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Theoretical Investigations on the Solvation Process

III. STO Double- ζ SCF Calculations on the Hydrated Proton H_5O_2^+

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STO double-zeta SCF wavefunctions for various configurations of the H_5O_2^+ associate have been computed. Results are discussed and compared with other authors' similar calculations on gaussian bases.

An electrostatic picture of the monosolvation of H_3O^+ is proposed as a fairly satisfactory one.

In a previous paper of this series [1], hereafter referred to as I, a simple electrostatic procedure for obtaining a first order picture of the conformational energy of hydration adducts was tested on the water dimer, where the association energy is about 5 kcal/mole. In the present note we make a similar test on $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ where the association energy is considerably larger, about 40 kcal/mole.

As in Paper I, the test is performed by comparing the results of the electrostatic procedure with a picture of the conformational energy obtained by "ab initio" SCF LCAO MO calculations on the whole associate.

In contrast with I the internal geometries of the partners are not kept fixed at the experimental ones because the association energy range does not allow one to neglect the hypothesis of sensible deformations.

All SCF calculations have been performed on a double- ζ STO basis set (ζ values for O in Ref. [2], for H in Ref. [3]). Such results may be used as a control of the compatibility of SCF geometry optimization via limited basis sets. There are, in fact, analogous investigations on the same associate relying on GTO basis sets of different complexity [4–6]. The essential information of the search for the best geometries is collected in Table 1.

The results on H_2O and H_3O^+ show that double- ζ STO basis sets give sufficiently correct geometries which compare well with the best calculations [7–8].

The optimized structure of H_5O_2^+ belongs to the D_{2d} symmetry group, i.e. it is linear with staggered terminal hydrogens, the other hydrogen lying at the molecular centre (see the model at the top of Fig. 1). The same disposition was found to be the optimum one also in Refs. [4–6]. Optimization of geometry was made in Ref. [6]: the best values quoted are $r_{\text{OH}} = 0.95 \text{ \AA}$, $r_{\text{O-O}} = 2.36 \text{ \AA}$, $\alpha = 115^\circ$.

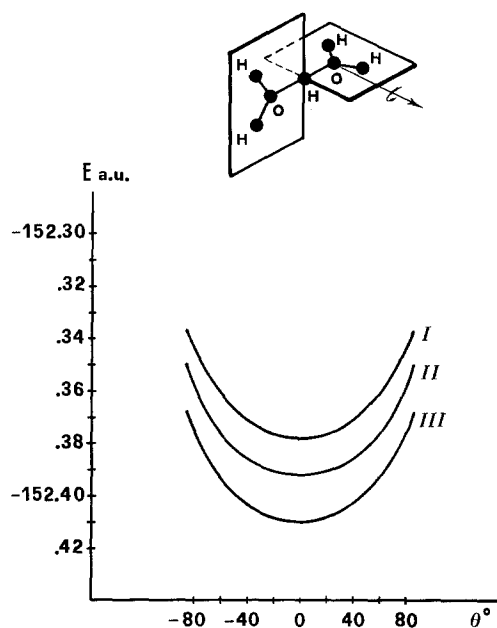


Fig. 1. Trend of the interaction energy for rotations of the HOH molecule, as shown at the top of the figure. The curves may be fitted by the following quartics (θ in radians, energy in atomic units): Eq. I $E^{\text{SCF}}(\theta) - E^{\text{SCF}}(0) = 0.012736 \theta^2 + 0.002487 \theta^4$. Eq. II $E^{\text{El}}(\theta) - E^{\text{El}}(0) = 0.006561 \theta^2 + 0.005519 \theta^4$. Eq. III $E^{\text{H}}(\theta) - E^{\text{H}}(0) = 0.011706 \theta^2 + 0.003010 \theta^4$

Table 1

	H ₂ O	H ₃ O ⁺	H ₅ O ₂ ⁺
$E(\text{a.u.})$	- 76.00574	- 76.30141	- 152.37793
$r_{\text{O-H}}(\text{\AA})$	0.962 (0.958)	0.970	0.966
α_{HOH}	108.8° (104.52°)	120°	114.4°
$r_{\text{O-O}}(\text{\AA})$	—	—	2.36
hydration energy ^d	—	185.5	44.4
(kcal/mole)		(172 ^a) (188.4 ^b)	(44.5 ^c) (38.5 ^b)

Experimental values in parenthesis.

^a: Ref. [9], ^b: [10], ^c: [11], all corrected for zero-point energy.

^d $\Delta E(\text{H}_{2n+1}\text{O}_n^+) = E(\text{H}_{2n+1}\text{O}_n^+) - E(\text{H}_{2n-1}\text{O}_{n-1}^+) - E(\text{H}_2\text{O})$.

The total energy of H₅O₂⁺ and binding energy ΔE relative to H₂O and H₃O⁺ reported in Table 1 are to be compared with those found by Kollman and Allen [4]: $E = -152.36230$ a.u., $\Delta E = 36.9$ kcal/mole, by Kraemer and Diercksen [5]: -152.42848 and 32.3 , by Newton and Ehrenson: -152.1791 and 44.0 .

The influence of the optimization of the internal geometry of the partners may be illustrated by examining the investigation made by Kraemer and Diercksen [5] on two possible reaction paths: a) H_2O and H_3O^+ approach each other retaining their internal geometries, b) two water molecules (at fixed internal geometries) approach each other keeping a proton fixed midway between the two O atoms. The minima they found are at $r_{\text{O-O}} = 2.47 \text{ \AA}$ for case a) and $r_{\text{O-O}} = 2.39 \text{ \AA}$ for case b), their difference in energy favouring b) by 0.6 kcal/mole. Furthermore a displacement of the proton along the O–O axis in the b) structure shows a very slight double well character.

Our results are very similar to those of Ref. [5] for large O–O distances. Near the equilibrium, if one releases the internal geometries of the partners, the difference between a) and b) structures increases notably. According to our calculations the difference between b) ($r_{\text{O-O}} = 2.45 \text{ \AA}$) and a) ($r_{\text{O-O}} = 2.36 \text{ \AA}$) is about 4 kcal/mole and further, the double well character of the proton displacement curve in b) structure disappears, leaving a very flat minimum. Such differences in stability between the two structures a) and b) show how in the present case geometry deformations are essential: it is, therefore, questionable whether the electrostatic assumption of Paper I may be still supported. Since the associate considered here may be regarded as a limiting case in the set of monohydration associates $\text{M}^+ \text{H}_2\text{O}$, where M^+ is a molecular ion, it is convenient to elucidate to what extent the electrostatic approximation is still valid. Simple estimates based on the interaction of a point dipole (H_2O) with a point charge (H_3O^+) have already shown [6] how it is possible in such a way to allow for about 70% of the interaction energy. A less naive approximation considers the two entities H_3O^+ and H_2O at the geometries of the associate (see Table 1) and calculates fully the electrostatic energy between them. Rotations of one of the partners around the corresponding O nucleus give an electrostatic picture of the potential energy hypersurface around the minimum. Such a picture is in fairly satisfactory accordance with the SCF one.

As an example Fig. 1 shows the energy hypersurface section corresponding to the rotation of H_2O around the axis visible in the figure. Curve I provides the SCF section, curve II the electrostatic one.

The application of point charge models performed in Paper I would not be appropriate in this case. A larger interpenetration of the charge clouds leads to the possibility of there being different models of the H_2O molecule, all reaching the same degree of reliability, as defined in I, which gives erratic results. Introduction of polarization effects is more influential in the present case. Curve III of Fig. 1 corresponds to a picture allowing for also the polarization (Hartree SCF function). The larger difference of $E_{\text{III}} - E_{\text{I}}$ with respect to $E_{\text{II}} - E_{\text{I}}$ is offset by a better approximation to I as far as curvature in the minimum region is concerned (compare the fitting with quartic curves reported at the bottom of Fig. 1).

In conclusion, it seems that the validity range of the electrostatic assumption may be extended to associates involving also “strong” hydrogen bonds, whereas the ultrasimple charge point model of Paper I seems to be too poor an approximation in such cases.

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