

# **Interior and Interfacial Aqueous Solvation of Benzene Dicarboxylate Dianions and Their Methylated Analogues: A Combined Molecular Dynamics and Photoelectron Spectroscopy Study**

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## **Abstract**

Aqueous solvation of benzene dicarboxylate dianions ( $\text{BCD}^{2-}$ ) was studied by means of photoelectron spectroscopy and molecular dynamics simulations. Photoelectron spectra of hydrated ortho-, and para- $\text{BCD}^{2-}$  with up to 25 water molecules were obtained. An even-odd effect was observed for the *p*- $\text{BCD}^{2-}$  system as a result of the alternate solvation of the two negative charges. However, the high polarizability of the benzene ring makes the two carboxylate groups interact with each other in *p*- $\text{BCD}^{2-}$ , suppressing the strength of this even-odd effect compared with the linear dicarboxylate dianions linked by an aliphatic chain. No even-odd

effect was observed for the *o*-BCD<sup>2-</sup> system, because each solvent molecule can interact with the two carboxylate groups at the same time due to their proximity. For large solvated clusters, the spectral features of the solute decreased while the solvent features became dominant, suggesting that both *o*- and *p*-BCD<sup>2-</sup> are situated in the center of the solvated clusters. Molecular dynamics simulations with both non-polarizable and polarizable force fields confirmed that all three isomers (*o*-, *m*-, and *p*-BCD<sup>2-</sup>) solvate in the aqueous bulk. However, upon methylation the hydrophobic forces overwhelm electrostatic interactions and, as a result, the calculations predict that the tetra-methyl *o*-BCD<sup>2-</sup> is located at the water surface with the carboxylate groups anchored in the liquid and the methylated benzene ring tilted away from the aqueous phase.

## Introduction

The carboxylate functional group ( $-\text{COO}^-$ ) is ubiquitous in biological systems, as well as in many technologically important materials, and in polluted atmospheres. An interesting group of systems is formed by species containing more than one carboxylate group. In particular, dicarboxylic acids have been recognized as a class of global atmospheric pollutants and they are among the major organic compounds in urban aerosol samples.<sup>1,2</sup> Dicarboxylic acids are produced from photochemical reactions and from pyrolysis of plants and other organic materials. For example, low molecular weight dicarboxylic acids, such as glutaric acid, form by photooxidation of cyclohexene and cyclopentene.<sup>3</sup> Due to the presence of two carboxylate groups, dicarboxylic acids are less volatile than the corresponding monocarboxylic acids. In the atmosphere, they are primarily found in aerosols<sup>4</sup> unlike, e.g., the formic and acetic acids, which are mostly present in the gaseous phase. Dicarboxylic acids in atmospheric particles play an important role as cloud condensation nuclei.<sup>5,6</sup> Furthermore, they are responsible for the formation of many secondary organic aerosols.<sup>7</sup> Thus understanding the microsolvation of dicarboxylic acids and their behavior at the water/vapor interface is very important for atmospheric chemistry.

Previously, we have investigated by means of photoelectron spectroscopy, molecular dynamics, and electronic structure calculations dicarboxylate dianions in which the two  $\text{COO}^-$  groups are connected by an aliphatic chain of varying lengths (oxalate, succinate, adipate, suberate, etc.).<sup>8,9</sup> The focus was on the sequential solvation of these dianions in size-selected water clusters and on bulk vs. interfacial solvation in extended aqueous systems. The flexible aliphatic chains give rise to an interesting phenomenon of solvent-induced conformation changes for large solvated clusters as a result of the competition between Coulomb repulsion and water-water H-bonding and hydrophobic and hydrophilic solvation. In this study, we investigate dicarboxylate dianions in which the spacer between the two carboxylate groups is a rigid aromatic ring. The generic system is the ortho-benzene dicarboxylate dianion. This is the doubly

ionized form of the technologically and environmentally extremely important phthalic acids, the esters of which used as a PVC softener represent a widely discussed potential health hazard.<sup>10,11</sup> Here, we study the aqueous solvation of all three (ortho-, meta-, and para-) benzene dicarboxylate dianions (*o*-, *m*-, *p*-BCD<sup>2-</sup>) and of the tetramethylated *o*-BCD<sup>2-</sup>. Using photoelectron spectroscopy and ab initio calculations we investigate solvation of benzene dicarboxylate dianions in water clusters and the role of the aromatic ring in electronically connecting the partially hydrated carboxylate groups. By means of molecular dynamics simulations we explore the competition between electrostatic and hydrophobic interactions in bulk versus interfacial solvation of the parent and methylated dianions in aqueous slabs.

## Experimental methods

The experiment was carried out using an apparatus equipped with a magnetic-bottle time-of-flight photoelectron analyzer and an electrospray ionization (ESI) source.<sup>12</sup> Details of the experimental method have been given elsewhere<sup>12</sup> and the procedures were similar to our previous studies on the solvated dicarboxylate dianions.<sup>8,9</sup> We chose two of the three benzene dicarboxylate acids, *o*-BCD<sup>2-</sup> and *p*-BCD<sup>2-</sup>, for the PES experiments to represent two extreme cases, in which the two carboxylate groups are the closest and farthest to each other around the benzene ring, respectively. Briefly, solvated dianions with a wide range of solvent numbers, *o*-(*p*-)BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>x</sub>, were produced from electrospray of mixed solutions of 10<sup>-3</sup> M of the corresponding di-sodium salts in a water-acetonitrile mixed solvent (1:4 volume ratio). Anions produced from the ESI source were guided into a room-temperature ion-trap, where ions were accumulated for 0.1 second before being pulsed into the extraction zone of a time-of-flight mass spectrometer. During photoelectron spectroscopic experiments, the dianions of interest were mass-selected and decelerated before being intercepted by a probe laser beam in the photodetachment zone of the magnetic-bottle photoelectron analyzer. In the current study, the detachment photon energies used were 193 nm (6.424 eV) and 157 nm (7.867 eV).

Photoelectron time-of-flight spectra were collected and then converted to kinetic energy spectra, calibrated by the known spectra of  $\Gamma$  and  $O$ . The electron binding energies (EB) were obtained by subtracting the kinetic energy (KE) spectra from the detachment photon energy ( $EB = h\nu - KE$ ). The energy resolution ( $\Delta KE/KE$ ) was about 2%, i.e.,  $\sim 10$  meV for 0.5 eV electrons, as measured from the spectrum of  $\Gamma$  at 355 nm.

## Computational Methods

Classical molecular dynamics simulation were aimed at a Boltzman sampling of solvation structures of the ortho-, meta-, and para-benzene dicarboxylate dianions, as well as the tetra-methyl ortho-benzene dicarboxylate dianion in aqueous slabs. To construct the slab a (tetragonal) prismatic box of  $30 \times 30 \times 120 \text{ \AA}^3$  was used, containing 863 water molecules, two identical dianions (placed initially on each side of the slab) and four sodium counterions. Application of periodic boundary conditions at a constant volume with such a unit cell yields an infinite slab with two water/vapor interfaces perpendicular to the  $z$  axis.<sup>13</sup> The non-bonded interactions were cut off at 12  $\text{\AA}$  and long-range electrostatic interactions were accounted for using the particle mesh Ewald procedure.<sup>14</sup> All systems were first minimized (10,000 steps of steepest descent) in order to avoid bad contacts and equilibrated for several hundreds of picoseconds before a 1 ns production run. Simulations were performed at 300 K with a time step of 1 fs and all bonds involving hydrogen atoms were constrained using the SHAKE algorithm.<sup>15</sup>

Both non-polarizable and polarizable force fields were employed in the MD simulations. For water, we used either the SPCE<sup>16</sup> or the POL3<sup>17</sup> models. For the ions we employed the general amber force field parameter set.<sup>18</sup> Fractional charges for the dianions were evaluated at the level using the standard RESP procedure and all molecular dynamics calculations were performed using Amber 8 program,<sup>19</sup> while Gaussian 03 was employed for electronic structure calculations.<sup>20</sup>

## Results and Discussion

**Photoelectron Spectra at 193 nm and 157 nm.** The photoelectron spectra of *o*-, *p*-BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>*x*</sub> (*x* = 0-20) at 193 nm are displayed in Figs. 1 and 2, respectively. The photoelectron spectra of selected *o*-, *p*-BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>*x*</sub> at 157 nm are displayed in Fig. 3.

The difference of the spectral features and electron binding energies between bare *o*-BCD<sup>2-</sup> and *p*-BCD<sup>2-</sup> had been explained in our previous publication.<sup>21</sup> For the spectrum of *o*-BCD<sup>2-</sup>, the first broad band at very low binding energies is due to detachment of the O lone-pairs in the carboxylate groups. The extremely low binding energies are due to the strong Coulomb repulsion between the two carboxylate groups at the ortho position. The band centered at ~2.2 eV is assigned to be from the  $\pi$  system of the benzene ring. For *p*-BCD<sup>2-</sup>, the longer distance between the two carboxylate groups reduces the intra-molecular Coulomb repulsion and increases the electron binding energies of the O lone pairs. Since the binding energy of the  $\pi$  electron feature does not change in *p*-BCD<sup>2-</sup> relative to that in *o*-BCD<sup>2-</sup>, it overlaps with the spectral features from the carboxylate O lone pairs (Fig. 2).

Several observations can be made about the spectra of the hydrated species in Figs. 1-3. First, the spectral features shift steadily to higher binding energies with increasing solvent molecules in both *o*- and *p*-BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>*x*</sub> due to stabilization of the negative charges by water. Second, spectral features on the high binding energy side are cut off in both 193 and 157 nm spectra as a result of the repulsive Coulomb barrier (RCB), which exists universally in multiply charged anions and essentially prohibits slow electrons from being emitted.<sup>22</sup> The  $\pi$  electron feature quickly disappears with the addition of the first few water molecules due to the cut-off caused by the RCB. For the spectra of larger clusters, only the onset of the carboxylate features can be observed. Third, from *x* = 5 in *o*-BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>*x*</sub> and *x* = 4 in *p*-BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>*x*</sub>, a new band emerges at the high binding energy side. In the 193 nm spectra (Figs. 1 and 2), the relative intensity of the new band reaches maximum at *x* = 9 for both systems and gradually disappears

with increasing cluster size due to the RCB cutoff. In the 157 nm spectra (Fig. 3), the new emerging band becomes the dominant feature for large clusters. Fourth, some weak spectral features appear for large clusters ( $x > 10$ ) in the lower binding energy range in both systems in the 193 nm spectra (Figs 1 and 2), but not showing up in the 157 nm spectra (Fig. 3). The photon energy dependence suggests that these features might be due to two-photon processes.

**Interactions between the Carboxylate Groups in Solvated Clusters.** The adiabatic detachment energies (ADEs), estimated from the threshold of the photoelectron spectra shown in Figs. 1 and 2, are plotted as a function of solvent number ( $x$ ) in Fig. 4a. The differential ADE ( $\Delta$ ADE), defined as  $[ADE(x) - ADE(x-1)]$ , is the net stabilization of one water to the negative charge as water is sequentially added. It is plotted in Fig. 4b as a function of  $x$ .

The differential ADE (Fig. 4b, red curve) for hydrated  $p$ -BCD<sup>2-</sup> shows an even-odd oscillation at small cluster size ( $x < 5$ ). We observed this even-odd effect in a series of solvated linear aliphatic dicarboxylate dianions.<sup>8,9</sup> This is because the two carboxylate groups are solvated separately in these systems and each water molecule can only solvate one carboxylate. The two carboxylate groups in  $p$ -BCD<sup>2-</sup>(H<sub>2</sub>O) <sub>$x$</sub>  should also be solvated alternately by water molecules at small cluster sizes because they are separated by a rigid benzene ring. It is interesting to compare  $p$ -BCD<sup>2-</sup>(H<sub>2</sub>O) <sub>$x$</sub>  with solvated adipate dianion [<sup>-</sup>O<sub>2</sub>C(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub><sup>-</sup>] because the distances between the two carboxylate groups are similar in these two dianions. However, we noted that the even-odd effect shown in the differential ADEs for the adipate systems are much stronger than that shown in the  $p$ -BCD<sup>2-</sup>(H<sub>2</sub>O) <sub>$x$</sub>  system.<sup>9</sup> The difference is caused by the different polarizability of the spacer between the two carboxylate groups. On one hand, in adipate the aliphatic chain can be viewed as an insulator. The two carboxylate groups are solvated separately and independently with little electronic communication. On the other hand, in  $p$ -BCD<sup>2-</sup> with planar  $D_{2h}$  symmetry<sup>21</sup> the two carboxylate groups can interact with each other through the much more polarizable phenyl ring. Once the equivalence between the two carboxylate groups is broken by the solvent molecule for odd solvent numbers, the electron

densities can redistribute to compensate the less stabilized charge, which reduces the energy difference between the two carboxylate groups and suppresses the oscillatory pattern in the differential ADEs in  $p\text{-BCD}^{2-}(\text{H}_2\text{O})_x$ . The difference between the aromatic and aliphatic spacer between the two carboxylate groups can also be seen clearly from the corresponding highest occupied molecular orbitals (HOMO). Fig. 5 compares the HOMO (evaluated with the 6-31+G\* basis set) of  $p\text{-BCD}^{2-}$  with that of the adipate dianion. While for the system with the aromatic spacer the HOMO is delocalized over the carboxylate groups and the benzene ring (Fig. 5a), there is virtually no HOMO electron density on the aliphatic chain in adipate (Fig. 5b).

The ADEs of the hydrated  $o\text{-BCD}^{2-}$  (Fig. 4a, black curve), which are much lower than those for  $p\text{-BCD}^{2-}(\text{H}_2\text{O})_x$  due to the stronger intra-molecular Coulomb repulsion, exhibit a smooth increase with the solvent number. The differential ADE (Fig. 4b, black curve) shows a monotonic decrease without any even-odd effect within our experimental uncertainty. According to our previous study,  $o\text{-BCD}^{2-}$  has  $C_2$  symmetry with the carboxylate groups rotated  $\sim 54^\circ$  away from the plane of benzene ring due to the strong Coulomb repulsion.<sup>21</sup> Even with this rotated geometry, the two carboxylate groups are close enough that each water molecule can interact with both of them at the same time. Each carboxylate group gains roughly the same stabilization energy with the addition of every solvent molecule. Thus no odd-even effect is expected in these systems.

**Interior versus Surface Solvation.** The additional features emerging in the spectra of large clusters (Figs. 1-3) are similar to those observed in our previous PES studies on different solvated systems. These high binding energy features were found to be due to ionization of solvent water molecules,<sup>23-25</sup> because the ionization potential of water was significantly lowered in the presence of the two negative charges. Beside the rapidly increasing solvent band, another interesting observation is the fact that often the intensity of the solute features decreased gradually with the solvent number.<sup>23-25</sup> We see the same effect in the present systems, e.g., for  $o\text{-BCD}^{2-}(\text{H}_2\text{O})_{25}$  (left column in Fig. 3) the solute features become a low binding energy tail in the

presence of the dominant solvent band. Previously, we interpreted this phenomenon in hydrated  $\text{SO}_4^{2-}$  and  $\text{C}_2\text{O}_4^{2-}$  clusters as due to the fact that these solutes are solvated in the center of the solvated clusters.<sup>23-25</sup> The decrease of the  $\text{BCD}^{2-}$  photoemission intensity with increasing cluster size thus suggests that both *o*, *p*- $\text{BCD}^{2-}$  are solvated in the center of large water clusters so that the electron signals from the solutes are suppressed by the surrounding solvation layer. Based on this micro-solvation information, we can estimate that all the three *o*, *m*, *p*- $\text{BCD}^{2-}$  species prefer bulk aqueous solvation to that at the water/vapor interface.

## Computational Results

The benzene dicarboxylate dianions possess two strongly hydrophilic  $-\text{COO}^-$  groups connected by a hydrophobic aromatic ring. It is not *a priori* obvious which of the two interactions with water are stronger and, consequently, whether these dianions prefer bulk or interfacial aqueous solvation, even though the above photoelectron data seem to suggest that in the large solvated clusters they prefer to be in the center of the water clusters. To explore this issue, we performed molecular dynamics simulations of *o*, *m*, *p*- $\text{BCD}^{2-}$  in aqueous slabs employing both non-polarizable and polarizable force fields.

Over the nanosecond simulations we averaged the density profiles, i.e., histogrammed abundancies of the individual species in slices parallel with the surface, from the aqueous bulk across the water/vapor interface into the gas phase. The results for *o*, *m*, *p*- $\text{BCD}^{2-}$  are shown in Figs. 6-8. We see that in all cases and with or without explicit polarization the hydrophilicity of the carboxylate groups wins over the hydrophobicity of the benzene ring and, consequently, the dianions prefer bulk aqueous solvation leaving an ion-free surface layer.

Although the results of the non-polarizable and polarizable force fields are qualitatively similar upon closer inspection there are subtle differences. Upon inclusion of polarization, which generally favors asymmetrically (i.e., interfacially) solvated structures<sup>26</sup> the ion-free surface

layer becomes thinner. Moreover, the isomers which have the two carboxylic groups located close to each other (i.e., the ortho- and, to a lesser extent, also the meta- isomer) tend to orient in the subsurface. This is seen in Figs. 6a and 7a where the signal from the carbon atoms of the benzene ring is shifted toward the surface compared to that of the carboxylate oxygens.

The hydration shell around the dicarboxylate dianions is not symmetric due to the different affinity of the  $\text{-COO}^-$  groups vs. the benzene ring for water. This is similar to the situation for dicarboxylate dianions with an aliphatic spacer group (such as adipate) investigated in our previous study.<sup>9</sup> As a demonstration, Fig. 9 depicts the nearest 25 water molecules around the para-benzene dicarboxylate dianion from a typical snapshot from the simulation. While the water structure around the carboxylate groups is dense and compact one clearly sees the diluted structure and voids in the solvent around the benzene ring.

A simple way to shift the balance between hydrophilic and hydrophobic interactions is via methylation. Fig. 10 shows the density profiles for the tetra-methyl ortho-benzene dicarboxylate employing both polarizable and non-polarizable force fields. The takeover of the hydrophobic interactions caused by (tetra)methylation is obvious from the strong interfacial carbon and oxygen peaks. The heights and positions of these peaks are almost uninfluenced by the inclusion of polarization, confirming our previous finding that polarization effects are rather unimportant for strong (hydrophobic) ionic surfactants, such as tetra-butyl ammonium.<sup>27</sup> It also follows from Fig. 10 that the sodium counter-ions, which inherently favor bulk solvation, are pulled toward the interface by attractive interactions to the dianions.

The tetra-methyl ortho-benzene dicarboxylate dianions are strongly oriented at the water/vacuum interface as demonstrated by a snapshot from the simulation (see Fig. 11). Fig. 12 shows the statistically average data, i.e., the distribution of orientations of the molecular axis of the dianion (passing through the center of the benzene ring in between the two carboxylate groups) with respect to the normal to the surface. This non-uniform distribution sharply raises at small angles, peaking around  $50^\circ$  and having a long tail up to  $150^\circ$ . This indicates a preferential

orientation with the two  $\text{-COO}^-$  groups anchored in the interfacial water layer and with the benzene ring pointing into the gas phase but strongly tilted or lying on the surface.

## **Conclusions**

Solvation of benzene dicarboxylate dianions in water clusters and in aqueous slabs was investigated by means of photoelectron spectroscopy and molecular dynamics simulations. Photoelectron spectra of the ortho- and para-isomers with up to 25 water molecules indicate interior solvation of the dianions. For the para-isomer an even-odd effect in the electron detachment energies was observed as a result of alternate solvation of the two separated charged carboxylate groups. This effect is weaker than in dicarboxylate dianions with an aliphatic spacer, since the two carboxylic groups can to some extent interact with each other via the polarizable benzene ring. No even-odd effect was observed for the ortho-isomer because each water molecule can solvate both carboxylate groups simultaneously due to their proximity.

Molecular dynamics simulations in extended slabs predict bulk solvation for all three isomers of benzene dicarboxylate dianions, regardless the use of polarizable or non-polarizable force field, consistent to the observation in the solvated clusters. Upon tetramethylations, however, the dianions exhibit surfactant activity. The preferential position of tetra-methyl ortho-benzene dicarboxylate dianion is thus at the water/vapor interface with the charged carboxylic groups anchored in the aqueous phase and the hydrophobic benzene ring essentially lying on the top-most water layer.

## **Acknowledgements**

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and performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, operated for DOE by Battelle.

## Figure Captions

**Figure 1:** Photoelectron spectra of  $o$ -BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>x</sub> ( $x = 0-20$ ) at 193 nm (6.424 eV).

**Figure 2:** Photoelectron spectra of  $p$ -BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>x</sub> ( $x = 0-20$ ) at 193 nm (6.424 eV).

**Figure 3:** Photoelectron spectra of selected  $o$ -BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>x</sub> ( $x = 0-25$ ) and  $p$ -BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>x</sub> ( $x = 0-16$ ) at 157 nm (7.866 eV).

**Figure 4:** a) Adiabatic electron binding energies (ADE) of  $o$ -BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>x</sub> ( $x = 0-20$ ) (black) and  $p$ -BCD<sup>2-</sup>(H<sub>2</sub>O)<sub>x</sub> ( $x = 0-20$ ) (red) as a function of solvent numbers ( $x$ ). b) The differential ADE [ $\Delta$ ADE = ADE( $x$ ) – ADE( $x-1$ )] as a function of  $x$ .

**Figure 5:** The highest occupied molecular orbital (HOMO) of a)  $p$ -BCD<sup>2-</sup> and b) the adipate dianion. Note the delocalization of the HOMO of  $p$ -BCD<sup>2-</sup> in the aromatic ring and the localized HOMO on the carboxylates in adipate.

**Figure 6:** Density profiles (i.e., histogrammed densities of the electrolyte ions and water molecules in layers parallel to the surface, from the center of the slab across the interface into the gas phase) of water oxygens and carbons and oxygens of  $o$ -BCD<sup>2-</sup> in an aqueous slab employing a) polarizable and b) non-polarizable force fields.

**Figure 7:** Density profiles of water oxygens and carbons and oxygens of  $m$ -BCD<sup>2-</sup> in an aqueous slab employing a) polarizable and b) non-polarizable force fields.

**Figure 8:** Density profiles of water oxygens and carbons and oxygens of  $p$ -BCD<sup>2-</sup> in an aqueous slab employing a) polarizable and b) non-polarizable force fields.

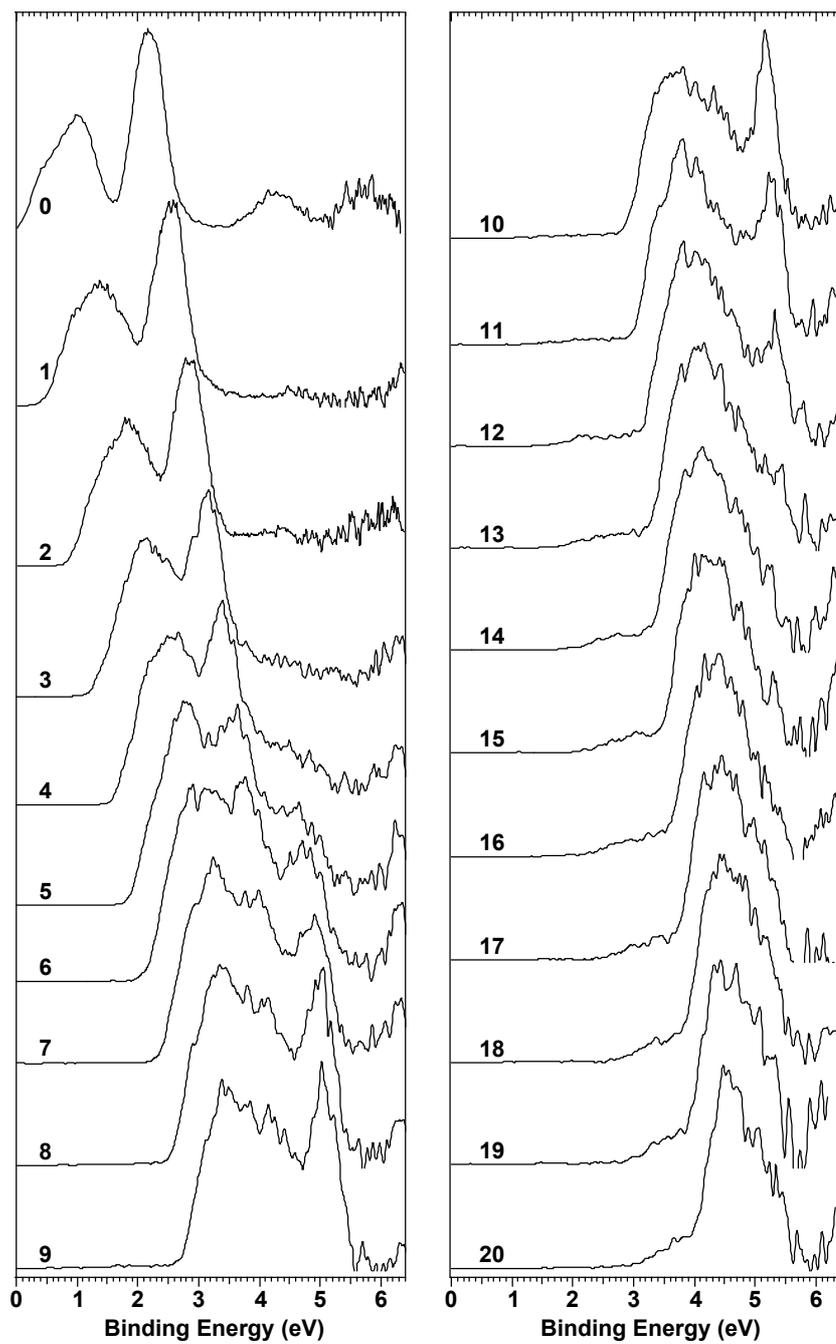
**Figure 9:** A snapshot of the first solvation shell (25 water molecules) of  $p$ -BCD<sup>2-</sup>. Note the reduced water density around the benzene ring compared to that around the -COO<sup>-</sup> groups.

**Figure 10:** Density profiles of water oxygens and carbons and oxygens of tetra-methyl *o*-BCD<sup>2-</sup> in an aqueous slab employing a) polarizable and b) non-polarizable force fields. Note the strong propensity of the ions for the air/water interface.

**Figure 11:** A snapshot from the molecular dynamics simulation depicting the tetra-methyl *o*-BCD<sup>2-</sup> at the air/water interface. Note the preferential orientation of the dianion with the hydrophilic -COO<sup>-</sup> groups “anchored” in the aqueous phase and the hydrophobic methylated benzene ring tilted and pointing toward the gas phase.

**Figure 12:** Orientation of the molecular axis of the tetra-methyl *o*-BCD<sup>2-</sup>, passing through the center of the benzene ring in between the two carboxylate groups, with respect to the normal to the surface (weighted by the factor  $1/\sin\theta$ ). The peak around 45° indicates a preferential orientation of the ion at the surface, with a tilted aromatic ring and carboxylate groups pointing toward the aqueous bulk.

**Figure 1**



**Figure 2**

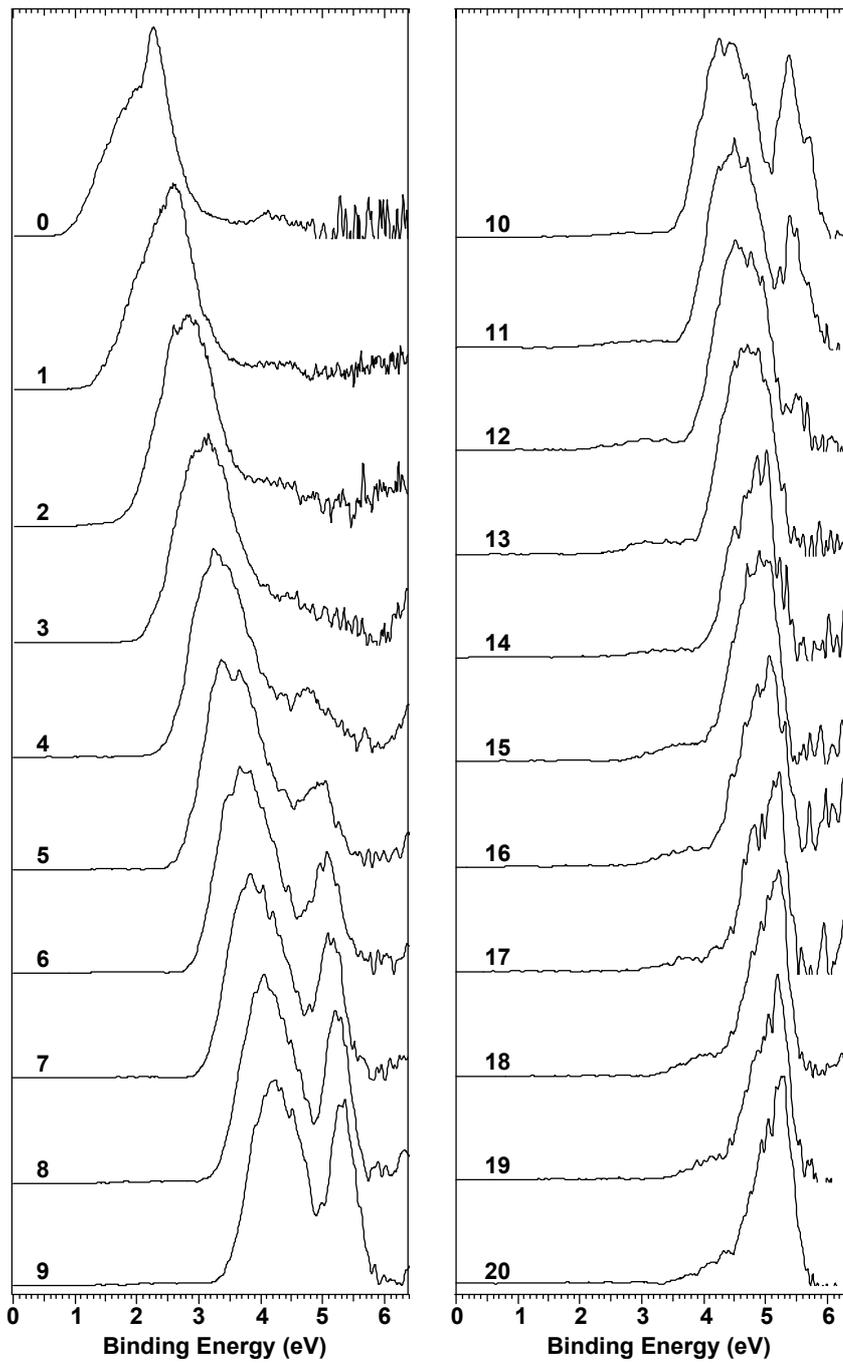


Figure 3

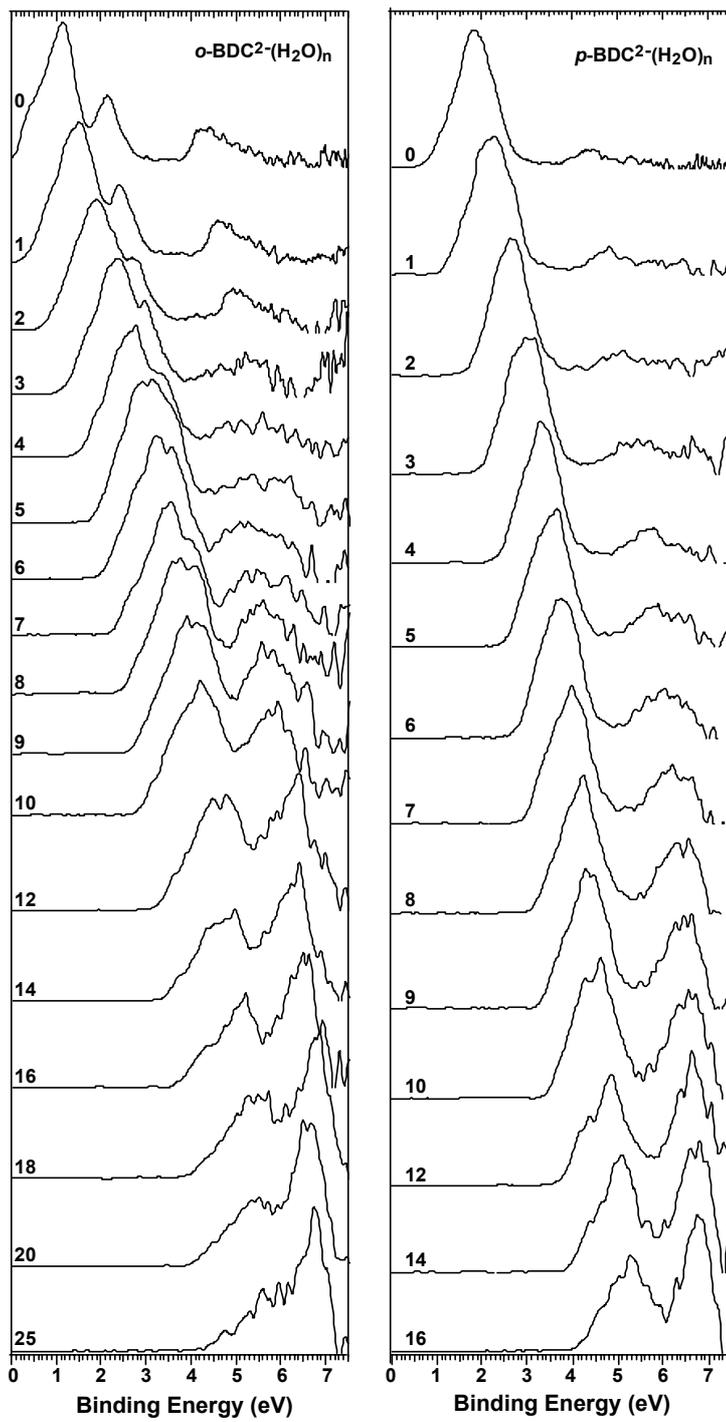


Figure 4

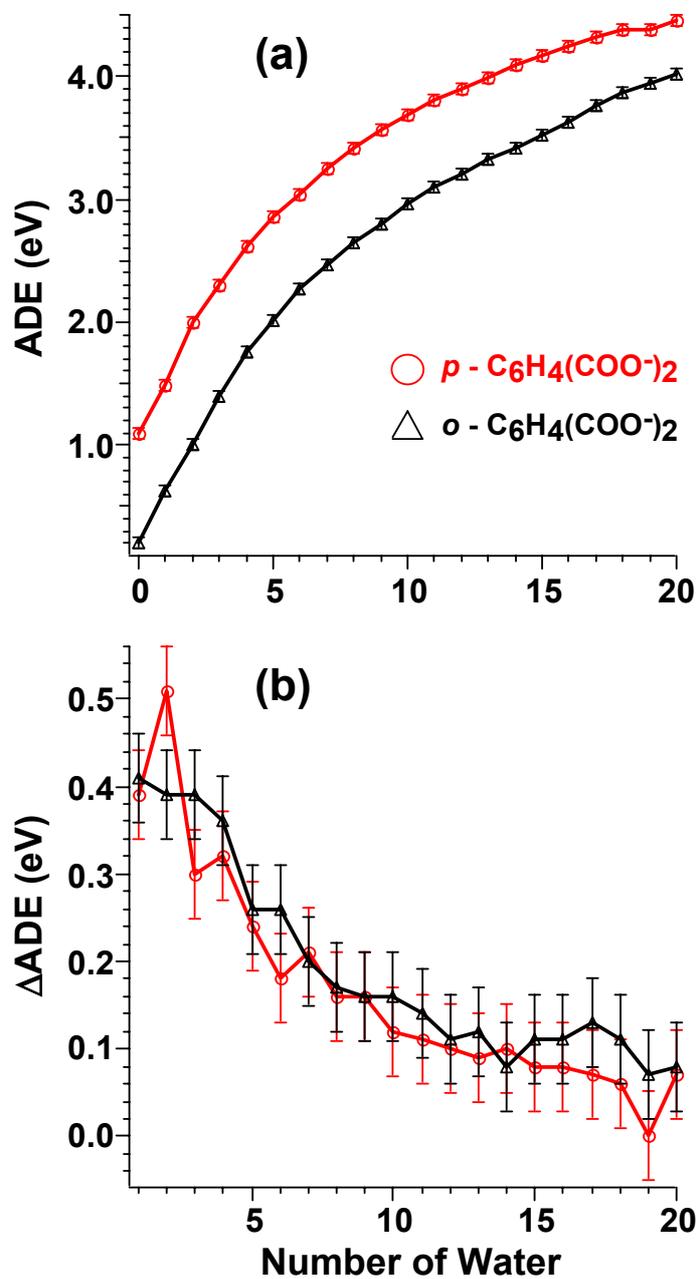
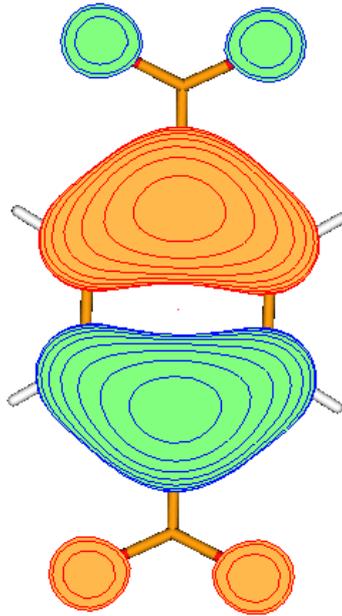


Figure 5a



**Figure 5b**

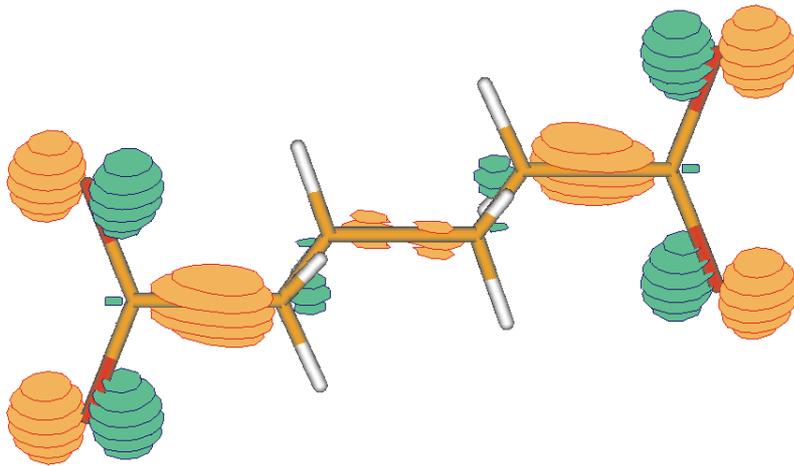


Figure 6a:

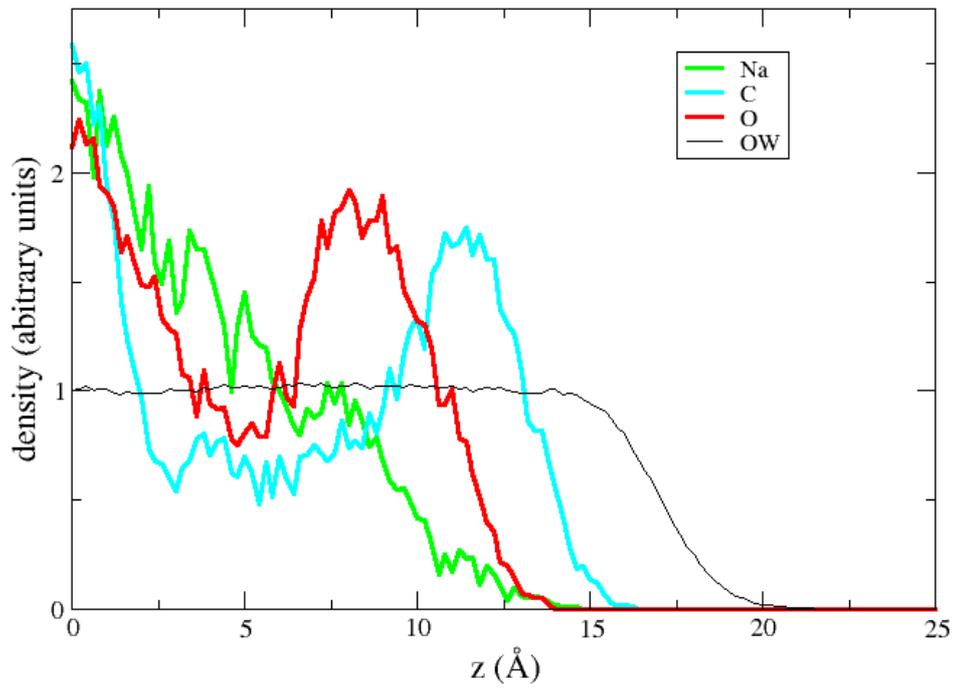


Figure 6b:

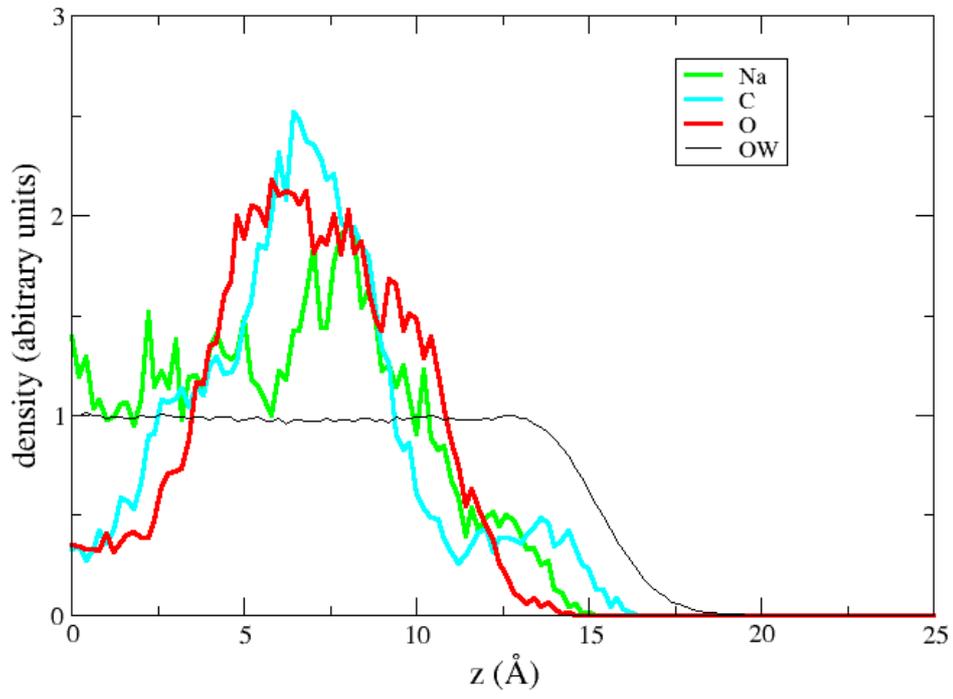


Figure 7a:

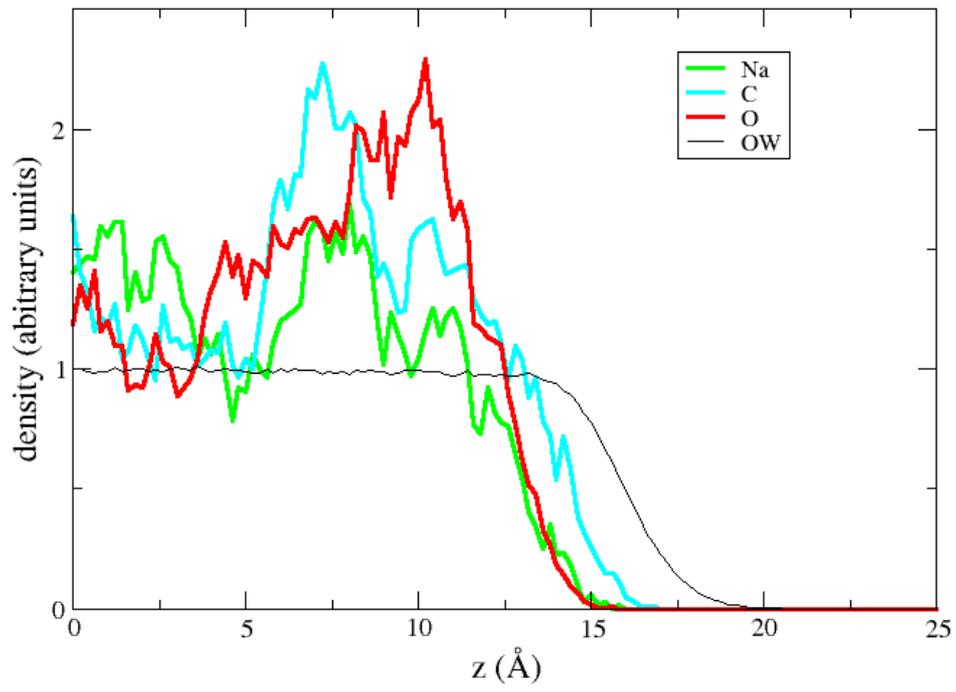


Figure 7b:

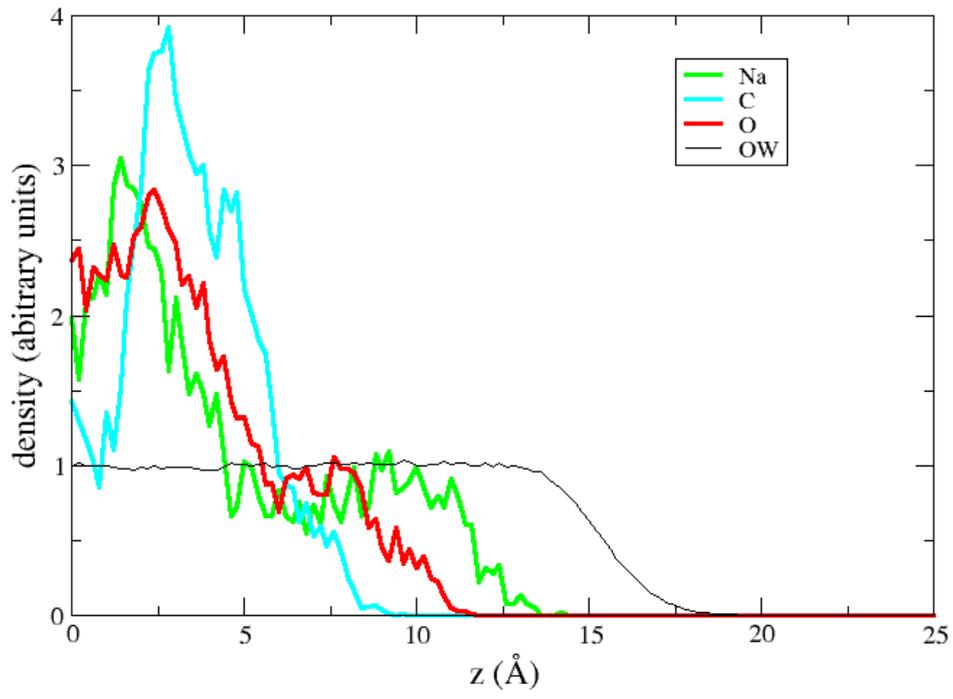


Figure 8a:

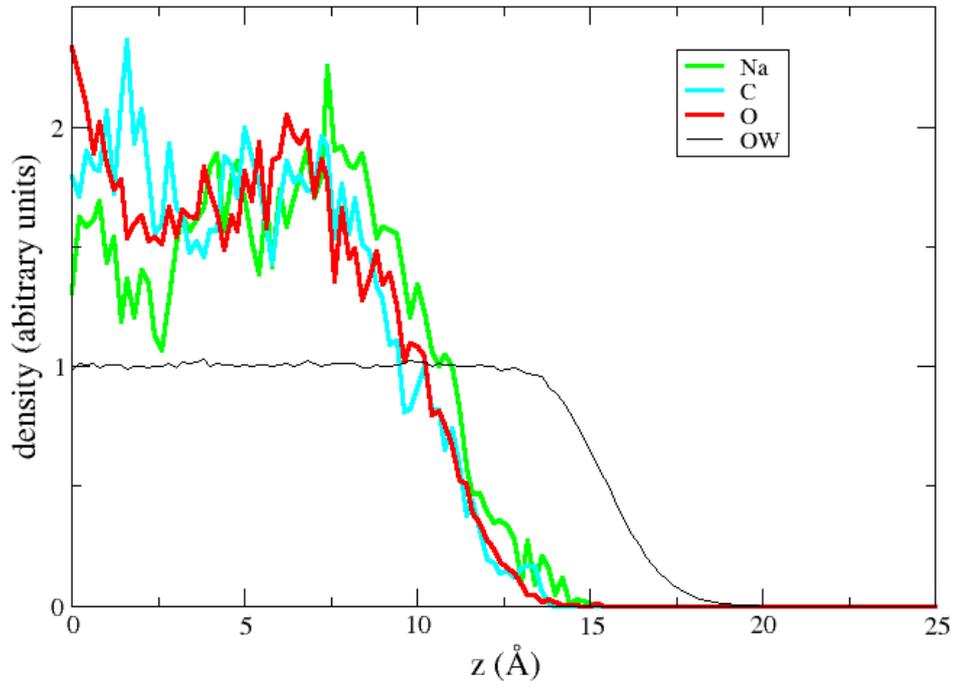


Figure 8b:

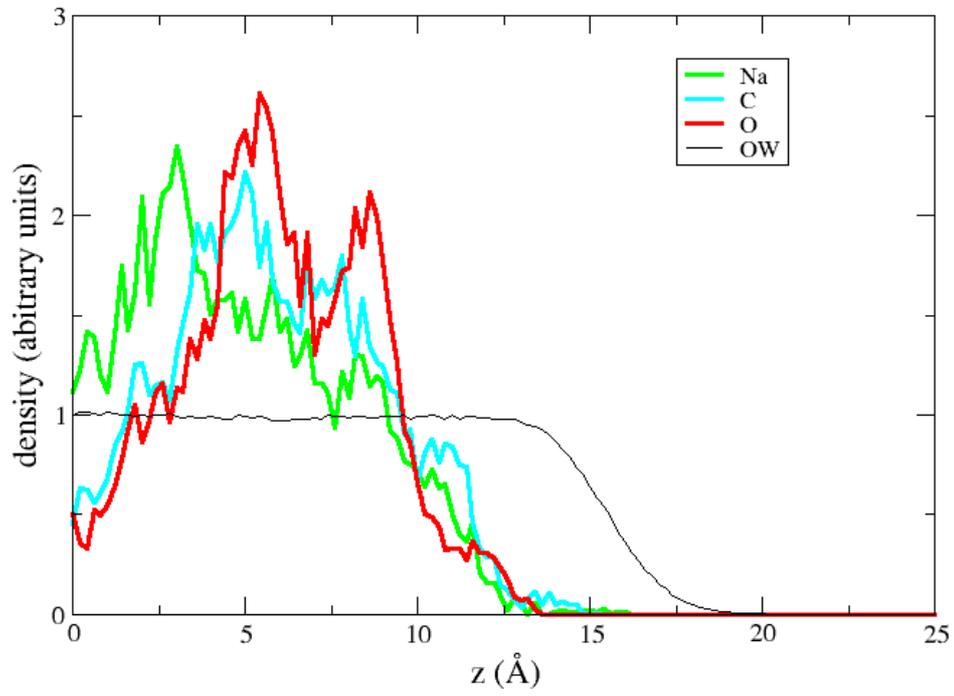


Figure 9:

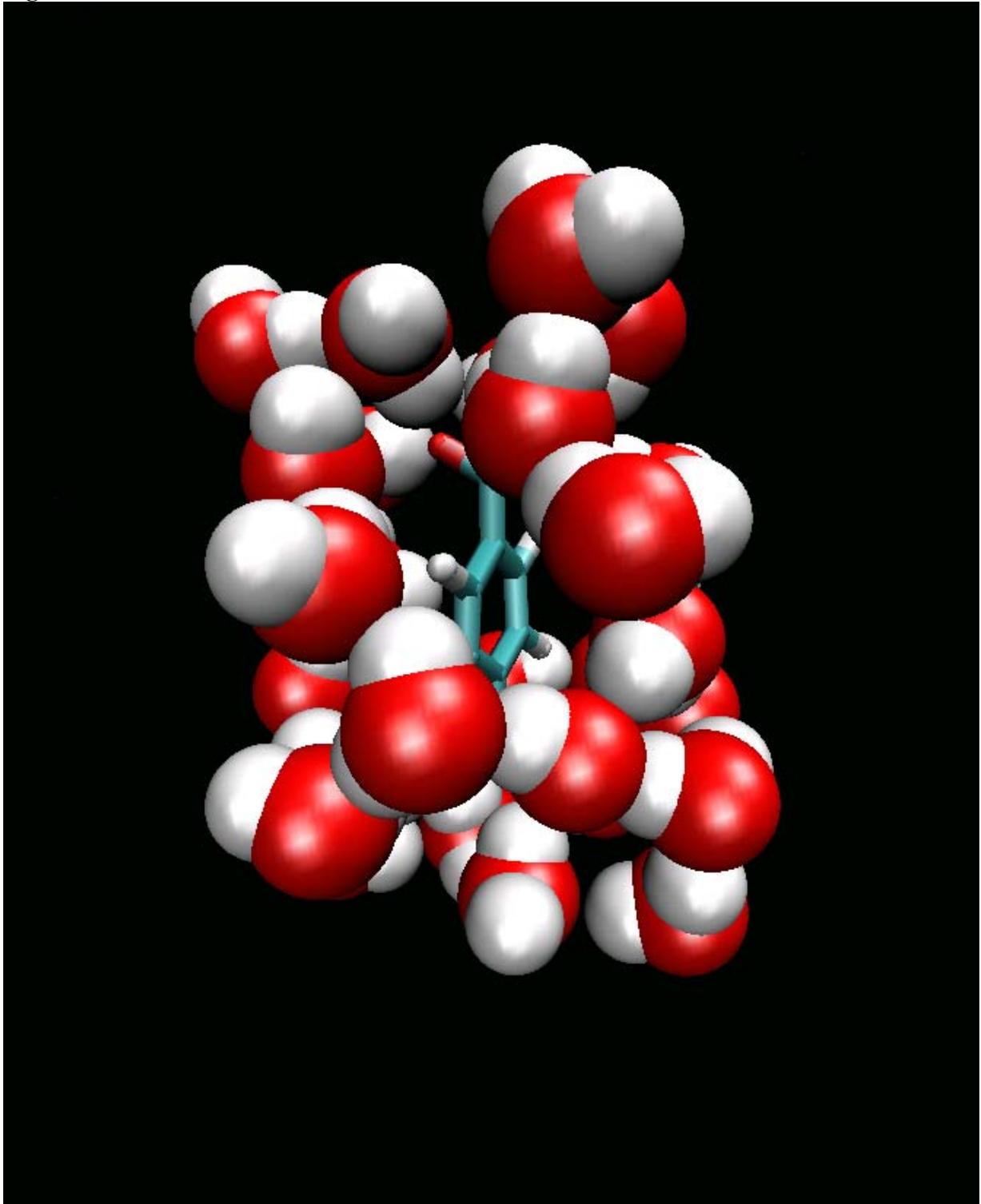


Figure 10a:

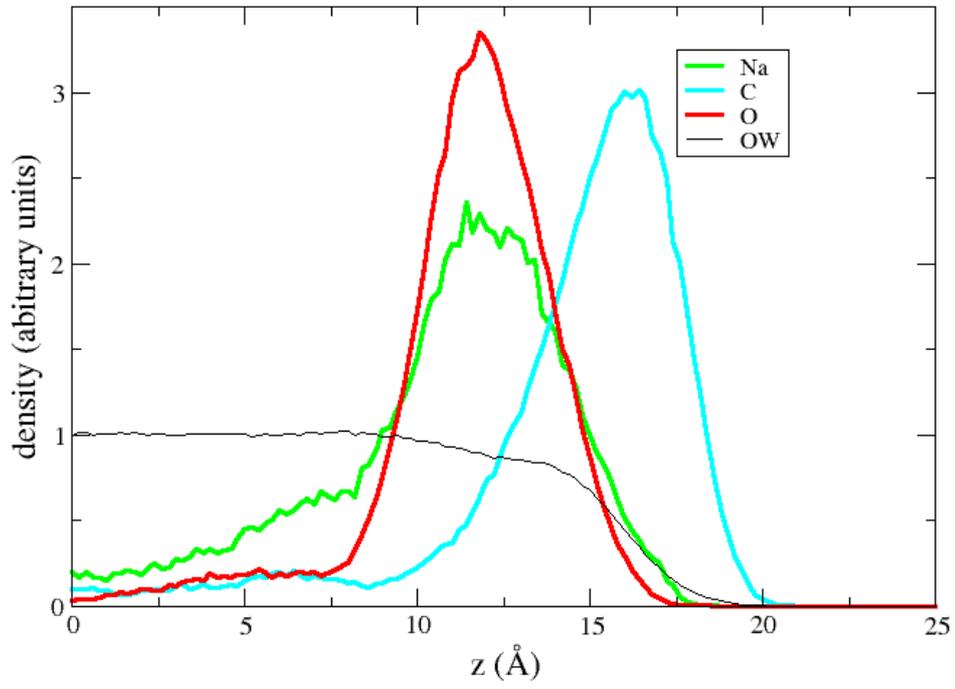


Figure 10b:

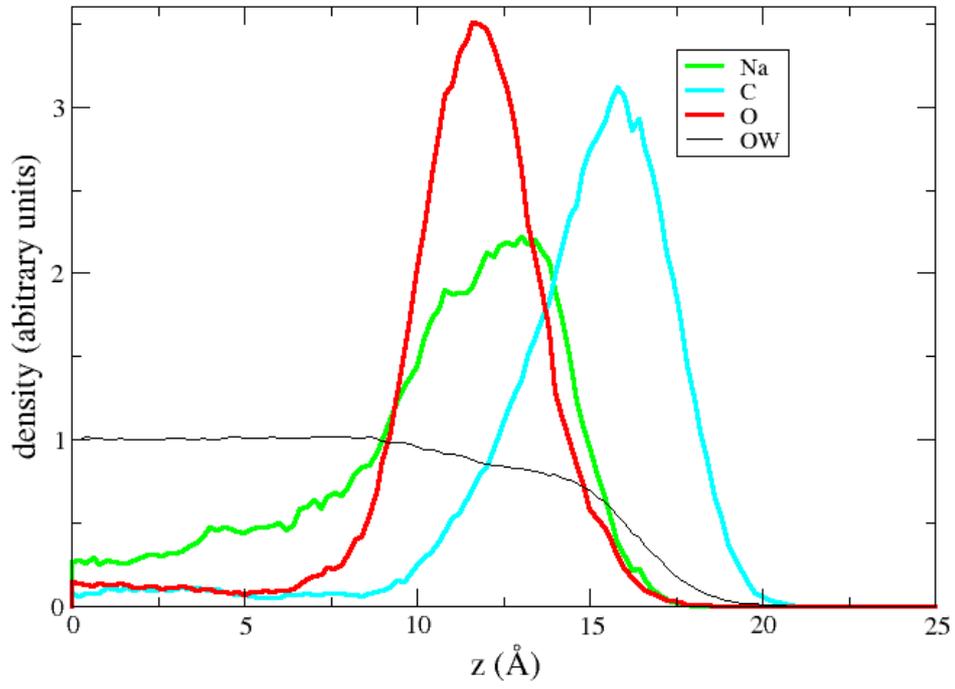
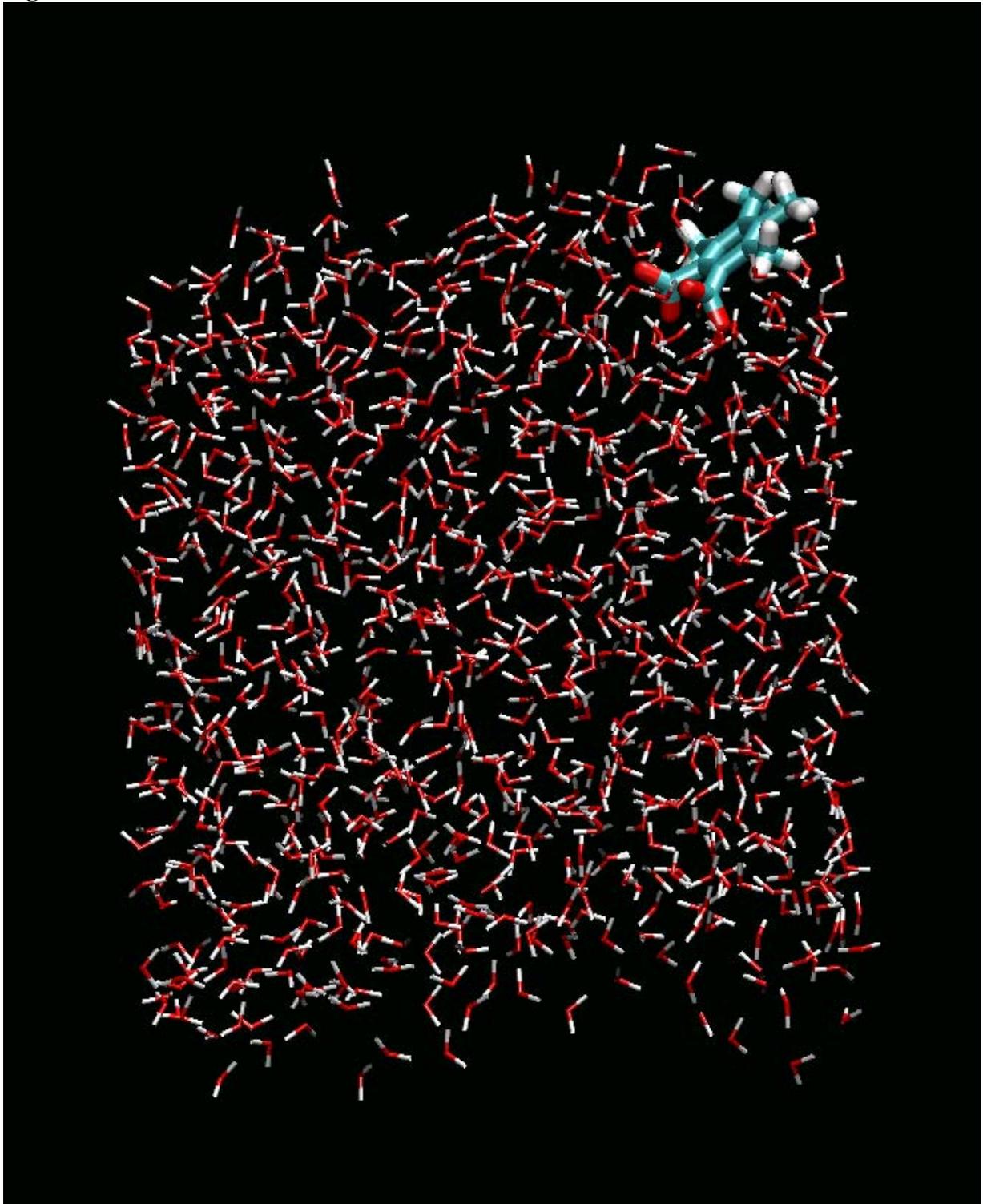
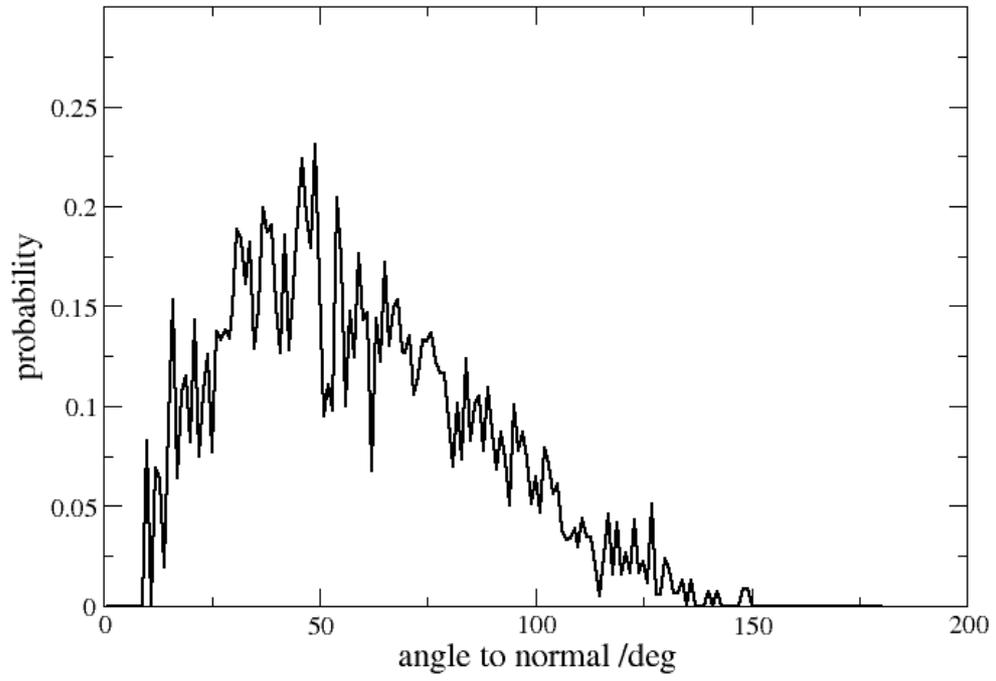


Figure 11:



**Figure 12:**



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