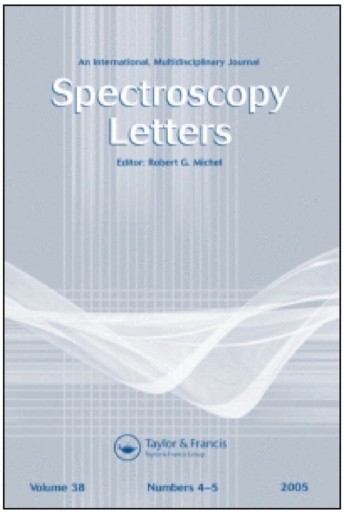

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Hydrogen Bonding and the Protonated Water Dimer

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HYDROGEN BONDING AND THE PROTONATED WATER DIMER

Key words: Protonated water dimer, Hydrogen Bonding, MOPAC

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ABSTRACT

A semi-empirical AM1 study of hydrogen bonding and protonation in water has been carried out to illustrate the two different O-H vibrational frequencies present in the protonated water dimer, $H_5O_2^+$. Using the MOPAC quantum mechanical program, it is shown that the optimized geometry for this species is C_{2h}, with an O-H bond distance of 1.20Å, and the fifteen normal frequencies have been determined. Results predict the two O-H vibrational frequencies at 553 and 3300 cm^{-1}, with the former being the H-bond stretching mode. A grid calculation illustrating how the potential energy surface of water varies with the H-O-H angle and the O-H bond distance is also presented.

INTRODUCTION

Proton transfers permeate many areas of chemistry. A significant distinction between O-H in a hydrogen bond and that in a protonated system is the separation distance of the two atoms. The protonation of water to produce the hydronium ion, or the protonation of an amine or nitrogen heterocyclic occurs at a distance of ~1.0 Å; however in hydrogen bonded systems the separation of 0···H and N···H is usually 2.5-3.5 Å. Of fundamental interest is how do we describe an 0···H and N···H distance between these limits? We have initiated a MOPAC [1], AM1 semi-empirical, study of the protonated dimer of water, $H_5O_2^+$, with the aim to better understand the energetic and geometrical factors that are involved. Of some interest is what is the difference between the transfer of a hydrogen bond and a proton transfer? Among the issues we address below are: i) what is the energy variation of the protonated dimer as the proton is moved along the O-O axis of the dimer? We will see that the simple D_{2h} structure does not represent the equilibrium geometry of the system, ii) the optimized geometry of $H_5O_2^+$, which is predicted to be C_{2h}, and the fifteen vibrational frequencies for this system, and iii) a grid calculation for water, which shows the dependence of the heat of formation of water on the O-H bond length and the H-O-H bond angle.

COMPUTATIONS

Initial structures for the semi-empirical AM1 calculation were generated from within Chem3D, version 3.5, or directly from construction of the Z-matrix. The keywords used are AM1, GNORM=0.001, CHARGE=1 and FORCE.

I. Potential Energy Surface of the Protonated Water Dimer. In proceeding with the AM1 calculation we started with a D_{2h} geometry with the two oxygen atoms separated by 2.78Å, with the proton at the midpoint between the oxygen atoms. The proton is allowed to move along the O-H-O axis, whose angle of 180° was held constant. The corresponding Z-matrix for this species is shown in Fig. 1.

The results of the calculation allow us to construct the energy diagram shown in Fig. 2, that clearly shows a double minimum at ~1.0Å O-H separation, which is the normal protonation distance found in the hydronium ion. A similar behavior was predicted by Scheiner [2], using the ab-initio method. It is noted that the midpoint separation of the proton between the two oxygen atoms is not a global minimum. As the proton moves towards either water molecule it becomes tetrahedral. Also plotted in Fig. 2. is the dipole moment of the system, which is

```
AM1 GNORM=0.001 CHARGE=1
PROTONATED WATER DIMER;O-O SEPARATION 2.78 ANGSTROMS
H
O   0.97612  1                                 1
H   0.97612  1  105.6524  1                    2   1
H   1.38815  0  127.5000  1  180.000  1        2   1   3
O   1.38815  0  180.0000  0  180.000  1        4   2   3
H   0.97612  1  127.5000  1  180.000  1        5   2   3
H   0.97612  1  127.5000  1  180.000  1        5   2   1
```

FIG. 1. Z-matrix for the D_{2h} structure of $H_5O_2^+$.

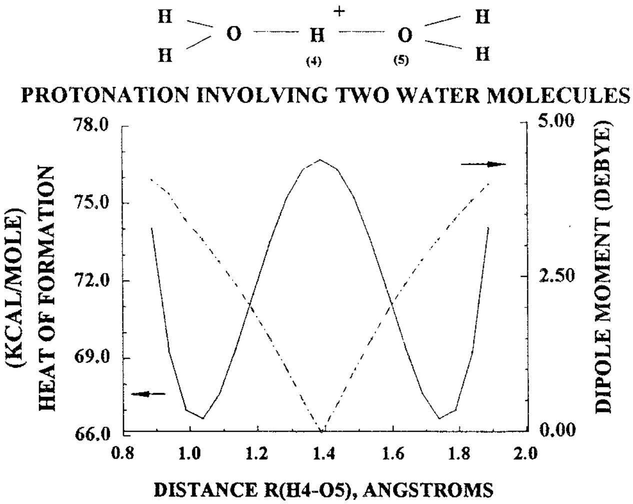


FIG. 2. Dependence of the heat of formation and dipole moment of $H_5O_2^+$ on the H(4)-O(5) separation distance. (Constrained motion along O-H^+-O axis).

zero for the symmetric D_{2h} structure, when the proton is at the midpoint, and which becomes polarized as the symmetry of the bisecting plane is lost. The dependence of the ionization potential of the protonated dimer on the R4-O5 separation distance is shown in Fig. 3, where it is seen that the maximum ionization potential occurs for the symmetric species. As the proton is moved from the center, the system becomes asymmetic and the influence of the proton is weakened on one side, which is reflected in the lower water ionization potential, i.e., it is easier to ionize an electron from water than from the hydronium ion.

II. Optimized Geometry of $H_5O_2^+$. The optimized geometry of the protonated dimer was determined to be C_{2h} , with a heat of formation value of 65.82 Kcal/mol. In Fig.4 we show the final optimized structure for the protonated dimer. At the outset the geometry was D_{2h} with the separation of the two oxygen atoms at 3.00Å, and all parameters were allowed to vary. The final optimized Z-matrix is given in Fig. 5, where it is seen that the longer H-bonded O-H distance is predicted to be 1.20Å. This result is in satisfactory agreement with ab-initio predictions reported by Schaefer et al.[3]. Calculation for the protonation of water results in an O-H distance of 1.0Å, in contrast to a value of 0.96Å for C_{2v} water. The equilibrium geometry for the protonated water dimer has an O-O distance of 2.39Å and a dipole moment estimated to be 5.75D.

In addition to determining the equilibrium geometry for $H_5O_2^+$ we have also calculated the 15 vibrational frequencies, and the corresponding symmetry species, which show some interesting effects. In particular the proton distance in a hydronium ion is 1.0Å, which is significantly shorter than the symmetric hydrogen bonded O-H separation of 1.20Å in the complex. This suggests two different types of O-H vibrations, namely, one that is associated with protonation, and a second one associated with the longer separation distance, that represents hydrogen bonding. A summary of the fifteen vibrational frequencies for the protonated dimer are given in Table I. These data show four stretching frequencies, and four angular bending modes of the two water molecules. An interesting vibrational mode is the one appearing at 553 cm^{-1}, which corresponds to the symmetric stretching of the two water molecules along the O-H-O axis. We label this as a

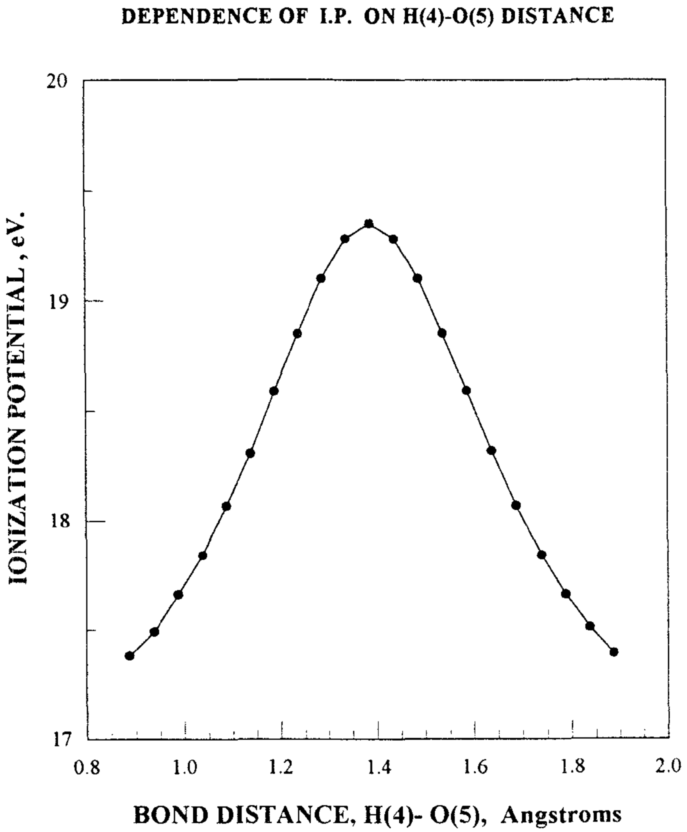


FIG. 3. Variation of the ionization potential for the protonated water dimer with H(4)-O(5) separation distance.

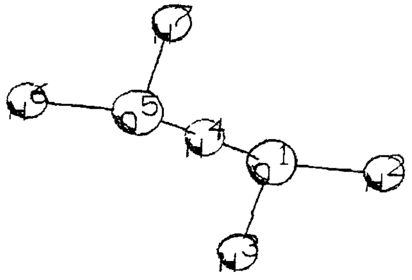


FIG. 4. Optimized structure, C_{2h} , of $H_5O_2^+$ with an O-O separation distance of 2.39Å, and heat of formation of 65.82 Kcal/mol.

```
AM1 GNORM=0.005 CHARGE=1
PROTONATED WATER DIMER;O-O SEPARATION 2.394 ANGSTROMS

O
H   0.97961  1                                  1
H   0.97963  1  106.02841  1                    1    2
H   1.19725  1  110.67018  1   120.03969   1    1    2    3
O   1.19714  1  179.78818  1  -157.77529   1    4    1    2
H   0.97963  1  110.64912  1   179.71994   1    5    4    2
H   0.97962  1  110.66691  1    62.49140   1    5    4    2
```

FIG. 5. Z-matrix for the optimized geometry of $H_5O_2^+$ with an O-O separation distance of 2.39Å.

hydrogen bond stretching mode, since the oxygen bonded to the proton each have a separation distance of 1.20Å, which is too large for protonation, and is consistent with a lower frequency, relative to the 3300 cm^{-1} stretch observed in the water molecule. It is to be expected that a larger O-H separation would be manifested as a shift to a lower O-H stretching frequency, consistent with increasing hydrogen bonding. The vector displacements for this symmetric mode are shown in Fig. 6, along with the symmetric O-H stretch of the two water molecules. An interesting experimental study of the vibrational frequencies for the hydrogen bonding complexation between phenols and carbonyl compounds has been reported to illustrate this effect [4]. The energetics of the protonation of water can also be determined from the heats of formation for H^+,H_2O, H_3O^+ and $H_5O_2^+$, each of which is obtained from the semi-empirical method. AM1 results for these species are 314.91, -59.25, 143.46 and 65.82 Kcal/mole, respectively. These values lead to the following enthalpy predictions:

$$H^+(g) + H_2O(g) \longrightarrow H_3O^+(g) \qquad \Delta H = -112.21 \text{ Kcal/mole} \qquad (1)$$

$$H_2O(g) + H_3O^+(g) \longrightarrow H_5O_2^+(g) \qquad \Delta H = -18.21 \text{ Kcal/mole} \qquad (2)$$

Table I

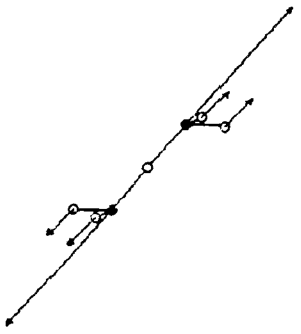
Predicted AM1 vibrational frequencies for the Protonated water dimer (C_{2h})

3416	(b_u)	O-H stretch of the two water molecules (radial)
3411	(a_g)	symmetric O-H stretch of the two molecules (radial)
3299	(a_u)	O-H stretch of the two water molecules (radial)
3295	(b_g)	O-H stretch of the two water molecules (radial)
1795	(b_u)	asymmetric angular bend of the two water molecules
1766	(a_g)	symmetric angular bend of the two water molecules
1540*	(a_u)	$H_5O_2^+$ bending mode with torsional motion of water molecules
1220*	(b_u)	$H_5O_2^+$ bending mode with asymmetic bend of the water molecules
999*	(b_u)	$H_5O_2^+$ bending mode (radial)
884	(b_g)	asymmetic torsion of the two water molecules
863	(a_g)	symmetric angular bend of the two water molecules
553	(a_g)	H-bond O-H stretch; symm. axial displacement of water (radial)
229*	(a_u)	torsion mode
182*	(b_u)	$H_5O_2^+$ bending mode, with antisymmetric angular bend of water
34*	(a_u)	$H_5O_2^+$ bending mode with torsion motion of water molecules

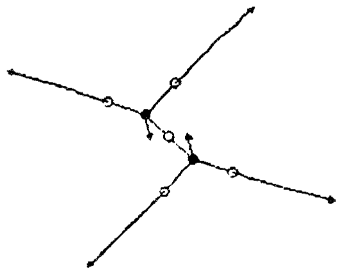
* indicates signficant displacement of the central hydrogen atom along z-axis.

The energetics of the second process has been experimentally determined to be -31.6 Kcal/mole [5]. It appears that an error occurs in the AM1 calculation for the calculated heat of formation of the proton, which has a value of 314.91 Kcal/mol, which is significantly different from the experimental value of 367.2 Kcal/mol [6]. In the case of H_2O and H_3O^+; however, the calculated heat of formation are correct within 2-4 Kcal/mol from the experimentally determined values [7].

III. Potential Energy Grid Calculation for Water. With the aim of understanding the energy dependence of the water molecule on bond length and bond angle, a



553 cm^{-1} (a_g)
H-Bond. R(O-H) =1.20Å



3411 cm^{-1} (a_g)
O-H stretch. R(O-H) = 0.98Å

FIG. 6. Symmetric stretching modes of $H_5O_2^+$ showing the two O-H stretches.

grid calculation involving the simultaneous variation of these two parameters was also carried out. A summary of these results is given in Fig. 7, where it is clearly seen that the optimum structure of water corresponds to an O-H bond distance of 0.96Å and a bond angle of 104°, in agreement with the known structure of water. The calculated heat of formation is –59.25 Kcal/mole, which is in reasonable agreement with the value of –57.80 Kcal/mole for $H_2O(g)$. Solvent interactions

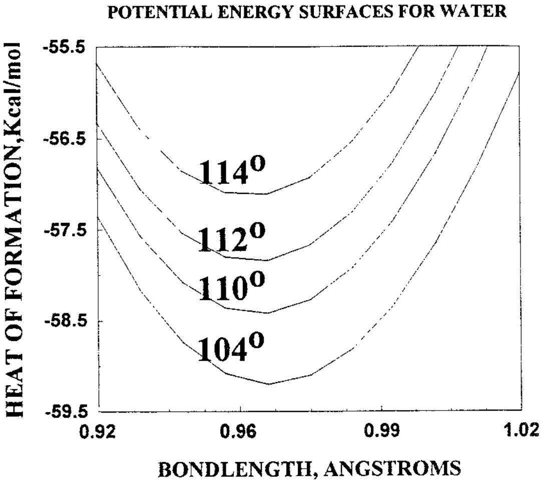


FIG. 7. AM1 grid calculation showing the dependence of the heat of formation of water on the O-H bond distance and H-O-H angle.

are not included in these calculations; consequently, they would apply to the gas phase or a non-polar hydrocarbon solvent.

Conclusion.

The results presented above show that AM1 successfully describes hydrogen bonding in the protonated water dimer, is consistent with ab-initio predictions, and illustrates the two different O-H vibrational frequencies present in this C_{2h} species.

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