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Influence of Structure on the Polarizability of Hydrated Methane Sulfonic Acid Clusters

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Abstract: The relationship between polarizability and structure is investigated in methane sulfonic acid (MSA) and in 36 hydrated MSA clusters. The polarizabilities are calculated at B3LYP and MP2 level and further partitioned into molecular contributions using classic and iterative Hirshfeld methods. The differences in the two approaches for partitioning of polarizabilities are thoroughly analyzed. The polarizabilities of the molecules are found to be influenced in a systematic way by the hydrogen bond network in the clusters, proton transfer between MSA and water molecules, and weak interactions between water molecules and the methyl group of MSA.

1. Introduction

Methane sulfonic acid (MSA) has received some attention in the literature recently due to its presence in aerosol. The mystery of its formation has been the main topic of the research around this compound,[1−4] as well as its concentration,[6,8−13] but its role in the growth of particle within the aerosol[7,14] and its role as catalyst in oxidation processes[5] have also been investigated. Wang examined the ability of MSA to act as a center of nucleation with water molecules by studying the stability of several hydrated MSA clusters.[21] He found that for the smaller clusters the hydrogen bonds network between MSA and the surrounding water molecules are the main stabilizing factor, whereas for clusters containing three water molecules or more a proton transfer occurs from MSA to a neighboring water molecule, thus creating an ion−pair complex. As the aggregation number increases the probability for a proton transfer increases, as well as the corresponding stabilization.

One of the factors that can influence the interaction of those clusters with the environment is their polarizability because of the electrostatic polarization and the proportional-ity of the van der Waals interactions to the polarizabilities of the interacting molecular moieties. The global polarizability of the cluster as well as the individual polarizability of the MSA and the different water molecules in the cluster are of great interest. One can expect the polarizabilities to be dependent on the structure of the clusters in a systematic fashion. The number and strength of hydrogen bonds between the molecules, the eventual proton transfer and the steric hindrance are some of the factors that can influence the values of polarizability. A thorough analysis of such relation can lead to a deeper understanding of this property.

In a previous work, a method for partitioning of cluster polarizabilities into molecular contributions, based on the Hirshfeld scheme,[15,16] was introduced and applied to water clusters.[17] This method was further extended to the iterative Hirshfeld scheme, recently introduced by Bultinck et al.[19] The iterative Hirshfeld scheme brought a number of fundamental improvements to the classic Hirshfeld weight function and the resulting atomic charges, such as the elimination of the random nature of the weight function and the extension of applicability to charged systems. In this work, the effect of the iterative nature of the new scheme on the values of polarizability will be examined by comparing the values obtained by means of both schemes.

In previous works,[17,18] the polarizabilities of the clusters were studied only at DFT level because of the extensive size

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of the systems. The quality of the values obtained at DFT level will be challenged here by comparison with MP2 method.

2. Method

The Hirshfeld method[15,16,19] allows us to write the *ij*-element of the polarizability tensor of a cluster as a sum of atomic contributions

$$\alpha_{ij} = \sum_A \alpha_{ij}^A + q_A^{(i)} j_A \tag{1}$$

where the *ij*-element of the intrinsic polarizability tensor of atom *A* and its first-order perturbed atomic charge in the Cartesian direction $j = x, y,$ or z are defined in eqs 2 and 3, respectively[17]

$$\alpha_{ij}^A = -\int i_A \omega_A(\mathbf{r}) \rho^{(j)}(\mathbf{r}) d\mathbf{r} \tag{2}$$

$$q_A^i = -\int \omega_A(\mathbf{r}) \rho^{(j)}(\mathbf{r}) d\mathbf{r} \tag{3}$$

The three first-order perturbed electronic densities $\rho^{(i)}$, $i = x, y, z$, can be obtained analytically by means of the CPHF method or numerically by means of the Finite Field method.

The atomic Hirshfeld weight function $\omega_A(r)$ can be defined in two ways:

• The classic Hirshfeld method,[15,16] where the weight function is constructed from the electronic densities of the spherical atoms

$$\omega_A(\mathbf{r}) = \frac{\rho_A^{(0)}(\mathbf{r})}{\sum_B \rho_B^{(0)}(\mathbf{r})} \tag{4}$$

• The iterative Hirshfeld method,[19] where the weight function is repeatedly constructed in each iteration from the atomic electronic densities obtained in the previous iteration, until conversion is achieved

$$\omega_A^n(\mathbf{r}) = \frac{\rho_A^{(n-1)}(\mathbf{r})}{\sum_B \rho_B^{(n-1)}(\mathbf{r})} \tag{5}$$

The electronic densities of the spherical atoms are used as an initial guess.

The intrinsic molecular polarizability of a molecule in a cluster is given by the sum of the intrinsic polarizabilities of the atoms in the molecule,

$$\alpha_{ij}^{\text{int,mol}} = \sum_{A(\text{mol})} \alpha_{ij}^A \tag{6}$$

whereas the total molecular polarizability also includes the intramolecular charge delocalization contribution

$$\alpha_{ij}^{\text{tot,mol}} = \sum_{A(\text{mol})} \alpha_{ij}^A + q_A^{(i)} (j_A - j_{\text{mol}}) \tag{7}$$

where j_{mol} represents the j coordinate of the geometrical center of the molecule.

Because the separate elements of the polarizability tensors are not rotationally invariable, only the isotropic values of the polarizabilities, given by the trace of the tensor, will be discussed in this work

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \tag{8}$$

3. Computational Details

The polarizabilities of MSA and 36 hydrated MSA clusters $CH_3SO_3H \cdot (H_2O)_n$, $n = 1, 5$, were calculated at the DFT level and the B3LYP functional and at the MP2 frozen-core level, using the 6−311++G(2df,p) basis set. The polarizabilities were subsequently partitioned using the classic and iterative Hirshfeld methods. The structures of the clusters were previously optimized by L. Wang[21] using the B3LYP/6−311++G(2df,p) method. The methodology for obtaining and partitioning the polarizabilities at the two levels of theory is as follows. In the first step, the density matrices in the presence of an electric field applied at the positive and negative x, y, and z directions were obtained using the Gaussian03 program.[20] The density matrices were further used to obtain the first-order perturbed density matrices by means of the Finite Field Theory using the Brabo program.[22] At last, the Stock program[16] was used to obtain the atomic charges and the atomic and molecular polarizabilities (eqs 2, 6, and 7).

4. Results and Discussion

4.1. Nomenclature. In the following discussion, the polarizabilities of the clusters will be related to their structures, in particular, the hydrogen bond (HB) network between the different molecules. The molecules will be classified according their HB pattern in the following way:
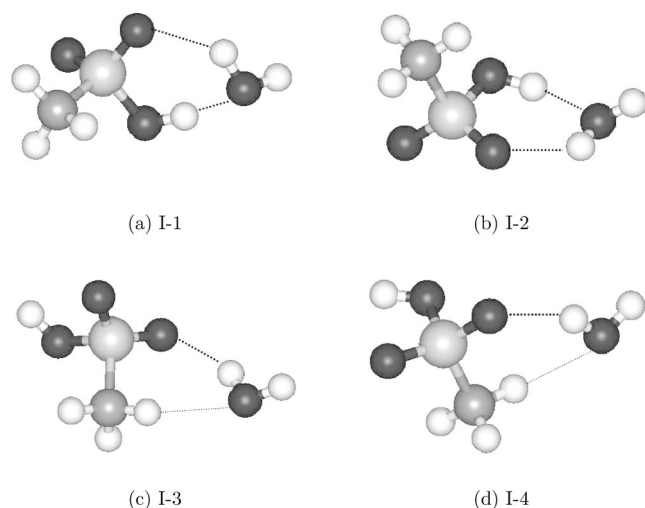
• A molecule that donates a hydrogen atom into a HB will be referred to as making a D-type HB.

• A molecule that accepts a HB through an oxygen atoms will be referred to as making an A-type HB.

• The water molecules in the clusters can be labeled by the number and type of HBs they make as A, D, AD, AAD, ADD, and AADD. The protonated ion H_3O^+ can be labeled as DDD.

• MSA can be labeled as A, AD, AAD, AAAD, and AAAAD according to the number and type of HBs it makes. The deprotonated ion SO_3^- can be labeled as AAA and AAAA.

4.2. Cluster Polarizabilities. Table 1 lists the polarizabilities of the free MSA and the hydrated MSA clusters, calculated at the B3LYP and MP2 levels and the 6−311++G-(2df,p) basis set. While B3LYP overestimates the polarizabilities by a mean 2.54%, the qualitative trends are identical for both levels of theory. It can be seen that the values depend on the number of water molecules that surround the MSA. Figure 1 depicts the strong linear relation between the number of water molecules n and the mean polarizability of the clusters containing n water molecules, for both levels of theory. The addition of a water molecule to a cluster causes a mean increase of the cluster polarizability by 9.40 or 9.08 au according to B3LYP or MP2 method, respectively.
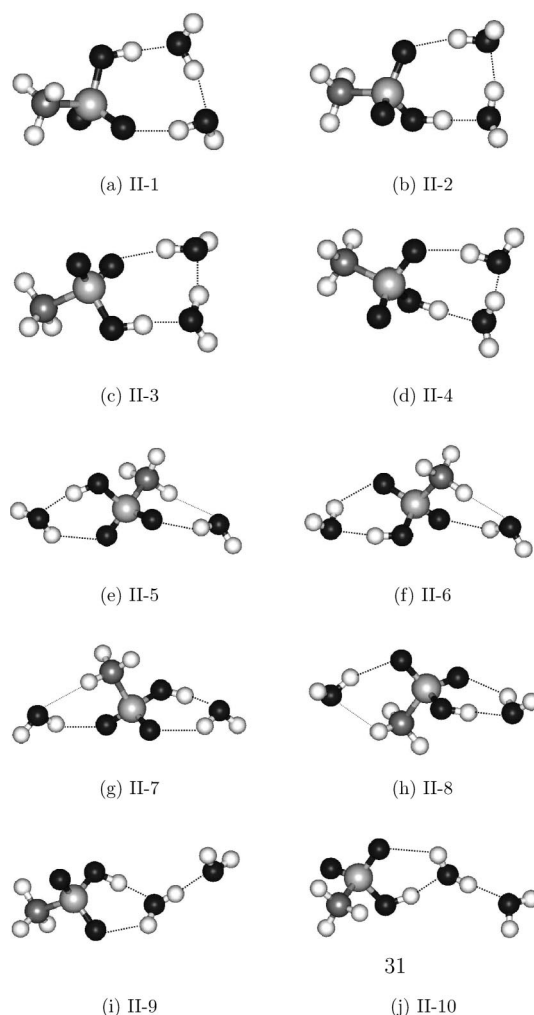
Examination of the values for clusters with identical number of water molecules n reveals that the polarizabilities are influenced by the structure of the clusters. For example, within the clusters containing one water molecule, two groups

Table 1. Calculated Polarizabilities of MSA and Hydrated MSA Clusters at B3LYP and MP2 Levels with 6-311++G(2df,p) Basis Set[a]

	B3LYP	MP2		B3LYP	MP2		B3LYP	MP2
MSA	43.059	42.551	II-9	61.340	59.917	IV-2	81.545	79.494
I-1	52.207	51.217	II-10	61.348	59.907	IV-3	82.449	80.421
I-2	52.215	51.212	III-1	72.281	70.680	IV-4	80.370	78.031
I-3	51.787	50.821	III-2	70.894	69.002	IV-5	80.197	77.871
I-4	51.808	50.851	III-3	71.541	69.709	IV-6	80.317	77.972
II-1	62.168	60.743	III-4	71.027	69.153	IV-7	80.388	78.198
II-2	62.078	60.665	III-5	70.726	68.877	IV-8	80.573	78.225
II-3	62.242	60.792	III-6	70.978	69.052	V-1	91.891	89.401
II-4	62.122	60.708	III-7	70.784	68.818	V-2	90.976	88.576
II-5	61.090	59.617	III-8	70.905	68.925	V-3	90.268	87.745
II-6	61.102	59.636	III-9	71.166	69.126	V-4	90.318	87.774
II-7	61.065	59.610	III-10	71.170	69.133			
II-8	61.093	59.639	IV-1	82.061	80.011			

[a] All values are in au.
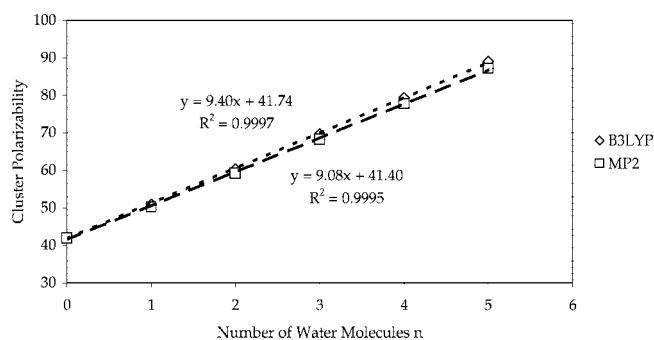
Figure 1. Mean polarizabilities of clusters containing identical number of water molecules *n* as function of *n* calculated at the B3LYP and MP2 levels with 6−311++G(2df,p) basis set.

(a) I-1   (b) I-2

(c) I-3   (d) I-4

Figure 2. $CH_3SO_3H \cdot H_2O$ clusters.

(a) II-1   (b) II-2

(c) II-3   (d) II-4

(e) II-5   (f) II-6

(g) II-7   (h) II-8

(i) II-9   (j) II-10

Figure 3. $CH_3SO_3H \cdot (H_2O)_2$ clusters.

can be identified; clusters I-1 and I-2, with polarizability values around 52.2(51.2) au for the B3LYP(MP2) method, and clusters I-3 and I-4 with polarizability values around 51.8(50.8) au. The first two clusters contain an AD-type MSA and an AD-type water molecule, whereas the latter two clusters contain an A-type MSA and a D-type water molecule that additionally interacts through its oxygen atom with a hydrogen atom of the methyl group. A similar relation between structure and polarizability can be found in the clusters containing two water molecules, where the polar-

izability values can be separated into three groups. The first group contains the clusters II-1 to II-4, with values around 62.2(60.7) au, that consist of two AD-type water molecules and an AD-type MSA. The second group contains clusters II-5 to II-8 with values around 61.1(59.6), that consist of an AD-type water molecule, D-type water molecule that also interacts with the methyl group, and AAD-type MSA. The third group contains clusters II-9 and II-10, with values
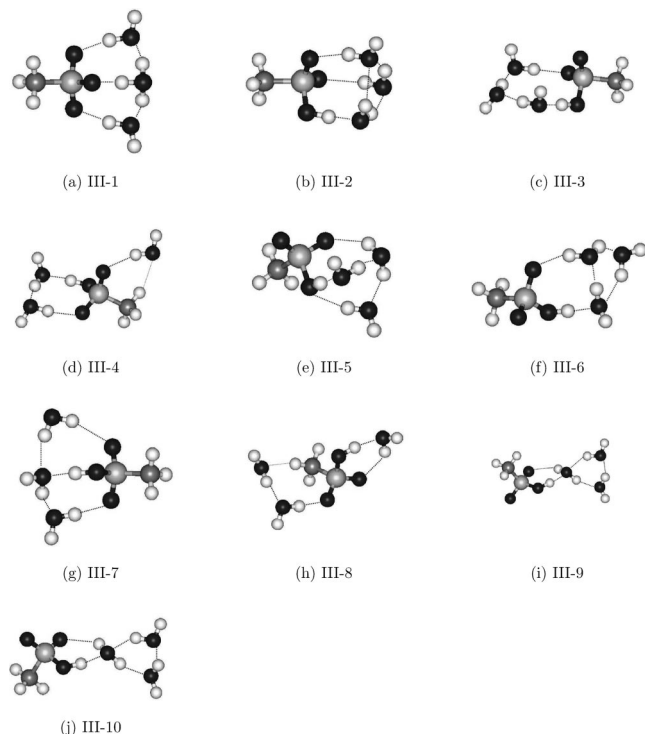
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(a) III-1   (b) III-2   (c) III-3

(d) III-4   (e) III-5   (f) III-6

(g) III-7   (h) III-8   (i) III-9

(j) III-10

Figure 4. $CH_3SO_3H \cdot (H_2O)_3$ clusters.

(a) IV-1   (b) IV-2

(c) IV-3   (d) IV-4

(e) IV-5   (f) IV-6

(g) IV-7   (h) IV-8

Figure 5. $CH_3SO_3H \bullet (H_2O)_4$ clusters.

(a) V-1   (b) V-2

(c) V-3   (d) V-4

Figure 6. $CH_3SO_3H \cdot (H_2O)_5$ clusters.

around 61.3(59.9), that are formed out of an AAD-type water molecule, an A-type water molecule, and an AD-type sulfuric acid.

As the number of water molecules in the cluster increases, such straightforward connection between the polarizability values and structure becomes less evident, although one can observe that clusters that contain an ion−pair complex resulting from a proton transfer, such as III-1 and IV-1−IV-3, have slightly larger values than clusters with equivalent aggregation number without proton transfer.

4.3. Atomic and Molecular Charges. Table 2 lists the mean charges for the different entities in the cluster, calculated with the classic Hirshfeld and iterative Hirshfeld methods, both at the B3LYP and MP2 levels of theory. The values for the mean charges of the SO_3^- entity are similar in the classic and iterative Hirshfeld schemes, being around −0.46 au and −0.54 au for the B3LYP and MP2 methods, respectively. However, this is not the case for the values of the charge of the SO_3H entity, where the classic Hirshfeld method assigns a slightly negative charge of −0.19(−0.21) au for the B3LYP(MP2) method, whereas the iterative Hirshfeld assigns a positive charge of 0.11(0.17) au. This disagreement in the sign is also present in the values for the methyl group of the MSA: the classic Hirshfeld method assigns a positive charge of around 0.11(0.13) au to the methyl group, whereas the iterative Hirshfeld method assigns it a negative charge of −0.22(−0.21) au.

These differences can be explained by the charges of the atoms, which are essentially different in the two schemes. In the classic Hirshfeld scheme, the charges of the atoms are rather small, amounting to around 0.5 au for the S atoms, −0.3 au for the O atoms, −0.1 au for the C atoms, and 0.05 au for the H atoms of the methyl group. On the other hand, in the iterative Hirshfeld scheme the atomic charges are
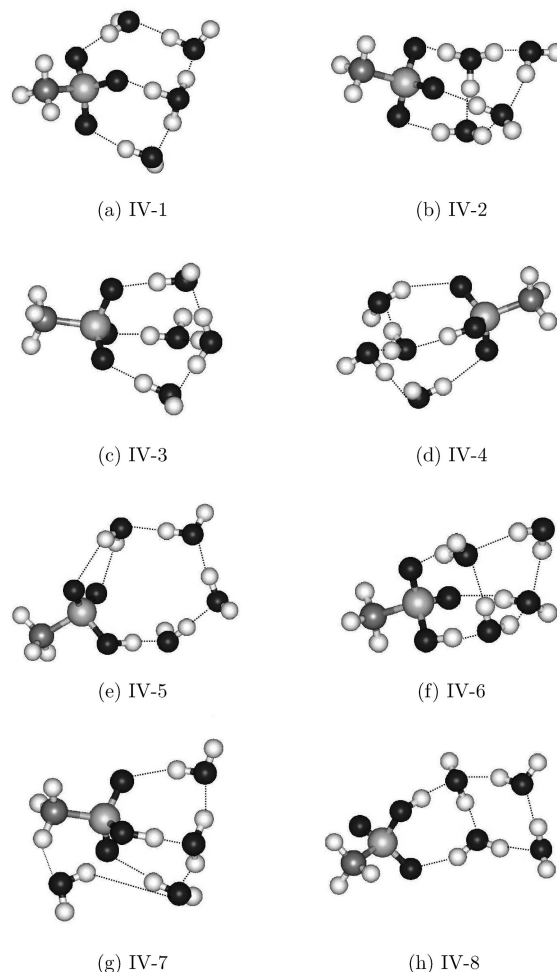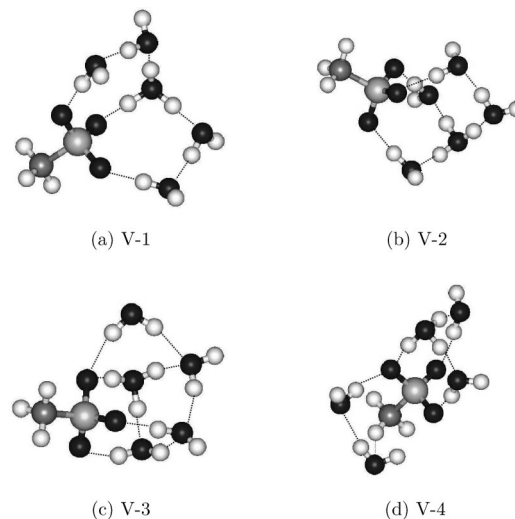
considerably larger, amounting to around 2.2 au for the S atoms, −0.9 au for the O atoms, −0.9 au for the C atoms, and 0.2 au for the H atoms of the methyl group. As stated in the ref 19 the larger charges are typical for the iterative Hirshfeld scheme and may be seen as a consequence of the iterative nature of the scheme, where the boundaries of the atoms within the molecule are allowed to differ considerably from the free spherical atoms, thus being independent of the

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Table 2. Mean Charges of the Different Entities in the Clusters Calculated at B3LYP and MP2 Levels with 6-311++G(2df,p) Basis Set and Partitioned with the Classic and Iterative Hirshfeld Schemes[a]

	B3LYP		MP2	
	classic	iterative	classic	iterative
SO_3^-	−0.47	−0.46	−0.54	−0.54
SO_3H	−0.19	0.17	−0.21	0.17
CH_3	0.11	−0.22	0.13	−0.21
A-H	0.12	0.05	0.11	0.03
D-H	−0.05	−0.01	−0.05	−0.01
AD-H	0.05	0.02	0.04	0.02
DD-H	−0.12	−0.04	−0.11	−0.02
AAD-H	0.07	0.02	0.06	0.01
ADD-H	0.02	0.03	0.02	0.02
AADD-H	0.06	0.03	0.05	0.01
DDD-H	0.26	0.63	0.31	0.72

[a] All values are in au.

initial choice of the promolecule. This effect is especially important for the atomic charge of the sulfur atom, which changes from 0.5 au to 2.2 au during the iterations, thus corresponding better with the high oxidation state of this atom in the molecule.

The values of the charges for the SO_3H and SO_3^- groups are not influenced by the number or type of HBs those entities form with the surrounding water molecules. However, the charges of the water molecules vary between positive and negative values according to the type of HBs they make. Generally, one can state that a D-type HB increases the electron density at the molecule, causing the D-type and DD-type of molecules to have a net negative charge, whereas an A-type HB decreases the electron density at the water molecule. Yet the relation between the charge of the water molecules and their type is not straightforward. Especially in the iterative Hirshfeld scheme, the net charges of the water molecules are smaller than in the classic Hirshfeld scheme, despite the larger values of atomic charges, and the charges are less dependent on the type of the molecules. For example, the ADD-type water molecule has a larger positive charge than the AAD-type water molecule in the iterative Hirshfeld scheme. This reduced charge transfer between molecules within a cluster implies that the molecules are better defined as separate entities within a cluster in the iterative Hirshfeld scheme.

4.4. Polarizability of MSA. MSA can be divided into two functional groups, the hydrophilic SO_3H or SO_3^- groups, that form HBs with the surrounding water molecules, and the hydrophobic methyl groups. Table 3 lists the mean intrinsic and total polarizabilities (eqs 6 and 7) of SO_3^- and SO_3H, calculated with the classical and iterative Hirshfeld schemes at the B3LYP and MP2 levels, as well as the correlation coefficient between the number of HBs and the polarizability values of the SO_3H entity. The polarizability values decrease with each additional HB, independent of its type.

The intrinsic polarizability values of SO_3H are strongly correlated with the number of HBs for both schemes at both levels of theory, as well as the total polarizability values for the classic Hirshfeld scheme at B3LYP and MP2 levels, having correlation coefficients above $R = 0.995$. However,

the correlation decreases to $R = 0.990$ for the total polarizabilities obtained with iterative scheme at both levels of theory. This can be attributed to the more drastic change in the definition of atoms in the cluster in the iterative scheme, resulting in a larger difference between the geometrical center of the group of atoms that is used as a reference point in eq 7 and the center of the electron density for those atoms. Another difference between the classic and iterative Hirshfeld scheme are the polarizability values of SO_3^-. In the classical scheme, the AAA- and AAAA-type SO_3^- have slightly lower values than the equivalent AAD- and AAAD-type SO_3H, while in the iterative Hirshfeld scheme the values for both entities are very similar for the same number of hydrogen bonds.

Although the values of the classic and iterative Hirshfeld schemes are quite similar, the contributions of the separate atoms are considerably different. For example, in the free MSA the sulfur atom has according to the classic Hirshfeld scheme an intrinsic polarizability (eq 2) of 3.7 au, while the oxygen atoms have an intrinsic polarizability of 3.2 au. The iterative Hirshfeld scheme assigns in the same molecule to the sulfur atom an intrinsic polarizability of 0.5 au and to the oxygen atoms an intrinsic polarizability of 4.1 au. This difference is in line with the differences in atomic charges between the two schemes: in the iterative Hirshfeld scheme, the sulfur atom has a significant positive charge and is therefore significantly less polarizable than the oxygen atoms.

Within the same type of SO_3H or SO_3^-, the values are also slightly influenced by the structure of the cluster. For example, Table 4 lists the polarizability values of the different AD-type SO_3Hs from different clusters. Those molecules can be classified into three different groups. The first group, that has the lowest values, contains the III-3 cluster, where SO_3H forms a ring with three water molecules. The second group, that has slightly larger values, contains the clusters II-1−II-4, III-6, and IV-8, where SO_3H forms a ring with two water molecules. Note that the fact that in the larger clusters those water molecules form also HBs with other water molecules outside the ring does not reflect on the polarizability values of the SO_3H. The third group, which has the largest values, contains the clusters I-1, I-2, II-9, II-10, III-9, and III-10, where the SO_3H forms a ring with only one water molecule. One can conclude that structures where the molecules form larger rings result in lower polarizabilities of the molecules involved. This can be explained by the weaker HBs that are formed in structures with smaller rings, because of ring strain, because it has been shown in previous studies[17,18] that weaker HBs lead to higher polarizability values.

The polarizabilities of the methyl groups in the clusters can be divided in two groups. The first group consists of the methyl groups that do not interact in any way with the water molecules and have values similar to the values of the methyl group in the free MSA. The second group, that has lower polarizability values, consists of the methyl groups that have one hydrogen atom interacting with an oxygen atom in a water molecule, thus forming a weak HB. Table 5 lists the mean values of the polarizabilites for both groups. An evident outlier in the second group is the methyl group in cluster III-8, that has polarizability values lower by 0.2 au than the

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Table 3. Mean Intrinsic and Total Polarizabilities of the SO_3^- (AAA- and AAAA-types) and SO_3H (non-HB, A-, AD-, AAD-, and AAAD-types) Entities Calculated at B3LYP and MP2 Levels with 6-311++G(2df,p) Basis Set and Partitioned with the Classic Hirshfeld (H-C) and Iterative Hirshfeld (H-I) Schemes[a]

| | intrinsic polarizability | | | | total polarizability | | | |
| | B3LYP | | MP2 | | B3LYP | | MP2 | |
	H-C	H-I	H-C	H-I	H-C	H-I	H-C	H-I
				SO_3^-				
AAA	11.586	11.563	11.692	11.795	19.237	20.626	19.584	21.204
AAAA SO_3	10.819	10.919	10.948	11.169	18.136	20.174	18.515	20.866
				SO_3H				
non-HB	14.384	13.495	14.267	13.471	25.298	25.507	25.264	25.668
A	13.727	13.090	13.653	13.096	24.006	23.439	24.062	23.485
AD	13.083	12.257	13.038	12.310	22.581	22.848	22.700	23.118
AAD	12.278	11.706	12.279	11.798	21.217	21.364	21.415	21.653
AAAD	11.371	11.009	11.430	11.155	19.738	19.832	20.003	20.122
R	0.997	0.996	0.997	0.996	1.000	0.990	1.000	0.983

[a] *R* stands for the correlation coefficient between the values of SO_3H and the number of hydrogen bonds. All values are in au.

Table 4. Intrinsic and Total Polarizabilities of the AD-Type SO_3Hs in the Different Clusters Calculated at B3LYP and MP2 Levels with 6-311++G(2df,p) Basis Set and Partitioned with the Classic Hirshfeld (H-C) and Iterative Hirshfeld (H-I) Schemes[a]

| | intrinsic polarizability | | | | total polarizability | | | |
| | B3LYP | | MP2 | | B3LYP | | MP2 | |
	H-C	H-I	H-C	H-I	H-C	H-I	H-C	H-I
III-3	12.494	11.810	12.489	11.907	21.382	21.528	21.565	21.872
II-1	12.752	11.994	12.727	12.075	21.997	22.467	22.148	22.825
II-2	12.767	12.003	12.740	12.081	22.025	22.319	22.175	22.636
II-3	12.769	11.995	12.741	12.074	21.980	22.455	22.134	22.798
II-4	12.790	12.009	12.759	12.086	22.011	22.417	22.167	22.757
III-6	12.803	12.045	12.787	12.116	22.119	22.153	22.286	22.393
IV-8	12.807	12.042	12.789	12.116	22.115	22.133	22.280	22.379
I-1	13.386	12.499	13.315	12.530	23.285	23.560	23.353	23.795
I-2	13.423	12.541	13.350	12.568	23.339	23.672	23.404	23.915
III-9	13.443	12.560	13.381	12.582	23.258	23.221	23.343	23.384
III-10	13.444	12.552	13.382	12.575	23.269	23.523	23.354	23.730
II-9	13.597	12.638	13.512	12.650	23.409	23.676	23.467	23.888
II-10	13.603	12.657	13.523	12.674	23.367	23.894	23.429	24.162

[a] All values are in au.

Table 5. Mean Intrinsic and Total Polarizabilities of the HB CH_3 and non-HB CH_3 in the Different Clusters Calculated at B3LYP and MP2 levels with 6-311++G(2df,p) Basis Set and Partitioned with the Classic Hirshfeld (H-C) and Iterative Hirshfeld (H-I) Schemes[a]

| | intrinsic polarizability | | | | total polarizability | | | |
| | B3LYP | | MP2 | | B3LYP | | MP2 | |
	H-C	H-I	H-C	H-I	H-C	H-I	H-C	H-I
HB-CH_3	6.275	7.390	6.156	7.179	9.346	9.665	9.195	9.460
non-HB-CH_3	6.845	8.056	6.680	7.778	10.158	10.638	9.932	10.347

[a] All values are in au.

mean in Table 5. In this cluster, the methyl group forms a ring together with the MSA and two water molecules, as opposed to the rings with a single water molecule in the rest of clusters in the second group. Similar to the situation described above, the weak HB that the hydrogen atoms of the methyl group forms is shorter (2.21 au) than the mean HB length (2.46 au) between methyl groups and water molecules, resulting in lower polarizability values.

4.5. Polarizability of H_2O and H_3O^+. Table 6 lists the intrinsic and total polarizabilities of the different types of water molecules, calculated at the B3LYP and MP2 levels of theory and partitioned with the classic and iterative

Hirshfeld schemes. As a general trend the polarizabilities decrease with the number of HBs the molecule makes, although small differences can be distinguished between the different methods and schemes. The polarizability values of the DD-type water molecules are evident outliers because they consequently have the largest values, despite the fact that those molecules form two HBs. It must be noted that there are only three molecules of that type in the collection of clusters examined in this work, in clusters III-7, IV-6, and V-3. The reason for those high values will be discussed further below. The general order for the polarizability values of the different molecules calculated by the old Hirshfeld

Table 6. Mean Intrinsic and Total Polarizabilities of the Different Types of H_2O and the DDD-Type H_3O^+ Calculated at B3LYP and MP2 Levels with the 6-311++G(2df,p) Basis Set and Partitioned with the Classic Hirshfeld (H-C) and Iterative Hirshfeld (H-I) Schemes[a]

	intrinsic polarizability				total polarizability			
	B3LYP		MP2		B3LYP		MP2	
	H-C	H-I	H-C	H-I	H-C	H-I	H-C	H-I
				H_2O				
A	5.113	5.845	4.988	5.732	6.794	6.654	6.633	6.466
D	5.396	5.796	5.229	5.659	6.999	6.932	6.807	6.738
AD	4.784	5.332	4.682	5.268	6.149	6.219	6.034	6.103
DD	5.715	5.848	5.508	5.677	7.243	7.342	7.008	7.121
AAD	4.242	4.901	4.175	4.880	5.511	5.818	5.438	5.773
ADD	4.482	4.805	4.397	4.771	5.656	5.731	5.577	5.661
AADD	3.754	4.244	3.728	4.292	4.767	4.926	4.771	4.950
				H_3O^+				
DDD	4.060	3.905	3.941	3.846	5.064	4.756	4.957	4.676

[a] All values are in au.

scheme is D > A > AD > ADD > AAD > AADD, where the values decrease over a range of approximately 1.5 au or 30%. The order implies that A-type HBs have a larger influence on the polarizability than D-type HBs. This concept is not maintained in the intrinsic polarizabilities calculated by the iterative scheme: the D-type HBs have here larger influence because the values of A-type molecules are larger than the values of D-type molecules and the values of AAD-type molecules are larger than the values of ADD-type molecules. For the total polarizabilities obtained by the iterative Hirshfeld method the order is not altogether consequent, because the A-type molecules have larger values than the D-type molecules but the ADD-type moelcules have larger values than the AAD-type molecules. This lack of consequence can be explained by the drawback in the definition of total polarizabilities in the iterative scheme that has been mentioned above.

Table 7 lists the mean atomic polarizabilities of the oxygen, hydrogen-bonded hydrogen atoms (HB H), and non-hydrogen-bonded hydrogen atoms (non-HB H) in the different types of water molecules, calculated at the B3LYP and MP2 levels and partitioned with the classic and iterative Hirshfeld schemes. Although the values of the intrinsic polarizabilities of the molecules are quite similar for the classic and iterative Hirshfeld scheme, their distribution between the oxygen atom and the hydrogen atoms are very different. A similar situation was observed also for the SO_3H entity. The mean value encountered for the polarizabilities of oxygen atoms is 2.8 au in the classic Hirshfeld scheme and 4.3 au in the iterative Hirshfeld scheme. The HB Hs and non-HB Hs contribute 0.8 and 1.2 au in the classic scheme, whereas in the iterative scheme their values decrease to 0.3 and 0.6 au.

The DD-type water molecules appear to have polarizability values of oxygen atoms that are significantly higher than those in the rest of the water molecules, explaining the outlying values of intrinsic and total polarizabilities of those molecules in Table 6. This effect can be correlated to their somewhat remote position in the clusters, where the oxygen atoms experience less steric hindrance than the rest of water

Table 7. Mean Polarizabilities of the Oxygen Atoms, Hydrogen-Bonded Hydrogen Atoms (HB H), and Non-Hydrogen-Bonded Hydrogen Atoms (non-HB H) in the Different Types of Water Molecules Calculated at B3LYP and MP2 levels with 6-311++G(2df,p) Basis Set and Partitioned with the Classic Hirshfeld and Iterative Hirshfeld Schemes[a]

	B3LYP/classic Hirshfeld			B3LYP/iterative Hirshfeld		
	O	HB H	non-HB H	O	HB H	non-HB H
A	2.805		1.154	4.582		0.631
D	3.149	0.929	1.319	4.704	0.404	0.688
AD	2.768	0.794	1.222	4.352	0.327	0.653
DD	3.542	1.087		4.952	0.448	
AAD	2.406	0.650	1.186	3.953	0.284	0.665
ADD	2.764	0.859		4.075	0.365	
AADD	2.292	0.731		3.564	0.340	

	MP2/classic Hirshfeld			MP2/iterative Hirshfeld		
	O	HB H	non-HB H	O	HB H	non-HB H
A	2.778		1.105	4.575		0.578
D	3.096	0.885	1.248	4.673	0.361	0.625
AD	2.748	0.765	1.168	4.391	0.287	0.590
DD	3.455	1.027		4.873	0.402	
AAD	2.406	0.631	1.138	4.039	0.246	0.595
ADD	2.744	0.827		4.122	0.325	
AADD	2.302	0.713		3.688	0.302	

[a] All values are in au.

molecules in the cluster. As was shown in a previous study on methanol clusters,[18] steric hindrance tends to decrease the values of polarizabilities. Another possible effect is the difference in the local field those molecules experience compared to other water molecules in the clusters.

Examining the values in Table 7 closely allows us to recognize a certain cooperativity effect between the atoms. For example, the polarizability values of the oxygen atoms that make one A-type HB decrease with the number of HBs the hydrogen atoms make in the same molecule: A > AD > ADD. A similar effect is present in the values of the oxygen atoms that make two A-type HBs: AA > AAD > AADD. Note that this effect is larger in the iterative Hirshfeld scheme. In addition, the values for the HB Hs decrease in the order of D > AD > AAD and DD > ADD > AADD.

5. Conclusions

The polarizabilities of MSA and hydrated MSA clusters with up to five water molecules were calculated using the B3LYP and MP2 methods. The polarizabilities and the charges of the different entities in the clusters were partitioned using both classic and iterative Hirshfeld schemes. The quality of the values obtained with the B3LYP level in this study is overall high, with global polarizabilities varying by less than 2% from the MP2 values and the trends in the partitioned polarizability values and charges being very similar at both levels of theory.

The atomic and molecular charges obtained using classic and iterative Hirshfeld schemes tend to disagree. While according to classic Hirshfeld scheme the SO_3H group has a negative charge and the methyl group has a positive charge, the iterative Hirshfeld scheme claims the opposite. The atomic charges in the iterative Hirshfeld scheme are signifi-

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cantly larger, especially for the sulfur atom, where the classic Hirshfeld scheme assigns a charge of 0.2 au, whereas the iterative Hirshfeld scheme assigns a charge above 2 au, thus corresponding better with the high oxidation state of the sulfur atom in MSA.

The large differences in atomic charges results also in large differences in the atomic polarizability values, where for example in the iterative scheme the sulfur atom has a significantly smaller contribution to the polarizability of MSA because of its high charge. Nevertheless, the values for the molecular polarizabilities obtained by eqs 6 and 7 in the both schemes are mostly similar. Both schemes reveal a strong relation between the number, type, and strength of hydrogen bonds and the polarizabilities of the different entities in the cluster. A lack of consistency in the definition of the total molecular polarizability was detected for the iterative Hirshfeld scheme that most likely is connected to a larger shift of the center of the electron density of the molecule from its geometrical center, which is being used as a reference point for the intramolecular charge delocalization contribution.

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