

Theoretical Study of the Adsorption of Water on a Model Soot Surface: II. Molecular Dynamics Simulations

Sylvain Picaud* and Paul N. M. Hoang

Laboratoire de Physique Moléculaire, UMR CNRS 6624, Faculté des Sciences, La Bouloie, Université de Franche-Comté, F-25030 Besançon Cedex, France

Said Hamad, Jose Antonio Mejias, and Santiago Lago

Departamento de Ciencias Ambientales, Universidad Pablo de Olavide, Carretera de Utrera Km.1, 41013 Sevilla, Spain

Received: November 25, 2003; In Final Form: February 5, 2004

In this paper, we present results from molecular dynamic simulations devoted to the characterization of the interaction between water molecules and a soot surface modeled by the anchoring of COOH groups on the face side of a graphite surface. The molecular dynamics simulations are based on a classical potential issued from quantum chemical calculations. They provide a view of the dynamics and the structure of water clusters on the model soot surface at 250 K. The results of these simulations show that the COOH groups act as strong trapping sites for a few water molecules that then become nucleation centers for other water molecules that form larger aggregates tied to the COOH. They show also that water adsorption on a model soot surface depends on the type, the number, and the relative positions of active sites on the surface.

1. Introduction

Soot particles emitted into the troposphere by aircraft are partially responsible for the nucleation of artificial cirrus clouds,^{1,2} which may have a large influence on upper troposphere/lower stratosphere (UTLS) chemistry.³ However, a characterization of these soot particles at a molecular level is lacking, and despite their importance, experimental and theoretical works devoted to the study of their behavior with respect to water adsorption are scarce.

Recently, transmission electron microscopy (TEM) studies⁴ have shown that soot is made of spherical-like particles with diameters in the 20- to 50-nm range. These particles are composed of microcrystallites containing graphite-type layers concentrically arranged in an onionlike structure. Additional results of Raman spectroscopy reveal that these graphitic layers contain a certain number of surface OH and C=O groups. Unlike pure graphite, which is known to be rather hydrophobic, soot particles can acquire a substantial number of water molecules, as shown by thermodynamics measurements of the corresponding adsorption isotherms.⁵ A theoretical investigation of this hydrophilic behavior remains challenging because it is thought to be related to the morphology of the soot particles and to their chemical heterogeneities.⁶

In a series of papers, Gubbins et al. have used grand canonical Monte Carlo simulations to study the adsorption of water on activated carbons^{7–11} and have shown that the adsorption is strongly dependent on the presence and arrangement of hydrophilic groups. These calculations were based on rather simple interaction potentials between water molecules and the activated surface. In a very recent paper, the more sophisticated semiempirical PM3 method was used to study the interaction of a 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.¹² The main conclusion of this latter 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.

Although these previous simulations have taken into account the influence of active sites with hydrogen bonding ability, 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. Moreover, as far as we know, no molecular dynamics simulations have been done on the water nucleation around the active site or on the dynamics of the adsorbed water molecules.

In a companion paper,¹³ we have reported a quantum chemical characterization of a hydrophilic site modeled by a carboxyl group attached to one of the carbon atoms in the graphite layer. The quantum chemical calculations are aimed at providing the local structure of such a site as well as the surface rearrangements around it. They also supply values of point charges at the COOH site that have been used to derive a pair potential for the water–active site interaction. In the present paper, we present molecular dynamics simulations based on this potential to 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, the results from the molecular dynamics simulations are presented, and the implications of our results are discussed in section 4. The main conclusions are summarized in section 5.

2. Details of Molecular Dynamics Simulations

The molecular dynamics (MD) simulations have been carried out by standard methods.¹⁴ The graphite substrate is represented

* Corresponding author. E-mail: sylvain.picaud@univ-fcomte.fr. Tel: +33 3 81 66 64 78. Fax: +33 3 81 66 64 75.

by three rigid layers of C atoms that occupy the bottom of the simulation box. The two innermost layers have pure-graphite geometry, whereas the upper layer (i.e., the surface layer) contains a random distribution of COOH active groups (between 1 and 13). The geometry of these active groups is issued from the ab initio calculations presented in the companion paper.¹³

In the previous quantum calculations,¹³ only one active group on the graphite plane was considered. Here, in the molecular dynamics simulations, we modeled an activated graphite surface with several active sites scattered on this surface. A site contains the COOH active group, the extra H atom, and the 16 nearest C atoms (i.e., the atoms that have been relaxed along the z direction according to the quantum calculations). This site is then randomly scattered on the graphite surface, with the criterion that two sites must not overlap. Moreover, we assumed that the charge redistribution around a site is not modified by the presence of another COOH group.

The (x, y) size of the simulation box ($x = 46.86$ Å and $y = 46.74$ Å along the directions parallel to the graphite surface) corresponds to a repeated patch of size $11a_1 \times 19a_2$ (where $a_1 = 4.26$ Å and $a_2 = 2.46$ Å are the graphite unit cell parameters) and is consistent with the size of the microcrystallites observed in soot particles.⁵

Various coverages of water molecules have been considered in the calculations, and the simulation implies up to 240 moving water molecules. In fact, this number corresponds to the saturation of the graphite surface by one (nearly) commensurate hexagonal bilayer of ice.

The translational equations of motion are solved by using the Verlet algorithm, and a predictor–corrector method based on the quaternion representation of the molecular orientations is used for the orientational equations of motion, with a time step of 2.2 fs.¹⁴ Long time runs are performed, involving 80 000 time steps (i.e., 176 ps) of equilibration followed by 120 000 additional time steps (264 ps), to collect the data. The initial velocities of each molecule are taken from a Boltzmann distribution corresponding to the desired temperature. The total energy of the system is held constant during the production runs by scaling the velocities every 20 steps. The simulations have been performed at 250 K, a temperature that is typical of the troposphere.

The TIP4P model,¹⁵ which accurately reproduces the structure and dynamics of both ice and liquid water,¹⁶ is used to describe the interaction V_{ww} between the water molecules. This model involves three charges located on the two protons and on a site slightly displaced with respect to the oxygen position along the C_{2v} molecular axis. A fourth site located on the oxygen characterizes the dispersion–repulsion interaction. For the calculations of the lateral interactions between water molecules, a cutoff distance of 23.0 Å was used, a distance that is large enough to avoid the use of long-range correction methods such as the Ewald sum. The water molecules are treated as rigid bodies. Note that we have used the TIP4P model in the present calculations instead of the charges on water issued from the ab initio calculations¹³ because we are interested in the behavior of water aggregates above the graphite surface. The charges calculated in the companion paper are more representative of an isolated water molecule interacting with the COOH active group.

The interaction potential for the adsorbate–substrate system (V_{ws}) is written as the sum of the water molecules–carbon atoms interaction (V_{wc}) plus the water molecules–active group (H + COOH) interaction (V_{wd}). These potentials V_{wc} and V_{wd} are the sums of pairwise atom–atom Lennard-Jones and charge–charge

TABLE 1: Lennard-Jones Parameters for the Dispersion–Repulsion Interaction between TIP4P Water and the Defective Graphite Surface

interacting pair ^a	σ (Å)	ϵ (meV)
$C_{gr}-O_w$	3.276	4.033
$C-O_w$	3.451	5.540
$=O-O_w$	3.056	7.834
$O-O_w$	3.076	7.049
$H-O_w$	0.000	0.000

^a The usual Lorentz–Berthelot combination rules have been used for the determination of the cross parameters.

TABLE 2: Average Energy Per Molecule (kJ/mol) for Different Water Coverages When There Is Only One Defect on the Graphite Surface^a

	number of water molecules	V_{ws}	V_{ww}	V_{total}
bare graphite	1	−6.8	0.0	−6.8
	2	−6.8	−13.0	−19.8
	3	−6.8	−23.3	−30.1
	4	−6.7	−29.0	−35.7
	5	−6.6	−28.5	−35.1
	13	−3.9	−30.0	−33.9
	48	−3.4	−35.2	−38.6
	128	−2.6	−37.8	−40.4
defect H-down	240	−2.6	−39.0	−41.6
	1	−30.8	0.0	−30.8
	2	−17.1	−8.8	−25.9
	3	−13.0	−20.7	−33.7
	4	−11.5	−26.7	−38.2
	5	−10.1	−27.4	−37.5
	13	−3.9	−30.2	−34.1
	48	−3.9	−35.2	−39.1
defect H-up	128	−2.8	−37.7	−40.5
	240	−3.0	−38.8	−41.8
	1	−44.6	0.0	−44.6
	2	−33.9	−12.1	−46.0
	3	−18.9	−21.6	−40.5
	4	−15.8	−27.5	−43.3
	5	−12.5	−28.3	−40.8
	13	−6.3	−29.1	−35.4
	48	−2.7	−35.4	−38.1
	128	−3.1	−37.5	−40.6
	240	−2.9	−38.8	−41.7

^a For up to five molecules, the results are issued from an optimization procedure. For the larger aggregates, the results come from MD simulations at 250 K.

interactions. The Lennard-Jones parameters (Table 1) are issued from the literature,¹⁷ whereas the charges on graphite and atoms of the active groups have been determined from ab initio calculations.¹³ Note that the polarization effects between the adsorbate and the substrate have been disregarded. All of these interactions are calculated in the direct space.

3. Results of the Simulations

First, we have optimized (by using a conjugate gradient method) the adsorption energy of one water molecule above a graphite surface containing either one H-down COOH site or one H-up COOH site in order to check the accuracy of the classical potential used in the simulations. The geometry of the corresponding equilibrium configuration (not shown) in the two situations is very similar to that obtained with the ab initio method,¹³ and the adsorption energy ranges from −30.8 to −44.6 kJ/mol (Table 2) above the H-down and H-up sites, respectively. In both cases, the main contribution to the potential energy comes from the electrostatic interaction.

These results cannot be compared simply with those obtained by the ab initio procedure¹³ because in the cluster used in the

quantum chemical calculations only a small area of the graphite plane is taken into account. Above the H-up COOH site, the water molecule is quite far away from the graphite plane,¹³ and the corresponding contribution V_{wc} to the total potential energy is very small (-0.6 kJ/mol). As a consequence, the total potential energy comes mainly from the interaction V_{wd} with the active site. This value agrees very well with the value obtained from quantum chemical calculations. Above the H-down COOH site, the water molecule is located much closer to the graphite plane,¹³ and the interaction V_{wc} between water molecules and the carbon atoms of the surface contributes substantially to the total interaction V_{ws} ($V_{wc} = -11.9$ kJ/mol, i.e., 40% of the total energy $V_{ws} = -30.8$ kJ/mol). Only the remaining contribution $V_{wd} = -18.9$ kJ/mol can be fairly compared with the value obtained from quantum calculations (-16.8 and -12.34 kJ/mol for B3LYP/MBS and B3LYP/MBS calculations, respectively; see ref 13) because these calculations underestimate the contributions V_{wc} that mainly come from the dispersion–repulsion interactions.

On the basis of these results (equilibrium geometry + potential energy), we can reasonably conclude that our classical potential is accurate enough to model the water-activated graphite interaction.

3.1. Simulations with One Active Site on the Graphite Surface. First, let us detail the results obtained with only one H-down or H-up site implemented on the graphite surface for different water coverages.

To investigate the first steps of the adsorption process of water on the activated surface, we have performed an optimization of the adsorption energy for small clusters containing up to five water molecules. The comparison of the mean energies per molecule for these very low water coverages (Table 2) clearly indicates that the COOH site (H-down or H-up) acts as a strong trapping site for the water molecules because the adsorption energy on both activated surfaces is lower than on a bare graphite surface. On this latter surface, the influence of the water–graphite interaction is very small, and the water molecules tend to optimize their lateral interactions whatever the water coverage.

Then, we have performed molecular dynamics simulations for larger aggregates containing between 13 and 240 molecules. The first number corresponds to the number of molecules involved in three close-packed hexagons in one layer of hexagonal ice, whereas the last number corresponds to the saturation of the graphite surface by a commensurate layer of hexagonal ice. For these aggregates, the results of molecular dynamics simulations at 250 K show that the influence of the active group is not very sensitive from an energetic point of view, as indicated by the close values of the energies above the activated and the bare graphite surfaces (Table 2). This result is not surprising because only a few of the water molecules are located near the active group and their contribution to the mean energy per molecule decreases as the total number of molecules increases on the surface. Note that on the clean graphite surface the adsorbate–substrate contribution (V_{ws}) per molecule is on average twice as small as that for the smaller aggregates as a result of a bilayer arrangement of the water molecules at large coverages. Such bilayer structure is confirmed by the study of the centers-of-mass distribution function $p(z)$ (not shown), which is characterized by two peaks for the large water aggregates.

The results above show that, from an energetic point of view, the first steps in the adsorption process on the activated surface are strongly dominated by the presence of the active group (H-down or H-up). By contrast, above a certain water coverage,

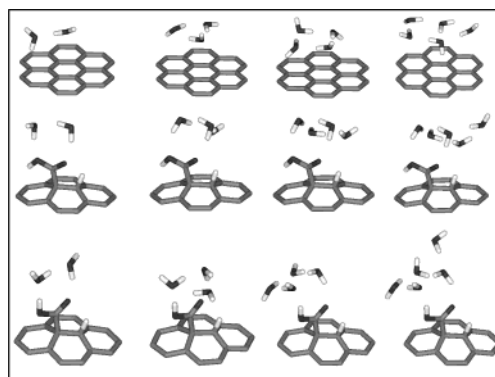


Figure 1. Equilibrium geometries of small water aggregates on a pure graphite surface (first row) and on a defective surface containing one H-down (second row) or one H-up (third row) defect (side views). Only a few C atoms are represented.

when the first water “shell” around the active group is completed, the energy of the system mainly depends on the lateral interactions between water molecules.

The geometry of the water aggregate above the COOH site (Figure 1) is mainly driven by the ability of that site to form hydrogen bonds with the water molecules and by the competition between these H bonds and those formed between water molecules. Note that in our classical simulations we will define H bonds with a geometrical criterion only (i.e., a H bond is formed when the O–H distance is around 2.0 Å).

On the two activated surfaces, the equilibrium geometry shows that the first adsorbed water molecule forms only one H bond through its oxygen atom (acting as a proton acceptor) on the H-up group and through one of its H atoms (acting as a proton donor) on the H-down group. As already mentioned, these configurations are in agreement with the *ab initio* results.¹³ On both groups, an additional water molecule tends to form two hydrogen bonds—the first one with the carbonyl group (C=O) and the second one with the neighboring water molecule (Figure 1). These two H bonds are preserved in the equilibrium geometry of larger aggregates (up to five water molecules in our optimization results).

For larger water aggregates, the formation of hydrogen bonds between the hydrophilic site and the water molecules has been characterized in MD simulations performed at 250 K through the calculation of some pair distribution functions (Figure 2). These functions $g_{XY}(r)$ reflect the probability of finding a distance r between an X atom of the water molecule and an Y atom pertaining to the COOH site. Indeed, $g_{HW-OC}(r)$ exhibits a well-pronounced peak around 2.0 Å, characteristic of the H-bond formation, for both H-down and H-up groups. On the H-up group, a second H bond is well evidenced by the presence of a sharp peak in $g_{OW-HO}(r)$ and corresponds to the binding between a water molecule of the aggregate and the hydroxyl (O–H) fragment of the active group. On the H-down group, a small shoulder around 2.0 Å is found in $g_{HW-OH}(r)$ instead of a sharp peak. This indicates that the second H bond is less stable on the H-down site than on the H-up site when the size of the water aggregate increases because of greater competition between the intermolecular and the water–active group bondings, as already observed in the comparison between the adsorption energies for the two groups.

Another way to characterize the geometry of the water aggregates during the simulations is the study of the water molecules’ positions through the distribution function of the oxygen atoms along the z direction perpendicular to the graphite surface ($p(z)$) and through the histogram $h(x, y)$ that reflects

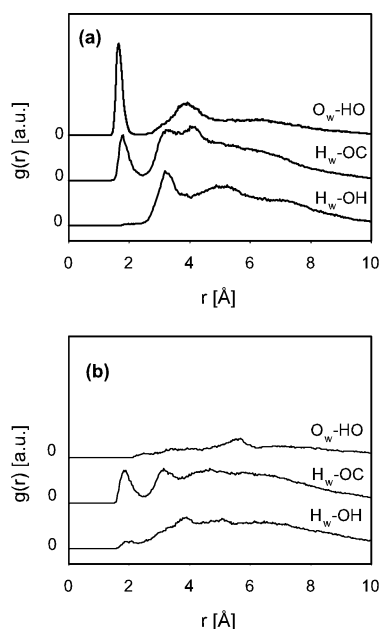


Figure 2. Pair distribution functions $g_{X,Y}(r)$ of the distance between an atom X pertaining to the water molecule and an atom Y of the COOH defect ((a) H-up and (b) H-down) issued from molecular dynamics simulations at 250 K of an aggregate containing 13 water molecules.

the probability of finding oxygen atoms of water at positions (x, y) whatever their z positions. Note that the ratio of water molecules close to the active group COOH over the total number of molecule in an aggregate becomes quite small when this aggregate grows. Because of the large size of the aggregates considered in the present simulations, the contribution to the distribution function $p(z)$ (not shown) of the water molecules located close to the COOH site is rather weak, and as a consequence, $p(z)$ mainly contains information on the water arrangement away from the vicinity of the site. On both surfaces, $p(z)$ for the various aggregates exhibit its first well-defined peak around 3.3 Å (the origin of the z axis is located on the graphite surface) and a less-pronounced second peak around 6.0 Å, indicating the bilayer arrangement of the water molecules that are located far from the active site. The distribution functions $h(x, y)$ for the smallest aggregate considered in the present simulations (13 water molecules) adsorbed on both kinds of active groups are given in Figure 3a and b. These functions not only give structural results but also contain also indirect information on the mobility of the aggregate because they are averaged over the simulation duration. On both activated surfaces, water molecules tend to remain bound to the active group as indicated by the density distribution around this group (high density in $h(x, y)$). On the contrary, water moves more freely on the pure graphite surface, as indicated by the spreading of the corresponding distribution (Figure 3c). Moreover, the dark dot on Figure 3a corresponds to the signature of the strong H bond between the hydroxyl of the H-up group and the nearest acceptor water molecule. Finally, because of the geometry of the H bonding between the active group and the water molecules, the water aggregate exhibits a more symmetrical shape on the H-up group than on the H-down group. Similar features are obtained for larger water aggregates (not shown).

3.2. Simulations with Several Active Sites on the Graphite Surface. After investigating the H bonding between a water aggregate and one active site, we performed simulations with a random distribution of active sites of the same type on the graphite surface to get information on the influence of such concentrations of sites on water adsorption. Note that as a first

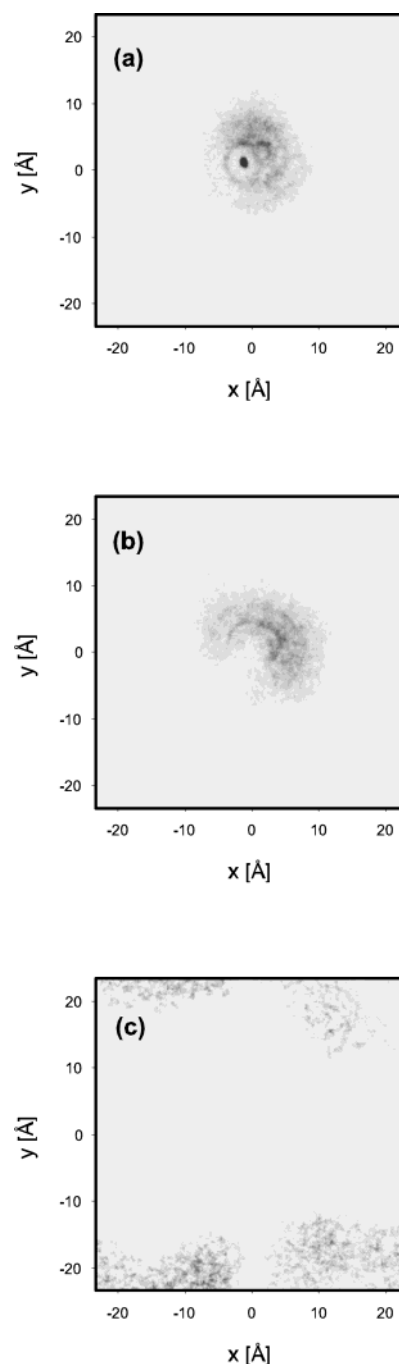


Figure 3. Distribution functions of the oxygen atoms' (of water molecules) positions projected in the (x, y) plane of the surface for an aggregate containing 13 water molecules at 250 K above a surface with (a) one H-up defect, (b) one H-down defect, or (c) above a pure graphite surface.

approximation we disregarded the possible coexistence of both types (H-up and H-down) of sites on the surface.

Let us illustrate these results by first considering a graphite surface containing three active sites. On these activated surfaces, various water coverages have been investigated; only the results obtained with 39 molecules are given here. This coverage corresponds to a ratio of 13 water molecules per site, a value equal to the number of molecules in the smallest aggregate considered in the simulations with only 1 site on the surface (see above). At the beginning of the simulations, the molecules were split into three small aggregates (of the same size) located above each site to ensure the optimization of the water–substrate interaction.

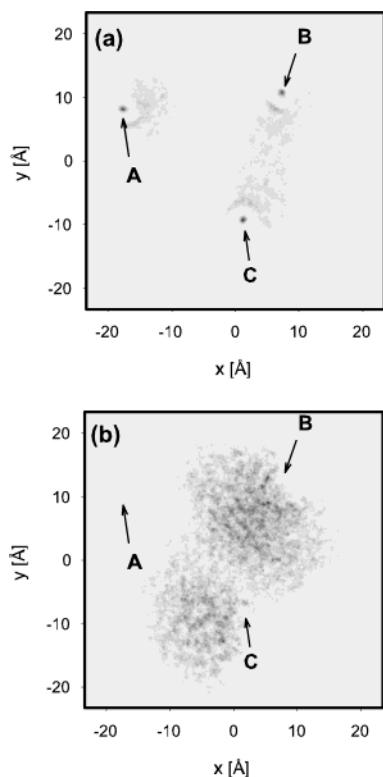


Figure 4. Distribution functions of the oxygen atoms' (of water molecules) positions projected in the (x, y) plane of the surface for an aggregate containing 128 water molecules at 250 K above a surface with 3 (a) H-up or (b) H-down defects.

The distribution functions $h(x, y)$ corresponding to these 39 molecules adsorbed on a graphite surface containing three H-down or H-up sites are given in Figure 4. This figure shows that the water molecules remain localized around the three H-up sites as indicated by the three dark spots in the corresponding $h(x, y)$ (Figure 4a). However, the strong lateral interactions between molecules lead to a merging of the water aggregates between the two closest sites (B and C in the figure). Such a feature is predominant on the surface containing H-down sites, but a careful analysis of the data issued from the corresponding simulation shows that only one aggregate is formed, attached to one of the three sites. During the simulation, this aggregate moves from one site to an adjacent site. This feature is confirmed by two gray zones appearing in Figure 4b, each of them corresponding to the attachment of the aggregate on one of the sites.

Then, we performed simulations with a maximum of 13 sites randomly distributed on the surface and with relatively high coverages, namely, 128 and 240 water molecules. The results are shown in Figure 5 where the distribution functions $h(x, y)$ exhibit very different behaviors on H-up (a and c) and H-down (b and d) groups, as already mentioned for the surface containing three sites. On these highly activated surfaces, only one large water aggregate is formed because of the large number of molecules considered in the simulation box. However, dark spots (maxima) in the $h(x, y)$ distribution functions indicate that the water molecules tend to maximize their interactions with H-up groups, and then the water molecules are gathered around the vicinity of active sites, leading to a corresponding aggregate as stretched as possible. This is specially evident in Figure 5c, where 13 maxima are obtained, coinciding with the positions of the 13 H-up active groups. By contrast, the water molecules tend to form a more compact aggregate on the surface containing

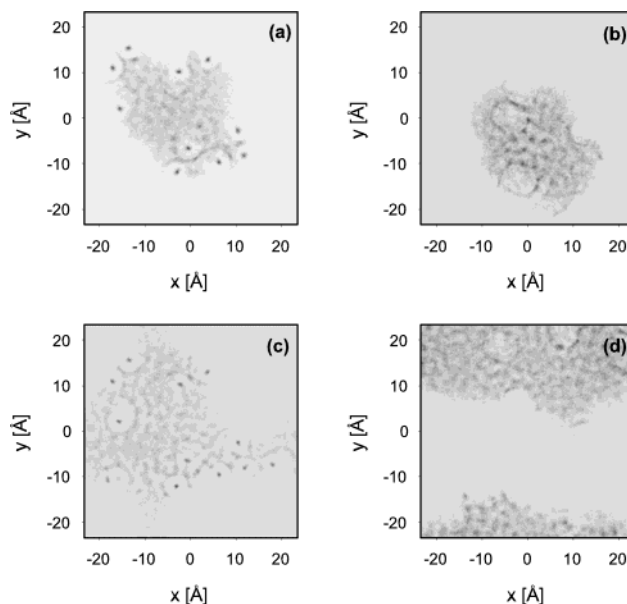


Figure 5. Distribution functions of the oxygen atoms' (of water molecules) positions projected in the (x, y) plane of the surface for a water aggregate above an active graphite surface: (a) 13 H-up active groups and 128 water molecules, (b) 13 H-down active groups and 128 water molecules, (c) 13 H-up active groups and 240 water molecules, and (d) 13 H-down active groups and 240 water molecules.

H-down groups as a result of a competition that favors water–water interactions with respect to water–COOH site interactions.

To characterize the influence of the COOH sites on the dynamics of the water molecules, we have compared the self-diffusion coefficients calculated for the water molecules adsorbed on a bare graphite surface to those calculated on an activated surface containing 13 sites (H-down or H-up). Note that to have better statistics we have considered only the case of large aggregates (i.e., those containing more than 128 water molecules) for the calculations of the diffusion coefficients (D). The results show that the values of D are similar ($1.1 \times 10^{-5} \text{ cm}^2/\text{s}$) on both activated surfaces and are more than twice as low as those on the bare graphite surface ($2.5 \times 10^{-5} \text{ cm}^2/\text{s}$). These results confirm that the sites affect not only the structure of the water aggregate but also the dynamics of the water molecules on the graphite surface.

4. Discussion

The objective of the present paper was to characterize the behavior of a model active graphite surface with respect to water adsorption. To our knowledge, very few publications have been devoted to the theoretical study of water adsorption on bare or activated graphite surfaces.

Gordillo and Marti¹⁸ have used molecular dynamics simulation to characterize static and dynamic properties of a layer of water molecules on a bare graphite surface between 200 and 350 K. In the present work, some simulations of water adsorption on a pure graphite surface have been done for comparison with the water behavior on activated surfaces. We should mention that the potential used in our study favors a cluster structure for the water molecules on bare graphite at 250 K because of the predominance of the water–water interactions with respect to the water–graphite interactions. This result is in contrast to the monolayer geometry obtained at the same temperature in ref 18 and based on a very different potential. This structural difference can also explain the different values for the diffusion coefficients that are close to that of bulk

ice in the paper of Gordillo and Marti,¹⁸ and they are rather characteristics of liquid water in the present work.

In a series of paper, Gubbins et al.^{7–10} have investigated adsorption equilibrium properties of water on porous activated carbons by using grand canonical Monte Carlo simulations. However, in these works, no detailed description of the activated surface was given in terms of surface reconstruction around the COOH anchoring point or in terms of charge redistribution on the graphite surface due to the presence of the active group. Moreover, they do not discuss the structure or the dynamics of the water molecules around these active groups. Nevertheless, the main conclusions drawn from these works are similar to those presented in the present paper on the basis of a more accurate potential (i.e., water adsorption on activated graphite surfaces is dependent on the species of active groups, on their number, and on their relative positions on the surface).

The only study that can actually be compared with the present work has been published in the very recent paper of Tarasevich et al.¹² These authors have studied the interaction of a few water molecules (up to three) with hydrophilic centers at a partially oxidized model graphite surface by using the semiempirical PM3 method. The graphite surface was simulated by a section of the edge of one or three 2D hexagonal graphene lattice sheets, with the hydrophilic center formed by the attachment of a COOH group (H-up only) to one of the boundary carbon atoms. The clusters modeling the graphite surface contained between 6 and 66 carbon atoms. These calculations have shown that the adsorption of the water molecules at the COOH site is a favorable process and leads to the formation of small water clusters tied to the carboxyl group by at least one hydrogen bond, in agreement with our own findings. The equilibrium geometry found for these small clusters (of up to three water molecules) is similar to that obtained in our work, and the adsorption enthalpies are also of the same order of magnitude. However, it is rather difficult to make a quantitative comparison between the results issued from these two studies because both the systems under investigation and the methods used are different.

A quantitative comparison between the present results and experimental data is not an easy task because it would require a precise characterization of the soot surface morphology and chemical composition. Although only one type of active site (COOH) has been considered in our calculations, we clearly show evidence of a stronger interaction between water molecules and the active graphite surface than between water and bare graphite. Such behavior is in agreement with the hydrophilic behavior of kerosene soot, as observed in the measurement of water adsorption isotherms.^{4,5,19} However, the specific interaction between water and soot is far from being understood, and further investigations are required by considering other types of active sites on the graphite surface (hydroxyl sites and sulfur-containing groups, for instance) and different geometries for the graphite substrate (i.e., not only the graphite plane but also edges and curved surfaces such as nanotubes, as evidenced by transmission electron microscopy⁴).

5. Conclusions

In this paper, molecular dynamics simulations based on quantum chemical results have been performed to characterize

the adsorption of water molecules on activated graphite surfaces from very low coverage up to the saturation of the graphite surface at a temperature that is typical of the troposphere (250 K).

The results of the molecular dynamics simulations show that, at low active-group concentrations on the graphite surface, these groups (H-down or H-up) act as strong trapping sites for a few water molecules due to the formation of hydrogen bonds between COOH and H₂O. These water molecules, directly H bound to the active group, thus become nucleation centers for other water molecules in order to form aggregates tied to the COOH site. The main difference between the two types of active groups comes from the number of H bonds that are formed with the water aggregate: one H bond for the H-down group and two H bonds for the H-up group. Moreover, at low water coverage, the water aggregate remains confined in the vicinity of the COOH site, in contrast with a bare graphite surface where the water aggregate is more free to move as a whole on the surface.

At higher water coverage and higher concentrations of active groups on the graphite surface, the present simulations demonstrate that water adsorption on activated graphite surfaces is dependent not only on the type of sites but also on their number and on their relative positions. Moreover, the dynamics of the water molecules is strongly slowed on the activated surface with respect to that on a bare graphite surface.

Acknowledgment. We acknowledge Professor J. Suzanne (Marseille) and Professor O. B. Popovitcheva (Moscou) for fruitful discussions. We thank the Ministère des Affaires Étrangères for financial support through the French/Spanish program PICASSO.

References and Notes

- (1) Chen, Y.; Kreidenweiss, S. M.; McInnes, L. M.; Rogers, D. C.; DeMott, P. J. *Geophys. Res. Lett.* **1998**, *25*, 1391.
- (2) DeMott, P. J.; Chen, Y.; Kreidenweiss, S. M.; McInnes, L. M.; Rogers, D. C.; Sherman, D. E. *Geophys. Res. Lett.* **1999**, *26*, 2492.
- (3) Seinfeld, J. H. *Nature* **1998**, *391*, 837.
- (4) Popovitcheva, O. B.; Persiantseva, N. M.; Trukhin, M. E.; Rulev, G. B.; Shonija, N. K.; Buriko, Y. Y.; Starik, A. M.; Demirdjian, B.; Ferry, D.; Suzanne, J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4421.
- (5) Popovitcheva, O. B.; Trukhin, M. E.; Persiantseva, N. M.; Shonija, N. K. *Atmos. Environ.* **2001**, *35*, 1673.
- (6) Kwon, S.; Vidic, R.; Borguet, E. *Surf. Sci.* **2003**, *522*, 17.
- (7) Maddox, M.; Ulberg, D.; Gubbins, K. E. *Fluid Phase Equilib.* **1995**, *104*, 145.
- (8) Müller, E. A.; Rull, L. F.; Vega, L. F.; Gubbins, K. E. *J. Phys. Chem.* **1996**, *100*, 1189.
- (9) Müller, E. A.; Gubbins, K. E. *Carbon* **1998**, *36*, 1433.
- (10) McCallum, C. L.; Bandosz, T. J.; McGrother, S. C.; Müller, E. A.; Gubbins, K. E. *Langmuir* **1999**, *15*, 533.
- (11) Brennan, J. K.; Bandosz, T. J.; Thomson, K. T.; Gubbins, K. E. *Colloids Surf., A* **2001**, *187–188*, 539.
- (12) Tarasevich, Y. I.; Aksenenko, E. V. *Colloids Surf., A* **2003**, *215*, 285.
- (13) Hamad, S.; Mejias, J. A.; Lago, S.; Picaud, S.; Hoang, P. N. M. *J. Phys. Chem. B* **2004**, *108*, 5405.
- (14) Allen, M. P.; Tildesley, D. J. In *Computer Simulation of Liquids*; Clarendon: Oxford, England, 1987.
- (15) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.
- (16) Nada, H.; Furukawa, Y. *Surf. Sci.* **2000**, *446*, 1.
- (17) Shevade, A. V.; Jiang, S.; Gubbins, K. E. *J. Chem. Phys.* **2000**, *113*, 6933.
- (18) Gordillo, M. C.; Marti, J. *J. Chem. Phys.* **2002**, *117*, 3425.
- (19) Seisel, S. Private communication, 2003.