Conclusions

We have generalized the simple PKS model to include explicitly both crystal-field and spin–orbit effects. This has been done in a systematic manner by using the Butler chain-of-groups approach. All matrix elements have been explicitly given so that direct application of the model to other symmetrical dimer systems is possible. Vibronic coupling has been explicitly included. As compared to the simple model, it is necessary to diagonalize matrices three times larger for a given vibrational basis. However, even strongly localized systems, which require large basis sets, can be easily handled with the computing power now routinely available. Of course the effects of vibronic coupling become increasingly pronounced as the system becomes increasingly localized.

We have pushed our model to the logical limit in analyzing the ESR and optical data available on the C–T ion, and the model has been found wanting. While it can simulate these data reasonably well, the electronic coupling parameters (ϵ_1, ϵ_2, ϵ_3) required are clearly unreasonable both on qualitative grounds and on the basis of detailed calculations.[15] It is possible that adding additional q-modes could help. In the case of the simple model, the addition of a second effective ("solvent") mode did add breadth to the high-energy side of the intervalence band in a plausible way.[16] In addition, the model really requires three distinct λ values, but this should not be a significant factor for the C–T ion because vibronic coupling is small in any event. We suspect that the problem is more fundamental, namely that the model in its present form simply does not take adequate account of the bridging ligand (the pyrazine ring) which must play a vital role in this strongly coupled system. In this regard, we note the recent very interesting work of Ondrechen and co-workers[15,17-19] which explicitly includes the bridging ligand in a three-site model (as opposed to our two-site model). A very important feature of her work is the explicit argument that the q_+ mode(s) play a vital and indeed even dominating role in systems in which the electronic coupling to the bridging ligand is sufficiently strong. (Such modes are decoupled from the problem to a very good approximation in the two-site model.[16])

It seems to us that a clear opportunity is present to attempt a synthesis of our present treatment and the three-site model of Ondrechen. The latter at present neglects spin–orbit coupling and does not explicitly consider the tetragonal and rhombic distortion parameters. It therefore cannot be used to calculate g values. It would clearly be of great interest to explicitly include the pyrazine bridge in our present treatment in the manner developed by Ondrechen et al. We have high hopes that in this way it will prove possible to rationalize the g values and intervalence band contour with sensible parameters, i.e., with ϵ_2 large and ϵ_1 and ϵ_3 small or negligible. We hope to pursue this point in future work. Such an approach may also suggest a framework for a detailed analysis of the MCD spectrum.[3]

Finally, we note that as the role of the bridging ligand diminishes, as for example in more localized systems, our present treatment becomes increasingly applicable. Obviously, examination of specific cases is required to test its usefulness.

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Theoretical Studies of the System $H_3O^+(H_2O)_n$ for n = 1–9

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Abstract: Monte Carlo calculations have been performed on the system $H_3O^+(H_2O)_n$ for n = 1–9, using approximate expressions to describe the interaction between H_3O^+ and H_2O and between two water molecules (MCY potential). The cluster formation energies through the reaction $H_3O^+(H_2O)_{n-1} + H_2O \rightleftharpoons H_3O^+(H_2O)_n$ are evaluated and compared to experimental data. Interesting information about the structure and the filling of the different solvation shells of water around H_3O^+ is obtained. In particular, we can note a tendency for large n, to fill the first shell with a fourth water molecule and to fill a third shell before the second one is complete.

I. Introduction

Since its existence was postulated in 1907,[1] the structure of H_3O^+ has been rather extensively discussed (see for instance ref 2–4). Many experimental data are available on crystalline hydrates of strong acids[5] or liquids[3,6] concerning H_3O^+ only, more recent work often being extended to larger systems $H^+(H_2O)_n$ in solids,[4,7-10] liquids,[11-13] or gas phase.[14-24] Parallel to this work in laboratory, observations in the stratosphere and lower tropo-

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sphere[25-28] showed that such systems are abundant in the atmosphere where their role is probably important.

Theoretical studies follow the same evolution. Most of them are based on the use of quantum mechanical methods,[2,29-53] sometimes with semiempirical approximations,[29-32] or with more or less extended ab initio basis sets or terms in a one-center expansion.[2,33-55] Most of these papers [2,31-49,55] are concerned with H_3O^+ and some[29,30,32,37,41,43,49-55] with $H_5O_2^+$. Quantum mechanical studies for $n = 3$ or 4 are found only in ref 32 and 43, while theoretical treatments for larger values of n are based on nonquantum mechanical methods.[11,14,15] In these last papers, particular attention has been paid to the case $n = 21$ which shows some unusual stability.[14,15]

In a recent paper,[54] quantum mechanical calculations have been performed for the system $H_3O^+\cdots H_2O$: the dispersion energy obtained from a perturbation treatment has been added to the SCF energy of the super-system. Ab initio basis sets of the type "double-ζ plus one polarization function" are used, the results being corrected for the basis set superposition error. An "atom–atom decomposition" was then proposed, the parameters being adjusted to fit the ab initio surface. Combined with MCY expression[56-58]

Table I. Cluster Formation Energies for the Reaction $H_3O^+(H_2O)_{n-1} + H_2O \rightleftharpoons H_3O^+(H_2O)_n$

n	$E_n - E_{n-1}$, kcal/mol	Newton et al.[43]	Kebarle et al.[22]	
9	−8.01 ± 0.64[a]			
8	−8.44 ± 0.53			
7	−9.12 ± 0.39			−10.3[b]
6	−9.25 ± 0.29			−11.7
5	−9.84 ± 0.20			−13
4	−10.29 ± 0.15	−17.70		−15.3
3	−26.25 ± 0.10	−26.11	−17.5[c]	−17
2	−27.58 ± 0.05	−30.95	−19.5	−22.3
1	−29.05 ± 0.02	−43.88	−31.6	−36.0

[a] The error is given by the sum of twice the standard deviation on n and $n - 1$ cluster energies. [b] From ref 22a. [c] From ref 22b.

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to describe the interaction energy between two water molecules, this approximation has been used, in the present work, to perform Monte Carlo calculations on the system $H_3O^+(H_2O)_n$ for $n = 1$ to 9. The structure of the clusters and the energy necessary for their formation through the reaction

$$H_3O^+(H_2O)_{n-1} + H_2O \rightleftharpoons H_3O^+(H_2O)_n$$

have been studied.

This work is the first step of a more general study of these systems and shows some of the problems which can be encountered before getting definitive answers.

II. Theoretical Treatment

Monte Carlo calculations have been performed with the program described in ref 57. Satellite programs for the analysis of the calculations have been written in Strasbourg. In the case of two water molecules, the parameters for the analytical formula fitting MCY ab initio results[56] are described in ref 57 and 58. Other formulas and parameters are available (see for instance ref 59 and 60); Monte Carlo calculations using different expressions of the potential have been performed[59a] and compared with experimental information on liquid water. In the present work, only one set of parameters has been used. Other sets could also be tried in the future; however, they would probably not change the general conclusions.

The interaction between H_3O^+ and H_2O is described by an atom–atom 12–6–1 expression.[56,59] The values of the parameters are given in ref 54. Though H_3O^+ is slightly pyramidal in crystals,[4,7-10] a planar structure has been chosen in the present calculations: it has been shown in a previous paper[54] that both structures give rather similar results for $H_3O^+\cdots H_2O$, the cost of the calculations with a planar structure being appreciably cheaper.

In the present step of our studies, proton tunneling between two water molecules has not been considered. As mentioned in ref 54, this important problem has been the subject of several theoretical works based on quantum chemical[30,50,52] or nonquantum chemical[11,14,15] calculations. Accurate quantum chemical calculations on $H_5O_2^+$ show[50] a very flat curve when the proton is shifted between the two water molecules. The energy difference is only 0.6 kcal/mol, explaining an easy tunneling. This energy is small compared to the stabilization energy of the clusters, maybe smaller than the inaccuracies introduced in our treatment by the use of approximate formulas to describe the energy. This suggests that it makes sense to start this study with a frozen geometrical configuration of H_3O^+ and to compare the theoretical energies to some experimental data obtained by measurement of reaction equilibria involving gazeous ions and molecules.[22] A more refined study would require the relaxing of the geometry of H_3O^+. In particular, we plan to perform similar calculations with a proton located on the middle of O–O in $H_5O_2^+$. However, as will be seen, some general tendencies will probably be obtained with a frozen configuration of H_3O^+ and are of great use in refining the theoretical method.

The analysis of the theoretical determinations gives information on the structure of the clusters. Of course, these structures concern only the limit case with a frozen H_3O^+. Similar calculations with other geometries for $H_5O_2^+$ should be performed. However, as will be seen, some tendencies, for instance those concerning the filling of the shells, could probably be generalized.

The planar geometry used for H_3O^+ is described in ref 54 and corresponds to $\alpha = 120°$ and $d_{OH} = 0.965$ Å. The experimental geometry is used for H_2O, with $\alpha = 104° 52'$ and $d_{OH} = 0.9572$ Å.

The energies of the clusters are computed as a sum of the energies of pairs of molecules, neglecting three-body effects. This last point will be discussed in the next section.

III. Results

Monte Carlo calculations have been performed at 300 K for $n = 1$ to 9. The results can then be compared with experimental data available at this temperature in the gas phase.

(a) Convergency of the Calculations. The number of moves considered in each calculation is 800 000 for $n = 1$–3 (where fast convergency is obtained), 2 400 000 for $n = 4$–5, and between 2 400 000 and 3 200 000 for $n = 6$–9 according to the convergency. About one-third of the configurations are retained for the low values of n and one-half for higher values. Compared to energies which vary from 29 to 15 kcal/mol per water molecule, the standard deviation per water molecule increases with n, from 0.008 to 0.024 kcal/mol, these values being multiplied by $2 \times n$ to have the error in the total system. If we draw the energy curves with respect to the number of the configurations considered (retained or not), the numbers of the moves given above correspond to the asymptotic part of the curve. We have checked that due to the relatively small size of these clusters which allow the start of the calculations with a reasonable configuration, it is not really necessary to discard the first moves as is generally done in the studies of liquid structures: the results obtained with the 800 000 first moves either discarded or not discarded are close, the statistical error being smaller in the nondiscarded case. To reduce the statistical error beyond the values given above would require a very much larger number of moves and would not change our qualitative conclusions.

(b) Cluster Formation Energies. Comparison between the Monte Carlo energy of a cluster and the energy of the most stable configuration shows that the discrepancies vary from 1.3 to 1.9 kcal/mol per water molecule when n increases. The Monte Carlo energy of the clusters varies from 29 to 15 kcal/mol per water molecule, giving an idea of the importance of the other geometrical configurations with respect to the most stable one.

Table I allows a comparison between our present results and other theoretical[43] or experimental determinations.[22] Monte Carlo calculations give a gap between the values obtained for $n = 3$ and 4, that is after that three water molecules are attached to the three H atoms of H_3O^+. In experimental data, the gap occurs between $n = 1$ and 2. This difference between the two determinations may be explained by the neglect in the theoretical treatment of the three (and higher)-body effect since the intermolecular energy is treated as a sum of the interactions between pairs of molecules. This 3 (and 4)-body effect is particularly important for $n = 2$ and 3 where the water molecules are close to H_3O^+, in the first solvation shell. We can note that our values, in good agreement with the experimental determinations for $n = 1$, become much larger for $n = 2$, 3 and somewhat smaller for the beginning of the second solvation shell. The discrepancy between theoretical and experimental values clearly decreases when n increases. This may suggest that the agreement could be much better for larger values of n and that correction in the theoretical treatment for the three-body effect could be necessary only when H_3O^+ is involved and maybe not for the interaction between three water molecules. The use of other parameters for the interaction between two water molecules could change somewhat the results but not the general features if the three-body effect involving H_3O^+ is important.

Work is now in progress in order to evaluate the effect of three-body forces involving H_3O^+. Preliminary SCF calculations on the most stable structures with $n = 1$, 2, 3 give energy differences of −30.306, −24.730, and −19.510 kcal/mol, respectively, while the sum of the SCF energies of pairs of molecules gives −30.306, −28.964, and −27.622 kcal/mol. The approximate formula used in MC calculations gives −30.684, −29.188, and −27.692 kcal/mol. We can see that the last two series of values are close; comparison with the first series of results shows that three-body forces can strongly decrease the results obtained in MC calculations for $n = 2$ and 3. On the contrary, when a fourth molecule is added in the second solvation shell, we have an SCF energy difference of 8.11 kcal/mol compared to the value of 7.76 kcal/mol given by the approximate formula. The three-body effect

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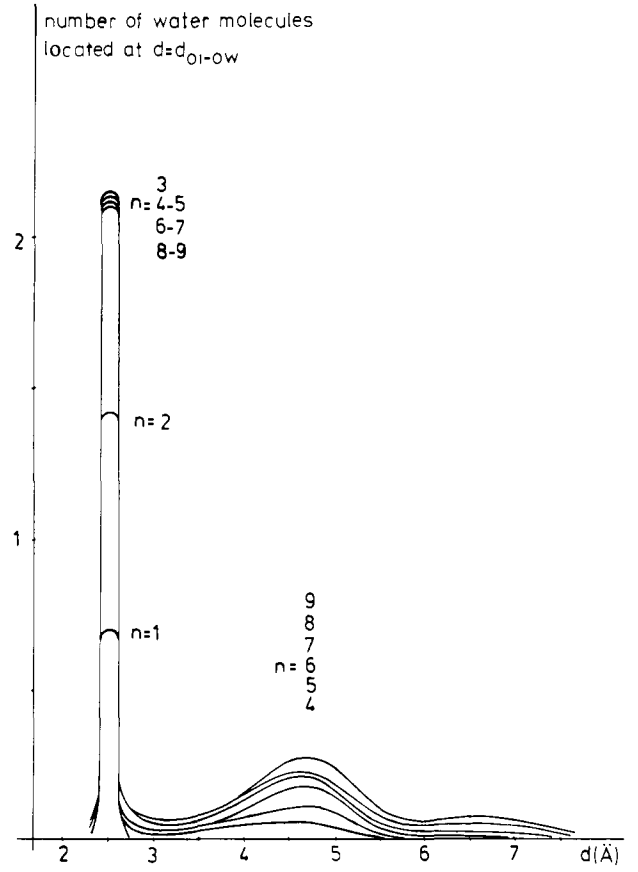

Figure 1. $H_3O^+(H_2O)_n$: number of water molecules located at distance d_{OI-OW}. For each peak, the values of n are given in the same order as the height of the curves.

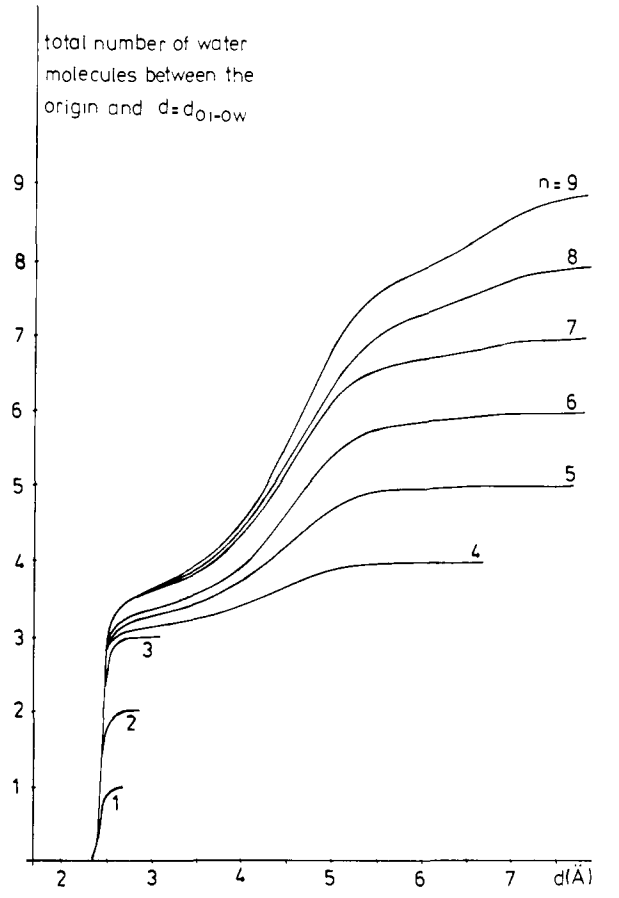

Figure 2. $H_3O^+(H_2O)_n$: total number of water molecules between the origin and distance d_{OI-OW}.

is then small in this case and gives somewhat larger values.

Some SCF calculations for $n = 2$ and 3 on different geometrical configurations show that the relative order of the stabilities is not strongly affected by the three-body effect. We can then expect that the properties described in the next section from the analysis of Monte Carlo calculations are generally significant. Further work will be done to check this assumption.

(c) Distribution of the Water Molecules around H_3O^+. Figure 1 gives the distribution of the water molecules around H_3O^+ as a function of the distance d_{OI-OW} between the oxygen atoms of the ion and of each water molecule. The curves are obtained from the analysis of the position of the water molecules in the geometrical configurations retained in Monte Carlo calculations. Histograms have been built, with a step of 0.1 Å. This gives, for each distance d, the number, N_W, of water molecules located at $d_{OI-OW} = d \pm 0.05$ Å. This number, divided by the total number of geometrical configurations retained in MC calculations gives a normalized value, N'_W, which is then smaller or equal to n. In Figure 1, N'_W is plotted as a function of d. The integration of this curve is plotted in Figure 2 and represents the number of water molecules within a volume surrounding the ion.

We can see a narrow peak at $d_{OI-OW} = 2.5$ Å for all values of n(Figure 1). The height of this peak is slightly decreasing from $n = 3$ to 9, but the basis is increasing such that the total number of the molecules corresponding to the region 2.2–3 Å increases till about 3.6 Å (Figure 2). This corresponds to a tendancy to accept either 3 or 4 molecules in the first solvation shell surrounding H_3O^+. The analysis of the geometry of the most stable configurations obtained in the course of Monte Carlo calculations shows that, for large n, a four-water-molecule configuration is most often found ($n = 6$, 7, 9), with $d_{OI-OW} \simeq 2.41$–2.52 Å, these values of the distances being close to those observed in crystals where H_3O^+ is surrounded by 3 water molecules. For $n = 8$, three- and four-water-molecule configurations are close in energy. Intermediate situations are found for $n = 4$ and 5, where three-water-molecule configurations are the most stable one, other low-energy configurations showing a fourth water molecule located at $d_{OI-OW} = 3.41$ and 2.69 Å, respectively.

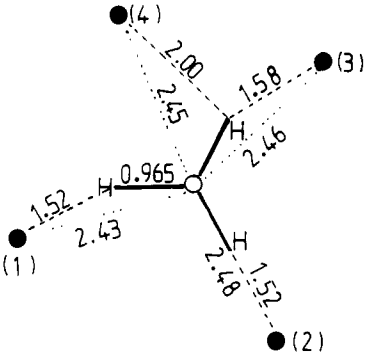

Figure 3. $H_3O^+(H_2O)_n$: geometry of the first solvation shell for $n = 6$.

The geometry of the first solvation shell is shown in Figure 3 for the most stable configuration obtained with $n = 6$. Cases $n = 7$–9 are quite similar. If we consider molecules 1, 2, and 3, we may assumed that they correspond to the three water molecules attached to H_3O^+ through hydrogen bonds in crystals. With respect to their initial position, we may suppose that molecules 1 and 3 are shifted by the approach of molecule 4 (they can be shifted in or out of the plane). While the hydrogen bond distance $d_{H-O} = 1.52$ Å for molecules 1 and 2, it is 1.58 for molecule 3 and 2.00 for molecule 4. This could be interpreted as an exchange between molecule 3, leaving molecule, and molecule 4 approaching molecule. This situation in the gas phase is then different from that in crystals where directional forces lead to 3 molecules in the first shell.[7,8,10]

We may question what the situation would be if we consider $H_5O_2^+$ as a central ion instead of H_3O^+. Given the very flat curve

obtained for proton tunneling in theoretical calculations,[50] we cannot know, at the present stage of the work, if $H_5O_2^+$ is or is not more favorable than H_3O^+. However, we can assume that some general conclusions would not be changed. For instance, if we replace, in Figure 3, H_3O^+ and molecule number 2 by $H_5O_2^+$, we may expect similar deformation of the position of molecules 1, 3, and 4 since H^+ should be shifted toward molecule 2. As mentioned in section II, further calculations will be performed to check this assumption but will not be available for some time.

The second peak around $d_{OI-OW} = 4.7$ Å is on the contrary very broad (Figure 1). This effect is illustrated in Figure 2 by the slope of the curve between $d_{OI-OW} = 4.0$ and 5.0 Å, compared to the nearly vertical wall at $d_{OI-OW} = 2.5$ Å. The peak is more pronounced for large values of n (Figure 1) and we can see, already for $n = 6$ or 7 but more clearly for $n = 8$ or 9, the formation of a third peak around $d_{OI-OW} = 6.8$ Å (the size of the box in Monte Carlo calculations has been chosen large enough to allow the study of this effect). It then exists some tendency to fill a third shell before the second one is complete. If we consider the limit of the three peaks are around 3.0, 5.9, and 10 Å, we find about 3.6, 4.2, and 1.2 molecules in each peak for $n = 9$. Figure 2 shows that the filling of the third shell is already noticeable for $n = 5$, with a very small number of molecules (0.1), this number increasing with n.

IV. Conclusions

As stated above, though the values of the cluster formation energies are not very good for small clusters, we expect that the description of the phenomena from the analysis of MC calculations is not strongly affected by this inaccuracy. A theoretical study of such clusters would be impossible without the use of approximate formulas, and the present treatment seems able to give interesting information about the structure and the filling of the solvation shells. Work is now in progress to extend this study to larger systems and to take into account three-body effects. Also, some studies considering $H_5O_2^+$ as the central ion, with the possibility of relaxing the geometry, will be undertaken.

Many questions are not yet answered about these systems. In this first step of our study, we have frozen the geometry of H_3O^+. We think that this treatment brings information which is essential for the understanding of these systems. The effect of the mobility of the proton in the clusters is of particular importance[11,14,15] and must be checked to get definitive answers.

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Monte Carlo Study of the Conformation-Dependent Hydration of the 18-Crown-6 Macrocycle

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Abstract: The conformation-dependent hydration of the [18]-O_6 macrocycle has been studied by Monte Carlo calculations on a cluster made up of 100 water molecules surrounding the solute in the C_i, D_{3d}, and C_1 conformations. The intrinsically most stable C_i form, unefficient for ion binding, is the least well hydrated and should be the least stable form in water. The D_{3d} conformer, with a preformed cavity suitable for cation binding and transport, is solvated to the same extent as the C_1 conformer and should be the most stable in the aqueous environment. A computer graphics analysis of the supramolecular clusters shows conformation-dependent patterns of hydrogen bonds in the first solvation shell, corresponding to different hydration energies in that shell. In the D_{3d} form, a cooperativity between solvent molecules H bonded one to another is observed, analogous to what is found in the X-ray structure of a [18]-O_6/water/*p*-nitrophenol complex. For C_1 three independent water molecules in a bridging position maintain firmly the distorted solute. The weak solvation of C_i results from linear H bonds to the solute and unfavorable water–water interactions. These results have an important bearing on conformational analysis in solution and on solvent-dependent cation complexation by ionophores, since conformations found in the solid state may not be those favored in water.

The [18]-O_6 crown ether, a simple model foor macrocyclic ion receptors and carriers, is flexible and displays several conformations in crystals, depending on the nature of its environment and on the presence and nature of the complexed cation:[1-4] e.g., the uncomplexed crown has C_i symmetry, the Na^+ and K^+ complexes are C_1 and D_{3d}, respectively. Flexibility is important not only to ensure the formation of the most favorable "cavity" for a given ion but also to facilitate the capture and release of the

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