

## Theoretical study of chlordecone and surface groups interaction in an activated carbon model under acidic and neutral conditions



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### ABSTRACT

Activated carbons (ACs) are widely used in the purification of drinking water without almost any knowledge about the adsorption mechanisms of the persistent organic pollutants. Chlordecone (CLD, Kepone) is an organochlorinated synthetic compound that has been used mainly as agricultural insecticide. CLD has been identified and listed as a persistent organic pollutant by the Stockholm Convention. The selection of the best suited AC for this type of contaminants is mainly an empirical and costly process. A theoretical study of the influence of AC surface groups (SGs) on CLD adsorption is done in order to help understanding the process. This may provide a first selection criteria for the preparation of AC with suitable surface properties. A model of AC consisting of a seven membered ring graphene sheet (coronene) with a functional group on the edge was used to evaluate the influence of the SGs over the adsorption. Multiple Minima Hypersurface methodology (MMH) coupled with PM7 semiempirical Hamiltonian was employed in order to study the interactions of the chlordecone with SGs (hydroxyl and carboxyl) at acidic and neutral pH and different hydration conditions. Selected structures were re-optimized using CAM-B3LYP to achieve a well-defined electron density to characterize the interactions by the Quantum Theory of Atoms in Molecules approach. The deprotonated form of surface carboxyl and hydroxyl groups of AC models show the strongest interactions, suggesting a chemical adsorption. An increase in carboxylic SGs content is proposed to enhance CLD adsorption onto AC at neutral pH conditions.

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### 1. Introduction

Chlordecone (CLD), decachloropentacyclo[5.3.0.0<sup>2,6</sup>.0<sup>3,9</sup>.0<sup>4,8</sup>] decan-5-one (CAS 143-50-0), is a chlorinated organic compound of chemical formula C<sub>10</sub>Cl<sub>10</sub>O (Fig. 1). It has been addressed as a Persistent Organic Pollutant (POP) by the Stockholm Convention since May, 2009 [1], and it has also been included in the Oslo and Paris Convention (OSPAR) as a substance of possible concern [2]. Between 1951 and 1975 about 1,600,000 kg of CLD were synthe-

sized in the U.S.A., the production was stopped in 1976, and finally in 1990 the authorization for its use was retired in France. However, it was extensively used as pesticide in banana crops until 1993 in the French West Indies: Martinique and Guadeloupe [3,4].

Chlordecone presents a low solubility in water (2.7 mg at 25 °C), except at pH > 9 where chlordecone hydrate appears, it has a high molecular weight (490.64 g/mol) and its vapor pressure is  $-2.25 \times 10^{-7}$  mmHg at 25 °C [5]. Due to chlordecone's persistence in natural environments and its high chemical and microbiological resistance, even after several years of not being used, 8–9% of cultivation areas of Guadeloupe contain CLD concentrations higher than 1 mg/kg in topsoil, and as high as 9 mg/kg in some banana fields [3]. CLD may be bound to soils for several decades to half a millennium, depending on soil type [3]. CLD has a strong affinity for lipids with a large bioaccumulation and biomagnification along of the food chain (log *K*<sub>ow</sub> = 4.5–6) [4,5], and it is known for its endocrine-disrupting

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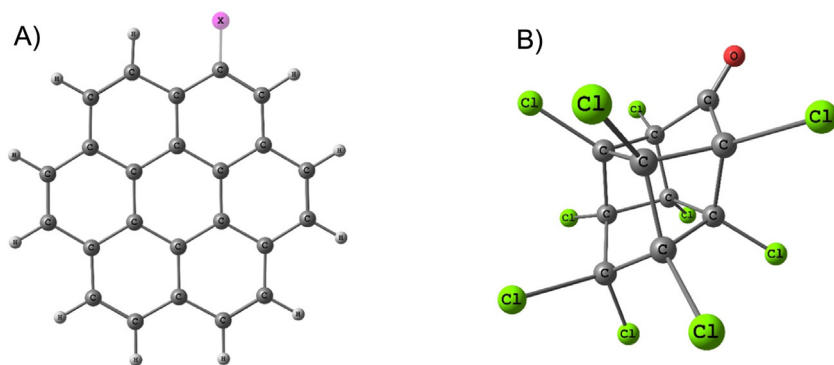


Fig. 1. (A) AC model consisting on coronene and its oxidized forms: X=H (Coronene), COOH, COO<sup>-</sup>, OH, O<sup>-</sup> and (B) CLD.

character [6,7] and its carcinogenic potential [8–10]. Before CLD proscription in the French West Indies, polluted tap water, local bottled spring water, and contaminated food have been consumed [11,12]. It has been recently shown that prenatal exposure is as well associated with a decreased length of gestation, hormone disruption and altered infants' cognitive and motor development [13,14]. The presence of chlordecone at high concentration (up to 10  $\mu\text{g/L}$ ) in several water resources [15], has risen awareness of CLD polluted consumption and residual waters as a serious issue. In order to limit CLD exposure for the population in Guadeloupe and Martinique, drinking water and production plants have been equipped with activated carbon (AC) filters [16,17].

ACs are very popular systems for treating water contaminated with persistent organic pollutants and to limit pesticide contamination [18–22]. The adsorption process onto AC is a very complex phenomenon ruled by multiple factors that range from chemical composition to textural properties [23,24]. The experimental procedures for determining the best-suited adsorbent are very time and resources consuming due to the high number of ACs types that are needed to be tested [16,25–27]. The influence of surface groups content over the adsorption properties has been reported and studied to some extent both experimentally and theoretically for porous carbons, mainly AC and soot particles [28–32]. Durimel et al. prepared sugarcane bagasse ACs with different textural characteristics and surface compositions, and used them to evaluate the influence of those factors along with the solution pH over the adsorption of CLD on AC. The results indicated that high carbon and acidic groups content favors the adsorption of CLD on AC [16]. The present work focuses on evaluating the influence of some AC surface groups (SGs) over the adsorption of CLD under acidic and neutral conditions. The interactions of CLD with two SGs of AC are studied using Multiple Minima Hypersurface (MMH) methodology [33–36]. MMH is a non-dynamical stochastic approach that allows estimating the thermodynamic association functions by means of the internal energy calculations with semiempirical Hamiltonians.

In a previous work [17,37], a methodology based on MMH was proposed for the study of the influence of AC surface groups over the adsorption process of small organic molecules on AC. The procedure has been successfully used to identify the main interactions responsible for hexachlorocyclohexane isomers ( $\gamma$  and  $\beta$ ) [17], paracetamol and <sup>125</sup>I-paracetamol [37] adsorption in similar systems. The current work aims to extend the methodology to a more complex system, using a bigger AC model as required by the size of the contaminant (CLD). Furthermore, in the present work the interactions between the CLD and AC surface groups are analyzed taking into account the energetic and geometrical aspects in order to better understand the adsorption process. Since the energy and geometric analysis suggests the possibility of chemisorption in some systems, the Quantum Theory of Atoms in Molecules (QTAIM)

approach [38] is used to provide a more rigorous classification of the nature of interactions. The final goal is to provide insights to improve the selection process of the best suited ACs according to its SGs compositions for the removal of chlordecone.

## 2. System under study

The interactions between the guest molecules and AC's surface have been studied with different theoretical procedures. Small polycycles and their oxidized derivatives are commonly used for building idealized models of carbon based materials [28,39–50]. In fact, naphthalene [17,44,45] coronene [37,43,49–51], and their derivatives have been repeatedly employed for this kind of theoretical studies. The use of such small models has both advantages and disadvantages, being the most obvious of the advantages the savings in computational resources allowing either the application of relatively high level calculations or a throughout exploration of the interactions space. On the other hand, the use of these small models brings along negative effects regarding their size, and, in some cases, the oversimplification of the structure. The dramatic reduction in size of these models with respect to the real structures can reduce the non-local contributions to the dispersion energies. In the specific case of AC, the use of oxidized forms of polycycles completely neglects the influence of pore shape, defects, pore size and pore connectivity. In return, it allows to explore the Potential Energy Surface (PES) and to perform a large number of calculations with a minimal computational cost in order to achieve a quantum chemical and statistical description of the edge SGs influence over the adsorption processes.

In a previous work, Durimel et al. showed that CLD adsorption onto the studied ACs is probably governed by hydrogen bonding of chlorine groups in CLD with carboxylic surface groups of AC and by hydrophobic interactions between the graphitic surface of the AC and the CLD [16]. It is known that ACs contains O, N, S and inorganic minerals according to its natural origin. These heteroatoms can be bonded on the graphene layers edges or in the aromatic rings in the graphene layers faces. In this last case the sp<sup>2</sup> character of the C atom is lost, but this oxidation occurs to a lesser extent compared to the oxidation over the sp<sup>2</sup> carbons situated on the edges. It is known that the presence of oxygen containing SGs on the graphene edges has a decisive influence over the AC properties [52] and that is why both, theoretical and experimental studies emphasize these SGs. In order to focus our attention on the SGs' influence over the adsorption process, the selected AC model consists of a seven ringed aromatic polycycles (coronene) with a functional group attached to the edge of the molecule (Fig. 1). As surface groups, hydroxyl (OH) and carboxyl (COOH) both directly attached to an sp<sup>2</sup> carbon lying on the edge, were selected since these are the most commonly encountered and abundant oxygenated SGs on ACs surfaces [39].

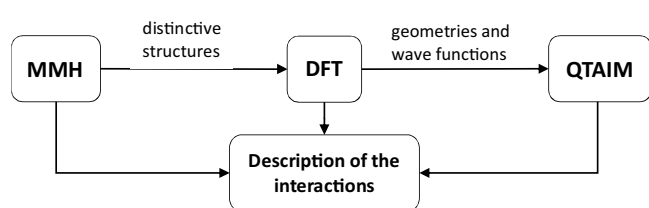


Fig. 2. General theoretical methodology used in the present work.

The coronene aromatic compound has been chosen herein to model the ACs. The edge of the coronene has been modified by carboxyl and hydroxyl groups to obtain the oxygen containing models of AC (see Fig. 1A). Note that the models provide both, the aromatic character (or graphene structure) and the SGs at the edges of ACs.

### 3. Methods and procedures

The general methodology employed in the present study consists of two main steps. In the first step the MMH methodology is utilized to explore the interactions space of the CLD with the AC SGs and select distinctive minima structure representing different types of interaction. The second step is a follow up step where the selected distinctive minima structures are re-optimized using DFT and the geometries and electronic structure are treated using QTAIM [38] to more accurately describe the nature of the interactions present. Fig. 2, describes the general methodology followed in this work.

MMH methodology combines a quantum semi-empirical methods for the evaluation of the energies with statistical mechanics to obtain thermodynamic quantities related to the molecular association process [53–61]. The main procedure of this approach will be outlined briefly.

An appropriate construction of several random molecular geometries initially generates a set of  $n$  non-redundant cluster configurations, starting from the independently optimized structures of AC, CLD and water. The random structures are optimized, normally following an energy gradient pathway, and a set of clusters of local minima in the configuration space is obtained. The energy,  $\varepsilon_i$ , of every  $i$ -th cluster of the ensemble is thus obtained.

The partition function of molecular association is calculated by choosing the same set of non-interacting molecules as reference value for the energy scale, which means that the association process is taken as isothermal.

Thermodynamic properties such as association energy ( $\Delta E_{\text{ASSOC}}$ ), entropy ( $\Delta S_{\text{ASSOC}}$ ), and Helmholtz free energy ( $\Delta A_{\text{ASSOC}}$ ) are then calculated by this procedure [34,35]. The term of association energy used, means the thermodynamic association energy calculated through the statistically weighted sum (i.e., partition function) of the representative “supermolecule” states. It will be called “mean association energy” from now on [34].

A Boltzmann distribution is used to calculate the thermally averaged state of the typical macroscopic system at room temperature (298.15 K).

Adsorption is a thermodynamic competitive process where the stronger interactions dominate over the weaker interactions. However, in a real system not only one type of interaction (the strongest) will determine the adsorption. It is well known that AC surface is very irregular (morphologically, topologically and chemically speaking) and many different adsorption sites are present. Even for similar adsorption sites, it is possible to find many different ways in which the solvent is adsorbed, especially for weakly interacting systems.

Association energy is defined as  $\Delta E_{\text{assoc}} = E_{\text{supermolecule}} - E_{\text{ref}}$ , where,  $E_{\text{supermolecule}}$  is the energy of the molecular complex formed

by the AC model and the solvent (water and chlordecone) and  $E_{\text{ref}}$  is the sum of the energies of each independent molecules. A favorable thermodynamic association implicates that the supermolecule will be more stable than the isolated molecules. Considering that the energy of the molecules are negative, then  $\Delta E_{\text{ASSOC}}$  will be negative. Thus, a major absolute value of  $\Delta E_{\text{ASSOC}}$  correspond to more energetically favorable associations.

The standard MMH procedure [33] puts the solute in the center of a cubic box and then generates the solvent molecules in random configurations. By this procedure, the region of space for generated solvent molecules cannot be restricted. In the present work, however, we utilized a modified version of the MMH methodology in order to improve the exploration of the configurational space [36].

The first modification relates to the program that generates the random configurations to allow specification of the region, orientation and dimensions of the solvent box [36]. This functionality can be used to make a more rational use of computational resources and improved analysis when exploring the configurational space involving an elongated shape solute molecule. The second modification consists of an additional step to select the minimum number of random configurations needed to ensure a correct exploration of the configurational space. The specifics to these modifications have been described in detail in previous works [17,37].

The number of different random configurations was set to 700 after testing to obtain the minimum number of initial configurations needed for a reasonable convergence of the  $\Delta E_{\text{ASSOC}}$ . The semiempirical Hamiltonian PM7 [62] was used for the optimization of the 700 different geometries and energies of each system, as implemented in MOPAC2012 program [63]. PM7 is a modern semiempirical Hamiltonian and it was parameterized using experimental and high-level ab initio reference data and it improves the description of non-covalent interactions with respect to previous semiempirical methods. The main disadvantage of using a semiempirical Hamiltonian is the lack of theoretical rigor. However, semiempirical methods have advantages on their own: these methods do not suffer from Basis Set Superposition Error (BSSE) because their basis sets are orthogonal, correlation effects are implicitly considered during the parameterization procedures using experimental data, and it allows to compute large systems, or in this case large number of supermolecules, efficiently [64]. For that reason, the use of semiempirical methods as a practical tool for modeling chemical systems has been extended to a wider range of species [62].

For the re-optimization of geometries, Becke's three parameter hybrid method using the correlation functional of Lee, Yang and Parr with the Coulomb-attenuating long-range correction: CAM-B3LYP [65–68] was used with the Pople's basis set 6-31+G(d,p). CAM-B3LYP yields atomization energies of similar quality to those from B3LYP, while benefiting from a reduced Self-Interaction Error [65]. The electronic structure was further refined by using the 6311++G(2df,2pd) basis set as implemented in Gaussian 09 [69].

The distinctive minima structures obtained for the systems SG/CLD/(H<sub>2</sub>O)<sub>n=0-3</sub> and their electronic structures were treated using Bader's QTAIM [38] in order to characterize the interaction types that take place during the adsorption process according to Nakanishi's criteria [70,71]. The QTAIM, enables us to analyze the nature of chemical bonds and interactions which is one of the main goals of this investigation.

## 4. Results and discussion

### 4.1. MMH calculations. Water clustering

Since adsorption of CLD occurs from aqueous solution, it is important to understand the role of water as solvent in the interac-

tions of CLD with OH and COOH SGs. In previous works by our group, the interaction of water molecules with the SGs has been studied using the present methodology for two models of AC, a naphthalene [17] and a coronene-based model [37]. This allows determining the minimum number of water molecules needed to saturate the SG, and the association energies obtained for the water cluster with the SGs can be used as a reference to compare with the inclusion of the contaminant.

Based on the results previously obtained for similar system, the maximum number of water molecules included in the calculations for the present study was set to three. The detailed procedure has been published and all programs for processing are available on a web site [17,29,37].

In an attempt to expand the range of applicability of semiempirical methods, PM7Hamiltonian was developed in 2012 with a subsequent significant increase in accuracy. The result was that the average unsigned error in the heats of formation of organic solids calculated using PM7 decreased by more than 50% relative to that for PM6, previously the most accurate of the NDDO method, at the same time, errors in PM7 geometries have been reduced by over one-third relative to those of PM6 [64]. In previous works our group had been working with the semiempirical Hamiltonian PM6-DH2X, but in view of the improved accuracy attained by PM7 we decided to switch to PM7 in the present work. Hence, the study of the interaction of SGs with water clusters up to three water molecules was carried out in order to compare and validate the results against previous ones and in order to have consistent reference association energy values for the present study. Table 1 shows the results obtained for the mean association energy per water molecule ( $\Delta E_{\text{ASSOC}}$ ) for water cluster around the SGs obtained in the present work as well as those obtained previously [17,37].

As shown in Table 1, the results obtained in the present work are consistent with previously obtained results from a qualitative standpoint. That is, the association of water is stronger for COOH group than for OH group. The lowest  $\Delta E_{\text{ASSOC}}$  for COOH group is achieved with a single adsorbed water molecule, and there are not significant differences in  $\Delta E_{\text{ASSOC}}$  after increasing the number of water molecules. This result indicates that the first water molecule saturates the COOH group and it is determinant for the solvation process. However, for OH group the saturation corresponds to an aggregate containing two or three water molecules, this behavior is also observed for the coronene/(H<sub>2</sub>O)<sub>n=1–3</sub> systems.

The pH influence has been taken into account by chemical modification of the SG. The association energy per water molecule for small water aggregates over O<sup>−</sup> and COO<sup>−</sup> surface groups is shown in Table 1. From these results it can be seen that affinity between charged SG and water molecules is higher for COO<sup>−</sup> than O<sup>−</sup> group. Besides, as expected,  $\Delta E_{\text{ASSOC}}$  is lower for charged SG than for neutral SG showing stronger coulomb-dominated interactions leading to higher affinity between water and charged SG. For both charged SG a single water molecule is enough to reach saturation.

Again, the trends obtained in the present work are consistent with those obtained by Enriquez-Victorero et al. [17] and Hernández-Valdés et al. [37], further confirming the validity of the procedure. However, the values of the individual association energies differ. As expected, difference is bigger for the results of Enriquez-Victorero et al. [17] since in that study both the AC model and the Hamiltonian differ from the ones used in this work, while the results of Hernández-Valdés et al. [37] correspond to a study where only the Hamiltonian has been changed. For coronene model the negative partial charge on the O<sup>−</sup> and COO<sup>−</sup> groups should be more delocalized over the aromatic system compared with the naphthalene model.

Summing up, according to the association energies, the affinity order between water molecules and SG is as follows: COO<sup>−</sup> > O<sup>−</sup> > COOH > OH > coronene. The saturation of the surface

groups COO<sup>−</sup>, O<sup>−</sup>, and COOH occurs when the first water molecule is added to the systems, while two or three water molecules are needed to saturate OH surface group and coronene. The electrostatic interactions are dominant and the most stable structures are mainly dominated by the formation of hydrogen bonds, being the most stable structures those with the highest number of H-bonds. This behavior was also obtained by Hernández-Valdés et al. [37].

In order to take into account the solvation process of CLD in water, systems CLD/(H<sub>2</sub>O)<sub>n=1–5</sub> were studied. MMH calculations for the solvation of chlordecone were carried out in order to be consequent with the energy criterion used in the present work (Figures SF21 and SF22). The lowest  $\Delta E_{\text{ASSOC}}$  for chlordecone/water cluster is achieved with a single adsorbed water molecule.

#### 4.2. MMH calculations. CLD adsorption

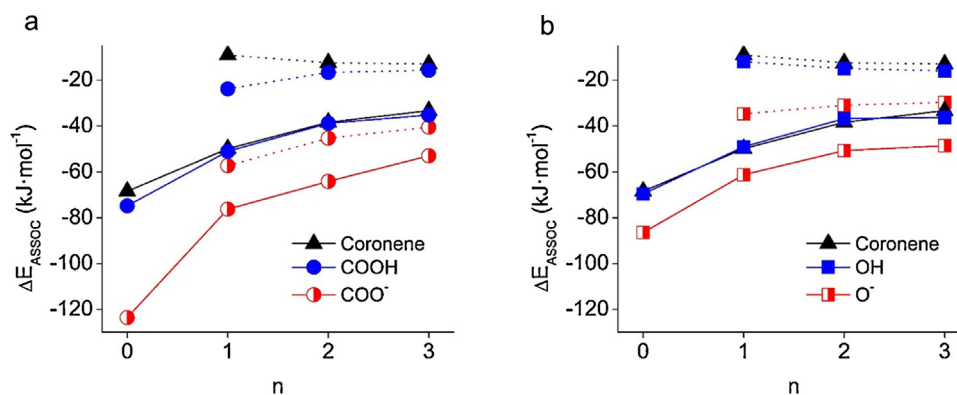
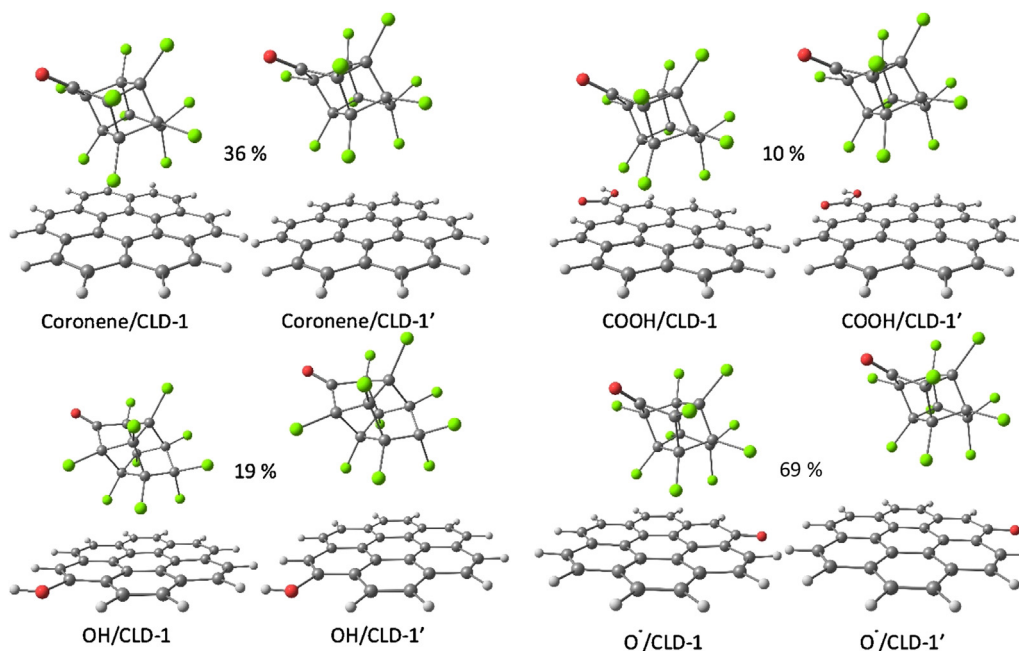
The conformational space corresponding to the interaction of each SG with CLD was explored in presence and absence of water molecules, and modified SGs were included in order to take into account the solvent and pH influence. A total of 35 systems were studied, 15 systems for SG/(H<sub>2</sub>O)<sub>n=1–3</sub> and 20 for SG/CLD/(H<sub>2</sub>O)<sub>n=0–3</sub>. For each system, 700 random individual configurations were generated and evaluated for each system. Fig. 3 summarizes the mean association energy results obtained for CLD interaction with different surface groups COOH, COO<sup>−</sup>, OH, and O<sup>−</sup> without water and with up to three water molecules at 298 K.

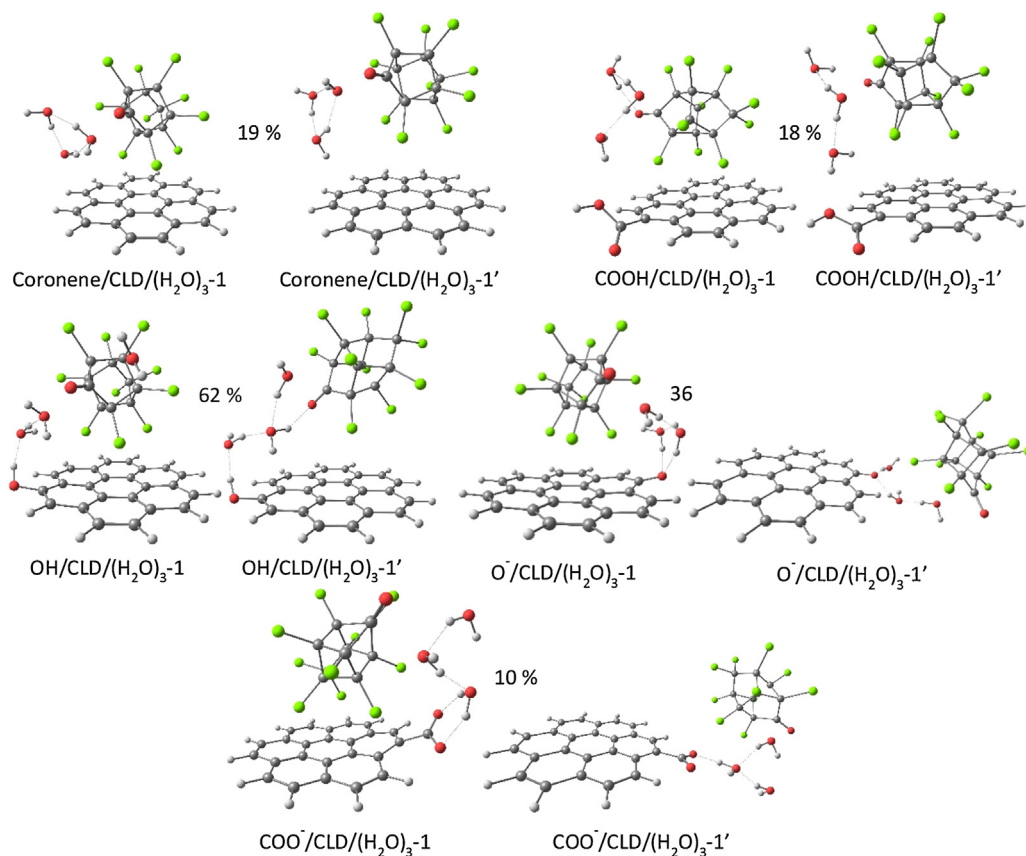
As it can be observed from Fig. 3, the behavior of  $\Delta E_{\text{ASSOC}}$  for the neutral SG/CLD/(H<sub>2</sub>O)<sub>n</sub> systems (SG = Coronene, COOH, and OH) is very similar for all of them, while for charged SG (COO<sup>−</sup> and O<sup>−</sup>), the  $\Delta E_{\text{ASSOC}}$  is clearly lower. Interestingly, for every system the  $\Delta E_{\text{ASSOC}}$  values were considerably lower in the presence of the contaminant compared to the corresponding association of the AC model with water molecules alone. Moreover, the stability of the systems SG/CLD was considerably higher than SG/CLD/(H<sub>2</sub>O)<sub>n=1–3</sub> systems (although these were still energetically favored). This behavior suggests that if a CLD molecule is associated with the SG, the molecules of water would not be able to compete for the adsorption sites and easily displace the CLD. However, it is important to note that in real systems CLD is very diluted and its adsorption constant will be displaced due to this fact. Numerical values of  $\Delta E_{\text{ASSOC}}$  for SG/(H<sub>2</sub>O)<sub>n=1–3</sub> and SG/CLD/(H<sub>2</sub>O)<sub>n=0–3</sub> systems are shown in Tables ST1 and ST2 (Section T, Supplementary information). Moreover, Figs. SF1 to SF20 in Section F, supplementary information, show geometries, interaction distances, association energies and contribution to the mean association energy (according to the Boltzmann distribution) for all obtained minima structures with a population over 5%.

A comparison of the  $\Delta E_{\text{ASSOC}}$  (Section T, Supplementary information) for coronene versus the other neutral SGs indicates a very little dependence of the adsorption process with the SGs composition at low pH conditions, where all studied SGs remain mostly in neutral form. On the other hand, at pH ≈ 5–7, which is most likely the case for drinking water, a rough estimation gives a deprotonation of OH surface groups lower than 3% and can be neglected, while only COOH groups are deprotonated to a considerable extent (≈90%) [51]. Taking into account that COO<sup>−</sup> is the only charged surface group, it is predicted that carboxylic surface groups will be the main contributors to enhance CLD adsorption onto AC at neutral or slightly acidic pH condition. These results are consistent with recent experimental findings by Durimel et al. [16]. In that work, the adsorption of CLD onto ACs of different SGs content was tested, and AC with the highest content of COOH SGs was selected as the best-suited for CLD adsorption [16]. The effects of basic pH conditions in the CLD adsorption onto AC will be the subject of future investigations.

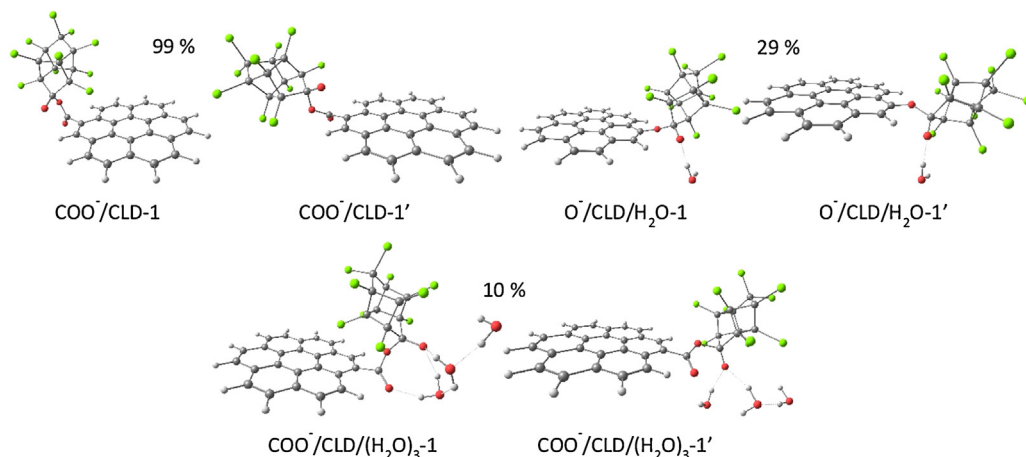
**Table 1**Mean association energy per water molecule ( $\Delta E_{\text{ASSOC}}$ ) for small water aggregates containing up to three molecules of  $\text{H}_2\text{O}$  with AC-SG. Energies are given in kJ/mol.

Surface group	$n\text{H}_2\text{O}$	$\Delta E_{\text{ASSOC}}$	$\Delta E_{\text{ASSOC}}^a$	$\Delta E_{\text{ASSOC}}^b$	$\Delta E_{\text{ASSOC}}^a - \Delta E_{\text{ASSOC}}$	$\Delta E_{\text{ASSOC}}^b - \Delta E_{\text{ASSOC}}$
Coronene	1	-9.0	-7.8	-	1.2	-
	2	-12.4	-11.9	-	0.5	-
	3	-12.9	-12.1	-	0.8	-
OH	1	-11.9	-16.9	-17.7	-5.0	-5.8
	2	-14.9	-25.9	-26.8	-11.0	-11.9
	3	-16.0	-24.9	-28.3	-8.9	-12.3
COOH	1	-23.8	-38.0	-36.4	-14.2	-12.6
	2	-16.6	-30.7	-33.8	-14.1	-17.2
	3	-15.7	-31.1	-31.1	-15.4	-15.4
$\text{O}^-$	1	-34.7	-43.9	-52.1	-9.2	-17.4
	2	-30.9	-41.5	-49.7	-10.6	-18.8
	3	-29.7	-37.5	-50.1	-7.8	-20.4
$\text{COO}^-$	1	-57.2	-57.0	-64.0	0.2	-6.8
	2	-45.3	-53.8	-56.8	-8.5	-11.5
	3	-40.5	-48.9	-53.5	-8.4	-13.0

<sup>a</sup> Values from Hernández-Valdés et al. based on a similar AC model [33].<sup>b</sup> Values from Enriquez-Victorero et al. based on a naphthalene based AC model [17].**Fig. 3.** Mean association energies for  $\text{SG}/(\text{H}_2\text{O})_n$  (dotted lines) and  $\text{SG}/\text{CLD}/(\text{H}_2\text{O})_n$  (solid lines) systems. (a) Carboxylic SGs, (b) hydroxyl SGs. “ $n$ ” is the number of water molecules added.**Fig. 4.** Distinctive minima structures and their populations (%) for the systems  $\text{SG}/\text{CLD}$ . Cl... $\pi$ -cloud interactions. Numbers denote structures found at PM7 while quoted numbers account for the corresponding re-optimized structures at CAM-B3LYP/6-31 + G(d,p) level of theory.



**Fig. 5.** Distinctive minima structures and their populations (%) for the systems SG/CLD/(H<sub>2</sub>O)<sub>n=1-3</sub>. Cl $\cdots$  $\pi$ -cloud interactions. Numbers denote structures found at PM7 while quoted numbers account for the corresponding re-optimized structures at CAM-B3LYP/6-31 + G(d,p) level of theory.



**Fig. 6.** Distinctive minima structures and their populations (%) for the systems SG/CLD/(H<sub>2</sub>O)<sub>n=0-3</sub>. O $\cdots$ CO interactions. Numbers denote structures found at PM7 while quoted numbers account for the corresponding re-optimized structures at CAM-B3LYP/6-31 + G(d,p) level of theory.

As a result of MMH-PM7 calculations two distinctive types of interaction were obtained for the systems under study (Figs. 4–6). The first type of interaction consist of the chlorine atoms of CLD interacting with the  $\pi$ -cloud of coronene (Cl $\cdots$  $\pi$ -cloud), giving rise to a relatively weak interaction. The second type is a donor–acceptor interaction between negatively charge oxygen of SGs (COO $^-$  and O $^-$ ) and the electronically deficient carbonyl carbon of CLD (O $^-$  $\cdots$ CO). These interactions are further described in Section 4.4 by means of QTAIM.

The first interaction type is mostly non-covalent in nature between chlorine atoms of CLD as a Lewis acid and carbon atoms

of coronene AC model as a Lewis base. This kind of interaction can be observed for the complexes including CLD (Figs. 4 and 5). The introduction of water molecules promotes this type of interaction, as can be seen from the complexes COOH/CLD/(H<sub>2</sub>O)<sub>3-1</sub> and OH/CLD/(H<sub>2</sub>O)<sub>3-1</sub> (neutral SGs), and from COO $^-$ /CLD/(H<sub>2</sub>O)<sub>3-1</sub> and O $^-$ /CLD/(H<sub>2</sub>O)<sub>3-1</sub> (charge SGs) in Fig. 5. The second interaction type is only present in the charged systems and shows clear signs of covalence, the bonding distance between the charged oxygen of the SG and the carbonylic carbon of the CLD (O $^-$  $\cdots$ CO interactions) are in the range between 1.5 and 1.6 Å (Fig. 6). Furthermore, the carbonylic groups of the CLD in the complexes lose their planar

configuration (i.e., the carbon  $sp^2$  character) with the corresponding increase of the C–O bond distance from 1.19 Å to 1.24 Å. This evidence suggests that a chemical sorption may occur at neutral and basic pH conditions between CLD and AC.

The  $Cl \cdots \pi$ -cloud interactions are easily found and appear to be favored from an entropic perspective since most starting geometries lead to this type of final structure. Nevertheless, the  $O^- \cdots CO$  interactions are much stronger, and taking into account that the population percentage value (99%) of the  $COO^-/CLD-1$  complex (Fig. 6) suggests the occurrence of chemical sorption, this kind of interaction had not been previously reported. For the  $O^-/CLD$  system (absence of water) no close  $O^- \cdots CO$  interaction was found, however, it is readily found after the addition of the first water molecule (system  $O^-/CLD/H_2O-1$ , Fig. 6), pointing to a major role of the solvating water molecules over the association process.

Regarding the aromaticity in the behavior of AC, two main effects are observed in our systems. First, the presence of interactions involving the delocalized electrons of the aromatic model. Second, the stabilization of the electron density in negatively charged surface groups.

As mentioned before, Enriquez-Victorero et al. [17] studied  $\beta$ -HCH and  $\gamma$ -HCH adsorption on AC SGs. Since CLD and HCH are simultaneously present in water bodies as persistent organic pollutants, a competitive relationship with regards to the adsorption on AC should be expected and studies addressing this issue should be carried out in the future. However, although, the selected semiempirical Hamiltonians and AC models are somewhat different, by comparing the nature of the interactions present in both systems it can be speculated that CLD adsorption should be favored over HCH by the present of  $COO^-$  as SG in AC. This suggests that under neutral pH conditions CLD adsorption onto AC should be favored over  $\beta$  and  $\gamma$ -HCH.

#### 4.3. Re-optimization using CAM-B3LYP DFT

In order to obtain a higher quality electronic structure and geometry to characterize the nature of the interactions present, a further minimization process was carried out. The criterion used for the selection of the geometrically representative structures was mainly visual and based on general chemical knowledge. Hence, a further statistical analysis will be meaningless. From the full set of minima obtained by MMH, 12 distinctive minima structures for the systems  $SG/CLD/(H_2O)_n=0-3$  were selected and each PM7 geometry was re-optimized using CAM-B3LYP/6-311++G(2df,2pd)/CAM-B3LYP/6-31+G(d,p) density functional method. This re-optimization is especially relevant in the present study due to the presence of relatively strong interactions ( $O^- \cdots CO$ ). CAM-B3LYP is a type of range-separated hybrid functional designed to minimize the self-interaction error while being relatively fast, and thus more suitable than most popular functional for this type of system where certain degree of charge transfer may occur. Figs. 4–6 show the geometries and population (in percent) obtained by MMH procedure and its re-optimized geometries using DFT. An analysis of these figures shows that for the most complexes presented in Figs. 4 and 5, the main interactions are of the type  $Cl \cdots \pi$ -cloud. However, Fig. 6 show that some structures ( $COO^-/CLD-1$  and  $O^-/CLD/H_2O-1$ ) present an interaction between the negatively charge oxygen of the SG and the electronically deficient carbonylic carbon of the CLD ( $O^- \cdots CO$ ), as mentioned above. It is noteworthy that upon re-optimization by CAM-B3LYP both interaction types found by MMH were practically unchanged for most complexes, supporting the validity of the results obtained by the semiempirical method.

When using different methods (such as PM7 and CAM-B3LYP), it is expected to obtain some rearrangement in the water clusters and even in the interactions with the AC model, due to differences

between the PESs when calculated with different methods as it is expected for weak interacting systems. The difference between the structures of minima between the methods reflects the flat nature of the PESs, which is expected for weakly interacting systems. This reinforces the need to make the largest possible and efficient exploration of the PESs, as it is proposed in our study.

For  $Cl \cdots \pi$ -cloud interaction types (Figs. 4 and 5), optimization methods yielded some differences: while for PM7 the average interaction distances are about 2.7 Å, CAM-B3LYP/6-31 + G(d,p) re-optimizations yield an average of 3.6 Å. This result suggests that the semiempirical Hamiltonian PM7 used in MMH procedures overestimates this kind of interactions, which leads to variation in structures such as  $COO^-/CLD/(H_2O)_3-1$  and  $O^-/CLD/(H_2O)_3-1$  (Fig. 5) during CAM-B3LYP/6-31 + G(d,p) re-optimization process. Nevertheless, most of the structures of minima obtained from PM7 and CAM-B3LYP conserved the main interaction types. This supports the use of the semiempirical Hamiltonian to describe the main interactions in the PESs. This conclusion emerges from a comparison of trends between both methods to reproduce the relative association energies between all distinctive structure (see Fig. SF23 in Supporting information).

#### 4.4. QTAIM analyses

In order to further ascertain the possibility of a chemisorption process, a QTAIM study was carried out in order to have a more detailed characterization of the interactions present in the systems under study. The polar coordinate ( $R, \theta$ ) representation of the plot for  $H_b(\mathbf{r})_c$  versus  $(\hbar^2/8m)\nabla^2\rho_b(\mathbf{r})_c$  and has been shown to be useful to classify, evaluate and understand the nature of molecular interactions in a unified and rigorous way [70,71].

The application of QTAIM allowed to characterize the topology of the electron density and its Laplacian at bond critical points (BCPs), and hence, to describe intermolecular interactions, and classify them from weak to strong, according to generally accepted criteria. Other density based functions, namely total energy density ( $H_{BCP}$ ), the ratio between potential and kinetic energy density ( $V_{BCP}/G_{BCP}$ ), and the ellipticity of the electron density ( $\varepsilon$ ) were also used for classifying. The values of these properties at BCPs of  $SG/CLD$  and  $SG/CLD/(H_2O)_{n=1-3}$  distinctive complexes are presented in Tables 2 and 3, also the corresponding structures are shown in Figs. 7 and 8, respectively. The corresponding electron densities were obtained used CAM-B3LYP/6-311++G(2df,2pd) functional density.

The interactions showed in Fig. 7 are mainly of dispersive nature (vdW). The ellipticity of the electron density ( $\varepsilon$ ) for  $Cl \cdots \pi$ -cloud interactions has high values that are characteristic of directionless or weak dispersive interactions, meaning that these are not typical bonding interactions between atoms, but halogen-bond interactions with the  $\pi$ -cloud of the AC model. Halogen bonding is a weak non-covalent interaction where halogen atoms function as electrophilic species [72]. These types of interactions are present a wide range of distances and energies ranging from vdW to charge transfer [73].

The interactions between water molecules and CLD are mostly either closed shell hydrogen bonds (HB) with a high dispersive character or charge transfer  $H_2O \cdots CO$  (CT) types. Few structures (Table 3) show covalent interactions between the negatively charged oxygen in the SG and the electronically deficient carbon in CLD ( $O^- \cdots CO$ ). This confirmed the conclusion drawn from the analysis of the results from MMH and the subsequent DFT re-optimizations (Fig. 6) where it was suggested the possibility of a chemisorption of CLD in the presence of charged SGs. The low  $\varepsilon$  in these cases accounted for straight cylindrical single bonds, and density based functions verify weak to strong covalent bonds. Taking into account that  $COO^-$  is the only charged SG at neutral pH con-

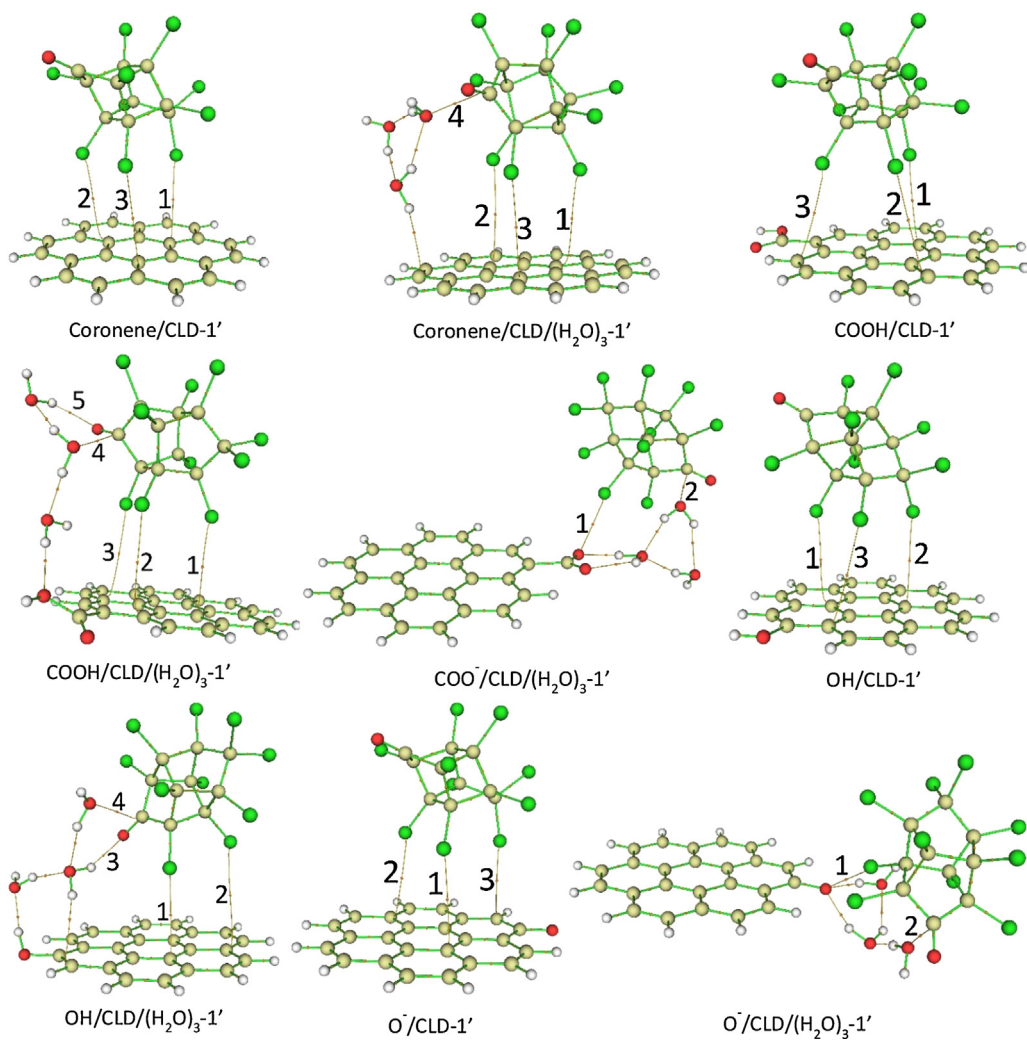


Fig. 7. Interactions and bond paths obtained by QTAIM for distinctive minima structures for the systems with interactions of the type Cl...π-cloud.

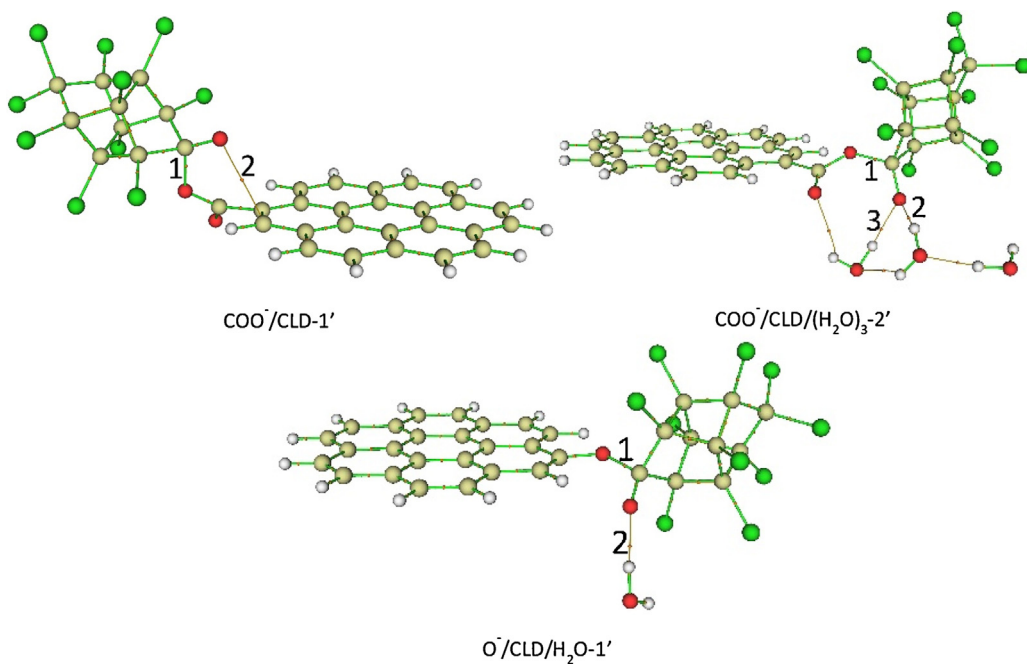


Fig. 8. Interactions and bond paths obtained by QTAIM for distinctive minima structures for the systems with interactions of the type O...CO.



**Table 2**

Interatomic distances ( $d$ ), electron density ( $\rho_{\text{BCP}}$ ), Laplacian of electron density ( $\nabla^2\rho_{\text{BCP}}$ ), total energy density ( $H_{\text{BCP}}$ ), potential-kinetic energy density ratio ( $V_{\text{BCP}}/G_{\text{BCP}}$ ) and ellipticity of the electron density ( $\varepsilon$ ) at the BCPs for the systems with interactions of the type  $\text{Cl}\cdots\pi$ -cloud.

Complex	Interaction	Atoms <sup>a</sup>	$d$ (Å)	$\rho_{\text{BCP}}$ (a.u.)	$\nabla^2\rho_{\text{BCP}}$ (a.u.)	$H_{\text{BCP}}$ (a.u.)	$V_{\text{BCP}}/G_{\text{BCP}}$	$\varepsilon$	Type <sup>b</sup>
Coronene/CLD-1'	1	C...Cl	3.59	0.0040	0.0134	0.0008	-0.6921	0.39	vdW
	2	C...Cl	3.83	0.0032	0.0101	0.0006	-0.7011	2.01	vdW
	3	C...Cl	3.83	0.0032	0.0100	0.0006	-0.6999	1.61	vdW
Coronene/CLD/(H <sub>2</sub> O) <sub>3</sub> -1'	1	C...Cl	3.76	0.0035	0.0114	0.0007	-0.6973	2.24	vdW
	2	C...Cl	4.09	0.0019	0.0058	0.0003	-0.6909	1.14	vdW
	3	C...Cl	3.79	0.0033	0.0103	0.0006	-0.6948	1.23	vdW
	4	O...C	2.71	0.0144	0.0537	0.0016	-0.8653	0.76	CT
COOH/CLD-1'	1	C...Cl	3.60	0.0039	0.0132	0.0008	-0.6895	0.61	vdW
	2	C...Cl	3.86	0.0028	0.0090	0.0005	-0.7013	2.43	vdW
	3	C...Cl	3.78	0.0032	0.0108	0.0006	-0.7029	8.63	vdW
COOH/CLD/(H <sub>2</sub> O) <sub>3</sub> 1-1'	1	C...Cl	3.79	0.0030	0.0095	0.0006	-0.6872	0.44	vdW
	2	C...Cl	4.06	0.0022	0.0065	0.0004	-0.6990	2.88	vdW
	3	C...Cl	3.90	0.0026	0.0081	0.0005	-0.6966	1.54	vdW
	4	O...C	2.49	0.0230	0.0717	0.0009	-0.9499	0.24	CT
	5	H...O	2.03	0.0192	0.0730	0.0019	-0.8854	0.06	HB
COO <sup>-</sup> /CLD/(H <sub>2</sub> O) <sub>3</sub> 1-1'	1	O...Cl	3.00	0.0100	0.0382	0.0015	-0.8168	0.13	vdW
	2	O...C	2.44	0.0235	0.0815	0.0016	-0.9167	0.11	CT
OH/CLD-1'	1	C...Cl	3.72	0.0037	0.0118	0.0007	-0.7004	1.18	vdW
	2	C...Cl	3.72	0.0035	0.0110	0.0006	-0.6947	0.42	vdW
	3	C...Cl	3.90	0.0028	0.0091	0.0005	-0.7033	4.30	vdW
OH/CLD/(H <sub>2</sub> O) <sub>3</sub> -1'	1	C...Cl	3.63	0.0042	0.0135	0.0008	-0.6999	0.54	vdW
	2	C...Cl	4.25	0.0015	0.0047	0.0003	-0.6908	2.49	vdW
	3	H...O	1.92	0.0244	0.0866	0.0010	-0.9531	0.03	HB
	4	O...C	2.62	0.0162	0.0597	0.0017	-0.8684	0.38	CT
O <sup>-</sup> /CLD-1'	1	C...Cl	3.61	0.0042	0.0136	0.0008	-0.7000	1.01	vdW
	2	C...Cl	3.59	0.0045	0.0147	0.0008	-0.7102	1.92	vdW
	3	C...Cl	3.27	0.0084	0.0247	0.0012	-0.7575	0.35	vdW
O <sup>-</sup> /CLD/(H <sub>2</sub> O) <sub>3</sub> -1'	1	O...Cl	2.91	0.0126	0.0465	0.0015	-0.8483	0.10	vdW
	2	O...C	2.48	0.0216	0.0774	0.0017	-0.9019	0.18	CT

<sup>a</sup> Atoms in the left side of the column correspond to AC model or water molecules, and atoms in the right side are of CLD.

<sup>b</sup> Interaction types: (vdW) van der Waals dispersive interactions, (HB) hydrogen bonds, and (CT) charge transfer interactions between water and CLD electron deficient carbon.

**Table 3**

Interatomic distances ( $d$ ), electron density ( $\rho_{\text{BCP}}$ ), Laplacian of electron density ( $\nabla^2\rho_{\text{BCP}}$ ), total energy density ( $H_{\text{BCP}}$ ), potential-kinetic energy density ratio ( $V_{\text{BCP}}/G_{\text{BCP}}$ ) and ellipticity of the electron density ( $\varepsilon$ ) at the BCPs for the systems with interactions of the type  $\text{O}^-\cdots\text{O}$ .

Complex	Interaction	Atoms <sup>a</sup>	$d$ (Å)	$\rho_{\text{BCP}}$ (a.u.)	$\nabla^2\rho_{\text{BCP}}$ (a.u.)	$H_{\text{BCP}}$ (a.u.)	$V_{\text{BCP}}/G_{\text{BCP}}$	$\varepsilon$	Type <sup>b</sup>
COO <sup>-</sup> /CLD-1'	1	O...C	1.63	0.1599	-0.0989	-0.1141	-2.2768	0.05	Cov-w
	2	C...O	2.83	0.0134	0.0487	0.0017	-0.8339	1.98	vdW
COO <sup>-</sup> /CLD/(H <sub>2</sub> O) <sub>3</sub> 1-2'	1	O...C	1.53	0.1991	-0.3406	-0.1990	-2.7478	0.05	Cov-w
	2	H...O	1.87	0.0296	0.0916	-0.0009	-1.0386	0.01	HB
	3	H...O	1.83	0.0319	0.0979	-0.0016	-1.0606	0.07	HB
O <sup>-</sup> /CLD/H <sub>2</sub> O-1'	1	O...C	1.50	0.2178	-0.4515	-0.2404	-2.8849	0.06	Cov-s
	2	H...O	1.77	0.0370	0.0975	-0.0046	-1.1595	0.03	HB

<sup>a</sup> Atoms in the left side of the column correspond to AC model or water molecules, and atoms in the right side are of CLD.

<sup>b</sup> Interaction types: (vdW) van der Waals dispersive interactions, (HB) hydrogen bonds, (Cov-w) weak covalent interactions, and (Cov-s) strong covalent interactions.

ditions (over 90%), these results are consistent with the idea that chemical sorption occurs between CLD and COO<sup>-</sup> SG at this pH, as reported experimentally by Durimel et al. [16]. These results can potentially help to improve the design of better AC for the removal of CLD from drinking water.

## 5. Conclusions

MMH methodology, together with a simplified model of AC was successfully employed to explore the PESs of the systems of interest and evaluated their thermodynamic association energy for different pH and solvation conditions. For acidic conditions, the results suggest a non-dependence of the association energy with the SG composition, while under neutral conditions the SG COO<sup>-</sup> (>90% COOH deprotonated) should enhance CLD adsorption. A DFT re-optimization of some minima structures showed that, although

PM7 overestimates the strength of dispersive interactions, it provides a correct qualitative description of the types of interactions that dominate the molecular association in these systems. The study using QTAIM showed a predominance of dispersive interactions for acid conditions and confirmed the presence of covalent interactions between the negatively charged oxygen of the SGs and the carbonylic carbon of the CLD, further suggesting the possibility of a chemical sorption of CLD on charged SGs, especially for COO<sup>-</sup> under neutral pH conditions.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmglm.2016.02.008>.

## References

- [1] Stockholm Convention. Listing of POPs in the Stockholm Convention: Annex A (Elimination), 2011.
- [2] OSPAR Convention. Available from: <http://context.reverso.net/traduccion/ingles-espanol/ospar+convention>.
- [3] Y.M. Cabidoche, R. Achard, P. Cattani, C. Clermont-Dauphin, F. Massat, J. Sansoulet, Long-term pollution by chlordecone of tropical volcanic soils in the French West Indies: a simple leaching model accounts for current residue, *Environ. Pollut.* 157 (2009) 1697–1705.
- [4] S. Coat, D. Monti, P. Legendre, C. Bouchon, F. Massat, G. Lepoint, Organochlorine pollution in tropical rivers (Guadeloupe): role of ecological factors in food web bioaccumulation, *Environ. Pollut.* 159 (2011) 1692–1701.
- [5] INCHEM, Chlordecone, environmental health criteria 43, in: International Programme on Chemical Safety, World Health Organization, Geneva, 1984.
- [6] H. Fang, W. Tong, W.S. Branham, C.L. Moland, S.L. Dial, H. Hong, Study of 202 natural synthetic, and environmental chemicals for binding to the androgen receptor, *Chem. Res. Toxicol.* 16 (2003) 1338–1358.
- [7] H.T. Tapiero, B.G. Nguyen, New estrogens and environmental estrogens, *Biomed. Pharmacother.* 56 (2002) 36–42.
- [8] M. Landau-Ossondo, N. Rabia, J. Jos-Pelage, L.M. Marquet, Y. Isidore, C. Saint-Aime, M. Martin, P. Irigaray, D. Belpomme, Why pesticides could be a common cause of prostate and breast cancers in the French Caribbean Island, Martinique. An overview on key mechanisms of pesticide-induced cancer, *Biomed. Pharmacother.* 63 (2009) 383–395.
- [9] L. Multigner, J.R. Ndong, A. Giusti, M. Romana, H. Delacroix-Maillard, S.B. Cordier, B. Jegou, J.P. Thome, P. Blanchet, Chlordecone exposure and risk of prostate cancer, *J. Clin. Oncol.* 28 (2010) 3457–3462.
- [10] EPA, Toxicological Review of Chlordecone (Kepone), US-EPA Publications, 2009, EPA/635/R-07/004F.
- [11] F. Clostre, P. Letourmy, M. Lesueur-Jannoyer, Organochlorine (chlordecone) uptake by root vegetables, *Chemosphere* 118 (2015) 96–102.
- [12] S. Jurjan, C. Jondreville, M. Mahieu, A. Fournier, H. Archimède, G. Rychen, C. Feidt, Relative bioavailability of soil-bound chlordecone in growing lambs, *Environ. Geochem. Health* 36 (2014), <http://dx.doi.org/10.1007/s10653-014-9608-5>.
- [13] S. Cordier, E. Bouquet, C. Warembourg, C. Massart, F. Rouget, P. Kadhel, H. Bataille, C. Monfort, O. Boucher, G. Muckle, L. Multigner, Perinatal exposure to chlordecone, thyroid hormone status and neurodevelopment in infants: the timoun cohort study in Guadeloupe (French West Indies), *Environ. Res.* 138 (2015) 271–278.
- [14] O. Boucher, M.N. Simard, G. Muckle, F. Rouget, P. Kadhel, H. Bataille, et al., Exposure to an organochlorine pesticide (chlordecone) and development of 18-month-old infants, *Neurotoxicology* 35 (2013) 162–168.
- [15] C. Dubuisson, F. Héraud, J.C. Leblanc, S. Gallotti, C. Flamand, A. Blateau, P. Quenel, J.L. Volatier, Impact of subsistence production on the management options to reduce the food exposure of the Martinican population to Chlordecone, *Regul. Toxicol. Pharm.* 49 (2007) 5–16.
- [16] A. Durimel, S. Altenor, R.A. Miranda-Quintana, P. Couespel Du Mesnil, U. Jáuregui-Haza, R. Gadiou, S. Gaspard, pH dependence of chlordecone adsorption on activated carbons and role of adsorbent physico-chemical properties, *Chem. Eng. J.* 229 (2013) 239–349.
- [17] C. Enriquez-Victorero, D. Hernández-Valdés, A.L. Montero-Alejo, A. Durimel, S. Gaspard, U. Jáuregui-Haza, Theoretical study of  $\gamma$ -hexachlorocyclohexane and  $\beta$ -hexachlorocyclohexane isomers interaction with surface groups of activated carbon model, *J. Mol. Graphics Modell.* 51 (2014) 137–148.
- [18] A. Bemnowska, R. Pelech, E. Milchert, Adsorption from aqueous solutions of chlorinated organic compounds onto activated carbons, *J. Colloid Interface Sci.* 265 (2003) 276–282.
- [19] V.O. Njoku, B.H. Hameed, Preparation and characterization of activated carbon from corncob by chemical activation with  $H_3PO_4$  for 2,4-dichlorophenoxyacetic acid adsorption, *Chem. Eng. J.* 173 (2011) 391–399.
- [20] B.H. Hameed, J.M. Salman, A.L. Ahmad, Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones, *J. Hazard. Mater.* 163 (2009) 121–126.
- [21] J.M. Salman, V.O. Njoku, B.H. Hameed, Bentazon and carbofuran adsorption onto date seed activated carbon: kinetics and equilibrium, *Chem. Eng. J.* 173 (2011) 361–368.
- [22] C. Faur, A. Cougnaud, G. Dreyfus, P. Le Cloirec, Modelling the breakthrough of activated carbon filters by pesticides in surface waters with static and recurrent neural network, *Chem. Eng. J.* 145 (2008) 7–15.
- [23] Report of the Persistent Organic Pollutants Review Committee on the work of its second meeting, Addendum: Risk profile on Chlordecone, Stockholm Convention on Persistent Organic Pollutants, Persistent Organic Pollutants Review Committee. Second meeting (2006), UNEP: Geneva 1–27.
- [24] S.S. Barton, M.J.B. Evans, E. Halliop, J.A.F. MacDonald, Acidic and basic sites on the surface of porous carbon, *Carbon* 35 (1997) 1361–1366.
- [25] D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulou, E. Otal, J.O. Valle, C. Fernandez-Pereira, Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse, *Chem. Eng. J.* 144 (2008) 42–50.
- [26] I.D. Mall, V.C. Srivastava, N.K. Agarwal, Adsorptive removal of auramine-O: kinetic and equilibrium study, *J. Hazard. Mater.* 143 (2007) 386–395.
- [27] M. Valix, W.H. Cheung, K. Zhang, Role of heteroatoms in activated carbon for removal of hexavalent chromium from wastewaters, *J. Hazard. Mater.* 135 (2006) 395–405.
- [28] M. Oubal, S. Picaud, M.T. Rayez, J.C. Rayez, A theoretical characterization of the interaction of water with oxidized carbonaceous clusters, *Carbon* 48 (2010) 1570–1579.
- [29] C. Faur, H. Métivier-Pignon, P. Le Cloirec, Multicomponent adsorption of pesticides onto activated carbon fibers, *Adsorption* 11 (2005) 479–490.
- [30] S. Furmaniak, A.P. Terzyk, P.A. Gauden, P. Kowalczyk, G.S. Szymanski, Influence of activated carbon surface oxygen functionalities on  $SO_2$  physisorption—simulation and experiment, *Chem. Phys. Lett.* 578 (2013) 85–91.
- [31] A.P. Terzyk, P. Gauden, A.W. Zielinski, S. Furmaniak, R.P. Wesolowski, K.K. Klimek, First molecular dynamics simulation insight into the mechanism of organics adsorption from aqueous solutions on microporous carbons, *Chem. Phys. Lett.* 515 (2011) 102–108.
- [32] A.P. Terzyk, Molecular properties and intermolecular forces—factors balancing the effect of carbon surface chemistry in adsorption of organics from dilute aqueous solutions, *J. Colloid Interface Sci.* 275 (2004) 9–29.
- [33] Available by request: <http://karin.qct.fq.oc.uh.cu/mmh/>.
- [34] L.A. Montero, A.M. Esteva, J. Molina, A. Zapardiel, L. Hernández, H. Márquez, et al., A theoretical approach to analytical properties of 2,4-diamino-5-phenylthiazole in water solution. Tautomerism and dependence on pH, *J. Am. Chem. Soc.* 120 (1998) 12023–12033.
- [35] L.A. Montero, J. Llano, J. Molina, J. Fabian, Multiple minima hypersurfaces of water clusters for calculations of association energy, *Int. J. Quantum Chem.* 79 (2000) 8–16.
- [36] D. Hernández Valdés, C. Enríquez Victorero, U. Jáuregui Haza, P. Hernández, S. González Santana, Granada modificado con restricción geométrica. Granada modificado with geometric restriction, *Rev. Cubana Cien. Inform.* 7 (2013) 9–15.
- [37] D. Hernández-Valdés, C. Enriquez-Victorero, L. Pizarro-Lou, D. Turión-Pérez, L. Ducat-Pagés, M. Arias, U. Jáuregui-Haza, Interaction of paracetamol and  $^{125}I$ -paracetamol with surface groups of activated carbon: theoretical and experimental study, *J. Radioanal. Nucl. Chem.* 305 (2) (2015) 609–622.
- [38] R.F.W. Bader, A quantum theory of molecular structure and its applications, *Chem. Rev.* 91 (1991) 893–928.
- [39] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Modification of the surface chemistry of activated carbons, *Carbon* 37 (1999) 1379–1389.
- [40] S. Picaud, P.N.M. Hoang, S. Hamad, J.A. Mejias, S. Lago, Theoretical study of the adsorption of water on a model soot surface: II. Molecular dynamics simulations, *J. Phys. Chem. B* 108 (2004) 5410–5415.
- [41] B. Collignon, P.N.M. Hoang, S. Picaud, J.C. Rayez, Ab initio study of the water adsorption on hydroxylated graphite surfaces, *Chem. Phys. Lett.* 406 (2005) 430–435.
- [42] B. Collignon, P.N.M. Hoang, S. Picaud, J.C. Rayez, Clustering of water molecules on model soot particles: an ab initio study, *Comput. Lett.* 1 (2005) 277–287.
- [43] G.R. Jenness, K.D. Jordan, DF-DFT-SAPT investigation of the interaction of a water molecule to coronene and dodecabenzocoronene: implications for the water graphite interaction, *J. Phys. Chem.* 123 (2009) 10242–10248.
- [44] E.M. Cabaleiro-Lago, J. Rodríguez-Otero, Á. Peña-Gallego, Computational study on the characteristics of the interaction in naphthalene  $\cdots (H_2X)_n = 1,2$  ( $X = O, S$ ) clusters, *J. Phys. Chem. A.* 112 (2008) 6344–6350.
- [45] Y. Cho, S.K. Min, J. Yun, W.Y. Kim, A. Tkatchenko, K.S. Kim, Noncovalent interactions of DNA bases with naphthalene and graphene, *J. Chem. Theor. Comput.* 9 (2013) 2090–2096.
- [46] P. Lazar, S. Zhang, K. Šafářová, Q. Li, J.P. Froning, J. Granatier, et al., Quantification of the interaction forces between metals and graphene by quantum chemical calculations and dynamic force measurements under ambient conditions, *ACS Nano* 7 (2013) 1646–1651.
- [47] P. Lazar, F. Karlický, P. Jurečka, M. Kocman, E. Otyepková, K. Šafářová, et al., Adsorption of small organic molecules on graphene, *J. Am. Chem. Soc.* 135 (2013) 6372–6377.
- [48] J. Granatier, P. Lazar, R. Prucek, K. Šafářová, R. Zbořil, M. Otyepka, et al., Interaction of graphene and arenes with noble metals, *J. Phys. Chem. C* 116 (2012) 14151–14162.
- [49] J. Granatier, P. Lazar, M. Otyepka, P. Hobza, The nature of the binding of Au, Ag, and Pd to benzene, coronene, and graphene: from benchmark CCSD(T) calculations to plane-wave DFT calculations, *J. Chem. Theor. Comput.* 7 (2011) 3743–3755.

- [50] M. Oubal, S. Picaud, M.T. Rayez, J.C. Rayez, Interaction of water molecules with defective carbonaceous clusters: an ab initio study, *Surf. Sci.* 604 (2010) 1666–1673.
- [51] S. Picaud, B. Collignon, N.M. Hoang, J.C. Rayez, Adsorption of water molecules on partially oxidized graphite surfaces: a molecular dynamics study of the competition between OH and COOH sites, *Phys. Chem. Chem. Phys.* 10 (2008) 6998–7009.
- [52] H. Marsh, F. Rodríguez-Reinoso, *Activated Carbon*, Elsevier, Amsterdam; London, 2006.
- [53] C. Morera, E. Alonso, R. González, L.A. Montero, J.M. García, A theoretical approach to the solvation of brassinosteroids, *J. Mol. Graphics Modell.* 27 (2009) 600–610.
- [54] C. Morera, N. Mora, L.A. Montero, E. Alonso, R.H. González, J.M. García, Interaction of brassinolide with essential amino acid residues: a theoretical approach, *J. Mol. Graphics Modell.* 5931 (2009) 1–8.
- [55] J.L.G. Coronado, E. Martín, L.A. Montero, J.L.G. Fierro, J.G. de la Vega, Effects of the 3- and 4-methoxy and acetamide substituents and solvent environment on the electronic properties of N-substituted 1,8-naphthalimide derivatives, *J. Phys. Chem. A* 111 (2007) 9724–9732.
- [56] E. Codorniu, A. Mesa, R. Hernández, L.A. Montero, F. Martínez, J.L. Santana, T. Borrmann, W.D. Stohrer, Essential amino acids interacting with flavonoids: a theoretical approach, *Int. J. Quantum Chem.* 103 (2005) 82–104.
- [57] E. Codorniu, A. Mesa, L.A. Montero, F. Martínez, T. Borrmann, W.D. Stohrer, Theoretical study of flavonoids and proline interactions: aqueous and gas phases, *J. Mol. Struct.: THEOCHEM* 623 (2002) 63–73.
- [58] R. Crespo, Y. Pérez, J.A. Padrón, L.A. Montero, Exploring the potential energy surfaces of association of NO with amino acids and related organic functional groups: the role of entropy of association, *Theor. Chem. Acc.* 118 (2007) 649–666.
- [59] L.A. Montero-Cabrera, Y. Pérez-Badell, M.J. Mora-Fonz, An approach to hydration of model silica materials by exploring their multiple minima hypersurfaces. The role of entropy of association, *J. Phys. Chem.* 112 (2008) 2880–2887.
- [60] M. Mascini, M. Del Carlo, D. Compagnone, G. Perez, L.A. Montero-Cabrera, S. González, H. Yamanaka, in: G. Neri, et al. (Eds.), *Multiple Minima Hypersurfaces Procedures for Biomimetic Ligands Screening in Sensors and Microsystems*, Springer, Netherlands, 2011, pp. 403–407.
- [61] Y. Pérez-Badell, L.A. Montero-Cabrera, Multiple minima hypersurfaces studies of aluminosilicate hydration, *Int. J. Quantum Chem.* 110 (2010) 586–594.
- [62] J.J.P. Stewart, Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters, *J. Mol. Model.* 19 (2013) 1–32.
- [63] J.J.P. Stewart, MOPAC2012, *Stewart Computational Chemistry*.
- [64] K.I. Ramachandran, G. Deepa, K. Namboori, Principles and applications, in: *Computational Chemistry And Molecular Modeling*, Springer, 2008, pp. 397, <http://dx.doi.org/10.1007/978-3-540-77304-72008>.
- [65] T. Yanai, D.P. Tew, N.C. Handy, A new hybrid exchange–correlation functional using the Coulomb–attenuating method (CAM-B3LYP), *Chem. Phys. Lett.* 393 (2004) 51–57.
- [66] A.P. Limacher, K.V. Mikkelsen, H.P. Lüthi, On the accurate calculation of polarizabilities and second hyperpolarizabilities of polyacetylene oligomer chains using the CAM-B3LYP density functional, *J. Chem. Phys.* 130 (2009).
- [67] R. Kobayashi, R.D. Amos, The application of CAM-B3LYP to the charge-transfer band problem of the zincbacteriochlorin–bacteriochlorin complex, *Chem. Phys. Lett.* 420 (2006) 106–109.
- [68] Katsuki Okuno, Yasuteru Shigeta, Ryohei Kishi, Hiroshi Miyasaka, Masayoshi Nakano, Tuned CAM-B3LYP functional in the time-dependent density functional theory scheme for excitation energies and properties of diarylethene derivatives, *J. Photochem. Photobiol. A* 235 (2012) 29–34.
- [69] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A. 01, Gaussian, Inc., Wallingford CT, 2009.
- [70] W. Nakanishi, S. Hayashi, K. Narahara, Atoms-in-molecules dual parameter analysis of weak to strong interactions: behaviors of electronic energy densities versus laplacian of electron densities at bond critical points, *J. Phys. Chem. A* 112 (2008) 13593–13599.
- [71] W. Nakanishi, S. Hayashi, K. Narahara, Polar coordinate representation of  $H_b(r_c)$  versus  $(\hbar^2/8m)\nabla^2\rho_b(r_c)$  at BCP in AIM analysis: classification and evaluation of weak to strong interactions, *J. Phys. Chem.* 113 (2009) 10050–10057.
- [72] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, Halogen bonding in supramolecular chemistry, *Angew. Chem. Int. Ed.* 47 (2008) 6114–6127.
- [73] M.H. Kolář, D. Palanisamy, A. Hareh, A. Pecina, P. Hobza, Characteristics of a  $\Sigma$ -hole and the Nature of a Halogen Bond, Springer, Berlin Heidelberg, 2014, pp. 606 <http://link.springer.com/10.1007/128>.