

Effect of Structural Parameters on the Polarizabilities of Methanol Clusters: A Hirshfeld Study

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Abstract: The polarizabilities of fifty methanol clusters $(\text{CH}_3\text{OH})_n$, $n = 1$ to 12, were calculated at the B3LYP/6-311++G** level of theory and partitioned into molecular contributions using the Hirshfeld-I method. The resulting molecular polarizabilities were found to be determined by the polarizabilities of the two parts of the molecule, the hydrophilic hydroxyl group and the hydrophobic methyl group, each exhibiting a different dependency upon the local environment. The polarizability of the hydroxyl group was found to be dependent on the number, type, and strength of the hydrogen bonds a methanol molecule makes, whereas the polarizability of the methyl groups is mostly influenced by sterical hindrance. The findings were compared with the results obtained in a previous study on water clusters. The influence of the BSSE correction was investigated and found to increase polarizability values by up to 8.5%.

1. Introduction

One factor determining the impact of liquid methanol on today's chemistry is its very frequent use as a solvent. For this reason, comprehensive studies have investigated the structure of liquid methanol as well as its properties. Although the earlier studies could use only experimental techniques,^{1–7} as the power of computational chemistry was yet to be established, nowadays it is common to find experimentalists and theoreticians together tackling this inexhaustible subject together.^{8–11}

However, computational studies of liquids still form a challenge, since the system to be investigated has an extensive size and is of a dynamic nature. Therefore, many of the studies employ hybrid quantum mechanical/molecular mechanical (QM/MM) methods or conduct MD simulations.^{12–17} Another possibility is to apply conventional electronic structure methods on methanol clusters in the gas phase, which allows for the examination of the properties of the clusters in closer detail.^{18–23} Recently, Boyd et al.²³ have published an extensive study on the potential surfaces

of methanol clusters $((\text{CH}_3\text{OH})_n, n = 2$ to 12), considering various types of isomers for each aggregation number. A selection of fifty of those clusters will be used in this study with the purpose of studying the polarizability of the methanol molecules within the clusters.

For solvents, different properties of the solvent and solute can influence the resulting interaction. As an attempt to understand this complex system, one may first start looking at the pure solvent, where each molecule can be considered as a solute, surrounded by similar solute molecules. Among the different properties that can be studied, electronic properties, and polarizability in particular, are of substance.^{24–26} Furthermore, when considering polar solvents as methanol, the relation between the properties of the solvent molecules and the hydrogen bonds that the solvent molecules make with each other and with the solute is of great importance.

Although the structure of a single molecule in a cluster is simple to obtain, the knowledge of its properties usually requires a partitioning method, of which the Hirshfeld method is our method of choice. The Hirshfeld method^{27,28} was introduced in 1977 primarily as a method for the partitioning of electron density for the purpose of obtaining atomic charges and dipoles. Later it was extended for the partitioning of properties such as quadrupole moments,²⁹ similarities,^{30,31}

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Fukui functions,^{32–34} energies,³⁵ and polarizabilities.³⁶ In our previous study,³⁶ the Hirshfeld method was used for the partitioning study of polarizabilities of water molecules in water clusters. In that study the molecular polarizabilities were found to be strongly dependent upon the hydrogen bond network and, moreover, to have highly transferable values between the clusters. Methanol clusters form a greater challenge, possessing a hydrophobic methyl group that disturbs the ordered hydrogen-bond network that can be found in water clusters. The balance between the polar and nonpolar parts of the molecule and the influence of the hydrogen bond network will be a determining factor for eventual polarizability of the solvent molecules and the resulting interactions with the solute. Recently, a new version of the Hirshfeld method has been introduced by Bultinck et al.³⁸ improving some aspects of the conventional method, such as arbitrariness of the choice of the promolecular density and the restriction of applicability to neutral systems. In this study, the revised method is applied for the first time to the study of polarizabilities. As a result, the obtained numerical results cannot be compared with those obtained in ref 36, yet the trends that are observed using both methods remain unchanged.

2. Method

The partitioning of polarizabilities of clusters into atomic and molecular contributions is accomplished in this study by means of the Hirshfeld method.^{27,28} Using this scheme, elements of the total polarizability tensor of the cluster can be reproduced exactly from atomic contributions

$$\alpha_{ij} = \sum_{A=1}^N (\alpha_{ij}^A + q_A^i j_A) \quad (1)$$

where i and j stand for the Cartesian directions x , y , or z . In this equation the summation runs over all atoms A in the system, α_{ij}^A is referred to as an intrinsic atomic polarizability, while q_A^i is referred to as a perturbed charge, i.e., it is the atomic Hirshfeld charge calculated using the first-order perturbed density matrix for an electric field oriented along the i axis.³⁶ The second term in the summation in eq 1 can thus be interpreted as a charge delocalization polarizability, which describes the contribution of charge transfer between the atoms to the total polarizability of the system. The intrinsic atomic polarizability α_{ij}^A and the perturbed atomic charge q_A^i are given by

$$\alpha_{ij}^A = \int (i - i_A) \omega_A(\vec{r}) \rho^i(\vec{r}) d\vec{r} \quad (2)$$

and by

$$q_A^i = \int \omega_A(\vec{r}) \rho^i(\vec{r}) d\vec{r} \quad (3)$$

respectively. In these i_A is the Cartesian coordinate of atom A in the i direction, and ρ^i and ρ^j are the first-order perturbed density matrices obtained using a coupled perturbed Kohn–Sham procedure for an electric field perturbation in the i and j direction, respectively. $\omega_A(\vec{r})$ is the Hirshfeld weight function of atom A .

To obtain the intrinsic polarizability of a molecule in a cluster, one needs to sum these quantities over the atoms of the molecule:

$$\alpha_{ij}^{int(mol)} = \sum_{A(mol)} \alpha_{ij}^A \quad (4)$$

Finally, the total polarizability of a molecule in a cluster is obtained by adding the intramolecular charge delocalization contribution:

$$\alpha_{ij}^{tot(mol)} = \alpha_{ij}^{int(mol)} + \sum_{A(mol)} q_A^i j_A \quad (5)$$

This intramolecular charge delocalization contribution is translationally invariant, when it is defined with respect to the geometrical center of the molecule.

In this study, only the isotropic part of the polarizability, which is independent of the orientation of the system, will be discussed. Therefore the values reported in this paper for the polarizabilities are always the trace of the corresponding polarizability tensor:

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (6)$$

In the classic version of the Hirshfeld method the weight function is constructed from the free atomic densities ρ_A^0 of the atoms in the system:

$$\omega_A(\vec{r}) = \frac{\rho_A^0(\vec{r})}{\sum_{B=1}^N \rho_B^0(\vec{r})} \quad (7)$$

Recently, Bultinck et al. have revised this method and proposed an iterative version, Hirshfeld-I, which is more in line with information theory.³⁸ In this revised version, the weight function is constructed in each iteration from the atomic densities ρ_A^{n-1} that normalize to the atomic populations that were obtained during the previous iteration:

$$\omega_A^n(\vec{r}) = \frac{\rho_A^{n-1}(\vec{r})}{\sum_{B=1}^N \rho_B^{n-1}(\vec{r})} \quad (8)$$

This procedure is repeated until convergence of the atomic populations. The converged weight function can then be used for the partitioning of properties such as polarizabilities, according to eqs 2 and 3.

3. Results and Discussion

The polarizabilities of fifty methanol clusters, with aggregation numbers ranging between 2 and 12, were calculated at the DFT level, using the B3LYP/6-311++G(d,p) method and the Gaussian03³⁹ program. The calculated polarizabilities were subsequently partitioned using the program STOCK.²⁸ The geometries used were those optimized by Boyd et al.²³ in a study of the energies of the methanol clusters.

Three different types of methanol clusters were used in this study: (1) Chainlike structures, with aggregation numbers ranging between $n = 2$ and $n = 12$, noted as nc . For

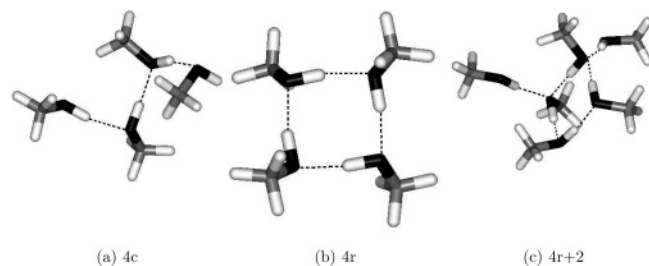


Figure 1. The three different types of clusters that were used in the study.

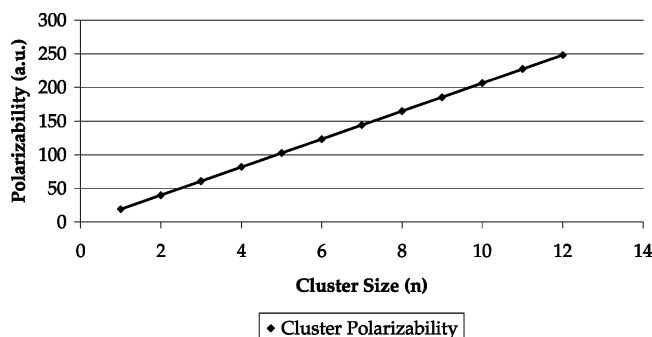


Figure 2. Isotropic part of the cluster polarizability (eq 6) for different aggregation numbers n .

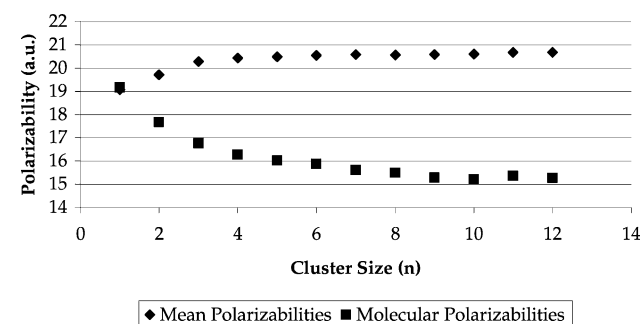


Figure 3. Polarizability of a molecule in a cluster of size n . Diamonds are mean polarizabilities and squares are molecular polarizabilities (eq 5).

example, cluster 4c is depicted in Figure 1a. (2) Ring structures, with aggregation numbers ranging between $n = 3$ and $n = 12$, noted as nr . For example, cluster 4r is depicted in Figure 1b. (3) Substituted ring structures, where the substituents can be a number of single methanol molecules (denoted as $nr + m$), a number of chains of two methanol molecules (denoted as $nr + md$), or a number of chains of three methanol molecules (denoted as $nr + mt$). Only in the first of these cases structures were considered with $m > 1$; in all other cases $m = 1$. For example, cluster $4r + 2$ is depicted in Figure 1c.

Figure 2 illustrates the isotropic cluster polarizabilities as function of the size of the cluster. The relation between the size of the cluster and the isotropic cluster polarizability appears to be highly linear, with an $R^2 = 1.0000(1)$ for a two parameter fit, suggesting a good transferability of the polarizability values between the molecules in the different clusters. Figure 3 displays both the mean molecular polarizabilities, obtained by dividing the isotropic cluster polar-

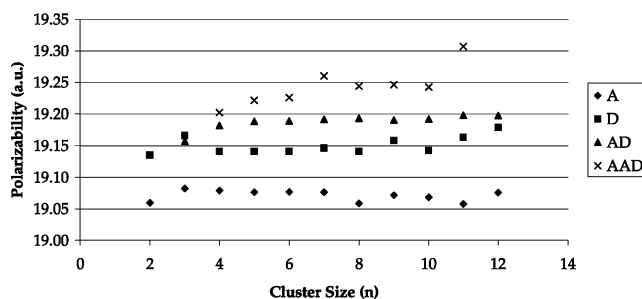


Figure 4. Polarizabilities of isolated molecules for the four types of hydrogen-bonded methanol molecules.

izability by the aggregation number n , and the molecular polarizabilities, obtained from eq 5. The mean molecular polarizability increases for the smaller clusters and reaches saturation quickly for clusters with an aggregation of 4–5 at value around 20.7 au, whereas the molecular polarizability decreases with the size of the cluster and stabilizes at a value around 15.3 au only at larger clusters of aggregation 9–10. The difference in behavior between these two properties is due to the charge delocalization contribution, which is dependent on the coordinates and thus on the size of the cluster, as can be seen from eq 1. The charge delocalization contribution increases for larger clusters as result of the extension of the volume of the system, resulting in the increase of mean molecular polarizabilities. However, Figure 3 also illustrates that the polarizability of a methanol molecule in a cluster decreases in going from gas phase to condensed phase, as the values for the molecular polarizability obtained from eq 5 decrease with the size of the cluster. A similar effect was observed for a water molecule in a cluster in ref 36. This behavior can be attributed to different effects, such as the change in geometry of the methanol molecule, the hydrogen-bonding network that the methanol molecules engage in in the clusters, the change of net charge of the molecule in the cluster, steric hindrance, and other local effects.

To investigate the effect of the change in geometry on the polarizability of the methanol molecules in the different clusters, the coordinates of each molecule were used to calculate its polarizability in the absence of the rest of the molecules in that particular cluster. These “isolated” polarizabilities were calculated using the same method and basis set as were used for the calculation of the polarizabilities of the clusters. The average “isolated” polarizability was found to amount to 19.24 au, being 0.17 au above the polarizability of an optimized single methanol molecule (19.07 au). This change in the polarizability on can be ascribed to the geometry deformation due to the formation of hydrogen bonds between the methanol molecules.

A methanol molecule can form up to three hydrogen bonds with neighboring molecules, by either acting as an acceptor through the oxygen atom (A) or by donating a hydrogen atom into the bond (D). In the clusters examined in this study, four different types of methanol molecules are present, namely methanol molecules of type A, type D, type AD, and type AAD. Figure 4 depicts the “isolated” polarizabilities for the four types of methanol molecules as a function of

Table 1. Average “isolated” Polarizabilities and Average BSSE Corrected “isolated” Polarizabilities of the Four Types of Methanol Molecules^a

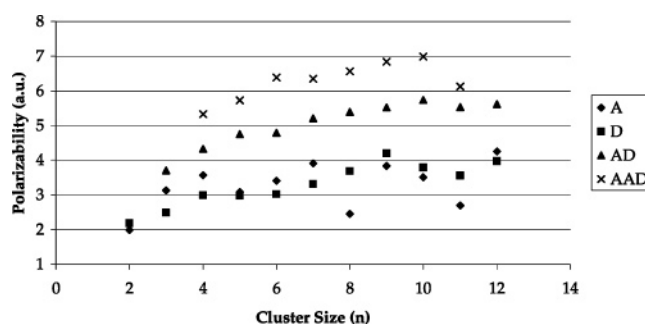
<i>n</i>	“isolated” polarizabilities				BSSE corrected polarizabilities			
	A	D	AD	AAD	A	D	AD	AAD
2	19.06	19.14			19.71(3.31)	19.81(3.39)		
3	19.08	19.17	19.16		20.10(5.07)	20.03(4.36)	20.22(5.26)	
4	19.08	19.14	19.18	19.20	20.09(5.01)	20.18(5.13)	20.47(6.27)	20.61(6.81)
5	19.08	19.14	19.19	19.22	20.13(5.22)	20.17(5.08)	20.58(6.76)	20.71(7.19)
6	19.08	19.14	19.19	19.23	20.28(5.93)	20.21(5.29)	20.58(6.77)	20.87(7.86)
7	19.08	19.15	19.19	19.26	20.28(5.93)	20.28(5.61)	20.67(7.17)	20.93(7.98)
8	19.06	19.14	19.19	19.24	20.03(4.87)	20.36(6.00)	20.73(7.40)	20.96(8.20)
9	19.07	19.16	19.19	19.25	20.22(5.67)	20.49(6.51)	20.77(7.59)	21.00(8.33)
10	19.07	19.14	19.19	19.24	20.10(5.13)	20.42(6.25)	20.79(7.69)	21.01(8.42)
11	19.06	19.16	19.20	19.31	19.97(4.56)	20.38(5.97)	20.76(7.50)	20.96(7.87)
12	19.08	19.18	19.20		20.21(5.617)	20.48(6.37)	20.78(7.63)	

^a The values between brackets give the percentage of the contribution of BSSE. All values are in au.

the size of the clusters. Each additional hydrogen bond appears to increase the “isolated” polarizabilities of the methanol molecules by lengthening the bonding distances and thus increasing the volume of the molecule. A D-type hydrogen bond has a larger effect than an A-type hydrogen bond, as the mean “isolated” polarizabilities of the former type of methanol molecules are larger than those of the latter type. The “isolated” polarizabilities are approximately independent of the size of the cluster, although the value for the AAD-type methanol molecule for aggregation number $n = 11$ seems to be exceptionally high. However, keeping in mind that Figure 4 displays only an average value, computed on all molecules of a given type within a cluster, the value for this point is still within the observed deviation (0.04 au). Although values of this magnitude also appear for the lower aggregation numbers, they are eventually averaged out, whereas for aggregation number $n = 11$ this is the only point available.

In order to distinguish the effect of geometry on the polarizability of a molecule from other effects, it is convenient to look at the difference between the “isolated” molecular polarizabilities and the molecular polarizabilities (eq 5) of the methanol molecules in the clusters. As such, the Basis Set Superposition Error (BSSE) can be taken into account, as the basis functions situated on neighboring methanol molecules in the clusters may influence the polarizability significantly. Furthermore, one cannot assume the BSSE error to be constant because of the wide range of aggregation numbers of the clusters. Indeed, the BSSE error of a cluster with aggregation number $n = 3$ can be expected to be smaller than the BSSE error of a cluster with aggregation number $n = 10$.

The BSSE error was calculated by means of the counterpoise method.^{40,41} The polarizability of a given molecule was calculated by replacing all other atoms in the clusters by ghost atoms. The average values of those BSSE corrected “isolated” polarizabilities are compared with the previously mentioned “isolated” polarizabilities in Table 1, for each type of methanol molecule. The BSSE corrected values are larger, as expected, increasing for the smaller clusters and stabilizing for the larger clusters. The correction also appears to increase with the number of hydrogen bonds, reaching 1.64 au for the AAD-type water molecules, which amounts to approximately 8.5% of the original value.

**Figure 5.** The average difference ($\Delta\alpha^{mol}$) between the BSSE corrected “isolated” polarizabilities and the total molecular polarizabilities for the four types of methanol molecules.

Taking the difference between the BSSE corrected “isolated” polarizabilities and the total molecular polarizabilities, obtained from eq 5, yields the change in the polarizability of the methanol molecule due to the rearrangement of the electron density, that is brought forth by bonding effects, such as hydrogen bonding, and nonbonding effects, such as steric hindrance or other local effects. Figure 5 shows the average change in polarizability ($\Delta\alpha^{mol}$) for the four types of methanol molecules. The values are lowest for the A- and D-type methanol molecules, that appear to be overlapping, and highest for the AAD-type methanol molecules. Note that higher $\Delta\alpha^{mol}$ values imply lower total molecular polarizabilities, in agreement with the values depicted in Figure 3. All the values tend to increase slightly for the smaller clusters and stabilize for the larger clusters. To understand this behavior it is necessary to compute the contributions of the different parts of the molecules to the intrinsic polarizabilities. A methanol molecule consists of a hydrophilic part, namely the hydroxyl group, and a hydrophobic part, namely the methyl group. Since the hydroxyl group can take part in the hydrogen-bonding network, one can expect the intrinsic polarizabilities to be directly influenced by it. On the other hand, the methyl groups do not make hydrogen bonds and can therefore only experience a secondary effect of the hydrogen-bonding network on their intrinsic polarizabilities. Furthermore, the methyl groups are much more voluminous than the hydroxyl group and can therefore be influenced to a greater extent by steric hindrance. Figures 6 and 7 illustrate

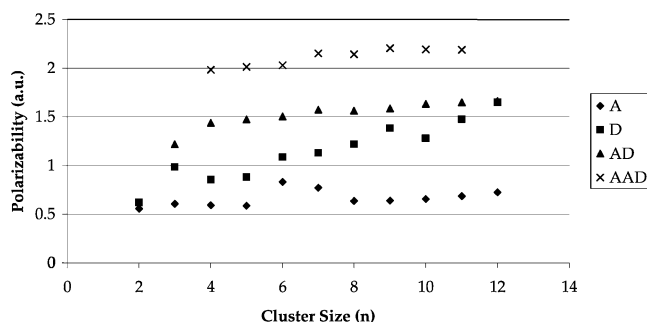


Figure 6. The average difference between the contribution of the hydroxyl groups to the BSSE corrected “isolated” polarizabilities and the molecular polarizabilities ($\Delta\alpha^{OH}$) in the four types of hydrogen-bonded methanol molecules.

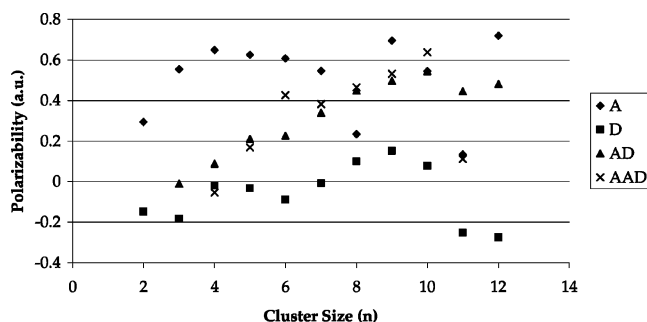


Figure 7. The average difference between the contribution of the methyl groups to the BSSE corrected “isolated” polarizabilities and molecular polarizabilities ($\Delta\alpha^{CH_3}$) in the four types of hydrogen-bonded methanol molecules.

the difference in intrinsic polarizabilities obtained from the BSSE corrected “isolated” molecules and the clusters, for the hydroxyl ($\Delta\alpha^{OH}$, Figure 6) and methyl ($\Delta\alpha^{CH_3}$, Figure 7) groups, respectively. The polarizabilities of the BSSE corrected “isolated” molecules are obtained by applying the same Hirshfeld-I scheme as was done for the clusters. The intrinsic polarizabilities of a group are obtained by summing over the intrinsic polarizabilities of the atoms in the group, analogous to eq 4. The values for the hydroxyl groups are again separated into four different populations, increasing with the number of hydrogen bonds and a D-type hydrogen bond having a greater influence on the values ($A < D < AD < AAD$), whereas the values for the methyl group exhibit less obvious behavior.

On the other hand, in Figure 7 the A-type molecules have the highest values and the D-type molecules have the lowest values. This difference in behavior from the $\Delta\alpha^{OH}$ causes the overlap in the values of those two types of molecules in Figure 5. The values for the AD- and AAD-type molecules in Figure 7 overlap and are situated between the values for A- and D-types, which may suggest that the polarizabilities of the methyl groups are not significantly influenced by the hydrogen-bonding network and that the primary effect for the change in their polarizability is due to local effects such as steric hindrance.

To investigate the sterical effects further, the structures of the different methanol clusters will be examined closer for the three types of methanol clusters.

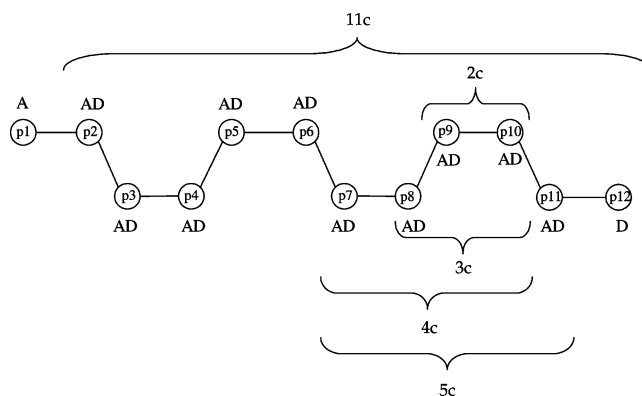


Figure 8. Schematic illustration of the positioning nomenclature of the methanol molecules in the chainlike clusters. The type of hydrogen-bonded methanol molecules is illustrated for the 12c cluster.

3.1. Chains. The chainlike clusters have a structure that allows analysis of the dependence of polarizabilities on the local environment in a straightforward way. The presence of a methyl group in the molecules causes this group of clusters to have a bent structure for the lower aggregation number and a helical structure for the larger aggregation numbers. The chains were constructed in a way that preserves the local environment at a given position throughout the range of the clusters. This local environment is characterized by the length of the hydrogen bonds the molecule makes and the steric hindrance it undergoes from the neighboring molecules.

The chains consist of an A-type molecule at one end and a D-type molecule at the other end, with several AD-type molecules in between connecting them. Each cluster nc was constructed by adding a molecule either to the A end or the D end of an $(n - 1)$ cluster, preserving the topology of the $n - 1$ molecules of the previous cluster. This way, the structure and the surroundings of a molecule in a certain position in the chain is approximately unchanged throughout all the clusters, even after reoptimization. This allows analysis of the correlation between the polarizability values of the molecules at a certain position and the specific environment at that position.

This concept is schematically illustrated in Figure 8. The two molecules that are grouped together under the label of 2c are the molecules that constitute the starting dimer, the left one being an A-type molecule and the right one being a D-type molecule. The trimer is constructed by adding a molecule to the left side of the dimer. The A-type molecule in the dimer becomes now an AD-type molecule in the trimer. This process is repeated to construct the 4c cluster. For the 5c cluster, a molecule was added to the right D-type side of the 4c cluster. As result, the molecule that was consistently a D-type molecule for clusters 2c to 4c, becomes an AD-type molecule in the 5c cluster. After subsequent addition of another seven molecules to either the A-side or the D-side one finally arrives to the structure of the 12c cluster. The molecules are then assigned numbers according to their position in the 12c cluster, which are also used to label the molecules in the smaller cluster. During the construction of the clusters, the molecules were more

Table 2. Average $\Delta\alpha^{mol}$ s, $\Delta\alpha^{OH}$ s, and $\Delta\alpha^{CH_3}$ s of the Different Types of Molecules in the Chainlike Clusters^a

position	$\Delta\alpha^{OH}$			$\Delta\alpha^{CH_3}$			$\Delta\alpha^{mol}$		
	A	D	AD	A	D	AD	A	D	AD
p1	1.25			1.1			4.26		
p2	1.21		2.31	0.55		0.64	2.70		4.33
p3	1.19		2.14	1.06		1.00	3.52		5.14
p4	1.17		2.16	1.07		1.28	3.84		5.63
p5	1.16		2.28	0.52		0.45	2.45		4.70
p6	1.28		2.52	1.00		1.13	3.66		5.89
p7	1.05		1.93	1.05		1.47	3.33		5.69
p8	1.11		2.47	0.94		1.31	3.14		6.11
p9	0.88		2.46	0.54		0.85	2.00		5.32
p10		1.26	1.92		0.10	0.90		2.51	4.65
p11		1.53	2.41		0.13	0.44		2.76	4.66
p12		2.20			0.21			3.84	

^a According to their placement in the chain—all values are in au.

frequently added to the A-side of the previous cluster than to the D-side. As result, the two molecules that originally constituted the dimer are located at the ninth and tenth position in the 12c cluster. This means that the A-type molecules can only occupy positions p1 to p9, while D-type molecules can only occupy positions p10 to p12.

Table 2 summarizes the average $\Delta\alpha^{OH}$ s, $\Delta\alpha^{CH_3}$ s, and the $\Delta\alpha^{mol}$ s of the different types of molecules, according to their position in the molecule. The averaging is performed as follows: the molecules that occupy position px are first separated according to their type (A, D, or AD), and then the values for each type at a given position are averaged. The values for the hydroxyl group follow the already established order $A < D < AD$. The values of $\Delta\alpha^{OH}$ for the A-type molecules have an average of 1.15 au, with an evident outlier at position p9, which has a value of 0.88 au. This low value can be explained by the relatively longer hydrogen bond in the dimer, 1.9 au, whereas the average hydrogen bond in the larger clusters is around 1.73 au. The hydrogen bond length is defined here as the distance between the hydrogen atom and the oxygen atom that participate in the bond. This effect can also be seen in the average value of $\Delta\alpha^{OH}$ of D-type molecules at position p10 (1.26 au). There are two molecules that contribute to this value, namely the molecules in this position in clusters 2c and 3c. Both molecules take part in longer hydrogen bonds, the value for the 3c cluster being 1.81 au, causing the $\Delta\alpha^{OH}$ of the D-type molecules at this position in the chain to be lower than the average value of 1.68 au. The hydrogen bond at this position is consequently longer throughout the whole range of the clusters, as part of the conservation of the local surroundings of the molecules. As result, also the values of $\Delta\alpha^{OH}$ of the AD-type molecules at position p10 (1.92 au) are lower than the average (2.26 au). It can also be observed that the length of the hydrogen bond has a larger effect on the polarizability of the hydrogen atom than that of the oxygen atom participating in the bond, which will be discussed further at a later stage. Similar arguments can be used to explain the outlier at position p7 for the AD-type molecules. The average hydrogen bond length at this position is 1.77 au, which is higher than the average by 0.04 au.

Table 3. Average $\Delta\alpha^{OH}$ s, $\Delta\alpha^{CH_3}$ s, and $\Delta\alpha^{mol}$ s of the Methanol Molecules in the Clusters with Ring Structures^a

cluster size	$\Delta\alpha^{OH}$	$\Delta\alpha^{CH_3}$	$\Delta\alpha^{mol}$
3	1.78	0.32	3.65
4	2.06	0.39	4.21
5	2.20	0.69	4.84
6	2.16	0.51	4.46
7	2.25	0.77	4.92
8	2.27	0.89	5.20
9	2.40	0.97	5.42
10	2.42	0.97	5.49
11	2.41	0.97	5.42
12	2.46	1.14	5.80

^a All values are in au.

The values of the methyl group again follow a less obvious pattern. The D-type molecules have low values, around 0.15 au, indicating that the intrinsic polarizabilities of the atoms in the methyl group are only slightly influenced by the transition from gas phase to a cluster. The methyl groups in the D-type molecules are not influenced by the hydrogen bond formation and undergo little steric hindrance due to their position at the end of the molecule. The values for the A- and the AD-types molecules are slightly higher, cover a wider range of values than in the case of the hydroxyl groups, and overlap extensively. The overlap of the values indicates that the polarizabilities of the atoms in the methyl groups in those two types of molecules are also not strongly influenced by the type or number of hydrogen bonds the molecule forms. The change in the values in going from single molecules to a cluster must therefore be sought in the steric hindrance effect. Although the A-type molecules are also placed at the end of the chain, they undergo more steric hindrance than the D-type molecules because they are connected to the chain through the oxygen atom, which is situated in the middle of the molecule, and not by the hydrogen atom, which is situated at the end of the molecule. The methyl groups are therefore oriented in such a fashion that they still undergo steric hindrance from the other methyl groups. It is also noticeable from Table 2 that the values for those two types of methanol molecules follow the same pattern. For example, the values at positions p2, p5, and p9 are considerably lower for both types of molecules. Examining the structures closely reveals that the methyl groups at those positions undergo less steric hindrance due to turns in the curve of the chain, resulting in a smaller change in the polarizabilities of those groups.

3.2. Rings. The ring structures, consisting only of AD-type molecules, allow a more thorough analysis of the factors that influence the polarizability within a single type. Table 3 summarizes the average $\Delta\alpha^{OH}$ s, $\Delta\alpha^{CH_3}$ s, and the $\Delta\alpha^{mol}$ s for the molecules in those clusters, according to the aggregation number. The values for the hydroxyl groups and the methyl groups, and as consequence also of the molecules, increase with the aggregation number. Two possible explanations for this behavior, that have been mentioned up till now, are the decreasing hydrogen bond lengths and the increasing steric hindrance. The correlation between the intrinsic polarizability of the hydrogen atoms and the length of the hydrogen bonds those atoms form was found to be 0.66, indicating that some connection must exist between those

two properties but that the polarizabilities must also be influenced by other factors. The polarizabilities seem to be influenced by substantial changes in the length of the hydrogen bonds but are less straightforwardly dependent on small changes. Moreover, there seems to be no correlation whatsoever between the length of the hydrogen bond and the intrinsic polarizability of the oxygen atoms, as has been noticed in the previous subsection. This finding is somewhat surprising, in light of the results that were obtained on water clusters in previous work, where correlations of 0.979 and 0.948 were found between the length of the hydrogen bonds and the intrinsic polarizabilities of the hydrogen atoms and oxygen atoms in DA-type water molecules, respectively. A possible explanation in this change of behavior is the more complicated structure of the methanol clusters, where new effects come to light, influencing the polarizabilities of the atoms and therefore reducing the correlation. One of the effects is the steric hindrance, which was found to increase the $\Delta\alpha^{CH_3}$ in the previous section and can therefore be responsible for the increasing trend in the clusters with the ring structures.

Another possible influencing factor on the polarizabilities can be the charge of the molecules. The reorganization of the charge density in going from gas phase to cluster can result in a net charge of the molecule in the cluster and a rearrangement of the charge within the molecule. The atomic charges of the atoms in the methanol clusters were calculated using the Hirshfeld-I scheme. The methanol molecules in the clusters were found to have a negligible net charge, never surpassing 0.01 au, but there seems to be a charge separation within the molecule, between the negatively charged hydroxyl groups and the positively charged methyl groups. The average value of the charge separation, defined as the absolute value of the difference of the charge of the hydroxyl group and the charge of the methyl group, is 0.37 au. A reasonable correlation was found between the $\Delta\alpha^{OH}$'s and the charges of the hydroxyl groups (-0.8932) and between the $\Delta\alpha^{CH_3}$'s and the charges of the methyl groups (0.9001). The polarizabilities of the hydroxyl groups increase with the negative charge, whereas the polarizabilities of the methyl groups increase with the positive charge, resulting in increasing polarizabilities of the molecules with the charge separation.

3.3. Substituted Rings. In this class of structures, the effect of the attachment of methanol molecules through a hydrogen bond was investigated by looking at the $\Delta\alpha^{OH}$'s, $\Delta\alpha^{CH_3}$'s, and $\Delta\alpha^{mol}$'s of a group of clusters $nr + m$ with $n = 5$ and m varying from 0 to 5. The values for the three different types of methanol molecules are summarized in Table 4.

The values for the hydroxyl groups follow the usual order of $D < AD < AAD$ and seem not to be influenced directly by the number of additional methanol molecules attached to the ring. For the methyl groups the situation is once again different: the D-type molecules have the lowest values that are independent of the size of the cluster or the extent of substitution and the values for the AD- and AAD-type molecules appear to be higher, to overlap and to increase with the extent of substitution. Also in this case, the increase

Table 4. Average $\Delta\alpha^{OH}$'s, $\Delta\alpha^{CH_3}$'s, and $\Delta\alpha^{mol}$'s of the Three Types of Methanol Waters in the Different $5r + m$ Ring Substituted Clusters

cluster	$\Delta\alpha^{OH}$			$\Delta\alpha^{CH_3}$			$\Delta\alpha^{mol}$		
	D	AD	AAD	D	AD	AAD	D	AD	AAD
5r	2.20			0.69			4.84		
5r+1	1.68	2.24	2.95	0.66	0.77	0.66	3.61	4.93	6.40
5r+2	1.57	2.31	2.93	0.41	0.89	1.07	2.99	5.41	6.49
5r+3	1.55	2.35	2.97	0.42	1.11	1.23	3.22	5.70	6.88
5r+4	1.84	2.18	3.00	0.64	1.68	1.31	3.95	6.07	7.07
5r+5	1.79		3.02	0.60		1.56	3.47		7.45

in the values can be ascribed to the rising steric hindrance between the different methyl groups, as more methanol molecules are placed on the ring. The combination of the trends established for the hydroxyl groups and for the methyl groups can be found in the values for the molecule. The values for the different types of molecules are all well separated and increase with the number of hydrogen bonds the molecules form. The values for the D-type molecules are stabilized around an average of 3.45 au, whereas the values for the AD and AAD-types molecules increase with the extent of substitution.

4. Conclusion

In conclusion, the polarizabilities of fifty different methanol clusters containing up to twelve methanol molecules were calculated at the B3LYP/6-311++G** level of theory and subsequently partitioned into atomic and molecular contributions using the Hirshfeld-I method. The obtained molecular polarizabilities were analyzed with respect to the local environment of the molecules in the clusters.

The results demonstrate that in order to understand the trends in the total molecular polarizabilities, the methanol molecules must be considered as a junction of two entities of different nature, namely a hydrophilic hydroxyl group and a hydrophobic methyl group. The polarizabilities of both groups exhibit a behavior that is fundamentally different from each other, but consequently throughout the total collection of the clusters, resulting in a somewhat complicated picture when superpositioned together to form the total polarizability of the molecule.

The polarizabilities of the hydroxyl group is in line with the findings that were obtained in a previous study on water clusters.³⁶ The values are strongly dependent on the hydrogen bond network that the molecules take part in, decreasing with a rising number of hydrogen bonds. The polarizabilities also tend to decrease with the strength of the hydrogen bond, although the correlation is not as optimal as in the case of the water clusters. This effect emphasizes the complexity of the relation between the local environment and the polarizability, that is far more pronounced in the case of the methanol clusters. In this case the structures are less orderly due to the presence of the methyl group, bringing new parameters into light that influence the polarizability and reduce the high correlation that is present in the case of the water clusters.

On the other hand, the polarizabilities of the methyl groups are not directly influenced by the hydrogen bond network

in the cluster and are mostly influenced by steric hindrance effects, that reduce the values. This effect is less extensive numerically, amounting to only 50% of the effect of the hydrogen-bonding network on the polarizabilities of the hydroxyl groups.

As a result of the those deviating behaviors, the polarizabilities of the methanol molecules in the clusters are not as strongly dependent on the hydrogen bond network as was found in the case of water clusters. The effect of steric hindrance contributes to greater deviation in the values within each group of molecules, leading to occasional overlap. The values also tend to decrease with the aggregation number, as steric hindrance is generally more substantial in larger clusters. Another important difference between water and methanol clusters is the absence in the latter of a significant intermolecular charge transfer, which influences the polarizability. The difference between water clusters and methanol clusters will be further explored in future work by examining additional local effects, such as the variation of the local field.

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