bonded HCOOH–H$_2$O Complex as Calculated with Different Computational Methods[a]

	BHLYP cc-pVDZ	BHLYP MBS	BHLYP 6-311++G(2d,2p)	B3LYP MBS	B3LYP 6-311++G(2d,2p)
ΔE	−64.32 (−44.37)	−41.48	−43.06 (−40.69)	−39.12	−41.48 (−38.33)
ΔH	−55.92	−33.60	−33.87	−31.24	−31.51
ΔG	−16.02	5.51	5.25	9.45	9.19

[a] Enthalpies and Gibbs free energies are calculated assuming 298 K and 1 bar. BHLYP stands for Becke's correlation and 50% Hartree–Fock + 50% LYP exchange; B3LYP stands for Becke's three-parameter hybrid functional using the LYP correlation functional. MBS stands for mixed basis set. (See the text for more details.) Values in brackets are those that include the counterpoise correction for the BSSE.
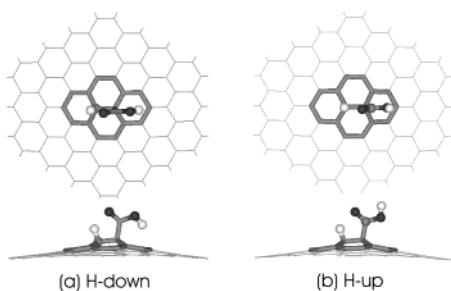
Adsorption of Water on a Model Soot Surface

J. Phys. Chem. B, Vol. 108, No. 17, 2004 **5407**

Figure 2. Geometry of the two stable structures optimized with the ONIOM method for the graphite surface containing the COOH group: (a) H-down and (b) H-up structures. Grey, black, and white circles represent C, O, and H atoms, respectively.

the 6-311++G(2d,2p) basis set or as compared to the results including the counterpoise correction. For example, the binding energy, ΔE, for the pure cc-pVDZ basis set is −64.32 kJ/mol, whereas the more accurate calculations predict values between −44.37 and −39.12 kJ/mol. The value obtained with the mixed basis set agrees within 1 kJ/mol with the most accurate value, 6-311++G(2d,2p) plus BSSE correction. The same good agreement is found for the ΔH and ΔG values. Thus, the use of the mixed basis set approach is considered to be valid for the study of the hydrogen bonding between water and carboxylic groups at the graphitelike surface. Additionally, to get an idea of the extrapolation to the complete basis set of interaction energy, we have computed ΔE with the aug-cc-pVTZ and aug-cc-pVQZ basis sets. The B3LYP interaction energies are −38.58 and −36.81 kJ/mol, respectively. That points to a basis set limit of about −36 kJ/mol. Thus, our BSSE-corrected energies lie within about 2 kJ/mol of the basis set limit.

Another important issue that deserves some consideration is the choice of the partition of the full cluster into two layers. We have tackled this question by making calculations with three different choices, as shown in Figure 1. In these models, 2 (partition A), 4 (partition B), and 10 (partition C) fused benzene rings were chosen as the DFT shell. These partitions are chosen so that both layers, DFT and PM3, are aromatic in all cases. The results of these calculations are also presented in section 3.

3. Results and Discussion

The structures optimized for the surface containing the COOH group are shown in Figure 2. The two layer partitions that we have used for this systems are those depicted for the bare surface, shown in Figure 1, plus the added HCOOH unit, which is included in the DFT layer. The geometries obtained with these three partitions are rather similar, so we show only the structures for partition B. The main characteristic of this structure is the loss of planarity near the active group due to relaxation along the z direction. This is a result of the rehybridization of the carbon atoms to which the hydrogen atom and the COOH group are connected. It is not an artifact of the model (i.e., finite size or partitioning into two layers) because geometry optimizations for the full aromatic structure yield planar geometry. For the
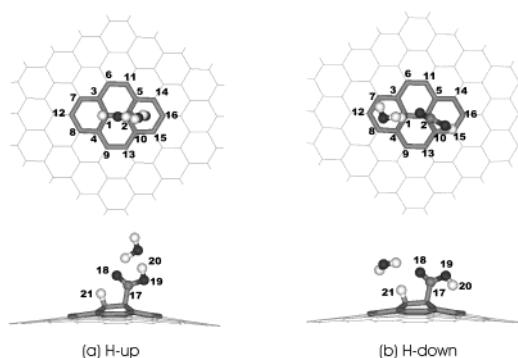

Figure 3. Geometry of the stable structure for a water molecule interacting with the (a) H-up and (b) H-down active site on the graphite surface, as issued from quantum chemical calculations. Grey, black, and white circles represent C, O, and H atoms, respectively. The numbers on the atoms correspond to the numbering used in Table 4 for the calculation of the charges issued from the present ab initio study.

COOH group, we have found two stable structures with the hydrogen of the acidic group pointing either to (H-down structure) or away from (H-up structure) the surface plane. The energy difference between them is small, about 1 kJ/mol.

The choice of the partition between two layers is an important issue. On one hand, one would like to do a full DFT calculation for the whole $C_{80}O_2H_{24}$ cluster. On the other hand, we would like to use a small DFT layer so that most of the system is treated at the semiempirical PM3 level. The first option is highly demanding from a computational viewpoint. The second one may not be accurate enough. To asses the effect of the separation between DFT and PM3 layers, we have studied the adsorption of water on the H-up structure for the three partitions described above. To this end, the geometry of a water molecule hydrogen bonded to the surface model has been fully optimized. The calculated adsorption energies are summarized in Table 2. These results show that the energy differences between the three models used here are rather small, within 1 kJ/mol. The BHLYP/cc-pVDZ results point to a substantial adsorption energy, $\sim$ −63 kJ/mol. However, the calculations with better basis sets, BHLYP/MBS and B3LYP/MBS, both point to an adsorption energy within about −40 kJ/mol. A similar basis set effect was observed for the $HCOOH-H_2O$ complex, with an adsorption energy influenced considerably by the basis set superposition error when the cc-pVDZ basis set is used. Such a BSSE is negligible for the larger 6-311++G(2d,2p) basis set as demonstrated in section 2. The optimized geometries (Figure 3) for the three partitions are almost identical as well. Because it is not necessary to use partition C, with the larger DFT layer, we decided to use partition B, containing four rings in the DFT layer, for the rest of the calculations.

These additional calculations include the full geometry optimization for water hydrogen bonded to the H-down site as well as the calculation of the vibrational frequencies in the harmonic approximation for the bare and hydrated surfaces with H-up and H-down sites. These frequencies have been used to calculate adsorption enthalpies and Gibbs free energies at $P =$

TABLE 2: Adsorption Energies, ΔE (kJ/mol), for H-Up and H-Down COOH Sites as Well as Different Partitions between DFT and PM3 Layers in the ONIOM Calculations[a]

| | BHLYP/cc-pVDZ | | BHLYP/MBS | | B3LYP/MBS | |
	H-up	H-down	H-up	H-down	H-up	H-down
A	−63.37		−40.12		−39.07	
B	−63.01	−31.93	−42.53	−16.80	−39.58	−12.34
C	−63.19		−41.24		−39.67	

[a] Three different combinations of DFT exchange-correlation potentials and basis sets have been used as explained in the text.

TABLE 3: Adsorption Enthalpies[a] and Gibbs Free Energies[a] for H-Up and H-Down Sites and Partition B

| | BHLYP/cc-pVDZ | | BHLYP/MBS | | B3LYP/MBS | |
	H-up	H-down	H-up	H-down	H-up	H-down
ΔH	−54.87	−24.68	−34.39	−9.55	−31.44	−5.09
ΔG	−14.97	14.18	5.51	29.31	8.46	33.77

[a] kJ/mol.

TABLE 4: Values of the Charges Located on the COOH Active Group and the Surrounding C Atoms, Issued from the Present ab Initio Study[a]

atom	number	q_{down} (e)	q_{up} (e)
C	(1)	−0.36234	0.03061
C	(2)	0.52443	0.14731
C	(3)	0.17111	0.01969
C	(4)	0.13470	−0.04232
C	(5)	−0.27410	−0.06614
C	(6)	−0.20624	−0.05713
C	(7)	−0.17564	−0.07994
C	(8)	−0.16092	−0.03808
C	(9)	−0.16308	−0.02978
C	(10)	−0.24093	−0.02432
C	(11)	0.16321	−0.01532
C	(12)	0.15588	0.08944
C	(13)	0.11175	−0.06398
C	(14)	0.13988	−0.00799
C	(15)	0.10289	−0.03800
C	(16)	−0.08893	0.02633
C	(17)	0.78904	0.70994
O	(18)	−0.46708	−0.50409
O	(19)	−0.55953	−0.58818
H	(20)	0.38520	0.45265
H	(21)	0.02070	0.07931

[a] q_{down} and q_{up} correspond to the H-down and H-up configurations, respectively. Note that there are no charges for the C atoms located far from an active group. The numbering of the atoms is indicated in Figure 3.

1 atm and $T = 298$ K. The adsorption energies, ΔE, for water on the H-down site are considerably smaller than on the H-up site, with values of ~ -17 and ~ -13 kJ/mol for BHLYP/MBS and B3LYP/MBS, respectively. The adsorption enthalpies and free energies are summarized in Table 3. As for the energies, the results from BHLYP/MBS and B3LYP/MBS are considered to be accurate within a few kJ/mol. The adsorption on the H-up site is more favorable than on the H-down site. The vibrational and thermal effects make the adsorption enthalpies less negative than the ΔE's and the Gibbs free energies of adsorption positive by a few kJ/mol.

To set up a pair potential for the water−surface interaction, we have calculated the charges on the atomic sites of our cluster model. These charges are determined by fitting the electrostatic potential around the cluster by means of the Merz−Singh−Kollman scheme.[28,29] Within this scheme, most charges on the cluster are negligible except for those on the COOH group and the anchoring carbon on the surface (Table 4). These values are rather similar to those used by Maddox et al.[16] Note that the charges on water following the same scheme as for the COOH group are −0.715 for O and 0.358 for H. The corresponding dipole moment is 1.9 D.

4. Conclusions

We have studied the adsorption of water on a carboxylic acid site on a graphitelike layer by means of the ONIOM(DFT:PM3) method. The system is a model of a soot surface with hydrophilic groups. For the DFT calculations, we use the BHLYP and B3LYP exchange-correlation functionals and a combination of cc-pVDZ and 6−311++G(2d,2p) basis sets. The geometry

optimization can be done with a cc-pVDZ basis set, and the final energy can be evaluated with the 6-311++G(2d,2p) basis set, providing results with a small basis set superposition error. The calculations can also be done with a partitioning in which the active site plus the three neighboring rings of graphite are included in the DFT layer, and the rest of the atoms can be included in the PM3 layer (partition B) The results are as accurate as when including more atoms in the DFT layer, such as in partition C. The comparison between BHLYP and B3LYP exchange-correlation functionals shows that they provide similar results. The presence of the COOH group at the surface produces a distortion of the planar graphite layer. The adsorption of water can take place on a COOH group in which the hydrogen atom is pointing either outward from or inward toward the surface plane. In the first case, water can act as a hydrogen donor−acceptor, whereas in the second case, it acts as a proton acceptor only. The adsorption energy in the donor−acceptor configuration is about −40 kJ/mol, but is it is only ~ -12 kJ/mol in the acceptor, H-down, structure. We have also calculated enthalpies and Gibbs free energies including vibrational contributions in the harmonic approximation. Our results point to adsorption enthalpies of −31 and −5 kJ/mol for the H-up and H-down COOH groups, respectively. The adsorption Gibbs free energies energies are about 8 and 34 kJ/mol. We have also calculated a set of point charges for the surface atoms by fitting the electrostatic potential around the active site. These charges, together with the structural and energetic data here provided, are used to set up a pair potential for molecular dynamics simulations in the accompanying paper.[18]

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Adsorption of Water on a Model Soot Surface

J. Phys. Chem. B, Vol. 108, No. 17, 2004 **5409**

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