INTERACTIONS OF IONS. AB INITIO SCF-MO-LCAO CALCULATIONS OF Li^+–H_2O–OH^- WITH A MINIMAL GAUSSIAN BASIS SET

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PE 128/40, 1975, 3-4.

ZÁKLADNÍ KNIHOVNA ČSAV PRAHA

Received March 22nd, 1974

The hydrogen bond in the Li^+–H_2O–OH^- system was investigated. The planar optimal structure of the complex was found for $d(O\cdots O) = 2{\cdot}35$ Å. The hydrogen bond energy is $-45{\cdot}1$ kcal/mol, by 11·5 kcal/mol higher than the hydrogen bond energy of H_2O–OH^- given by the same basis set. The population analysis suggests extremely high electron transfer (0·106 el.) from OH^- to Li^+–H_2O. Potential curves were examined for the proton motion in the hydrogen bond for various O···O distances.

In the last several years numerous *ab initio* calculations were reported on interactions of systems bound by a hydrogen bond[1,2]. To our knowledge, however, no calculation was reported for a system of the $M^+\cdots H_2O\cdots B^-$ type, where the anion is bound to water by a hydrogen bond which is affected by the presence of the cation M^+. Eigen and coworkers[3] have suggested structures called "water separed ion pairs" in which one or several water molecules are localized between two ions on the basis of measurements by the methods of relaxation kinetics[4]. For B^- being a hydroxyl anion, Robinson and Harned[5,6] assumed a structure in which water is strongly polarized by the field of a cation and the proton activated in this way is capable of forming a shortlived $M^+\cdots OH^-\cdots H^+\cdots OH^-$ bond. By means of this process called internal hydrolysis they accounted for the decrease of the activity coefficients in the series $Cs^+ > K^+ > Na^+ > Li^+$ with alkali metal hydroxides which is in contrast to most alkali metal salts. A special position of alkali metal hydroxides was also found with the phase diagrams of aqueous solutions of electrolytes[7]. This indicates that to arrive at the correct structure and properties of electrolytes one must consider not only the interaction of the cation with water but also the participation of the anion[8]. A detailed infrared spectroscopic study of aqueous solutions of electrolytes was performed by Zundel and collaborators[9–12]. A continuous absorption was assigned to the extremely high polarizability of hydrogen bonds[10,11] with a double minimum potential well or with a flat and broad potential. This polarizability is particularly high for compounds with symmetric bonds as in $H_5O_2^+$ and $H_3O_2^-$. With alkali metal hydroxides the symmetry of the bond in the $H_3O_2^-$ system can be perturbed by the presence of the ion M^+. Nevertheless it is still polarizable enough so that a continuous infrared absorption is observed at higher wavenumbers[9]. From the papers mentioned above it appears that the examination of the effect of a cation on the hydrogen bond between water and an anion might provide information useful for the understanding of the structure of electrolytes and their physicochemical properties.

The aim of this paper is to examine the hydrogen bond in the $Li^+\cdots H_2O\cdots OH^-$ system by the *ab initio* SCF calculations. Though the system is rather simple, we restricted ourselves to a minimal basis set of contracted Gaussian functions. Only semi-quantitative results are therefore to be expected.

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Method and Basis Set

The calculations were carried out with a modified program POLYATOM (ref.[13]), QCPE 47·1. For the lithium ion we selected the (7*s*) basis set[14] contracted to [2*s*], for oxygen the (7*s* 3*p*) basis set[15] contracted to [2*s* 1*p*] and for hydrogen the (3*s*) basis set[16] contracted to [1*s*]. Scaling factors of valence orbital exponents for oxygen and hydrogen were optimized for isolated water molecules and hydroxyl ion[17]. The total energy for water is −75·80426 a.u., the optimal OH bond length is 0·96 Å, the bond angle is 109° and the dipole moment is 2·58 D. For the OH^- ion the total energy is −75·11576 a.u. and the optimal bond length is 0·996 Å. The energy of the hydrogen bond in the water dimer is −8·72 kcal/mol, the O–O bond length 2·8 Å, and the angle θ between the line bisecting the bond angle in the proton acceptor molecule and the line passing through oxygen atoms is 30°.

The geometry parameters of the water dimer are somewhat more realistic than those given by other minimal basis sets of a comparable size[18]. Large basis sets predict the bond energy to be round 4·7–4·8 kcal/mol[19,20]. The bond energy given by the basis set used by us is greatly overestimated and is close to the bond energy given by the DZ basis set of Newton and Ehrenson[21]. Another feature of our basis set is a small effect of functions localized on the neighbouring molecule on the energy of the monomer of water. The change in the energy of dimerization brought about in this way was 1·13 kcal/mol with our basis at the O–O distance 2·8 Å, compared to 5·77 kcal/mol with the minimal STO-3 G basis set[22] at d(O–O) = 2·78 Å. The overestimation of the energy of dimerization is presumably due to a high dipole moment of the monomeric water which gives rise to the overestimation of the coulomb interaction. The charge trasfer and the polarization energy are better accounted for. The quantities derived from the Mulliken population analysis such as charge transfer and charge shift are realistic, too.

For the energy of the hydrogen bond in the H_2O–OH^- system we obtained the value of −33·55 kcal/mol. This matches more closely the value of −24·3 kcal/mol given by a large basis set[23] than does the energy of −40·72 kcal/mol given by the DZ 4–31 G basis set[21]. The O–O bond length of 2·57 Å given by our basis set agrees well with the value of 2·63 Å inferred by interpolation from the results of Kraemer and Diercksen[23] with a large basis set for an unsymmetric complex. Details on our basis set will be published elsewhere[17].

The 2*s* function for lithium was scaled by 2·1. The scaling factor was obtained by iterative optimization. This was done simultaneously with the Li–O bond length optimization in a planar (C_{2v}) Li^+–H_2O system, maintaining water in the geometry of the isolated molecule. The total energy of Li^+–H_2O is −83·11390 a.u. The optimal Li–O bond length and hydration energy of the lithium ion are 1·79 Å and 47·7 kcal/mol, respectively, compared to 1·84 Å and 35·2 kcal/mol given by a large basis set[24].

RESULTS

Geometry optimization. The optimization of the interaction energy between Li^+, H_2O and OH^- started from the optimal geometries of the pertinent components. First the location of hydrogen in the OH group, $H_{(3)}$, was optimized for the Li—$O_{(1)}$ distance fixed at 1·79 Å and the $O_{(1)}$—$O_{(2)}$ distance fixed at 2·45 Å (for numbering of atoms and the model configuration see Fig. 1). We assumed that the $O_{(1)}$—$O_{(2)}$ distance should be shortened due to the effect of Li^+, compared to the $O_{(1)}$—$O_{(2)}$ distance in $H_3O_2^-$. The energy dependence on the angle β is plotted in Fig. 2. The optimal angle β was interpolated to be 50°, *i.e.* the hydrogen $H_{(3)}$ is in the *trans*

configuration to the Li^+ ion. In next calculations we have taken β of 60° which corresponds to the point of lowest calculated energy. The second minimum at $\beta = -40°$, belonging to the *cis* configuration of the hydrogen $H_{(3)}$ to lithium, is 1·07 kcal higher in energy than the minimum for the *trans* configuration. The potential barrier is 1·82 kcal/mol for the *trans-cis* transformation and 0·75 kcal/mol for the *cis-trans* transformation. On moving $H_{(3)}$ from the *xz* plane by 45°, with $\beta = 60°$, the energy increased by 0·56 kcal/mol. In all subsequent calculations the planar structure of Li^+–H_2O–OH^- was considered. The $O_{(1)}$—$O_{(2)}$ and then Li—$O_{(1)}$ distance were optimized for $\beta = 60°$ (energies are entered in Table I); the resulting values are 2·35 Å and 1·7 Å, respectively. Next, maintaining the optimal Li–$O_{(1)}$ and $O_{(1)}$–$O_{(2)}$ bond lengths fixed, the position of $H_{(2)}$ (in the hydrogen bond) was optimized. The optimal $O_{(1)}$–$H_{(2)}$ distance of 1·135 Å is markedly longer than it is in the water monomer (0·96 Å). This implies that $H_{(2)}$ is only slightly nearer to the water oxygen, $O_{(1)}$, than to oxygen in OH^-. This is in agreement with Robinson and Harned's[5,6] assumption of a strongly polarized water O–H bond in a complex.

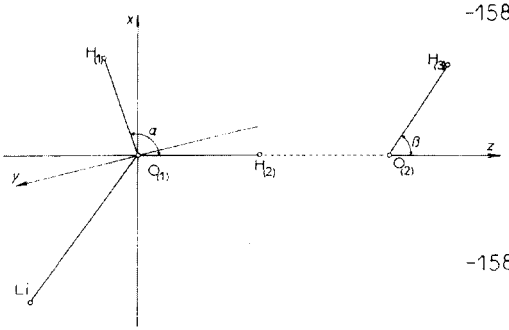

FIG. 1
The Structure of Li^+–H_2O–OH^-

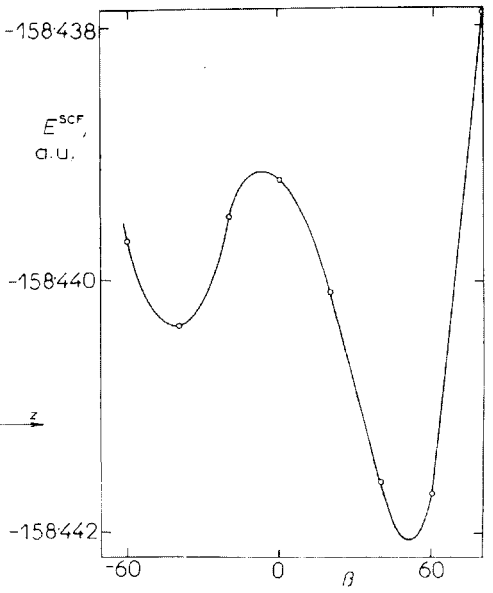

FIG. 2
Optimization of the Position of the Hydroxyl Hydrogen
Energy dependence on the β angle. The O_1—O_2 distance is 2·45 Å.

TABLE I

Total SCF Energies of the Li^+–H_2O–OH^- System ($\beta = 60°$, bond lengths in Å, energies in a.u.) For meaning of geometry parameters see Fig. 1.

$d(Li–O_{(1)})$	$d(O_{(1)}–O_{(2)})$	$d(O_{(1)}–H_{(2)})$	E(SCF)
1·79	2·35	0·96	−158·442 65
	2·25		−158·438 54
1·70	2·35		−158·444 37
1·60			−158·441 14
1·70	2·40		−158·444 34
	2·35	1·06	−158·457 60
		1·11	−158·459 54
		1·135	−158·459 72
		1·14	−158·459 71
		1·16	−158·459 46
		1·21	−158·457 64
		1·31	−158·447 93
	2·50	0·96	−158·441 36
		1·06	−158·454 36
		1·16	−158·457 31
		1·21	−158·457 22
		1·26	−158·456 63
		1·31	−158·455 57
		1·41	−158·450 83
		1·51	−158·437 42
1·70	2·65	0·96	−158·432 55
		1·06	−158·443 70
		1·16	−158·444 81
		1·26	−158·443 42
		1·31	−158·442 99
		1·36	−158·442 96
		1·41	−158·443 24
		1·51	−158·443 43
		1·61	−158·438 70
		1·66	−158·431 83
	2·80	0·96	−158·421 43
		1·06	−158·430 19
		1·16	−158·428 47
		1·21	−158·426 31
		1·31	−158·422 61
		1·41	−158·421 88
		1·51	−158·424 69
		1·61	−158·429 39
		1·71	−158·431 85
		1·81	−158·424 75

We also carried out calculations on the bifurcated hydrogen bond. In this structure the OH^- ion was forced to approach the water molecule symetrically with respect to $H_{(1)}$ and $H_{(2)}$ (the atoms Li, $O_{(1)}$, $O_{(2)}$, and $H_{(3)}$ were lying on a straight line). The optimal $O_{(1)}$–$O_{(2)}$ distance was found at 2·31 Å. Since the structure was 18·83 kcal/mol higher in energy than that with a linear hydrogen bond, the bifurcated structures were disregarded in the next considerations.

Many-body interactions. The $O_{(1)}$–$O_{(2)}$ and Li–$O_{(1)}$ bond lengths in the complex are shorter by 0·22 Å and 0·09 Å than they are in $H_3O_2^-$ and Li^+–H_2O. This implies a strong effect of Li^+ and OH^- ions on the interaction of pertinent subsystems. By substraction of the energy of subsystems Li^+–H_2O (d(Li—O) = 1·7 Å) and OH^- from the energy of the complex in the optimal structure (Table I) we get the interaction energy of 0·23162 a.u., *i.e.* −145·33 kcal/mol. Of course, this is not the energy of the hydrogen bond because it also comprises the interaction between Li^+ and OH^- ions. For this reason we considered it useful to make an analysis of the interaction energies. We made use of the relationship which was employed by Hankins and coworkers[19] for the study of many-body interactions. Thus the total energy is expanded over the energies of single molecules, $E^{(1)}$, pair interactions, $V^{(2)}$, triplet terms *etc.* In our case,

$$E(x_1, x_2, x_3) = E_1^{(1)}(x_1) + E_2^{(1)}(x_2) + E_3^{(1)}(x_3) + V_{12}^{(2)}(x_1, x_2) +$$

$$+ V_{23}^{(2)}(x_2, x_3) + V_{13}^{(2)}(x_1, x_3) + V_{123}^{(3)}(x_1, x_2, x_3) .$$

Here the index (1) stands for lithium, (2) for H_2O, (3) for OH^-. The results presented in Table II were obtained for $d(O_{(1)}–H_{(2)}) = 0·96$ Å; the other parameters refer to the optimal structure of the complex. A large value of $V_{123}^{(3)}$ confirms the anticipated nonadditivity of interactions. The nonadditivity of interaction energies was also found

TABLE II

Pair Energies and Interactions Energies in Li^+–H_2O–OH^-

$d(O_1—H_2) = 0·96$ Å, the other geometry parameters refer to the optimal structure of the complex.

Pair energy	a.u.	Interaction energy	kcal/mol
$E_{12} = E(Li^+\cdots H_2O)$	− 83·112 34	$V_{12}^{(2)}$	− 46·64
$E_{23} = E(H_2O\cdots OH^-)$	−150·959 48	$V_{23}^{(2)}$	− 24·76
$E_{13} = E(Li^+\cdots OH^-)$	− 82·509 30	$V_{13}^{(2)}$	−100·26
		$V_{123}^{(3)}$	− 10·68

with neutral systems such as water polymers[19,25]. This conforms to the conception of Frank[26,27] about the cooperation in the hydrogen bond formation.

The energy of the hydrogen bond between Li^+-H_2O and OH^- is estimated to be $-0{\cdot}05648$ a.u. ($-35{\cdot}44$ kcal/mol). It is obtained by summation of $V_{23}^{(2)}$ and $V_{123}^{(3)}$ and applying the reasoning which was used by Kollman and Kuntz[28] for the estimation of the hydrogen bond energy in the $Li^+-H_2O-H_2O$ system. In fact it is simply the energy given by the subtraction of the interaction energy of Li^+ and OH^- ions from the total interaction energy of Li^+-H_2O with OH^-. In the same way we also treated the optimal structure of the complex with $d(O_{(1)}-H_{(2)}) = 1{\cdot}135$ Å. The estimated hydrogen bond energy is 0·07183 a.u., *i.e.* $-45{\cdot}07$ kcal/mol. Compared to $H_3O_2^-$, it is 11·52 kcal/mol higher. This does not seem to be unrealistic, confronted with the results for the water dimer[28], where the effect of the Li^+ ion brings about the increase of 3·6 kcal/mol in the hydrogen bond energy.

Population analysis. Fig. 3 presents the gross atomic and overlap populations for the complex in the optimal geometry and for all its subsystems. Since the overlap

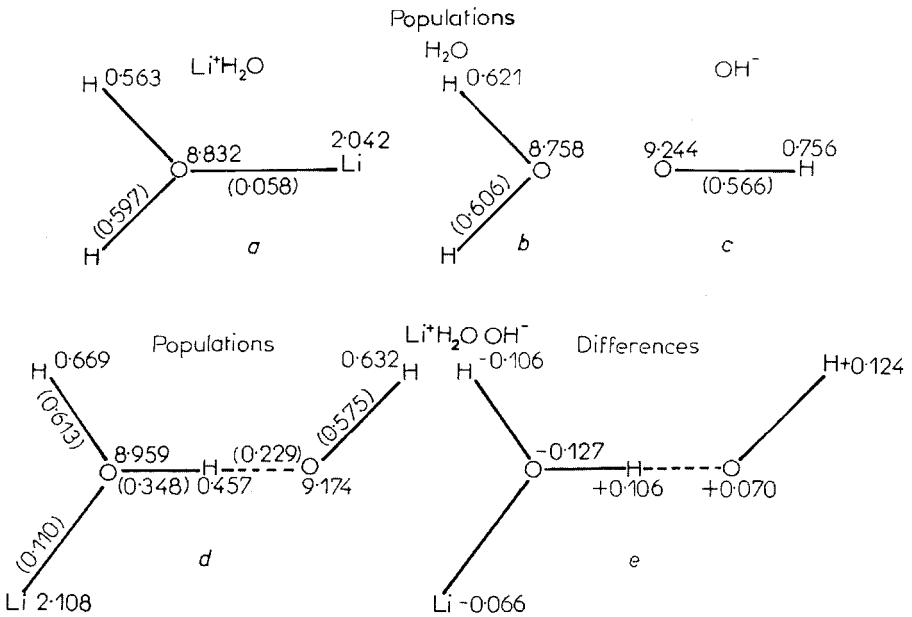

FIG. 3

Gross Atomic and Overlap (in parentheses) Populations

a: Li^+-H_2O; *b*: H_2O; *c*: OH^-; *d*: $Li^+-H_2O-OH^-$; *e*: Differences in gross atomic populations between $Li^+-H_2O-OH^-$ and subsystems Li^+-H_2O and OH^-. Optimized geometry in all instances.

populations (given in parentheses) reflect the covalency of bonds in some way, the hydrogen bond appears to be considerably covalent. The $O_{(2)}$–$H_{(2)}$ overlap population is appreciably high (0·115) even for the unshifted position of hydrogen H_2 *i.e.* for the position which corresponds to the O–H bond length of 0·96 Å in water. The effect of the Li^+ ion on the enhanced ability of water to form a hydrogen bond is due to the increased positive charge on hydrogen. A considerable charge redistribution upon the complex formation between Li^+–H_2O and OH^- is depicted in Fig. 3*e*. The trend conforms to what is to be expected in the formation of the hydrogen bond[1]. The overall electron transfer from OH^- to Li^+–H_2O is 0·193 el. which is a very high value. It is presumably affected by the fact that the location of $H_{(2)}$ in the optimal configuration is near the middle of the O···O bond. In such a case it is difficult to treat electrons localized on $H_{(2)}$ as though they belong solely to Li^+–H_2O. Any charge separation then becomes artificial. A similar situation was found by Clementi[29] in the reaction of NH_3 with HCl (for discussion see also ref.[1]). In the complex with the unperturbated water geometry ($d(O_{(1)}$–$H_{(2)}) = 0·96$ Å), the electron transfer is lower compared to that in the optimal structure but its value of 0·106 el. is still high enough.

The potential curve for the proton motion. The potential curve for the motion of a proton bound in the hydrogen bond is plotted in Fig. 4. It possesses only one minimum with the optimal $O_{(1)}$–$O_{(2)}$ distance of 2·35 Å. Its shape can be well fitted

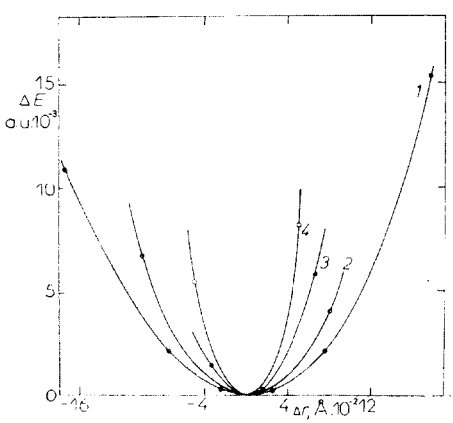

FIG. 4

Potential Curves for the Proton Motion in the Hydrogen Bond and the O–H Stretching Vibration in Water

1 Li^+–H_2O–OH^-; *2* H_2O–OH^-; *3* H_2O–H_2O; *4* H_2O.

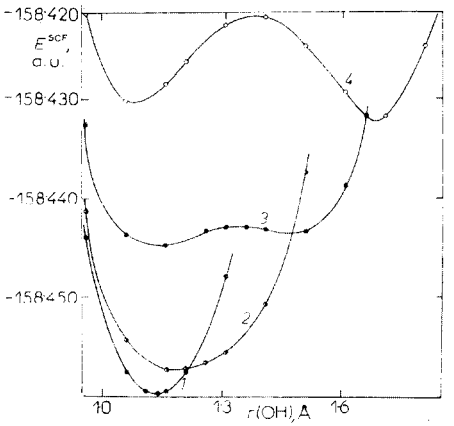

FIG. 5

Potential Curves for the Proton Motion in the Hydrogen Bond in Li^+–H_2O–OH^-

1 $d(O_1—O_2) = 2·35$ Å; *2* $d(O_1—O_2) = 2·50$ Å; *3* $d(O_1—O_2) = 2·65$ Å; *4* $d(O_1—O_2) = 2·80$ Å.

by a parabola which is broader than for H_2O–H_2O and H_2O–OH^- systems. This indicates qualitatively a frequency shift of the OH stretching vibration in water owing to the change in energy of the hydrogen bond. The fact that we found a single minimum for $d(O_{(1)}$–$O_{(2)}) = 2{\cdot}35$ Å is in agreement with the results of Diercksen and coworkers[30]. These authors concluded that a single minimum is found in all cases if the separation of heavy atoms is smaller than about 2·4 Å.

Nevertheless our results do not permit us to decide unambiguously whether there is a double-well or a single-well minimum on the potential curve of the optimal configuration. The reasons are the following: *a*) As other minimal basis sets, our basis set underestimates the O···O distances. It is therefore to be expected that the actual $d(O_{(1)}$–$O_{(2)})$ in the optimal structure is about 2·4 Å or slightly larger. *b*) It is well-known that the minimal basis set gives a single-well potential curve for such distances between heavy atoms for which a larger basis set gives a double-well minimum (see ref.[31] for NH_4^+–NH_3). *c*) If a hydration of the complex were accounted for, the O···O distance would most likely increase.

More detailed information about the proton motion in the hydrogen bond is provided by the potential curves for various $O_{(1)}$–$O_{(2)}$ distances. These are shown in Fig. 5. For $d(O_{(1)}$–$O_{(2)}) = 2{\cdot}5$ Å a distortion appears on the parabola. For $d(O_{(1)}$–$O_{(2)}) = 2{\cdot}65$ we found a double-well unsymetric minimum, the well of lower energy being on the side of the proton donor (*i.e.* water). For $d(O_{(1)}$–$O_{(2)}) = 2{\cdot}8$ Å we also found a double-well minimum but the well of lower energy was located on the side of the OH^- ion. Hence, there may be roughly a symetric double-well minimum for $d(O_{(1)}$–$O_{(2)})$ ranging from 2·65 to 2·8 Å. In any case the shapes of the potential curves provide an account of the continuous infrared absorption[9–12].

DISCUSSION

As noted above, incomplete hydration of the complex is one of the drawbacks of the model used. The complex treated represents an isolated particle in the gas phase. On relaxing the fixed parameters ($O_{(1)}$–$H_{(1)}$, $O_{(2)}$–$H_{(3)}$, Li–$O_{(1)}$ bond lengths and angles α and β), a further optimization at longer $O_{(1)}$···$O_{(2)}$ distances would lead to the LiOH . H_2O system. This can be inferred from the presence of a lower minimum of the Li^+–H_2O–OH^- complex on the side of OH^- at $d(O_{(1)}$–$O_{(2)}) = 2{\cdot}8$ Å. Actually, the complex is unstable towards LiOH + H_2O by 11·0 kcal/mol. Obviously, more water molecules are necessary as the Li–O bond in LiOH would be weakened. It should be noted that the type of the hydrogen bond dealt with in this study is also present in a LiOH . H_2O crystal. Evidence for this was provided by the X-ray analysis[32]. Observed shifts in OH stretching vibrations[33] also indicate strong hydrogen bonds in a LiOH . H_2O crystal.

Our results were obtained by making use of the minimal basis set and cannot therefore be regarded as quantitative. For this reason no attempt was made to correct

the energies for zero-point and correlation energies. Several studies have already been reported on the use of the minimal basis set in calculations on the hydrogen bond in a cluster of more than two particles[18,25,34]. As some of the results are not consistent with those given by large basis sets[35], the interpretations based on the minimal basis set must be taken with caution. On the other hand, for sometime to come a larger than minimal basis set will hardly be manageable for systems involving more water molecules and more complex ions (especially bivalent cations and larger inorganic anions seem to be of interest[3]). Hence, the next studies with the basis sets of this type appear to be expedient. Moreover, it is possible to presume that at least the relative values for different systems will be plausible.

The authors thank the Computing Research Centre of United Nations at Bratislava for providing a grant of computer time on CDC 3300.

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Translated by P. Čársky.