

## A Point Charge Model of the Hydronium Ion, $\text{H}_3\text{O}_4^+$

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A simple point charge model, including electrostatic, repulsive, and dispersive interactions, is suggested for complexes including hydrogen bonds. The model is expected to give the equilibrium distance and the binding energy due to the intermolecular hydrogen bonds. It has at present been applied to the hydronium ion,  $\text{H}_3\text{O}_4^+$ .

A theoretical investigation of the strength of the hydrogen bond is specially important when experimental investigations are incomplete. This is the case with the hydronium ion,  $\text{H}_3\text{O}_4^+$ . Quantum mechanical calculations by SCF-MO-LCAO treatment on this ion have previously been performed by Grahn.<sup>1</sup> He has used only  $1s$ ,  $2s$ , and  $2p$  orbitals in oxygen and  $1s$  in hydrogen, *i.e.* a minimal basis set. The atomic orbitals (AO's) in his calculations are all of the Slater type<sup>2</sup> except  $2s$  (in oxygen), which has been given a node by mixing the Slater function  $2s'$  with  $1s$  (in oxygen) and making these two ( $2s$  and  $1s$ ) orbitals orthogonal. The method is, however, too complicated to be suitable for the variation of the conformation of the ion under consideration. In the present paper a simplified model is suggested for this ion. This model makes possible the variation of the distances between the constituent parts ( $\text{H}_3\text{O}^+$  and three water molecules) of the  $\text{H}_3\text{O}_4^+$ -ion in order to find the equilibrium distance by minimizing the energy needed to build up the ion out of its constituent parts. The aim of this paper is to give some information on how this simple model works in the case of  $\text{H}_3\text{O}_4^+$  and to indicate how it, hopefully, may be extended to other complex systems.

A simple point charge model for the  $\text{H}_3\text{O}_4^+$ -ion is suggested under the assumption that the ion is planar, symmetric and consisting of four parts, namely a  $\text{H}_3\text{O}^+$ -ion and three water molecules that are bound to the  $\text{H}_3\text{O}^+$ -ion by hydrogen bonds (Fig. 1). The distances between O and O', O'', O''', have been varied symmetrically while the O—H distances within the four constituent parts have been kept fixed and made equal, *i.e.* the O—H distance in the  $\text{H}_3\text{O}^+$ -ion has been assumed to be 0.96 Å, which is equal to the O—H distance in a water molecule. These distances have been fixed in accordance with the assumptions made in the paper by Grahn.<sup>3</sup> The model suggested in the present paper includes the pure electrostatic interactions between the different point

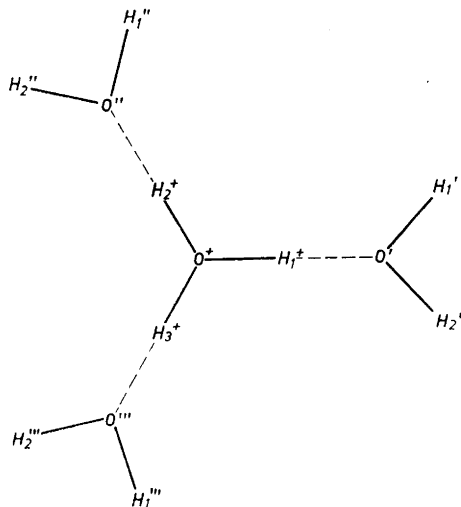


Fig. 1. A  $\text{H}_9\text{O}_4^+$  complex formed by  $\text{H}_3\text{O}^+$  ion and three water molecules. It is assumed to be planar.

Table 1.  $x$ ,  $y$ , and  $z$  are the position coordinates in  $\text{\AA}$  of the point charges in  $\text{H}_9\text{O}_4^+$ -ion (see Figs. 1 and 2),  $Q$  is the strength of the point charges in  $e^+$ , where  $e^+ = +4.8 \times 10^{-10}$  e.s.u., and  $d$  is the distance varied.

The name of the point charge	$x$	$y$	$z$	$Q$
$\text{O}^+$	0	0	0	+0.38
$\text{H}_1^+$	+0.96	0	0	+0.59
$\text{H}_2^+$	-0.48	+0.83	0	+0.59
$\text{H}_3^+$	-0.48	-0.83	0	+0.59
$\text{n}_1^+$	+0.48	0	0	-0.38
$\text{n}_2^+$	-0.24	+0.42	0	-0.38
$\text{n}_3^+$	-0.24	-0.42	0	-0.38
$\text{O}'$	$d$	0	0	+4.12
$\text{H}_1'$	$d+0.58$	+0.76	0	+0.28
$\text{H}_2'$	$d+0.58$	-0.76	0	+0.28
$\text{n}_1'$	$d+0.29$	+0.38	0	-0.34
$\text{n}_2'$	$d+0.29$	-0.38	0	-0.34
$\text{L}_1'$	$d-0.06$	0	+0.09	-2.00
$\text{L}_2'$	$d-0.06$	0	-0.09	-2.00
$\text{O}''(\text{O}''')$	$-0.50d$	$(\frac{+}{-}) 0.87d$	0	+4.12
$\text{H}_1''(\text{H}_1''')$	$-0.50d+0.37$	$(-)(0.87d+0.89)$	0	+0.28
$\text{H}_2''(\text{H}_2''')$	$-0.50d-0.95$	$(\frac{+}{-})(0.87d+0.13)$	0	+0.28
$\text{n}_1''(\text{n}_1''')$	$-0.50d+0.18$	$(\frac{+}{-})(0.87d+0.44)$	0	-0.34
$\text{n}_2''(\text{n}_2''')$	$-0.50d-0.48$	$(\frac{+}{-})(0.87d+0.06)$	0	-0.34
$\text{L}_1''(\text{L}_1''')$	$-0.50d+0.03$	$(\frac{+}{-})(0.87d-0.05)$	+0.09	-2.00
$\text{L}_2''(\text{L}_2''')$	$-0.50d+0.03$	$(\frac{+}{-})(0.87d-0.05)$	-0.09	-2.00

charges, the dispersive interactions (mainly those due to dipole-dipole interactions) and the repulsive interactions (being partly due to the Pauli-principle). The two last-mentioned interactions, originating from the dispersive and repulsive forces, are the main interactions between  $H_1^+$  and  $O'$  ( $H_2^+ - O''$  and  $H_3^+ - O'''$ ) (Fig. 1).

The choice of the strength of point charges for the different atoms has been done in accordance with the calculated total net atomic populations<sup>4</sup> derived from the results obtained by Grahn.<sup>3</sup> Negative charges have been placed midway between the atoms in the four constituent parts of the  $H_3O_4^+$ -ion (see Table 1 and Fig. 2). This has been done in order to give the right

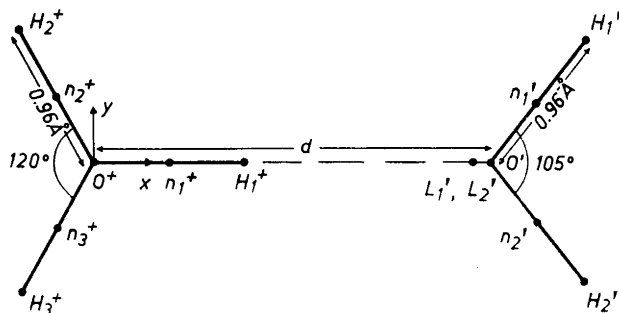


Fig. 2. Relative positions of the point charges for the central  $H_3O^+$ -ion and one of the water molecules (see also Fig. 1). The  $z$  axis is perpendicular to the plane of the paper, *i.e.* the plane of the  $H_3O_4^+$ -ion. The "lone pair" electrons ( $L_1'$  and  $L_2'$  in this figure) of the water molecule are shown in projection only (see Table 1).

Table 2.  $x, y, z$  are the position coordinates in Å of the point charges in two water molecules as shown in Fig. 3,  $Q$  is the strength of the corresponding point charges in  $e^+$ , where  $e^+ = 4.8 \times 10^{-10}$  e.s.u. and  $d$  is the distance varied.

The name of the point charge	$x$ (Å)	$y$ (Å)	$z$ (Å)	$Q$
$O'$	0	0	0	+4.12
$H_1'$	+0.96	0	0	+0.28
$H_2'$	-0.25	+0.93	0	+0.28
$n_1'$	+0.48	0	0	-0.34
$n_2'$	-0.12	+0.46	0	-0.34
$L_1'$	-0.04	-0.05	+0.09	-2.00
$L_2'$	-0.04	-0.05	-0.09	-2.00
$O$	$d$	0	0	+4.12
$H_1$	$d+0.34$	-0.76	+0.48	+0.28
$H_2$	$d+0.34$	+0.76	+0.48	+0.28
$n_1$	$d+0.17$	-0.38	+0.24	-0.34
$n_2$	$d+0.17$	+0.38	+0.24	-0.34
$L_1$	$d-0.11$	0	0	-2.00
$L_2$	$d+0.04$	0	-0.105	-2.00

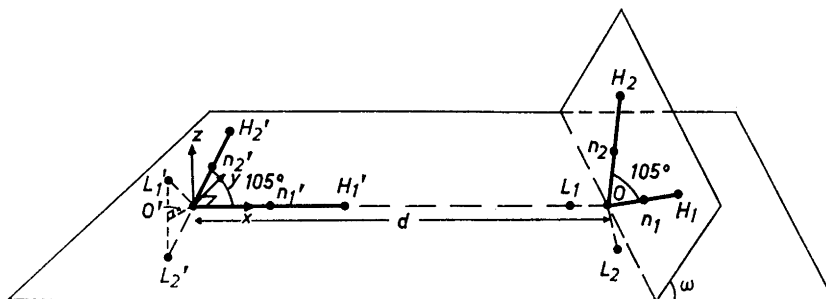


Fig. 3. Relative positions of the point charges in two water molecules in an ice-like structure.  $\omega = 55^\circ$ . See also Table 2.

total charge to the water molecules and to the  $\text{H}_3\text{O}^+$ -ion. This way of handling the problem gives wrong dipole moments to the water molecules; therefore two pairs of "lone-pair" electrons have been represented by charges placed in such a way that each pair is situated symmetrically relative to the water molecule on a line forming a  $55^\circ$  angle with the plane of the water molecule and far enough from the oxygen atom to give the experimentally measured dipole moment to this molecule (see Table 2 and Fig. 3). Assuming a vacuum in the space between the point charges, the electrostatic potential energy can be calculated.

The potential energy,  $V(r_{AB})$ , of the form

$$V(r_{AB}) = a_{AB} \exp(-b_{AB}r_{AB}) - (c_{AB}/r_{AB}^6) \quad (1)$$

where

$$c_{AB} = \frac{\frac{3}{2}(e\hbar/\sqrt{m}) \alpha_A \alpha_B}{\sqrt{\alpha_A/N_A} + \sqrt{\alpha_B/N_B}} \quad (2)$$

is assumed to take care of the interactions between atoms A and B that are due to dispersive and repulsive effects.  $\alpha_A$  and  $\alpha_B$  are atomic polarizabilities, while  $N_A$  and  $N_B$  are effective numbers of outer-shell electrons for atoms A and B.<sup>5</sup> In the present paper  $\alpha$  is assumed to vary strongly only when the effective number of outer-shell electrons varies strongly in comparison with the total number of outer-shell electrons in the neutral atom, while  $\alpha$  is assumed to be constant when comparatively small variations of the effective number of outer-shell electrons are considered. Negligible variations can be expected to be present for heavier atoms. In the present case where only oxygen and hydrogen atoms are present, the following assumptions have been made about  $\alpha_H$  (H stands for hydrogen) and  $\alpha_O$  (O for oxygen):

1)  $\alpha_H$  is assumed to be directly proportional to the effective number of electrons,  $N_H$ , i.e. directly proportional to  $(1 - Q_H)$ , where  $Q_H$  is the point charge given to the hydrogen atom when calculating the electrostatic energy.

$$\alpha_H = \text{const.} \times N_H = \text{const.} \times (1 - Q_H) \quad (3)$$

2)  $\alpha_o$  is assumed to be constant because  $N_o$  varies only between 5 and 6, *i.e.* the relative change of the effective number of the outer-shell electrons is comparatively small and consequently  $N_o$  has been kept constant.

$$\alpha_o = \text{const.} \quad (4)$$

The value of  $c_{OH}$  in eqn. (2) for the neutral case, where no consideration is taken of the charge on the atom in the molecule, has been put equal to 90.4  $\text{\AA}^6$  kcal/mole.<sup>6</sup> Then the actual value,  $c'_{OH}$ , according to (2), (3), and (4) is

$$c'_{OH} = (1 - Q_H) c_{OH} \quad (5)$$

where

$$c_{OH} = 90.4 \text{ \AA}^6 \text{ kcal/mole} \quad (6)$$

$a_{OH}$  and  $b_{OH}$  have been calculated by assuming

$$\left\{ \begin{array}{l} a_{OH} = \sqrt{a_{OO} \times a_{HH}} \\ b_{OH} = \frac{1}{2}(b_{OO} + b_{HH}) \end{array} \right. \quad (7a)$$

$$\quad (7b)$$

$a_{OO}$  and  $b_{OO}$  have been determined semi-empirically by Scott and Sheraga.<sup>6</sup>

$$a_{OO} = 1.35 \times 10^5 \text{ kcal/mole} \quad (8)$$

$$b_{OO} = 4.59 \text{ \AA}^{-1} \quad (9)$$

$a_{HH}$  and  $b_{HH}$  have been calculated<sup>7</sup> from an accurate quantum mechanical calculation for the interaction between two hydrogen molecules by assuming a potential energy of the following form:

$$V(r_{HH}) = a_{HH} \exp(-b_{HH} r_{HH}) \quad (10)$$

(*i.e.* without the  $-c_{HH}/r_{HH}^6$ -term). The repulsive centra in that case have been moved from the positions of the atoms into the corresponding bonds, which would correspond to the correction for the dipole-dipole interactions. The values of  $a_{HH}$  and  $b_{HH}$  determined from very accurate quantum mechanical calculations are not especially suitable for the present calculation under the assumption (1). But since the assumption (7) according to Mason and Rice<sup>8</sup> is not expected to give a high accuracy, the values of

$$a_{HH} = 5.01 \times 10^3 \text{ kcal/mole} \quad (11)$$

and

$$b_{HH} = 3.73 \text{ \AA}^{-1} \quad (12)$$

from Ref. 7 have been used as initial values.

Because of the uncertainty in the choice of the parameters  $a_{OH}$ ,  $b_{OH}$ , and  $c_{OH}$ , these have been tested on a corresponding model for the interaction between two water molecules that were assumed to have the same relative positions as in ice (see Fig. 3 and Table 2). For this reason  $c_{OH}$  has been calculated according to the description given earlier in this paper,

$$c_{OH} = (1 - 0.28) \times 90.4 = 65.1 \text{ \AA}^6 \text{ kcal/mole} \quad (13)$$

$b_{\text{OH}}$ , as calculated from (7b), has been kept fixed, while  $a_{\text{OH}}$  has been varied in order to give minimum total energy (electrostatic+dispersive+repulsive) at the experimentally measured equilibrium distance of 2.76 Å between the oxygen atoms in the interacting water molecules. It has been necessary to ascribe a value of  $0.52 \times 10^4$  kcal/mole, or just 20 % of the value originally calculated from (7a), to the parameter  $a_{\text{OH}}$ . For the following calculations on  $\text{H}_9\text{O}_4^+$ -ion this corrected value of  $a_{\text{OH}}$ ,

$$a_{\text{OH}} = 0.52 \times 10^4 \text{ kcal/mole} \quad (14)$$

and the value from (7a) of

$$b_{\text{OH}} = 4.16 \text{ Å}^{-1} \quad (15)$$

have been used while the value of  $c_{\text{OH}}$  has been calculated for this case according to the earlier description,

$$c_{\text{OH}} = (1 - 0.59) \times 90.4 = 37.1 \text{ Å}^6 \text{ kcal/mole}. \quad (16)$$

This resulted in an equilibrium distance between the oxygen atoms, corresponding to the minimum position for the total energy, of about 2.45 Å for  $\text{H}_9\text{O}_4^+$ -ion.

The energy calculated for the interaction between two water molecules, by letting this energy have its minimum for the equilibrium distance of 2.76 Å between the oxygen atoms, is  $-2.5$  kcal/mole (see Fig. 4). The corresponding experimental value is  $-6.1$  kcal/mole which indicates that the value given by the present model is too low by a factor of 2.4. The corresponding energy

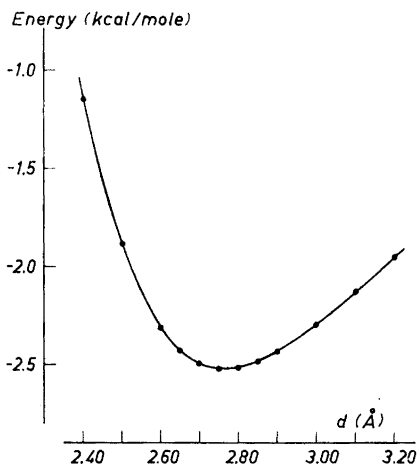


Fig. 4. Variation of the interaction energy around the equilibrium distance of 2.76 Å for two water molecules (cf. Fig. 3 and Table 2).

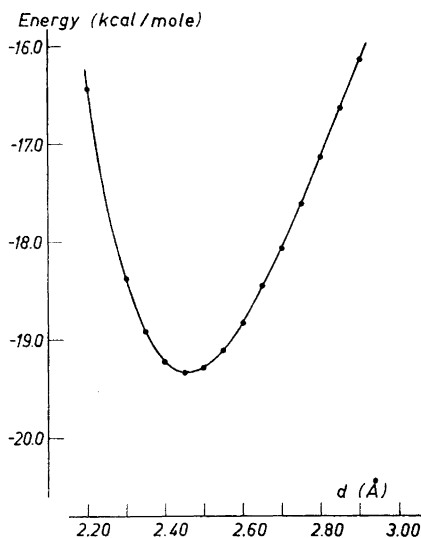


Fig. 5. Variation of the interaction energy for  $\text{H}_3\text{O}^+$  and a water molecule in hydronium ion,  $\text{H}_9\text{O}_4^+$ , at equilibrium distance of 2.45 Å (cf. Fig. 2 and Table 1).

for the  $\text{H}_3\text{O}^+ - \text{H}_2\text{O}$  interaction at the equilibrium distance of about 2.45 Å is approximately  $-19.3$  kcal/mole (see Fig. 5). If the same factor of 2.4 is assumed to be valid here, the energy drops to a value of  $-46.3$  kcal/mole. This is close to the energy calculated by Grahn<sup>1</sup> for the distance of the 2.55 Å between the oxygen atoms. The short equilibrium distance and rather high interaction energy value point to quite a strong interaction between the  $\text{H}_3\text{O}^+$ -ion and the three closest water molecules. The variations of the energy around the equilibrium positions can be seen in Fig. 4 for  $\text{H}_2\text{O} - \text{H}_2\text{O}$  interaction and in Fig. 5 for  $\text{H}_3\text{O}^+ - \text{H}_2\text{O}$  interaction.

The values of the parameters  $b_{\text{HH}}$  (see (12)) and  $b_{\text{OO}}$  (see (9)) divided by van der Waals radii of hydrogen,  $r(\text{W}_{\text{H}})$ , and oxygen,  $r(\text{W}_{\text{O}})$ , give a constant value,  $k$ , where  $r(\text{W}_{\text{H}}) = 1.2$  Å and  $r(\text{W}_{\text{O}}) = 1.5$  Å.

$$\frac{b_{\text{HH}}}{r(\text{W}_{\text{H}})} \approx \frac{b_{\text{OO}}}{r(\text{W}_{\text{O}})} \approx k = 3.1 \quad (17)$$

We hope that eqn. (17) can be used for the calculation of the parameter  $b_{\text{AA}}$  for atom A in general by letting it be equal to  $k r(\text{W}_{\text{A}})$ , where  $r(\text{W}_{\text{A}})$  is van der Waals radius for the atom A. This assumption will be tested in continued studies of the hydrogen bond at this laboratory.

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#### REFERENCES

1. Grahn, R. *Arkiv Fysik* **21** (1962) 13.
2. Slater, J. C. *Phys. Rev.* **36** (1930) 57.
3. Grahn, R. *Arkiv Fysik* **19** (1961) 147.
4. Mulliken, R. S. *J. Chem. Phys.* **23** (1955) 1833.
5. Pitzer, K. S. *Advan. Chem. Phys.* **2** (1959) 59.
6. Scott, R. A. and Scheraga, H. A. *J. Chem. Phys.* **42** (1965) 2209.
7. Williams, D. E. *J. Chem. Phys.* **43** (1965) 4424.
8. Mason, E. A. and Rice, W. E. *J. Chem. Phys.* **22** (1954) 522.

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