The Effect of Intermolecular Interactions in Some Water Clusters and Hydrates of the Hydronium and Hydroxyl Ions, on their Polarisability and Hyperpolarisabilities. A Comparative Study

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The polarisability and hyperpolarisabilities of $(H_2O)_n$, $H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$ are computed by the CHF-PT-EB-CNDO method. The basis set has been optimized with respect to the polarisability and second hyperpolarisability of H_2O. The effect of intermolecular interactions, in the water clusters and the hydrates of the ions on their polarisability and hyperpolarisabilities, and their variation with charge, shape and size of the aggregates is discussed.

1. Introduction

It has been found that the electric dipole moment of the H_2O molecule in ice is greater than the moment of an isolated water molecule (which is 1.84 D), due to the electric field of the neighbouring molecules [1].

Several values have been reported for the dipole moment of a water molecule in the liquid or solid state [1–6]. For example Onsager and Dupuis estimated the dipole moment of a water molecule in ice as being 3.67 D [1, 5]. More recent values are 2.91 D and 2.93 D [2, 6].

Considering the increased polarity of the water molecules in ice [6], the charge transfer (there is evidence that it plays an important role in H-bonded complexes [7a]), which has been associated with large electric nonlinearities [7b], as well as the possibility that some of the bulk properties may be interpreted in terms of relatively small agregates [7c], it was considered useful to study the dipole moment (μ), the polarisability (α) [8a, b], its anisotropy (ζ^2) and the hyperpolarisabilities (β and γ) of some water clusters (Figure 1).

It is known that the dependence of electric nonlinearities on environmental interactions is of current interest [9–11]. Further the influence of these interactions on the electric hyperpolarisabilities has also been demonstrated experimentally [12]. The present analysis aims at illuminating the effect of intermolecular interactions, existing in water clusters, on their dipole moment, polarisability and hyperpolarisabilities. This is achieved by changing the various parameters (charge, size, configuration) of the clusters and observing the changes which occur in these properties. Then the resulting trends are discussed and generalized.

Of essential importance in the analysis of the present results is the cooperative effect (that is each interaction enhances the effect of the next one), which has been previously observed in water aggregates for hydrogen bond energies and dipole moments [13]. Qualitative suggestions of the cooperative effect in the interactions between water molecules were reported in 1957 (as Minton states [14a] by Frank and Wen [14b]). The present comparative study allows one to monitor the effect of cooperativity on five properties (the dipole moment, the polarisability, its anisotropy and the two hyperpolarisabilities β and γ), as well as the variation of this effect with changes in structure.

For this study several hydrates of the hydronium and hydroxyl ions have also been employed (Figures 2, 3). It is known that the solvated ions have been the subject of a large number of works aimed at illuminating various aspects of their structure and properties [15–17].

To the best of our knowledge this is the first study reported in the literature concerning the hyperpolarisabilities of the hydronium and hydroxyl hydrates. Thus the results reported here are complementary to previous studies which deal with the properties of H-bonded complexes (neutral and charged).

The tensor components required to determine μ, α, β and γ of the considered aggregates have been com-

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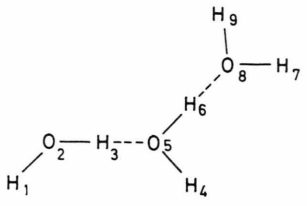

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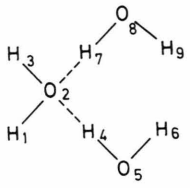

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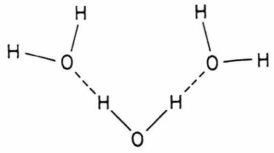

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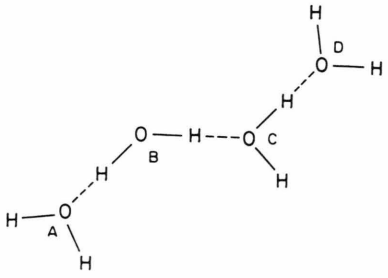

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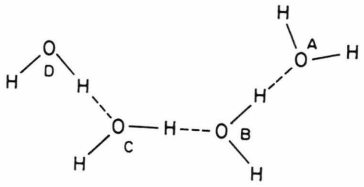

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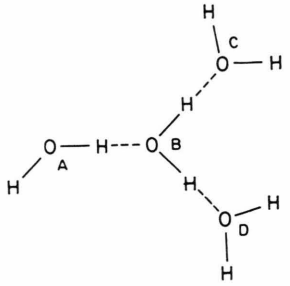

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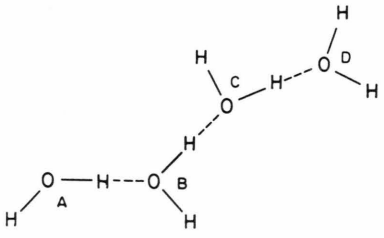

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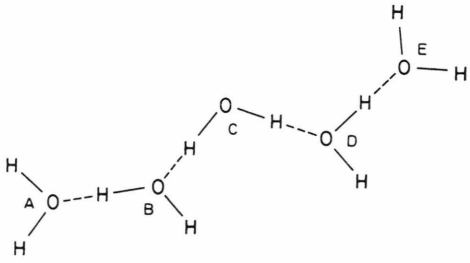

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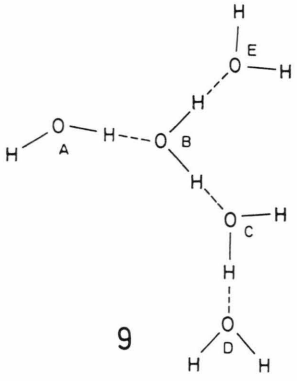

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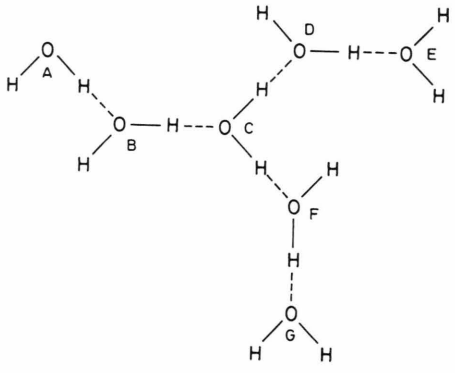

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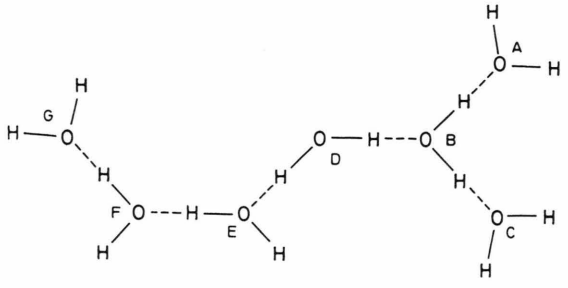

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Fig. 1. Structure of the various configurations of $(H_2O)_n$, where $n = 3-5, 7$.

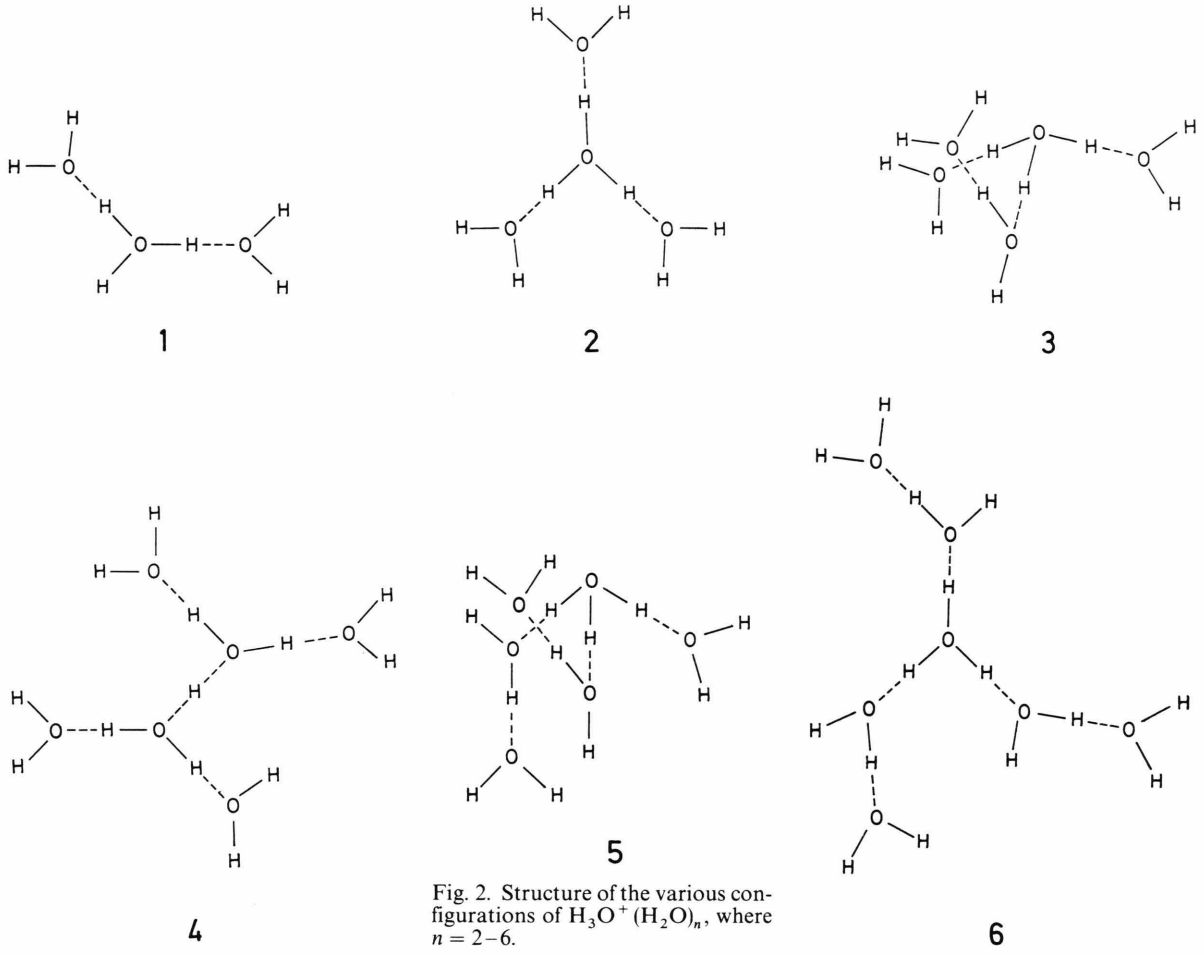

Fig. 2. Structure of the various configurations of $H_3O^+(H_2O)_n$, where $n = 2-6$.

puted by employing the CHF-PT-EB-CNDO method [11, 18–20]. Several precautions have been taken to safeguard the validity of the reported findings.

II. Method

A) Definition and Justification of the Model

Our CHF-PT-EB-CNDO method relies on:

(a) An extended basis (EB)CNDO [21 a] wave function. This model uses the standard CNDO/2 parameters [21 a]. For extended basis sets the parameter k [21 b], which premultiplies the bonding parameters, is also used. This parameter allows for different interactions between the various orbitals (occupied-occupied, virtual-virtual and occupied-virtual). It is known that several authors have used the CNDO approximations for problems related to polarisabilities and hyperpolarisabilities [22].

(b) McWeeny's et al. [23] coupled Hartree-Fock perturbation theory (CHF-PT). This method involves a direct self-consistent calculation of the perturbed Fock-Dirac density matrix, it avoids the intermediate determination of perturbed orbitals and offers quite substantial computational advantages [24]. Further it has been argued that large time savings are attained by employing perturbation theory in preference to the finite field approach on which most calculations of electric properties rely [25].

(c) Carefully chosen basis sets, with exponents optimized to the properties (polarisabilities and/or hyperpolarisabilities) of some representative molecules. These bases are then used for the computation of the properties of molecules with similar structure [11, 18–20].

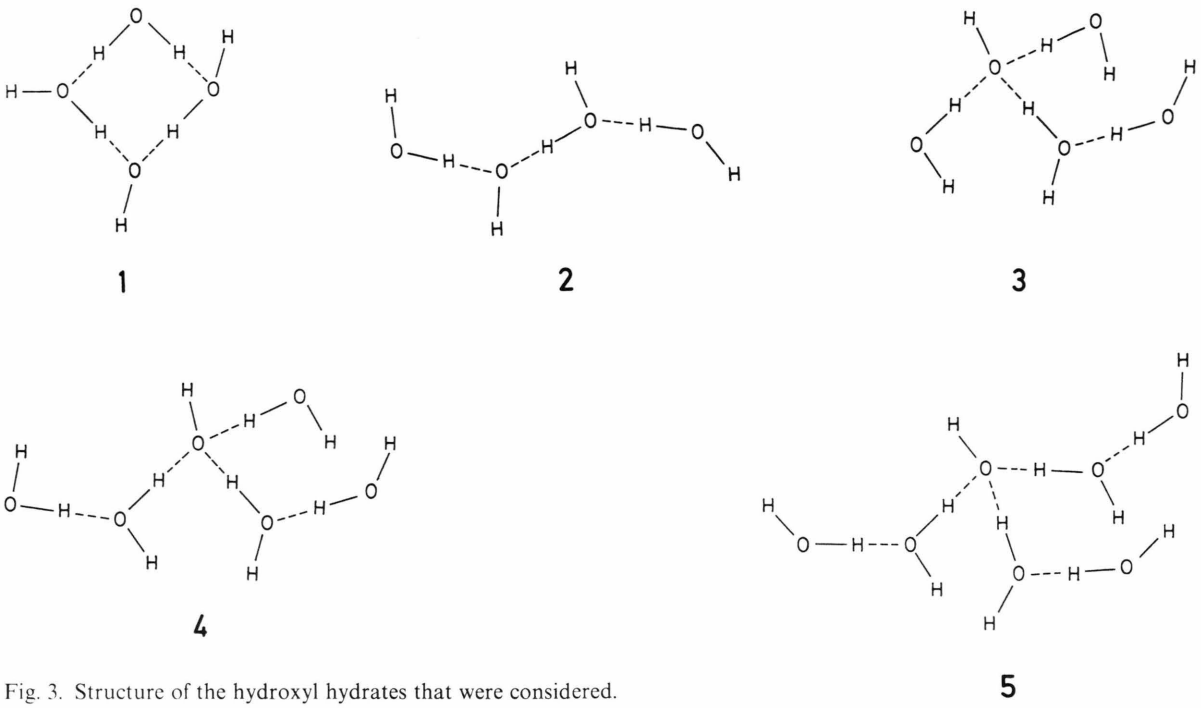

Fig. 3. Structure of the hydroxyl hydrates that were considered.

It is known that the quality of the basis set greatly affects the accuracy of quantum chemical calculations in many cases [26] and especially for the second hyperpolarisability, the choice of the right basis set is of paramount importance [18, 19a, 27]. Thus we have carried out extensive experimentation with numerous basis sets, involving up to d orbitals for H and up to f orbitals for C, N and O. Methane [18a], ethylene [18b], ammonia [19a] and water [28] have been chosen as test molecules on which the performance, as to the accurate determination of hyperpolarisabilities (and polarisabilities), of the basis sets has been tested. Analysis of the results has shown that high l AOs like f orbitals for C, N and O and d orbitals for H are sufficient (they can lead to reasonable results) but not necessary, within a semiempirical framework, in particular if one takes advantage of the freedom allowed within such schemes [18a, 18b, 19a].

It is added that correlation effects, which are significant for the accurate determination of γ [29] are taken into account at least partially, through the optimization of the basis set with respect to some judiciously chosen experimental results.

The CHF-PT-EB-CNDO method has given results, for the polarisability and the second hyperpolarisability of a large number of molecules, belonging to several classes of organic molecules (alkanes, polyenes, aromatics, amines, amides etc.) in good agreement with the experimentally determined data [11, 18, 19a, 19b]. These favourable comparisons give confidence in the model and in its aptitude for the present study.

The deficiency of standard CNDO/2 [21] to give accurate absolute values for properties like dimerization energies, equilibrium geometries, etc. [30] is not relevant to our objective because we are interested in polarisabilities (α) and hyperpolarisabilities (β and γ) at fixed geometries and in particular in trends which are based on property differences and ratios.

It is useful to state that CNDO approximations have been the basis for several interesting studies which consider the interaction of molecules with their neighbours [31].

B) The Basis Set

Analysis of numerous tests on H_2O, which involved basis sets including up to f orbitals for O and up to d for H, and relevant experience on other molecules (e.g. CH_4 [18a], C_2H_4 [18b], NH_3 [19a]), has led us to

Table 1. Normalized dipole moments, polarisabilities and hyperpolarisabilities of water clusters $(H_2O)_n$.

Cluster	Fig. 1	Normalized[m]				
		μ	α	ζ^2	β	γ
$(H_2O)_3$	**1**[a]	1.00	1.00	1.00	1.00	1.00
	1[b]	1.32	0.97	0.16	1.86	0.93
	2[c]	1.22	0.98	0.87	1.94	0.95
	3[d]	1.30	0.95	0.24	1.91	0.92
		1.21[n]	0.97[n]	0.57[n]	1.68[n]	0.95[n]
$(H_2O)_4$	**4**[e]	1.01	1.56	0.85	1.54	1.65
	5[f]	1.24	1.51	0.09	1.41	1.54
	6[g]	1.40	1.45	0.93	1.66	1.52
	7[h]	1.55	1.58	4.86	1.69	1.62
		1.30[n]	1.52[n]	1.68[n]	1.57[n]	1.58[n]
$(H_2O)_5$	**8**[i]	0.65	2.33	6.66	0.85	2.60
	9[j]	0.90	2.15	5.53	1.08	2.38
		0.77[n]	2.24[n]	6.09[n]	0.96[n]	2.49[n]
$(H_2O)_7$	**10**[k]	1.02	4.14	8.57	−2.15	4.73
	11[l]	0.83	4.00	21.31	1.41	4.59
		0.92[n]	4.07[n]	14.94[n]	−0.37[n]	4.66[n]

[a] The first water, Fig. 1, **1** ($H_1O_2H_3$) is on the plane of the paper. – The second water ($H_4O_5H_6$): The oxygen (O_5) is on the previous plane, but the hydrogens (H_4, H_6) are above the plane and away from the first water. The bisector of $H_4\hat{O}_5H_6$ forms an angle of 127.27° with O_2H_3. – The third water ($H_7O_8H_9$): The bisector of $H_7\hat{O}_8H_9$ forms an angle of 143° with the segment $O_5H_6O_8$. The plane of this water is approximately parallel to but above the plane of the first water.

[b] The geometry of this aggregate differes from that given in Fig. 1, **1**, in that, this water cluster has the third water ($H_7O_8H_9$) approximately perpendicular to the plane of the first water ($H_1O_2H_3$).

[c] The molecules $H_4O_5H_6$, $H_7O_8H_9$ and the O_2 are coplanar. The plane of $H_1O_2H_3$ is perpendicular to this plane.

[d] The geometry is defined in Fig. 4 of [35].

[e] We start with the configuration given in Figure 1, **1.** The extra water (A) is added such that H_2O(B) becomes a double proton donor [36].

[f] To the configuration given in Fig. 1, **1,** we add H_2O(D), such that H_2O(B), H_2O(C) and H_2O(D) form a sequential arrangement.

[g] We start with the configuration given in figure 1, **1.** The added water molecule (D), H_2O(A) and H_2O(B) have the geometry of the water cluster given in Figure 1, **1.**

[h] From Fig. 1, **1,** the added water molecule (D), with H_2O(C) and H_2O(B) have the geometry of the cluster given in Figure 1, **1.**

[i] We start with Figure 1, **4.** The added water molecule (A), H_2O(B) and H_2O(C) have the arrangement given in Figure 1, **1.**

[j] To Fig. 1, **6** is added water molecule (D), such that this, H_2O(C) and H_2O(B) have the geometry given in Figure 1, **1.**

[k] The molecules H_2O(B), H_2O(C), H_2O(D) and H_2O(E) have the geometry given in Figure 1, **7.** – The molecules H_2O(A), H_2O(B), H_2O(C) and H_2O(D) have the geometry given in Figure 1, **5.** – The molecules H_2O(B), H_2O(C), H_2O(D), H_2O(F) and H_2O(G) have the geometry given in Figure 1, **9.**

[l] The molecules H_2O(A), H_2O(B), H_2O(C) and H_2O(D) have the geometry given in Figure 1, **6.** – The molecules H_2O(D), H_2O(E), H_2O(F) and H_2O(G) have the geometry given in Figure 1, **5.**

choose the following basis set for the computation of μ and the components required to determine α, ζ^2, β and γ of the clusters considered here:

H: 1 s (0.8), 2 s (0.38), 2 p (0.475)

O: 2 s (1.975), 2 p (1.975)

This set of orbitals has been optimized with respect to the experimental $\alpha = 9.82$ a.u. [32] and $\gamma = 2310$ a.u. [33] values of H_2O (the resulting basis reproduced these values).

It is added that the computed dipole moment of H_2O is 1.78 D (3.26% in error with respect to the experimental value).

C) The Convergence Criteria

A detailed discussion concerning the convergence criteria for the self-consistent computation of $R^{(0)}$, $R^{(1)}$ and $R^{(2)}$ (which are the zeroth-order density matrix, the first and second order corrections respectively) is presented in references [20] and [34a].

D) Geometry of the Configurations

The geometry elements of the configuration used in this work are given in the footnotes of Table 1. We note that for the structure of $H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$, we have made extensive use of the information given in References [15] and [16].

Each cluster has been rotated in such a way that the dipole moment of the system coincides with the z axis.

The coordinates of all clusters (Fig. 1–3) are available on request.

III. Results and Discussion

The average μ of the considered neutral clusters (Table 1 and Fig. 1) shows a maximum for $(H_2O)_4$ and a minimum for $(H_2O)_5$. It is observed (Table 1) that change of geometry (configuration) may induce a considerable variation in the dipole moment of the cluster (e.g. the results for $(H_2O)_4$).

The dipole moment of the water molecule within the clusters considered here is not close to the value(s) of the dipole moment for a water molecule in ice [2, 6]. This is likely to be due to the specific configurations chosen and the rather small n (3 to 7), the number of

[m] The normalization has been performed with respect to the relevant property of $(H_2O)_3$, Figure 1, **1.**

[n] This is the average value of the property (normalized) for the clusters with the same n.

water molecules in a cluster. Thus each H_2O in the present aggregates is within an environment which is not similar to that which exists in ice.

The average values for the polarisability, its anisotropy and the second hyperpolarisability of $(H_2O)_n$ increases with n (Table 1).

The first hyperpolarisability (β) is a property very sensitive to inter-molecular interactions. Thus Levine and Bethea [34b] have found that β of p-nitroaniline is a factor of 3.4 larger in a polar solvent in comparison to that found in a non-polar one. Our results demonstrate this remarkable sensitivity of the first hyperpolarisability. In particular one may note the β results for $(H_2O)_3$ and $(H_2O)_7$. In the latter case we have even a change of sign (Table 1). One sees the comparatively small anisotropy of $(H_2O)_3$ having the configuration given in Figure 1, **5** in comparison to all other configurations of $(H_2O)_n$, $n = 3-5$, 7 (Table 1).

We have considered 4 configurations of $(H_2O)_3$ and $(H_2O)_4$ and 2 configurations for $(H_2O)_5$ and $(H_2O)_7$. Change of geometry (expressed by changing the configuration) may induce variations which are more marked for the anisotropy of the polarisability and the first hyperpolarisability of the considered clusters than other reported properties (Table 1). However it is observed that the cyclic OH^- double proton acceptor structure (Fig. 3, **1**) is associated with remarkably larger second hyperpolarisability in comparison to that of the planar-chain structure (Fig. 3, **2**) [15].

Analysis of the results of $H_3O^+(H_2O)_n$ shows that their polarisability and the second hyperpolarisability increases with n while the anisotropy shows a minimum and a maximum (Table 2). A maximum and a minimum is shown by the first hyperpolarisability of the clusters $H_3O^+(H_2O)_n$, when it is varied as a function of n (Table 2).

For $H_3O^+(H_2O)_5$ we have considered two configurations (Fig. 2, **4** and 2, **5**). The properties of these two configurations do not change greatly (Table 2).

For $OH^-(H_2O)_3$ we have two configurations (Fig. 3, **1** and 3, **2**). The polarisability anosotropies of these configurations show a large difference (Table 3).

The polarisability and the second hyperpolarisability of the considered clusters, $OH^-(H_2O)_n$, where $n = 3-7$ increases with n (for the two configurations of $OH^-(H_2O)_3$ the average value has been considered), while the anisotropy and the first hyperpolarisability show a maximum (Table 3).

The second hyperpolarisabilities of all clusters (with the same n value) are within the same order of magnitude. The largest ratio observed is

$$\gamma\,[OH^-(H_2O)_3]/\gamma\,[(H_2O)_3] = 2.1\,. \qquad (1)$$

Computations of the hyperpolarisability (γ) of a large number of molecular anions have shown that the non-linearity of the negatively charged species can be several orders of magnitude larger than that of their neutral precursors (and even more so in comparison to that of the resulting molecular cation).

For the isoelectronic clusters, $OH^-(H_2O)_n$ and $(H_2O)_{n+1}$, it is observed (average values are considered where more than one configuration is available for a specific n):

$$P\,[(H_2O)_{n+1}] > P\,[OH^-(H_2O)_n] \qquad (2)$$

for $n = 4$, 6, where P denotes the polarisability or the second hyperpolarisability. This relationship is reversed, when $n = 3$ for the above properties (Tables

Table 2. Normalized polarisabilities and hyperpolarisabilities of the hydrated hydronium ion, $H_3O^+(H_2O)_n$.

Cluster	Fig. 2	Normalized[d]			
		α	ζ^2	β	γ
$H_3O^+(H_2O)_2$	**1**[a]	0.90	0.70	−0.25	0.79
$H_3O^+(H_2O)_3$	**2**[b]	1.35	0.65	0.0	1.28
$H_3O^+(H_2O)_4$	**3**[b]	1.90	0.37	0.25	1.96
$H_3O^+(H_2O)_5$	**4**[b]	2.45	0.89	0.0	2.63
	5[b]	2.55	1.15	0.10	2.8
		2.5[e]	1.02[e]	0.05[e]	2.71[e]
$H_3O^+(H_2O)_6$	**6**[c]	3.17	0.80	0.43	3.70

[a] The information for the geometry of $H_3O^+(H_2O)_2$ is from [15]. This aggregate is centro-symmetric.
[b] The information for the geometry of this ion cluster is from [16].
[c] One water is added to each peripheral H_2O of $H_3O^+(H_2O)_3$, Figure 2, **2**.
[d] Footnote m of Table 1. [e] Footnote n of Table 1.

Table 3. Normalized polarisabilities and hyperpolarisabilities of the hydrated hydroxyl ion, $OH^-(H_2O)_n$.

Cluster	Fig. 3	Normalized[b]			
		α	ζ^2	β	γ
$OH^-(H_2O)_3$	**1**[a]	1.38	0.51	0.32	1.94
	2[a]	1.25	0.04	0.58	1.45
		1.31[c]	0.27[c]	0.45[c]	1.69[c]
$OH^-(H_2O)_4$	**3**[a]	1.81	0.27	1.42	2.12
$OH^-(H_2O)_5$	**4**[a]	2.47	3.49	0.63	2.94
$OH^-(H_2O)_6$	**5**[a]	3.17	2.10	0.14	3.83

[a] Footnote a of Table 2. [b] Footnote m of Table 1.
[c] Footnote n of Table 1.

1, 3). This inequality (2) is followed by the polarisability anisotropies. A different pattern is shown by the normalized first hyperpolarisability (Table 1, 3).

For the isoelectronic pair $(H_2O)_{n+1}$, $H_3O^+(H_2O)_n$ we have:

$$P[(H_2O)_{n+1}] > P[H_3O^+(H_2O)_n], \tag{3}$$

where P denotes the polarisability or the second hyperpolarisability (Tables 1, 2). The polarisability anisotropy follows this trend for $n = 3$, 4, 6, while for $n = 2$, the opposite inequality exists. The first hyperpolarisability shows a different pattern (the trend for $n = 2-4$ is reversed for $n = 6$).

Analysis of the results for the isoelectronic pair $OH^-(H_2O)_n$, $H_3O^+(H_2O)_n$ shows:

$$P[OH^-(H_2O)_n] > P[H_3O^+(H_2O)_n], \tag{4}$$

where P denotes the second hyperpolarisability (Tables 2, 3). The reverse trend is followed by the polarisability (except for $n = 6$, where the clusters of the pair have approximately the same value). The normalized first hyperpolarisability follows the inequality (4) for $n = 3-5$ and the reverse for $n = 6$, while for the polarisability anisotropy the inequality (4) holds for $n = 5$, 6 and the opposite for $n = 3$, 4 (Tables 2, 3).

In general the positive charge contracts the charge cloud (and reduces the ability to polarise) while the negative charge expands the charge cloud (thus making it more diffuse and enhances its ability for polarisation). However the present results show (Tables 1, 2):

$$P[H_3O^+(H_2O)_n] > P[(H_2O)_n], \tag{5}$$

for $n = 3-5$, where P denotes the polarisability or the second hyperpolarisability. For the polarisability anisotropy the above inequality (5) holds only for $n = 3$ (for $n = 4$, 5 the opposite inequality is followed). The normalized first hyperpolarisability values exhibit the opposite inequality to (5).

In order to have a relative assessment of the effect of intermolecular interactions on the polarisability and hyperpolarisabilities as well as the variation of this effect with charge and shape (geometry), we define the approximation;

$$\text{Pint} = P[(H_2O)_n] - n \times P[H_2O], \tag{6}$$

$$P' = \frac{\text{Pint}}{m} \text{ and } m = \frac{n(n-1)}{2},$$

where P may be the polarisability, the first hyperpolarisability or the second hyperpolarisability. The index P' gives a measure of the average effective pair intermolecular interactions on the property P. In the present work this property is used in its normalized form in order to safeguard the validity of the observed trends. The effects of interactions between H-bonded and non H-bonded water molecules are considered but not distinguished. The results of Table 4 are presented by employing the formula $H^+(H_2O)_n$ instead of $H_3O^+(H_2O)_{n-1}$. The average P' increases with the size of the water cluster (Table 4). The properties $\zeta^{2\prime}$ and β' show much greater sensitivity than α' and γ' to variations of configuration. Comparison of the average P' for $(H_2O)_3$ and $(H_2O)_7$ clearly demonstrates that the cooperative effect is an important factor for the rationalization of the electric porperties (linear and nonlinear) of H-bonded clusters. From the results of Table 4, we note that the influence of the cooperative effect on the properties which have been considered here appears to follow the ordering (neutral clusters):

$$\text{polarisability anisotropy} > \text{first hyperpolarisability} > \text{second hyperpolarisability} > \text{polarisability} \tag{7}$$

The results show (Table 4) that the positive charge differentiates the behaviour of $\zeta^{2\prime}$ and β' from α' and γ' (in the neutral clusters, $(H_2O)_n$, however, the variation of P' – for all four properties – with n was following the same trend).

IV. Conclusions

This work demonstrates and analyses the changes of the polarisability and the hyperpolarisabilities of water clusters neutral and charged due to intermolecular interactions. This is a problem of current interest.

In general, change of the polarisability and the second hyperpolarisability, induced by varying the number of water molecules in the cluster (which may be neutral, positively or negatively charged), follow the same trend. The polarisability anisotropy and the first hyperpolarisability follow their own different patterns of behaviour.

Changes of geometry induce greater variations in β in comparison to α or γ. The results for $(H_2O)_7$ clearly demonstrate this. The remarkable sensitivity of the first hyperpolarisability to geometry changes has been noted before [19a].

Table 4. Variation of α', $\zeta^{2'}$, β' and γ' (normalized) with the size and shape of $(H_2O)_n$ and $H^+(H_2O)_n$.

Cluster[a]	m[b]	Normalized[c]				Cluster[d]	m	Normalized[c]			
		α'[a]	$\zeta^{2'}$	β'	γ'			α'	$\zeta^{2'}$	β'	γ'
$(H_2O)_3$	3	1.00	1.00	1.00	1.00	$H^+(H_2O)_3$	3	0.63	0.68	2.22	0.32
	3	0.88	0.10	0.16	0.77						
	3	0.93	0.86	0.08	0.83	$H^+(H_2O)_4$	6	0.71	0.30	1.32	0.59
	3	0.82	0.19	0.11	0.73						
		0.91[e]	0.54[e]	0.34[e]	0.83[e]	$H^+(H_2O)_5$	10	0.76	0.09	0.91	0.78
$(H_2O)_4$	6	1.09	0.41	0.56	1.17	$H^+(H_2O)_6$	15	0.74	0.16	0.79	0.80
	6	0.99	0.0	0.63	0.99		15	0.81	0.22	0.77	0.91
	6	0.88	0.45	0.51	0.97			0.77[e]	0.19[e]	0.78[e]	0.85[e]
	6	1.13	2.55	0.49	1.03						
		1.02[e]	0.85[e]	0.55[e]	1.04[e]	$H^+(H_2O)_7$	21	0.77	0.10	0.60	0.96
$(H_2O)_5$	10	1.23	2.10	0.74	1.40						
	10	1.03	1.74	0.67	1.18						
		1.13[e]	1.92[e]	0.70[e]	1.29[e]						
$(H_2O)_7$	21	1.29	1.28	0.96	1.43						
	21	1.22	3.22	0.46	1.36						
		1.25[e]	2.25[e]	0.71[e]	1.39[e]						

[a] The structure of the employed clusters is given in Fig. 1 and it is defined in detail in Table 1 (second column), where the ordering is the same as here.
[b] The symbols (m, α', $\zeta^{2'}$, β' and γ') are defined in the text.
[c] The normalization has been performed with respect to the relevant property of $(H_2O)_3$, Figure 1, **1.**
[d] The structure of the employed clusters is given in Fig. 2 and it is defined in detail in Table 2 (second column), where the ordering is the same as here.
[e] This is the average value in the considered configurations for each cluster.

Relationships referring to various isoelectronic pairs have been reported. These help to elucidate the effect of the charge on the properties and provide some more examples where one may compare the changes in the properties with the variation of n.

An index P' has been defined, which gives a measure of the average, effective pair intermolecular interactions on the properties. Employing $(H_2O)_n$ and $H_3O^+(H_2O)_n$ the considerable impact of the cooperative effect of the H-bond and other intermolecular interactions on the polarisability anisotropy, the first and second hyperpolarisabilities have been demonstrated (this effect is notable but less pronounced in the polarisability). The role of the positive charge on the above effect has also been shown.

The components of the considered properties have been computed by employing the CHF-PT-EB-CNDO method. Several arguments have been presented to support the adequacy of this method for the present study. In particular we note the numerous comparisons between the computed and the experimentally determined results [11, 18, 19a, 19b], which demonstrate that the method (CHF-PT-EB-CNDO) provides reasonably accurate molecular polarisabilities (α) and hyperpolarisabilities (γ). The basis set used for the computations has been optimized with respect to the polarisability and the hyperpolarisability (γ) of H_2O. Furthermore the validity of the reported findings, which are mainly trends, is strengthened by relying on the analysis of normalized property values.

This work, however, should be considered only as a first step towards a more refined study which will give due consideration to various other important factors (e.g. explicit treatment of electron correlation) and including the basis set superposition effects. Furthermore, analysis of the charge rearrangement in the individual molecules due to the presence of other molecules is likely to add more insight to the problems considered here.

[1] C. A. Coulson and D. Eisenberg, Proc. Roy. Soc. London A **291,** 445 (1966).
[2] J. F. Nagle, Chem. Phys. **43,** 317 (1979).
[3] O. Wörz and R. H. Cole, J. Chem. Phys. **51,** 1546 (1969).
[4] G. P. Johari and S. J. Jones, J. Glasiology **21,** 259 (1978).
[5] L. Onsager and M. Dupuis, Electrolytes, Ed. B. Pesce, Pergamon, London 1962.
[6] C. A. Coulson and D. Eisenberg, Proc. Roy. Soc. London A, **291,** 454 (1966).
[7] a) H. Umeyama and K. Morokuma, J. Amer. Chem. Soc. **99,** 1316 (1977). – b) B. F. Levine and C. G. Bethea, J. Chem. Phys. **66,** 1070 (1977). – c) S. Tomoda and K. Kimura, Chem. Phys. Letters **102,** 560 (1983).
[8] a) The average polarisability, first and second hyperpolarisabilities are given by [8b]:

$$\alpha = 1/3\,(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$
$$\beta = 3/5\,(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}),$$
$$\gamma = 1/5\,(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\,\gamma_{xxyy}\,2\,\gamma_{xxzz} + 2\,\gamma_{yyzz}).$$

The polarisability anisotropy is defined by:

$$\zeta^2 = 1/2\,[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2].$$

b) A. D. Buckingham and B. J. Orr, Q. Rev. Chem. Soc. **21,** 195 (1967).
[9] J. Waite and M. G. Papadopoulos, Chem. Phys. Letters **114,** 539 (1985).
[10] a) J. Zyss and G. Berthier, J. Chem. Phys. **77,** 3635 (1982). – b) G. R. Meredith and B. Buchalter, J. Chem. Phys. **78,** 1938 (1983).
[11] J. Waite and M. G. Papadopoulus, J. Chem. Phys. **83,** 4047 (1985).
[12] I. Ledoux and J. Zyss, Chem. Phys. **73,** 203 (1982).
[13] S. Scheiner and J. F. Nagle, J. Phys. Chem. **87,** 4267 (1983).
[14] a) A. P. Minton, Trans. Faraday Soc. **67,** 1226 (1971). – b) H. S. Frank and W. Y. Wen, Disc. Faraday Soc. **24,** 133 (1957).
[15] M. D. Newton and S. Ehrenson, J. Amer. Chem. Soc. **93,** 4971 (1971).
[16] M. D. Newton, J. Chem. Phys. **67,** 5535 (1977).
[17] a) M. De Paz, S. Ehrenson, and L. Friedman, J. Chem. Phys. **52,** 3362 (1970). – b) W. P. Kraemer and G. H. F. Diercksen, Chem. Phys. Letters **5,** 463 (1970). – c) M. Eigen, Angew. Chem. Int. Ed. Engl. **3,** 1 (1964) and references therein. – d) E. P. Grimsrud and P. Kebarle, J. Amer. Chem. Soc. **95,** 7939 (1973). – e) R. Triolo and A. H. Narten, J. Chem. Phys. **63,** 3624 (1975).
[18] a) C. A. Nicolaides, M. Papadopoulos, and J. Waite, Theor. Chim. Acta **61,** 427 (1982). – b) M. G. Papadopoulos, J. Waite, and C. A. Nicolaides, J. Chem. Phys. **77,** 2527 (1982). – c) J. Waite, M. G. Papadopoulos, and C. A. Nicolaides, J. Chem. Phys. **77,** 2536 (1982).
[19] a) J. Waite and M. G. Papadopoulos, J. Chem. Phys. **82,** 1427 (1985). – b) M. G. Papadopoulos and J. Waite, J. Chem. Phys. **82,** 1435 (1985).
[20] J. Waite and M. G. Papadopoulos, J. Chem. Soc. Faraday Trans. II, **81,** 433 (1985).
[21] a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York 1970. – b) H. Shinoda and T. Akutagawa, Bull. Chem. Soc. Japan **48,** 3435 (1975).
[22] a) E. N. Svendsen, C. S. Willard, and A. C. Albrecht, J. Chem. Phys. **83,** 5760 (1985). – b) V. J. Docherty, D. Pugh, and J. O. Morley, J. Chem. Soc. Faraday Trans. II, **81,** 1179 (1985). – c) E. N. Svendsen, T. Stroyer-Hansen, and H. F. Hameka, Chem. Phys. Letters **54,** 217 (1978). – d) M. Spiekerman, D. Bougeard, H.-J. Oelichman, and B. Schrader, Theor. Chim. Acta **54,** 301 (1980). – e) J. J. C. Teixeira-Dias and J. N. Murrell, Mol. Phys. **19,** 329 (1970).
[23] a) R. McWeeny, Phys. Rev. **126,** 1028 (1962). – b) G. Diercksen and R. McWeeny, J. Chem. Phys. **44,** 3554 (1966). – c) J. L. Dodds, R. McWeeny, W. T. Raynes, and J. P. Riley, Mol. Phys. **33,** 611 (1977).
[24] J. L. Dodds, R. McWeeny, and A. J. S. Sadlej, Mol. Phys. **34,** 1779 (1977).
[25] G. T. Daborn, W. I. Ferguson, and N. C. Handy, Chem. Phys. **50,** 255 (1980).
[26] I. Shavitt, "Advanced Theories and Computational Approaches to the Electronic Structure of Molecules", Ed. C. E. Dykstra, Reidel Pub. Company, Holland 1984.
[27] R. M. Berns and P. E. S. Wormer, Mol. Phys. **44,** 1215 (1981).
[28] J. Waite and M. G. Papadopoulos, unpublished results.
[29] a) R. J. Bartlett and G. D. Purvis III, Phys. Rev. A **20,** 1313 (1979). – b) G. D. Purvis III and R. J. Bartlett, Phys. Rev. A **23,** 1594 (1981).
[30] a) S. N. Mohammad and A. J. Hopfinger, Int. J. Quant. Chem. **22,** 1189 (1982). – b) V. A. Zubkov, B. I. Kolegov, and T. M. Birshtein, Russian Chem. Rev. **52,** 1057 (1983).
[31] a) D. A. McDonaill and D. A. Morton-Blake, Theor. Chim. Acta **65,** 13 (1984). – b) O. N. Ventura and J. P. Bartolucci, Theor. Chim. Acta **64,** 229 (1984). – c) J. L. Ravail and D. Rinaldi, Chem. Phys. **18,** 233 (1976). – d) O. Tapia, C. Lamborelle, and G. Johannin, Chem. Phys. Letters **72,** 334 (1980). – e) O. Tapia and G. Johannin, J. Chem. Phys. **75,** 3624 (1981).
[32] A. J. Sadlej, Mol. Phys. **34,** 731 (1977).
[33] J. F. Ward and C. K. Miller, Phys. Rev. A **19,** 826 (1979).
[34] a) J. Waite and M. G. Papadopoulos, J. Mol. Struct. **108,** 247 (1984). – b) B. F. Levine and C. G. Bethea, J. Chem. Phys. **69,** 5240 (1978).
[35] D. Hankins, J. W. Moskowitz and F. H. Stillinger, J. Chem. Phys. **53,** 4544 (1970).
[36] P. Kollman, J. Amer. Chem. Soc. **99,** 4875 (1977).