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Short Communications

The Influence of Metal Ions on Neighbouring Hydrogen Bonds

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The influence of metal ions on hydrogen bonds formed by their ligands to other molecules is studied at the example of the water dimer and lithium ion by means of *ab initio* calculations using a $8s/4p+P$ Gaussian basis set. Potential curves for the dimer separation and proton transfer are reported, and the results are used to discuss the ion influence on structure, rotation and the first part of the autoprotolysis reaction of the dimer. Several properties of electrolyte solutions can be related to the principal effects predicted by our calculations.

Key words: Metal complexes – Hydrogen bond – Proton transfer.

1. Introduction

The importance of hydrogen bonding for almost all kinds of chemical and biological systems has been recognized very much during the last decades so that there does not seem to be any need to refer to it generally, but rather to point out the detailed phenomena, which might be concerned by the results reported in the following.

Quantum chemical calculations proved to be one of the most powerful tools in the principal study of hydrogen bonding (for reviews see Ref. [1] and [2]) and form the basis of the investigations reported here.

As one of the most prominent and meaningful examples of hydrogen bonding, the water dimer has been studied very carefully in the past [3–6], including calculations almost at the Hartree–Fock limit. For our purposes, the water dimer seems to be a very good test system too, since the studies mentioned previously could be used for comparison with our data, and since the study of ion influence on hydrogen bonds between water molecules has a special importance for the understanding of effects in electrolyte solutions. It could be expected, that the results obtained for this system would hold generally also for other types of hydrogen bonds, at least in a qualitative sense, and have some

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significance, therefore also for larger hydrogen bonded molecules as encountered in biologically important species.

2. Method

The calculations reported here are of the *ab initio* MO SCF type, using Huzinaga's Gaussian lobe basis sets [7], the program being used is discussed in detail in Ref. [8].

The values for the dimerization energy of water calculated by this method range from 3.7 to 6.1 kcal/mole, the most extended basis set [6] led to the following data: total energy −152.1378 a.u., dimerization energy 3.7 kcal/mole for the linear arrangement ($0 \cdots 0 = 3.0$ Å), where the water molecules are distorted by an angle of 90 degrees.

Since in the studies reported here, we had to calculate a huge number of points of the potential surface of the dimer and the dimer connected with a metal ion, we could not use this very large basis set (13*s*, 8*p*, 2*d*, 1*f* for oxygen), but rather had to choose a smaller, but still sufficiently accurate one reflecting well even minor effects. After some test calculations we found a 8*s*, 4*p*, 1*d* (5111/31/1) set for oxygen and a 4*s*, 1*p* (31/1) set for hydrogen to fulfill these criteria satisfactorily. The exponents for the *s* and *p* functions were taken from Ref. [7], the polarization functions of oxygen and hydrogen had the exponents of 0.3 and 0.1, respectively. For the studies of the ion influence, lithium was chosen in a 8*s*, 1*p* (5111/1) set (Ref. [7], polarization function exponent 0.3). The use of the polarization functions seemed to be of special importance, since many effects of the ion are due to polarization effects and since we planned to study also rotational barriers in our system. For a good description of the potential curve of the $0 \cdots 0$ vibration these functions seemed to be essential, too.

The geometry of the water molecules was kept constant throughout the calculations ($O-H = 0.96$ Å, $H/O/H = 104.5°$), and the potential curves were constructed by calculation of 10 to 20 points for each of them. For the ion, C_{2v} symmetry with respect to the first water molecule was assumed and the distance to the oxygen was energy optimized.

All calculations were performed at the CDC Cyber 74 computer of the Interuniversity computer center at the Technical University of Vienna.

3. Results and Discussion

3.1. The Water Dimer

The total energy obtained by our basis set for the water dimer is −151.9819 a.u. and thus 0.1 percent higher than the "best" value of Ref. [6]. The geometry resulting with our basis set is identical to that of Ref. [6], the $O \cdots O$ distance being 3.0 Å. The corresponding potential curve is given in

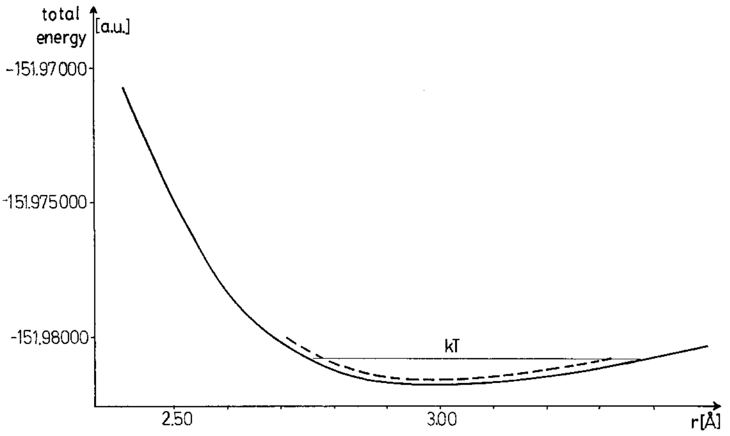

Fig. 1. Potential curve for $H_2O \cdots H_2O$ (dotted line = planar configuration)

Fig. 1. The dimerization energy in our system is 4.8 kcal/mole, the force constant for the $O \cdots O$ vibration in the harmonic approach 0.05 mdyn/Å.

3.2. *The Water Dimer – Lithium Ion – Complex*

Hydrated cations have been studied excessively during the past ten years (for a review of calculations, see Ref. [9]), but only recently second shells were included into such studies [10, 11], which allow some comparison with our data. This comparison is quite limited however, due to the use of small basis sets and rigid experimental geometries in these studies [10, 11]. Some other related studies concern rather stabilization energy data only [12, 13] and cannot be used, therefore, for a discussion of the ion influence on the hydrogen bond.

The potential curve for the lithium ion/water dimer system is given in Fig. 2.

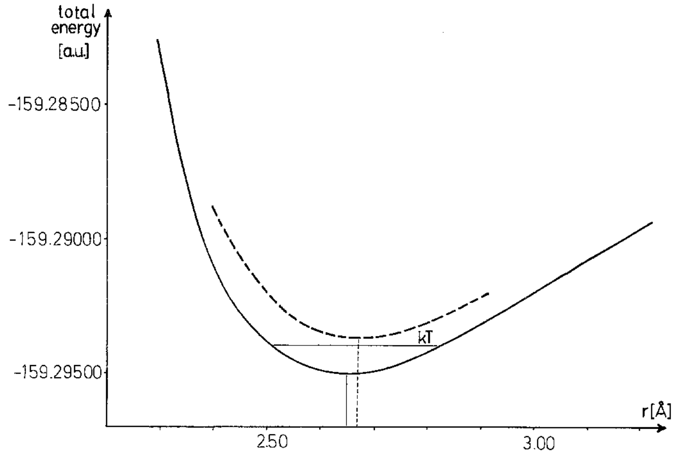

Fig. 2. Potential curves for $Li^+/H_2O \cdots H_2O$ (dotted line = planar conformation)

Regarding the shape of the potential curves, one of the most obvious influences of the ion seems to be the shortening of the O · · · O distance at the energy minimum (2.65 Å compared to 3.0 Å of the dimer), which corresponds to a reduction of the volume occupied by the water dimer by about 50%. At the same time, the stabilization energy for the hydrogen bond increases considerably to the value of 16.9 kcal/mole. Subtracting the value of 4.8 kcal calculated for the dimer, one obtains the net stabilization effect of the lithium ion interacting with the second water molecule to be 12.1 kcal/mole. This value agrees quite well with the second shell hydration energies calculated for fully solvated lithium ion (11.3 kcal for tetrahedral coordination, 12.3 kcal for the $C_{2v} - 1:2$ complex [11]). In connection with the above mentioned reduction of volume, some of the "structure forming" properties of the Li ion seem to be explained quite well even by this simple model system.

Another point of interest within this context seems to be the reduction of the width of the potential curve and its much steeper ascent at both sides, which is reflected also in the harmonic force constant of 0.19 mdyn/Å compared to 0.05 of the dimer itself. This data might be interpreted as "decreased flexibility" of the hydrogen bond induced by the ion.

3.3. *Rotation*

Accurate rotational barriers cannot be evaluated within the methodical framework of our calculations, since relaxation of other geometrical parameters than the O · · · O distance and correlation effects might change the absolute values. It could be expected, however, that the relative changes could be predicted correctly by this approach, leading to information about the rotability of water molecules linked by hydrogen bonds and the ion influence on it.

The dotted potential curves in Figs. 1 and 2 correspond to the dimer configuration, where both water molecules are in the same molecular plain, i.e. to the 90 degree rotated form of the dimer discussed above.

For the dimer, one observes an almost parallel potential curve, separated by the very low energy value of 0.2 kcal/mole, which is almost within the limit of methodical errors and in any case lower than kT. This means, that the water dimer shows almost free rotation. Under the influence of the lithium ion, a considerable change is observed. Parallelity of the potential curves is not given any longer, the minimum is located at an O · · · O distance of 2.70 Å (2.65 before rotation) and the "barrier" has increased to 0.9 kcal/mole, which is slightly higher than kT at room temperature. One can expect, therefore, a lesser mobility of the second water molecule not only due to its stronger stabilization, but also in regard to its rotation. This might be also one of the factors contributing to the "structure forming" behaviour of lithium and similar ions in aqueous solution [14].

3.4. Protolysis Reaction

Proton transfer along hydrogen bonds has been investigated extensively in the past ([15] and references therein). Only a few of these studies concern, however, the kind of proton transfer, where charged species are being produced, especially between identical molecules (autoprotolysis reaction), mainly since the process of dissociation into such species would not occur in the gas phase, for which the quantum chemical model system is valid. Only upon consideration of the interaction with solvent molecules (i.e. inclusion of solvation) one can expect a correct description of the whole dissociation process. It seems to be possible, however, to describe – at the equilibrium distance of both molecules involved in the reaction – the proton transfer which should necessarily be the first step of the dissociation reaction. In this first part of the autoprotolysis, solvent effects might be neglected in a first approximation. We thus have limited our studies to this part of the autoprotolysis reaction, which is of such great importance in aqueous and nonaqueous solvents. A semiempirical study on this reaction in the formic acid dimer [16], reported several years ago, showed, that even the simplified CNDO formalism allows a quite satisfactory description of the first part of the reaction, so that we could expect the results of this *ab initio* study to be reliable enough to reflect correctly the ion influence on autoprotolysis.

The calculated potential curves for the "autoprotolytic" proton transfer in the water dimer and the water dimer bonded to lithium ion are shown in Fig. 3. In

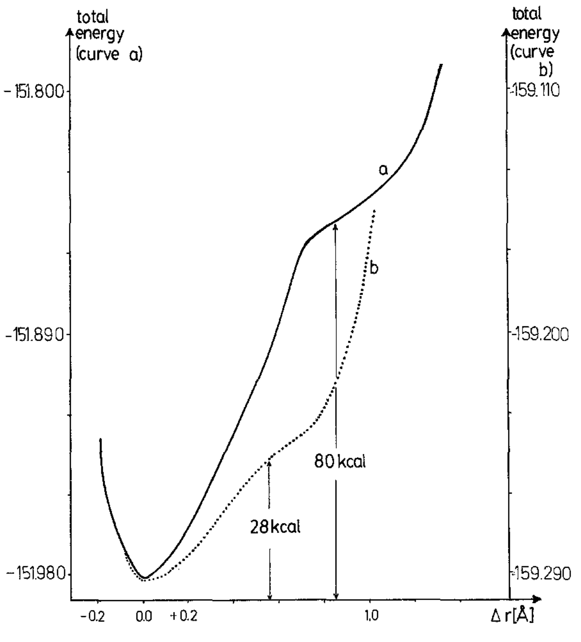

Fig. 3. Potential curves for proton transfer a) in $H_2O \cdots H_2O$ b) in $Li^+/H_2O \cdots H_2O$

both cases the O · · · O distance is kept at the equilibrium value resulting from the potential curves reported above. Both curves show the same shape characterized by a shoulder at that distance of the proton, where the attraction of the other oxygen atom compensates to some extent the energy loss due to the removement of the proton from its orignal water molecule. From this point, one can expect stronger changes in the O · · · O distance in the case of dissociation reactions. After this shoulder, the potential curves become much more steep because of the energy loss due to the additional repulsive forces between the proton and the second water molecule.

The striking difference between both curves is given, however, by the energy separation of the equilibrium geometry and the point, where the above mentioned shoulder is reached. This separation is about 80 kcal/mole for the water dimer, whereas it is only 28 kcal/mole, if the dimer is bonded to the ion, indicating a strongly facilitated autoprotolysis reaction or, in terms of solution chemistry, increased "acidity". This result fits very well Lewis' acid-base-concept as well as Gutmann's donor/acceptor concept [17]. The energy calculated for the products of the autoprotolysis reaction (OH^- or LiOH and H_3O^+) – which is compensated to a large extent in solution by the solvation energy – is 246 kcal/mole for the dimer and 110 kcal/mole for $Li^+(H_2O)_2$, also indicating the reaction to be strongly facilitated by the ion influence.

It should not remain unmentioned that electron correlation, which has been neglected throughout the calculations on proton transfer, has to be expected to have an increasing influence the more the proton is removed from its original site. This effect will surely induce some changes in the potential curve, but not alter its general shape. The contribution of correlation cannot be expected further, to be large enough to compensate fully the effects of the ion as being observed in the one-determinantal approach, since the absolute values for correlation contributions to hydrogen transfer processes are generally small [15].

4. Conclusion

The results reported in this work seem to give – despite the very simple model system being used – a good insight into some general features of ion influence on hydrogen bonds between the ligand of the ion and other molecules. Strengthening of these hydrogen bonds, meaning a kind of "fixation" of the neighbouring molecules and changes in structure due to volume reduction seem to be the most important effect, which might be of some importance not only in the case of water, but also other hydrogen bonded partners like nucleic acid/base pairs. Further, our simple model system seems to indicate also the theoretical background of some properties of electrolyte solutions like second shell solvation, electrostriction and the autoprotolysis reaction.

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