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Ab Initio Studies on the Structures and Energetics of Inner- and Outer-Shell Hydrates of the Proton and the Hydroxide Ion

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Abstract: *Ab initio* molecular orbital calculations using Gaussian orbital basis sets have been carried out for a large variety of structures of the hydrated proton and hydroxyl ion, $H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$, $n = 0, 4$. Calculated solvation enthalpies, based on energy-optimized structures, are within a few kilocalories of experimental values (after corrections for zero-point energy differences have been made), and the experimentally observed similarities of enthalpies for isoelectronic cations and anions are reproduced. Preliminary calculations indicate that there are no sharp discontinuities in solvation enthalpy associated with the transition from the inner to the outer solvation shell, in agreement with available cation data. Among the structural principles derived from the calculations are: (1) the general energetic preference for chain structures, with branching when possible, although cyclic species may be the favored structures for some of the larger hydrates; (2) an increase in interoxygen distances upon successive hydration; (3) a general tendency for bridging protons either to occupy asymmetric positions or to be associated with symmetric potentials characterized by essentially flat central regions; and (4) the reluctance of the hydronium ion and the hydroxyl ion to serve as a proton acceptor and a proton donor, respectively. Rules such as these, together with other features of the potential energy surfaces and charge distributions, lead to a comprehensive and apparently internally consistent picture of the hydrates of H^+ and OH^-. In the context of this picture, a detailed discussion of various static and dynamic properties of these complexes is given. General agreement is found with the previously suggested structure for the inner solvation shell of the proton ($H_9O_4^+$), while a new alternative structure is proposed for the hydroxyl ion inner solvation shell ($H_7O_4^-$). Although the present calculations are most directly related to the isolated species for which they were carried out, their relevance to higher hydration processes and to condensed-phase ion properties is emphasized.

The properties of solvated protons and hydroxyl ions have been a matter of long-standing chemical interest.[1] This interest has recently been heightened by new gas-phase kinetic[2] and thermodynamic data,[3,4] and the relevance of these data to ion-clustering processes in the upper atmosphere,[2] as well as to the behavior of H^+ and OH^- in solution.[1] Crystallographic[5,6] and spectroscopic[7,8] data are also available for several varieties of hydrated proton species in the solid phase. Needless to say, a comprehensive theoretical understanding of the properties of these ions would be of great value in correlating the rapidly accumulating experimental data. Considerable headway toward this goal was made in a recent molecular orbital study,

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employing the CNDO/2 method.[9] The intention of the semiempirical study was to build up a body of information relating to structure, energy trends, and charge shifts upon successive hydration of the primary ions, and to develop a picture of strong single and multiple hydrogen bonding in ions which could serve to orient future, more accurate studies. As demonstrated below, this purpose has been admirably served.

At the *ab initio* level, several calculations of varying degrees of accuracy have been carried out, but they have so far been limited to monomeric species (H_2O,[10-12] H_3O^+,[10,11a,12b-14] and (OH^-)[10,11a,15]), polymers of neutral water,[12a,16-19] and the solvated hydronium ion, $H_5O_2^+$.[12b,14] Both the semiempirical and *ab initio* investigations indicated that approximate Hartree-Fock calculations would provide an adequate framework for studying the properties of the H^+ and OH^- hydrated complexes. It therefore seemed appropriate to carry out a set of *ab initio* calculations, at a consistent level of approximation, for the entire set of species—$H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$, $n = 0, 4$. Such a set allows not only a thorough examination of the buildup of the so-called[1] inner solvation shell, but also the transition to the outer solvation shell ($n = 3 \rightarrow n = 4$). The basis set chosen for the molecular orbital studies we shall report is discussed in the following section. We are primarily interested in systematically following the structural and energetic changes which accompany the filling of the inner shell and the beginning of the outer shell, with the goal of elucidating as many structural principles as possible. In particular the relative preferences for linear and branched-chain structures and cyclic structures will be examined, as well as the relative preference of the oxygen atom for different types of coordination (two-, three-, and fourfold). Although our results will obviously be most directly relevant to isolated, gas-phase species, we nevertheless will use them as a basis for evaluating previous models for proton and hydroxyl ion solvation and mobility in aqueous solution.

After discussing computational matters in section I, we shall give a detailed account (Section II) of how the equilibrium geometries and other features of the potential energy surfaces were obtained, emphasizing the efficient use made of the previous structural predictions arising from the CNDO/2 study.[6] The remainder of the paper is mainly devoted to a discussion of the results and a comparison of calculated and experimentally obtained quantities. In an attempt to calibrate the current calculations, a detailed comparison is made between the present results and more accurate calculations which are available for a few of the smaller species. A special section is devoted to population analysis,[20] a potentially useful procedure for interpretive purposes, but one whose application in the context of extended basis set requires some critical evaluation.

It is hoped that the current set of calculations, beyond their intrinsic value as regards the proton and hydroxyl ion hydration processes, will convincingly illustrate the benefits to be obtained by systematically applying an accurate computational method to a set of related species large enough to permit the inference of general structural principles.

I. Computational Method and Choice of Basis Set

All calculations were carried out in the *ab initio* molecular orbital (MO) framework, using basis sets of contracted Gaussian-type orbitals (GTO's). The integral and SCF programs employed are those recently developed by Hehre and Pople.[21] We desired a basis set sufficiently flexible to give reasonable quantitative account of the structure and intermolecular energetics of the system under study while at the same time small enough so that a detailed study of potential energy surfaces of interest might be carried out economically. In preliminary minimal-basis calculations (STO-3G basis[21]), the stabilities of H_3O^+ (relative to H^+ and H_2O) and $H_5O_2^+$ (relative to H_3O^+ and H_2O) were found exaggerated by $\sim$2 and $\sim$3 eV, respectively.[22] For improved energetics we turned to the so-called 4-31G set recently introduced by Ditchfield, Hehre, and Pople.[23] This basis provides two functions for each valence atomic orbital (1s for H; 2s, 2p for O), consisting of a contraction of three GTO's and a single GTO, respectively. A single inner-shell function of four contracted GTO's completes the set. The free-atom basis functions are modified by "standard" scale factors appropriate to molecular environments.[23] The sets of scale factors are 0.99 and 0.98 for O and 1.20 and 1.15 for H, where the first and second members of each pair correspond to the contracted set of three GTO's and the single GTO, respectively. It was not feasible in the present study to add polarization functions to the above basis set (2p functions for H and 3d functions for O) because of the size of the systems involved. We shall conclude in section V, by comparison with calculations employing polarization functions, that the 4-31G basis has sufficient flexibility for the problem at hand.

Since the 4-31G basis employs fewer primitive GTO's than other similar basis sets (generally denoted as "double-ζ" basis sets[16,24]), it is not surprising that it leads to total energies somewhat smaller in magnitude than the usual double-ζ energies. These absolute energy effects (*e.g.*, $\sim$0.1 au for H_2O) have been found to result principally from nearly constant atomic errors

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Table I. Monomers and Neutral Water Polymers. Structures and Energies[a]

Species	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
H_2O	C_{2v}		**0.950**	**111.3**	−75.9086
H_3O^+	C_{3v} (D_{3h})		**0.964**	**120.0**	−76.2006
OH^-			**0.985**		−75.2298
$(H_2O)_2$[e,f]	C_s	**2.87**	0.95	**145** (XO2H2) 180 (dihed XH1)	−151.8303
		2.95			(+0.0001)
				130 (XO2H2)	(+0.0002)
$(H_2O)_3$[e,g]	C_3	**2.66**[h]	0.95	20 (H4O2O3) **0** (O2H6–plane)	−227.7643
				27.5 (O2H6–plane)	(+0.0007)

[a] Bond distances (R_{OO} and R_{OH}) are given in ångströms, angles (α) in degrees, and energies in atomic units. Except for the three monomers H_2O, H_3O^+, and OH^- (whose listed parameter values have been rounded off), the listed values of R and α are identical with the values employed in the calculations. Parameter values appearing in boldface are within 0.02 Å and 2° of optimal (as estimated by interpolation) bond lengths and angles, respectively, unless otherwise noted. In cases where several geometric variations of a given type of structure are considered, only those parameter values which are different from the original set are included in the later entries. [b] The structures have been partially or completely optimized by minimizing the total molecular energy, subject to the indicated symmetry constraint, except as noted. Entries in parentheses indicate the symmetry of the optimized structure, if different (higher) from that employed as a constraint. [c] Angles (α) correspond generally to bond angles or dihedral angles. Dihedral angles are denoted as (dihed XY), corresponding to the nonlinear chain of four atoms X–O—O–Y. The X–O, O–O, and Y–O bonds may in some cases involve bridging protons. For the case of cyclic systems the angle between an external OH bond and the plane of the oxygen atoms is denoted as (OH–plane). [d] The optimal total energy is presented for each species. For nonoptimal structures, the total energy is given relative to the optimal value. [e] Monomer components are maintained at optimal monomer geometry. [f] The dimer consists of a proton-donor molecule (H1O1H2) and a proton-acceptor molecule (H3O2H4), bonded by a linear H bond (O1H2O2). To simplify the geometry specification, the vector sum of the O2H3 and O2H4 bonds defines the ficticious atom X (O2X). The angle dihed XH1 was taken as 180°. [g] Figure 6 shows the cyclic trimer with an additional proton (H3), and should be consulted for the definition of atomic labels. [h] The optimal value by interpolation is ~2.69 Å.

associated with the small number of primitives used in the inner-shell functions of the 4-31G basis.[23] Thus atomization energies for small molecules differ from typical double-ζ atomization energies by only ~1–5 kcal.[23] As a test for possible effects arising from inner-shell deficiencies, we have calculated the energy of a water molecule in the presence of the entire basis set used for various typical complexes involving water [*e.g.*, $(H_2O)_2$, cyclic $(H_2O)_3$, and $H_2O \cdot H_3O^+$], but not the electrons or nuclear charges of the complexing species. The addition of these off-center basis functions typically lowered the water monomer energy by only ~1 kcal. Hence we find no evidence for any strong tendency of valence orbitals on a given center to compensate for inner-shell deficiencies on another center. Such an effect would, of course lead to undesirable distortions of intermolecular potential surfaces.

II. Energy Calculations and Selection of Molecular Structures

A. General Objectives. In this section we outline the procedures employed in studying the molecular energetics and structure for the following species: H_2O, $(H_2O)_2$, $(H_2O)_3$, $H_3O^+(H_2O)_n$, and $OH^-(H_2O)_n$ (n = 0, 4). Our first objective was to minimize the energy of these species with respect to important geometrical parameters, reasonable values being assumed for the nonoptimized parameters. As we shall see in the next section, the molecular energies so obtained are in good agreement with experimental solvation enthalpies, especially when estimates of zero-point vibrational energy are included. The parameter search was greatly facilitated by a knowledge of the results of the CNDO study.[9] The benefits to be obtained from the use of a semiempirical method in extensive preliminary examination of potential energy surfaces are clearly illustrated in the present study. In view of the good agreement between calculated and experimental energies, we felt justified in making a detailed examination of features of the calculated molecular potential energy surfaces, in hopes of uncovering basic principles by which the formation of the larger solvated aggregates could be inferred from properties of the smaller systems. A related, specific objective was to provide a theoretical examination of Eigen's model[1] for the proton and its inner solvation shell ($H_9O_4^+$) and perhaps to gain insight into the transition from the inner to the outer solvation shell.

We have viewed the formation of the solvated ions $H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$ in three distinct ways: (1) the combination of smaller solvated ions with an additional water molecule; (2) the combination of water or a neutral water polymer with H_3O^+ or OH^-; and (3) the abstraction of a proton from, or addition of a proton to, a neutral polymer of water. Presumably the first viewpoint is the most relevant to the available experimental data,[3,4] and we have concentrated most of our effort along this line. The following structural questions were pertinent to all three viewpoints. To what extent do the building blocks, H_3O^+ and OH^-, preserve their identity in the larger species; *i.e.*, is it reasonable to view the solvated species essentially as monomer units held together by charge–dipole interactions, somewhat perturbed by polarization and charge transfer, and can this view be generalized to other hydrogen-bonding situations? In the CNDO study[9] the monomer units were generally recognizable, although often appreciably distorted. A complementary question involves the softness of the various modes of framework- and H-bond stretching distortions and the relevance of these modes to the mechanism of formation of larger solvated species and isomerization within a given species. Intimately related to these considerations are the processes which account for the rapid effective proton and hydroxyl mobility[1] and the short lifetime of a particular ion (H_3O^+ or OH^-) in liquid water.[1] Also of interest are the relative energies of various isomeric alternatives corresponding

Table II. $H_5O_2{}^+$ Structures and Energies[a,e]

Species	Figure	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
(A) Chain						
(1) Optimized	1	D_2 (D_{2d})	**2.36**		**115** (H2O1H3) **90** (dihed H2H4)	−152.1791[f]
(2) Eclipsed conformation		D_{2h}			0 (dihed H2H4)	(+0.0021)
(3) Asymmetric H bond		C_{2v}		1.26		(+0.0005)
(4) $H_7O_3{}^+$-like H-bond distances		C_{2v}	2.46	1.04 (O1H1)	112 (H4O2H5) 120 (H2O1H3)	(+0.0023)
(5) Bare central proton[g]		D_{2d}			112 (H2O1H3)	(+0.0834)[h]
			2.52[i]		112 (H2O1H3)	(+0.0794)[h]
(6) CNDO (optimized)		C_2 (C_{2h})			107 (H2O1H3) 117 (H1O1H2)	(+0.0131)
(B) Four-coordinate oxygen						
(1) Bifurcated H bond	2	C_{2v}	**2.36**[j]	**0.95** (O1H2)	112 (H4O2H5) **110** (H2O1H3) 90 (dihed H2H4)	(+0.0248)
(2) H_2O-proton donor	3	C_s	2.36	1.00 (O2H4)	112 (H4O2H5) **100** (H1O1O2) 180 (dihed H1H5)	(+0.1377)[h]
		C_s	3.26	0.95 (O2H4)		(+0.0844)[h]
(3) Charge dipole (no H bond)	4	C_s	**2.61**[k]		**75** (H1O1O2) 90 (dihed H1H4)	(+0.0405)
		C_s			90 (H1O1O2)	(+0.0462)

[a–e] See footnotes *a–e*, Table I. Geometrical parameters R_{OO}, R_{OH}, and α are identified, when necessary, in terms of the atom labels presented in the appropriate figure, as indicated in the second column. R_{OH} refers to bridging protons; external OH bond lengths are fixed at 0.95 Å, as discussed in the text. [f] Bound by 0.0696 au with respect to H_3O^+ and H_2O. [g] No basis functions on the central proton. [h] Unbound with respect to H_3O^+ and H_2O. See footnote *f*. [i] Optimal $R_{OO} \sim 2.48$ Å by interpolation. [j] Optimal $R_{OO} \sim 2.45$ Å by interpolation. [k] Optimal $R_{OO} \sim 2.66$ Å by interpolation.

to linear, branched, and cyclic structures, and the relative preferences of H_2O, H_3O^+, and OH^- with regard to serving as proton donors or acceptors in hydrogen-bonding situations. As a final point, we recall the implication of previous experimental[4b] and theoretical[9] work that the effective sizes of corresponding cations and anions ($H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$) are very similar. The CNDO study[9] yielded almost identical framework-bond distances for both members of such a pair, and we wish to know to what extent the more elaborate *ab initio* calculations are consistent with this model.

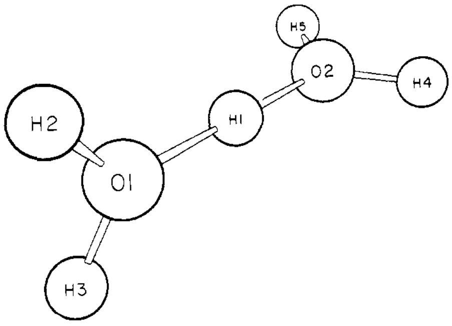

Figure 1. The optimized chain structure of $H_5O_2{}^+$ (II-A1). This and the subsequent structural drawings have been obtained from Cartesian coordinates with the aid of a computer (CRT plots). The perspective views have been chosen to illustrate as clearly as possible the most important structural features of each ion, and bonds have been inserted to point up the dominant interatomic interactions.

Answers to the above questions would combine to give a comprehensive understanding of the strong, multiple hydrogen bonding associated with these ionic systems, and, with this general objective in mind, we now proceed to a detailed discussion of the structural studies.

B. Details of the Geometry Search. The main results of the geometry search are in Tables I–IX. The principal features of the relevant molecular structures are defined in these tables by various bond lengths and angles, which we either optimized (listed in boldface) by minimizing the total energy or assigned reasonable values to, usually taken from calculations on smaller, related systems, or from the CNDO calculations.[9] In most cases, the geometry optimization was carried out subject to certain symmetry constraints, as indicated in the tables. The most important structures are presented in perspective drawings, Figures 1–16. The figures also provide the atomic labels used to define bond distances and angles in the tables. To facilitate the identification of various structures, unique symbols, based on identifiers in the tables, will be used; *e.g.*, the symbol IV-B2 represents the Eigen structure[1] for $H_9O_4{}^+$ (C_{3v} summetry). The first entries in each table (II–IX) are denoted as "chain" structures. For cations, chain refers to structures consisting of three-coordinate oxygen atoms linked in straight or

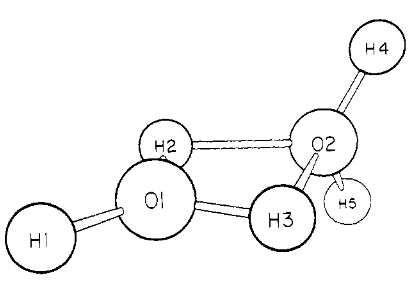

Figure 2. Bifurcated ring structure of $H_5O_2{}^+$ (II-B1).

Table III. $H_7O_3^+$ Structure and Energies[a,e]

Species	Figure	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
(A) Chain						
(1) Optimized	5	C_{2v}	**2.46**	**1.04** (O1H1)	**120** (O2O1O3) 112 (H4O2H5) 90 (dihed H3H4)	−228.1370[f]
(2) One symmetric H bond		C_s		1.23 (O1H1)		(+0.0091)
(3) $H_5O_2^+$-like symmetric H bonds		C_{2v}	2.36	1.18		(+0.0191)
(4) $H_5O_2^+$ (optimal)[g]–H_2O complex		C_s	2.36 (O1O2)	1.18 (O1H1) 0.95 (O1H2)	116 (H2O1H3)	(+0.0082)
(5) $H_5O_2^+$ (distorted)–H_2O complex		C_s		0.95 (O1H2)		(+0.0033)
(6) $(H_2O)_2$ (optimal)–H_3O^+ complex[e,h]		C_s	2.87 (O1O2)	0.95 (O1H1) 0.95 (O3H2)	111.2 (H1O1H3) 120 (H6O3H7)	(+0.0294)
(7) $(H_2O)_2$ (distorted)–H_3O^+ complex		C_s		0.95 (O3H2)		(+0.0195)
(8) H_2O–H_3O^+–H_2O		C_{2v}		0.95 (O1H1)		(+0.0064)
(9) CNDO (optimized)		C_{2v}	2.37	1.12 (O1H1)	107 (H4O2H5) 121 (H1O2H4) 135 (O2O1O3) 0 (dihed H3H4)	(+0.0214)
(B) Rings						
(1) Neutral cyclic trimer plus proton[i]	6		**2.66**[j]	1.00	110 (H1O1H2) 60 (OOO) 55 (OH–plane)	(+0.0927)[k]
(2) H_3O^+ double proton donor[e,l]	7	C_s	**2.51**	**1.00** (O1H2) **1.00** (O1H3) **0.95** (O2H4)	110 (H2O1H3) 70 (O2O1O3)	(+0.0253)
				1.04 (O1H2) 1.00 (O2H4)		(+0.0289)
(C) Central proton[m]		D_{3h}		**1.40**[n]		(+0.0650)[k]

[a–e] See footnotes *a–e*, Table I. [f] Bound by 0.0494 au with respect to $H_5O_2^+$ (II-A1) and H_2O. [g] The $H_5O_2^+$ moiety is given the optimal structure (II-A1) except for slight distortions in the angles of the terminal OH bonds. [h] The $(H_2O)_2$ moiety is assigned the optimal geometry (Table I). [i] The structure is obtained by adding a proton to the neutral cyclic trimer (Table I), adjusting the H_3O^+ moiety so that it symmetrically straddles the plane of the oxygen atoms, with all HOH angles equal to 110°, and extending the OH bonds involving bridge protons to 1.00 Å. [j] Optimal R_{OO} ~2.70 Å by interpolation. [k] Unbound with respect to $H_5O_2^+$ (II-A1) and H_2O. See footnote *f*. [l] The structure is planar except for the double-proton-acceptor H_2O, whose plane forms an angle of 145° with the O3O2 bond. H bonds are 20° off axis. [m] The planes of the three H_2O molecules complexed to the central proton are perpendicular to the plane of the oxygen atoms. [n] Optimal R_{OH} ~ 1.44 Å by interpolation.

Table IV. $H_9O_4^+$ Structures and Energies[a,e]

Species	Figure	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
(A) Straight chain						
(1) Optimized (symmetric central H bond)	8	C_2	**2.36** (O1O2) **2.54** (O1O3)	**1.00** (O1H2)	112 (H7O3H6) 120 (O2O1O3) 120 (H1O1H3) 90 (dihed O3O4)	(+0.0075)
(2) $H_7O_3^+$-like outer H-bond distances		C_2	2.46 (O1O3)	1.04 (O1H2)		(+0.0113)
(3) Planar oxygen framework		C_{2h}			180 (dihed O3O4)	(+0.0088)
(4) Asymmetric central H bond				1.14 (O1H1)		(+0.0076)
(B) Branched chain (Eigen)						
(1) Planar (optimized)	9	C_{3v} (D_{3h})	**2.54**	**1.00** (O1H1)	112 (H4O2H5) **120** (O2O1O3) 90 (dihed H2H4)	−304.0872[f]
(2) Pyramidal[g]		C_{3v}			117.3 (O2O1O3)	(+0.0022)
(3) CNDO (optimized)		D_{3h}	2.39	1.09 (O1H1)	127 (H1O2H4) 106 (H5O2H4)	(+0.035)
(C) Ring						
(1) Neutral cyclic tetramer plus proton[h]			2.75	1.00	90 (OOO)	(+0.1089)[i]
(2) H_3O^+ double proton donor[e,j,k]	10	C_{2v}	2.46 (O1O2) 2.80 (O2O3)	1.00	110 (H2O1H3) 90 (O2O1O4) 5 (H5O2O3)	(+0.0182)

[a–e] See footnotes *a–e*, Table I. [f] Bound by 0.0341 au with respect to $H_7O_3^+$ (III-A1) + H_2O. [g] The planes of the outer H_2O groups are kept parallel to the threefold molecular axis. [h] This structure is completely analogous to the corresponding $H_7O_3^+$ structure (see footnote *i*, Table III) with the exception of the OOO angles (90°) and the off-axis H-bond angle (8°). [i] Unbound with respect to $H_7O_3^+$ (III-A1) and H_2O. See footnote *f*. [j] Planar, except for the double-proton-acceptor H_2O. [k] The two unique interoxygen bond lengths have been partially optimized, subject to the constraints of C_{2v} symmetry and an O2O1O4 angle of 90°.

Table V. $H_{11}O_5^+$ Structures and Energies[a,e]

Species	Figure	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
(A) $H_9O_4^+$ (IV-A1)–H_2O complex[e,f]	8		2.54 (O5O1)	1.00 (O1H3)	90 (dihed H10H1)	(+0.0055)
(B) $H_9O_4^+$ (IV-B1)–H_2O complex[e,f]	9	C_s	2.70 (O5O2) 2.54 (O5O2)	1.00 (O2H4)	90 (dihed H10H1)	−380.0240[g] (+0.0008)
(C) $H_9O_4^+$ (IV-C2)–H_2O complex[e,f]	10	C_{2v}	2.54 (O5O1)	1.00 (H1O1)	90 (dihed H10H2)	(+0.0061)

[a-e] See footnotes *a–e*, Table I. [f] The $H_{11}O_5^+$ structures are obtained by adding a proton-acceptor water molecule (H10O5H11) to the appropriate $H_9O_4^+$ structure. Figure references are to the $H_9O_4^+$ moiety. The OH bond associated with the newly formed bridge is extended to 1.00 Å. [g] Bound by 0.0282 au with respect to $H_9O_4^+$ (IV-B1) and H_2O.

Table VI. $H_3O_2^-$ Structures and Energies[a,e]

Species	Figure	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
(A) Chain						
(1) Optimized (symmetric H bond)	11	C_2	**2.42**		**109** (H1O1H2) **160** (dihed H2H3)	(+0.0002)
(2) Cis conformation		C_{2v}			0 (dihed H2H3)	(+0.0027)
(3) Asymmetric H bond		C_s	**2.45**	1.11	180 (dihed H2H3)	−151.2033[f]
(B) Bifurcated H bond		C_{2v}	**2.48**	0.95[g]	**94** (HOH)[g]	(+0.0173)
(C) OH^- proton donor[h]		C_s	2.42 3.03	0.95	145 (XO2H1)	(+0.1247)[i] (+0.0878)[i]

[a-e] See footnotes *a–e*, Table I. [f] Bound by 0.0649 au with respect to OH^- and H_2O. [g] The OH bond length and HOH angle refer to the distorted H_2O molecule, whose protons are complexed to the hydroxyl ion oxygen atom. [h] Structure obtained by removing the nonbridging proton of the proton-donor H_2O molecule in $(H_2O)_2$. See footnote *f* of Table I for label definitions. [i] Unbound with respect to OH^- and H_2O.

branched chains by hydrogen bonds. The corresponding anion chains have similar oxygen frameworks, but the oxygen atoms may be two-, three-, or four-coordinate. Unless otherwise stated, all hydrogen bonds are constrained to be linear, and each three-coordinate oxygen atom is constrained to lie in the plane of its three ligands. The ligand planes associated with two adjacent three-coordinate oxygen atoms form a dihedral angle of 90°, except as noted. In the case of ring structures, nonlinear H bonds are expected. Using the minimal-basis-set results of Del Bene and Pople[19] as a guide, we have constrained these H bonds to lie in the plane of the oxygen framework and have adopted off-axis angles (in an exocyclic sense) of 20 and 5–10° for O_3 and O_4 rings, respectively. The off-axis angle is defined as the angle between O1H1 and O1O2 in the H-bonded system O1—H1···O2. Initially, ex-

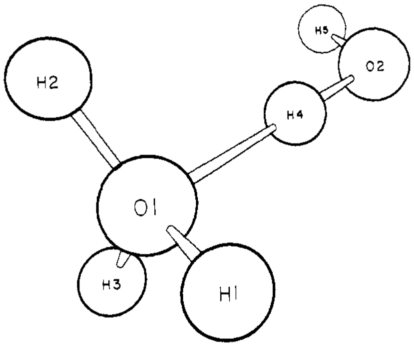

Figure 3. H_2O-proton donor structure of $H_5O_2^+$ (II-B2).

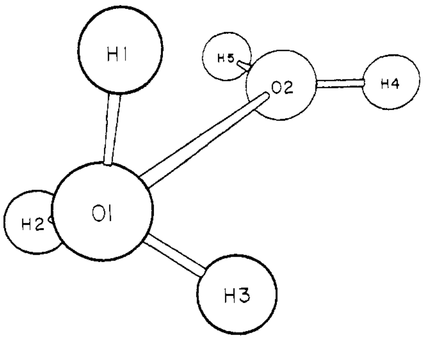

Figure 4. Charge–dipole structure of $H_5O_2^+$ (II-B3).

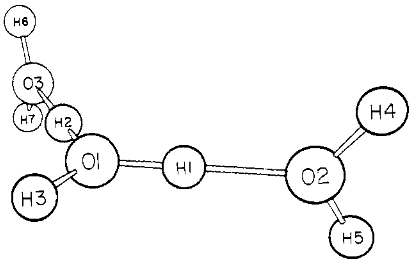

Figure 5. Optimized chain structure of $H_7O_3^+$ (III-A1).

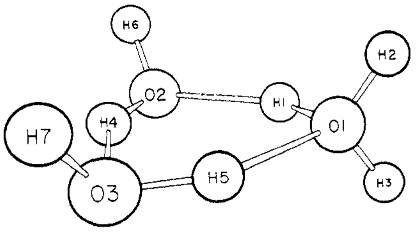

Figure 6. Cyclic structure of $H_7O_3^+$ obtained from neutral trimer plus proton (III-B1).

Table VII. $H_5O_3^-$ Structures and Energies[a,e]

Species	Figure	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
(A) Chain						
(1) Optimized	12	C_{2v}	**2.53**	**1.03** (O2H1)	**140** (O2O1O3)[f] 109 (H3O2H1) 180 (dihed H3H5)	−227.1599[g]
(2) Out-of-plane terminal OH's		C_{2v}			90 (dihed H3H5)	(+0.0009)
(3) $H_3O_2^-$-like symmetric H bonds		C_{2v}	2.42		90 (dihed H3H5)	(+0.0224)
(4) Terminal OH^-		C_s		1.50 (O2H1)		(+0.0195)
(5) Central H_2O (double proton donor)[e,h]		C_s		0.95 (O1H1) 0.95 (O1H2)	112 (O2O1O3) 90 (dihed H3H2) 180 (dihed H4H1)	(+0.0723)[i]
(6) Central OH^- (proton donor)[h]		C_s	2.50	1.00 (O1H1) 1.50 (O1H2)	90 (dihed H3H2)	(+0.0977)[i]
(7) CNDO (optimized)		C_{2v}	2.37	1.11 (O2H1)	106 (H3O2H1)	(+0.0132)
(B) Ring						
(1) Neutral cyclic trimer minus proton[j]			**2.66**	1.00	60 (OOO) 55 (OH–plane)	(+0.0653)[i]
(2) OH^- double proton acceptor[k]	13		**2.66**	1.00	100 (H2O2H3) 60 (OOO) 55 (O3H5–plane) 130 (H1O1O2), (H1O1O3)	(+0.0165)

[a–e] See footnotes *a–e*, Table I. [f] Optimal value ~135° by interpolation. [g] Bound by 0.0480 au with respect to $H_3O_2^-$ (VI-A3) and H_2O. [h] Structures of the type VII-A5 and VII-A6 are generated from the standard chain structure VII-A1 by transferring H5 (Figure 12) from the central oxygen atom to the terminal oxygen atom, O2, and orienting the plane of the resultant water moiety (H3O2H5) perpendicular to the oxygen atoms. [i] Unbound with respect to $H_3O_2^-$ (VI-A3) and H_2O. See footnote *g*. [j] Same structure as $(H_2O)_3$ (Table I), except for abstracted proton and extended internal OH bond lengths (1.00 Å). [k] The two external OH bonds are directed on opposite sides of the oxygen planes. The H bonds are 20° off axis, and the internal OH bonds are extended to 1.00 Å.

ternal OH bonds in the cyclic systems were oriented at an angle of 55° with respect to the oxygen plane.[19] Subsequent work, however, revealed that an in-plane orientation was preferred in the case of the cyclic cations and the symmetric (C_3) cyclic water trimer.[25]

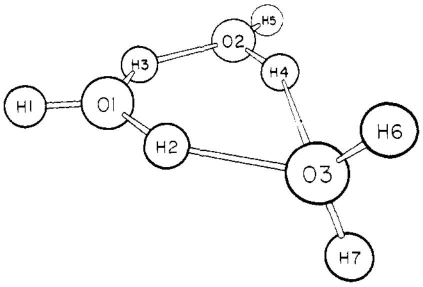

Figure 7. Cyclic H_3O^+–double proton donor structure of $H_7O_3^+$ (III-B2).

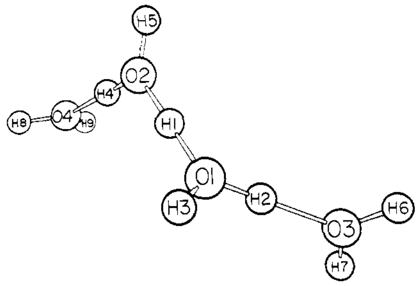

Figure 8. Optimized chain structure of $H_9O_4^+$ (IV-A1).

The O–H bond distances (R_{OH}) listed in Tables II–IX refer to internal H's involved in H bonds; terminal OH bonds are assigned the fixed value of 0.95 Å based on the optimized values listed in Tables II and VI. The HOH angles associated with water-like components of the complexes were generally assigned the calculated optimal H_2O value of 111.2° (Table I). Some excep-

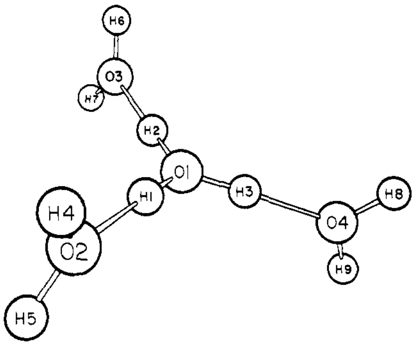

Figure 9. Optimized branched (Eigen type) structure of $H_9O_4^+$ (IV-B1).

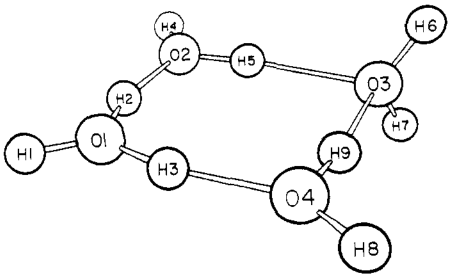

Figure 10. Cyclic H_3O^+–double proton donor structure of $H_9O_4^+$ (IV-C2).

[25] J. Del Bene and J. A. Pople, *J. Chem. Phys.*, in press, have shown that a slightly more stable neutral trimer ring can be obtained by letting one of the outer OH bonds be directed on the side of the oxygen plane opposite to that of the other two OH bonds.

Table VIII. $H_7O_4^-$ Structures and Energies[a,e]

Species	Figure	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
(A) Straight chain[f]						
(1) Optimized (symmetric central H bond)		C_2	**2.42** (O1O2) **2.61** (O1O3)	**0.99** (O3H2)	140 (O2O1O3) 110 (H6O1O2) 109 (H4O3H2) 90 (dihed O3O4) 180 (dihed H4H6)	(+0.0048)
(2) Planar oxygen framework	14	C_{2h}			180 (dihed O3O4)	(+0.0052)
(3) $H_5O_3^-$-like outer H bonds		C_2	2.53 (O1O3)	1.03 (O3H2)		(+0.0071)
(4) Asymmetric central H bond				1.13 (O1H1)		(+0.0047)
(5) CNDO (optimized)		C_2	2.34 (O1O2) 2.40 (O1O3)	1.10 (O3H2)	143 (O2O1O3) 105 (H4O3H2) 180 (dihed O304)	(+0.0255)
(B) Branched chain	15	C_{3v}	**2.61**	**0.99**	**110** (O2O1O3) 109 (H3O2H2) 180 (dihed H1H3)	−303.1053[g]
(C) Ring						
(1) Neutral cyclic tetramer minus proton[h]			2.75	1.00	90 (OOO) 55 (OH–plane)	(+0.0772)[i]
(2) OH^- double proton acceptor[j,k]	16	C_s	2.53 (O2O3) 2.80 (O1O2)		10 (H4O3O2) 5 (H2O2O1) 90 (O2O3O4) 55 (O2H3–plane) 110 (H1O1O2)	(+0.0027)

[a–e] See footnotes *a–e*, Table I. [f] Labels for chain structures are defined in Figure 14, which depicts the planar conformation VIII-A2. [g] Bound by 0.0368 au with respect to $H_5O_3^-$ (VII-A1) and H_2O. [h] Same structure as the corresponding cation IV-C1 except that the H_3O^+ moiety of the latter species is replaced by a bridging OH^- group. H bonds are 8° off axis. [i] Unbound with respect to $H_5O_3^-$ (VII-A1) and H_2O. See footnote *g*. [j] The hydroxyl group (O1H1) is directed on the side of the oxygen plane opposite to that of the O2H3 and O4H7 bonds. [k] The two unique interoxygen bond lengths have been partially optimized, subject to the constants of C_{2v} symmetry on the oxygen framework and an O2O3O4 angle of 90°.

Table IX. $H_9O_5^-$ Structures and Energies[a,e]

Species	Figure	Symmetry constraint[b]	R_{OO}	R_{OH}	α[c]	E_{tot}[d]
(A) $H_7O_4^-$ (VIII-B)–H_2O complex[f]	15		2.70 (O2O5)	0.99 (O5H8)	125.5 (O1O2O5) 0 (dihed O5H1) 90 (dihed H9H2)	(+0.0076)
(B) $H_7O_4^-$ (VIII-C2)–H_2O complex[f,g]	16	C_s	2.70 (O1O5)	0.99 (O5H8)	110 (O5O1H1) 180 (dihed H9H1)	−379.0469[h]

[a–e] See footnotes *a–e*, Table I. [f] $H_9O_5^-$ structures are obtained by adding a proton-donor water molecule (H8O5H9) to the appropriate $H_7O_4^-$ structure. Figure references are to the $H_7O_4^-$ moiety. The OH bond (O5H8) associated with the newly formed bridge is extended to 0.99 Å. [g] The new OO bond (O5O1) is on the side of the oxygen plane opposite to that of the O1H1 bond. [h] Bound by 0.0330 au with respect to $H_7O_4^-$ (VIII-B) and H_2O.

tions are noted in the tables. The calculations based on CNDO-optimized geometries have employed an estimated corrected terminal OH distance of 0.97 Å, since CNDO consistently overestimates the equilibrium lengths of such bonds.[26] These calculations were done prior to the geometry optimizations (Tables II and VI) which indicated that 0.95 was the best terminal OH distance.

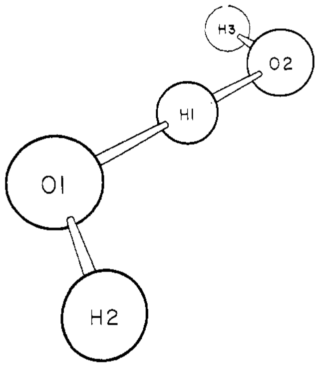

Figure 11. Optimized chain structure of $H_3O_2^-$ (VI-A1).

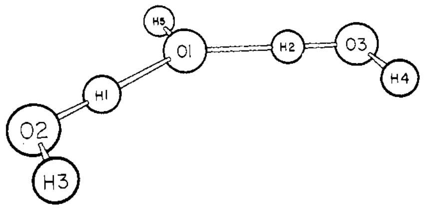

Figure 12. Optimized chain structure of $H_5O_3^-$ (VII-A1).

The general scheme for geometry optimization involved an initial guess based on other *ab initio* calculations or CNDO results, followed by optimization of O–O and internal OH distances, followed by op-

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(26) G. A. Segal, *J. Chem. Phys.*, 47, 1876 (1967).

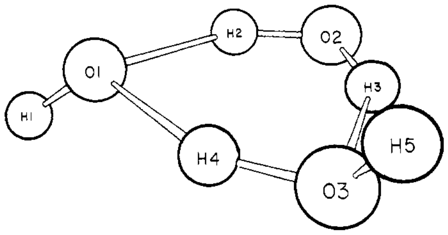

Figure 13. Cyclic OH^-–double proton acceptor structure of $H_5O_3^-$ (VII-B2).

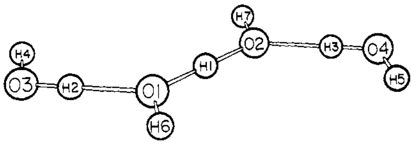

Figure 14. Planar-chain structure of $H_7O_4^-$ (VIII-A2).

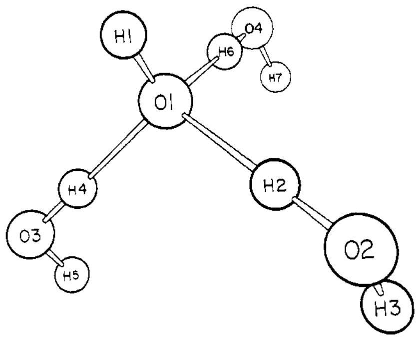

Figure 15. Optimized branched structure of $H_7O_4^-$ (VIII-B).

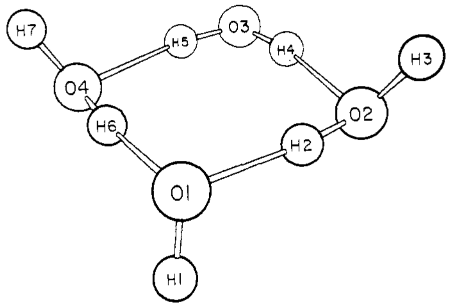

Figure 16. Cyclic OH^-–double proton acceptor structure of $H_7O_4^-$ (VIII-C2).

timization of framework-bond angles and dihedral angles. This procedure was sometimes repeated for another cycle. In cases where symmetric H bonds were assumed, stability of the energy with respect to asymmetric distortions was also tested. For the monomers, equal-spaced grids of 0.01 Å and 1° were employed, and the tabulated values were obtained by fitting to a parabola. Coarser grids were used for the larger systems, typically 0.04 Å and 5°. The parameter values listed as "optimal" (*i.e.*, in boldface) in the tables correspond to those grid points closest to the true optimal values, as estimated by parabola fitting. Unless otherwise noted in the tables, the boldface values are within 0.02 Å and 2° of the true optimal bond lengths and angles, respectively. We conclude this section with specific details for each species.

Monomer Units and Neutral Water Polymers. The geometries of the monomers H_2O, OH^-, and H_3O^+ were completely optimized to within 0.001 Å and 0.1° for bond distances and angles, respectively, subject to the overall symmetry constraints indicated in Table I. As a point of reference for calculating the relatively large solvation energies associated with charged-water complexes, it is of interest to see if the theory gives a reasonable account of the polymerization of neutral water. We therefore include several dimer and cyclic trimer calculations in Table I, which may be compared with the results of Pople.[19]

$H_5O_2^+$. The chain structure was first optimized within a constrained D_2 symmetry, and the resultant D_{2d} structure was then tested for stability with respect to asymmetric motion of the central proton (C_{2h}). The D_{2d} structure was most stable (Figure 1). Attempts to obtain an optimal structure of C_{2h} symmetry by a wagging distortion of the planar D_{2h} structure always resulted in collapse back to the D_{2h} structure. The effect of constraining the H-bond distances to be those found optimal for $H_7O_3^+$ (Table III) is indicated in II-A4. A charge–dipole model is provided in II-A5, where the optimal D_{2d} calculation is repeated with the constraint that the central proton remain bare (*i.e.*, it is given no basis functions, or, equivalently, the basis functions of the central proton are constrained to have zero coefficients in all MO's). Since the bifurcated structure of the neutral water dimer was found to be nearly as stable as the open structure,[16] we have included a bifurcated $H_5O_2^+$ structure (II-B1). Two other examples of four-coordinate oxygen are also considered. In II-B2 an H_2O acts as proton donor to H_3O^+. The linear H bond coincides with the threefold axis of the H_3O^+ moiety, which is allowed to relax from planarity. The structure was found to be unbound with respect to H_2O and H_3O^+. Structure II-B3 represents a non-H-bonded charge–dipole complex with the twofold axis of one water molecule collinear with the threefold axis of a nonplanar H_3O^+ group.

$H_7O_3^+$. The chain structure III-A1 was optimized, subject to a C_{2v} symmetry constraint. The CNDO oxygen framework angle was first assumed, and the internal bond distances were optimized. The framework angle was next optimized, and then the distances were reoptimized. Terminal HOH groups were assigned a bond angle of 112° (intermediate between the optimal H_2O and $H_5O_2^+$ angles) and were rotated perpendicular to the oxygen plane (*cf.* the dihedral angle of II-A1). The effect of constraining the optimal H-bond distances for $H_5O_2^+$ is indicated in III-A3. Constrained calculations of this type will be helpful (see below) in studying mechanisms of formation and interconversion of the various solvated ions. The optimal chain structure corresponds to a slightly distorted central H_3O^+ surrounded by two H_2O molecules. Different chain structures were obtained by appropriate distortions of the internal bond distances. In III-A4, we have a complex between a water molecule and an essentially optimal $H_5O_2^+$ molecule. The structure III-A5, obtainable from III-A1 by contracting one of the inner OH bond lengths to 0.95 Å, represents a possible transitional species arising in the conversion of the initial complex III-A4 into the optimal chain structure III-A1, *i.e.*, a complex between H_2O and $H_5O_2^+$ with a distorted framework.

As an alternative model for formation of $H_7O_3^+$, we considered H_3O^+ complexed to an optimal H_2O dimer (III-A6) and the transitional species III-A7, in which the dimer geometry is distorted. Finally an H_3O^+ is complexed to two H_2O molecules (III-A8), with all monomers given their optimal geometries. Structure III-B1 corresponds to a neutral cyclic trimer (see above) to which a proton has been added. In the second model (III-B2) an H_3O^+ donates two protons to a water dimer (one to each of the dimer oxygen atoms). Of the structures considered, those with two in-plane external OH bonds (O1H1 and O2H5, Figure 7) were found to be most favorable energetically. A three-coordinate proton structure consisting of a proton surrounded in a plane by three water molecules (III-C) was also tested. Structures III-B1 and III-C are unbound with respect to H_2O and $H_5O_2^+$.

$H_9O_4^+$. As a starting point (IV-A2) for optimizing the chain structure, a C_2 structure was assumed, with a symmetric central H bond taken from optimal $H_5O_2^+$ (II-A1) and terminal H bonds taken from optimal $H_7O_3^+$ (III-A1). Bond angles were assigned on the basis of III-A1 and an oxygen-framework dihedral angle of 90° was chosen on the basis of II-A1 and II-A2. First the inner and outer H-bond distances were optimized (IV-A1), and then the sensitivity to dihedral angle was tested in IV-A3. The presence of four oxygen atoms suggests branching as an energetically acceptable alternative to the linear-chain structure. In IV-B1 the branched (Eigen) structure[1] is optimized with respect to H-bond distances, with the constraint of C_{3v} symmetry. Ring structures were examined in a fashion analogous to the case of $H_7O_3^+$. As in the case of III-B2, structures with in-plane OH bonds (O1H1, O2H4, and O4H8, Figure 10) appeared to be most stable, although only a few out-of-plane deformations could be considered.

$H_{11}O_5^+$. A preliminary investigation of the outer solvation shell was undertaken by adding a water molecule to the three most favorable $H_9O_4^+$ structures, *i.e.*, the linear chain, the branched-chain (Eigen) structure, and the kite structure (IV-C2). No optimization was possible, and the new interoxygen bond distance in the complex was taken as either 2.54 or 2.70 Å.

$H_3O_2^-$. The planar-chain structure was optimized for a symmetric H bond (VI-A1). Sensitivity to dihedral angle and H-bond distortion are indicated in VI-A2 and VI-A3, respectively. As an alternative, the hydroxyl oxygen was complexed to a distorted water molecule, forming a bifurcated structure (VI-B), for which the interoxygen bond length and the water HOH angle were optimized. Finally, the H-bonding ability of the hydroxyl proton was tested by considering the structure obtainable by removing a terminal proton from the proton-donor molecule in a neutral water dimer. The complex is predicted to be unbound with respect to its monomer components. We have arbitrarily presented energies for two different interoxygen distances—the optimal chain value and a long-range value (3.03 Å).

$H_5O_3^-$. The optimal chain structure VII-A1 was arrived at as follows. From the results for $H_3O_2^-$, terminal HOH angles of 109° were assigned, with the terminal OH bonds trans to the central hydroxyl OH bond. The CNDO framework angle (140°) was assumed, and the H-bond distances were optimized. Framework-angle distortions and out-of-plane deformations (VII-A2) were then tested. An isomer with a terminal OH^- (VII-A4) was generated by reversing the asymmetry of one of the H bonds in VII-A1. Two other isomers involving respectively a central double-proton-donating water molecule (VII-A5) and a central proton-donating hydroxyl group (VII-A6) were also considered.

A cyclic structure was generated from a cyclic neutral trimer by removal of a terminal proton (*cf.* VI-C) and optimizing the interoxygen distance, keeping the equilateral triangle oxygen framework. A more favorable cyclic structure was obtained by allowing the hydroxyl to serve as a double proton acceptor (VII-B2).

$H_7O_4^-$. A planar-chain structure (C_{2h} symmetry) was constructed with appropriate bond distances and angles from the optimal $H_5O_3^-$ structure (VII-A1) and with a symmetric central H bond as optimized for $H_3O_2^-$ (VI-A1). The energy was then optimized with respect to H-bond distances and the oxygen-framework dihedral angle (VII-A1). Distortion to an asymmetric central H bond (VIII-A4) was also tested. The fact that branching leads to extra stability in the case of $H_9O_4^+$ (IV-B) led us next to investigate pyramidal structures corresponding to a central OH^- complexed to three water molecules. Based on $H_5O_3^-$ results, the terminal water molecules were assigned HOH angles of 109° and placed in trans conformations with respect to the central OH^-.

Finally, the usual two types of cyclic structures were investigated, the first obtained by removal of a proton from the square neutral tetramer (OH^- proton donor) and the second corresponding to OH^- in a double-proton-acceptor capacity. In the latter case (VIII-C2), a kite framework was found once again to be most favorable.

$H_9O_5^-$. Two preliminary structures relevant to the outer solvation shell of the hydroxyl ion were constructed by adding a water molecule to the two most stable $H_7O_4^-$ structures—the branched chain (VIII-B) and the cyclic kite (VIII-C2). The new interoxygen bond in the acyclic structure IX-A occurs at one of the outer oxygen atoms of $H_7O_4^-$ (VIII-B) and is placed in a cis conformation with respect to the central OH bond (O1H1). The new bond in the ring structure IX-B occurs at the hydroxyl oxygen atom (O1) and lies in the molecular symmetry plane, forming an angle of 110° with the hydroxyl group (O1H1). By analogy with the procedure used for the $H_{11}O_5^+$ species, the new interoxygen bond in both $H_9O_5^-$ structures was assigned a length of 2.70 Å, and the OH bonds involved in the newly formed bridges were extended from 0.95 to 0.99 Å.

III. Comparison with Experimental Enthalpies

The most direct experimental data on the properties of the H_3O^+ and OH^- hydrates come from mass spectrometric studies,[3,4] which yield enthalpies of formation of the higher hydrates from the lower members of the series and water, and cross sections for attenuation of the hydrate ion beams.[4] Of these two properties,

Table X. Calculated and Experimental Solvation Enthalpies for the Formation of the $H_3O^+ \cdot nH_2O$ and $OH^- \cdot nH_2O$ Hydrates[a]

	Positive ions				Negative ions		
	ΔE_{tot}		ΔE_{exptl}[c]		ΔE_{tot}		
Hydration no., *n*	Calcd	Corr for ZP energy[b]	Ref 4	Ref 3	Calcd	Corr for ZP energy[b]	ΔE_{exptl}[c] Ref 4
0	7.94	7.67	7.9	7.2[d]			
1	1.89	1.62	1.4	1.6	1.77	1.54[e]	1.5
2	1.34	1.15	1.0	0.97	1.31	1.12	1.0
3	1.13	0.97	0.75	0.74	1.00	0.84	~0.8
4	0.77[f]	0.66	0.70	0.66	0.90[f]	0.77	

[a] All enthalpies in electron volts. ΔE is the energy of the species relative to the energy of H_2O and the next lower hydrate. [b] Corrected for the zero-point energy differences accompanying hydration. Obtained from observed (corrected, see text) frequencies for H_2O, H_3O^+, and $H_5O_2^+$ and scaled proportionally to computed ΔE_{tot} through positive ion sequence $H_5O_2^+ \rightarrow H_{11}O_5^+$. Negative ion corrections taken equal to corresponding positive ion corrections, except as noted. The procedure of scaling within the negative ion series by ΔE_{tot} would, it should be observed, yield essentially identical results. The zero-point corrections were made for the deuterium isotope of hydrogen, since most of the experimental data refer to the perdeuterio species. A slightly larger (≤ 0.1 eV) correction would be obtained for the mass-1 isotope. [c] Experimental values are those of Friedman and coworkers[4] (perdeuterio species) and Kebarle, *et al.*[3] (normal hydrogen isotope), unless otherwise noted. [d] Reference 30. [e] The zero-point energy correction was taken as five-sixths of the $H_5O_2^+$ correction, since only five new vibrational modes are formed in the reaction $OH^- + H_2O \rightarrow H_3O_2^-$. [f] Geometry only partially optimized.

the former is most directly relatable to the theoretical results obtained in the present study. In Table X we have listed the following energy differences (ΔE_{tot}), based on the total energies (E_{tot}) associated with the optimal structures given in Tables I–IX.

$$\Delta E_{tot}(\text{cation}) = E_{tot}(H_3O^+ \cdot nH_2O) - E_{tot}(H_3O^+ \cdot (n-1)H_2O) - E_{tot}(H_2O)$$

$$\Delta E_{tot}(\text{anion}) = E_{tot}(OH^- \cdot nH_2O) - E_{tot}(OH^- \cdot (n-1)H_2O) - E_{tot}(H_2O)$$

The second column (Table X) for each type of ion contains the result of correcting the ΔE_{tot} values for zero-point energy differences.[27] These differences arise principally from the fact that new vibrational modes are created in the process of hydration (an increase of six in all cases except for the formation of H_3O^+ and $H_3O_2^-$, where three and five new modes are formed, respectively). Zero-point energy corrections are, of course, dependent on the particular isotopes involved, and the corrections included in Table X are for the perdeuterio species, from which most of the experimental solvation enthalpies have been obtained.[4] Similar, slightly larger, corrections would be found for the species containing the normal hydrogen isotope.

Before comparing the corrected ΔE_{tot} values with the experimental data, one might consider the importance of correlation energy differences attending the hydration processes. Of course, it is only meaningful discussing correlation energy effects to the extent that differences between the approximate and true Hartree–Fock energies cancel, and in the absence of polarization functions, we cannot be confident of such cancellations. At any rate, aside from the process $H_2O + H^+ \rightarrow H_3O^+$, where the decrease in correlation energy may be as much as ~1 eV,[29] correlation energy probably makes only a minor contribution to the solvation energies of interest.

The experimental data are primarily taken from the work of Friedman, *et al.*, on perdeuterio cations[4a] and anions[4b] and the work of Kebarle, *et al.*, on the cations, using the normal hydrogen isotope.[3] Aside from a 0.2-eV difference for $H_5O_2^+$ (some of which may be accounted for by the isotopic difference), the two sets of cation data agree to within 0.04 eV. The value of Friedman, *et al.*, for D_3O^+ [4a] is somewhat larger than previous values.[30] The corrected, calculated ΔE_{tot} values (second column for each ion) are seen to be in close agreement with experiment. Except for the case of D_3O^+, where disagreement exists among different experimental results, the calculated enthalpies which are obtained from *optimal* structures are consistently larger than the experimental quantities, with

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(27) In view of the scarcity of spectral data for the ionic species of interest, we have estimated the zero-point corrections as follows. The only perdeuterio species for which essentially complete vibrational frequency data are available are D_2O,[28a,b] D_3O^+,[7a,28c] and $D_5O_2^+$.[7b] Hence, our procedure was to calculate accurately the zero-point energy change for the formation of D_3O^+ and $D_5O_2^+$ and then assume that the ratio of the zero-point correction to ΔE_{tot} for $D_5O_2^+$ holds also for the higher hydrates. The zero-point correction for the anion $OD^-(D_2O)_n$ was assigned the value obtained for the corresponding cation D_3O^+-$(D_2O)_n$, except for $D_3O_2^-$, where the $D_5O_2^+$ value was scaled by five-sixths (see above discussion). Alternatively, the corrections for the anions could be made by using the same scale factor procedure as used for the larger cations, but essentially the same results would be obtained.

The available spectra for D_2O, D_3O^+, and $D_5O_2^+$ have been obtained from two basic types of environment, corresponding to essentially "free" species and species associated with their environment by varying degrees of hydrogen bonding and other interactions. A reasonably consistent set of frequencies for "unassociated" molecules was obtained from the gas-phase D_2O data,[28a] the liquid SO_2 solution D_3O^+ data,[7a] and the solid $D_5O_2^+ \cdot ClO_4^-$ data,[7b] corrected for the hydrogen bonds existing between the four terminal protons and the ClO_4^- oxygen atoms. The corresponding data for the "associated" molecules was taken from liquid D_2O,[28b] solid $D_3O^+ \cdot Cl^-$,[28c] and solid $D_5O_2^+ \cdot ClO_4^-$.[7b] The correction needed to obtain the zero-point energy for "unassociated" $D_5O_2^+$ was determined by assuming that the ratio of the zero-point energy in the free and associated states is the same for D_3O^+ and $D_5O_2^+$. This assumption leads to the reasonable correction of 0.94 kcal per OD bond, or a total of +3.76 kcal for the estimated zero-point energy of "free" $D_5O_2^+$, relative to that for $D_5O_2^+$ in the solid perchlorate salt. We finally obtain zero-point energy corrections of 0.27 and 0.34 eV for the formation of D_3O^+ and $D_5O_2^-$, respectively, using the "free species" data, and values of 0.22 and 0.28 eV from the corresponding "associated species" data. It is gratifying to find that similar values are obtained from the two approaches, and we adopt (Table X) the free species corrections as being most relevant to the calculated values.

(28) (a) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, N. Y., 1945. (b) R. A. More O'Ferrall, G. W. Koeppl, and A. J. Kresge, *J. Amer. Chem. Soc.*, **93**, 1 (1971). These authors quote frequency values from G. E. Walrafen (in "Hydrogen Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis, London, 1969, p 8) and R. E. Weston, Jr. [*Spectrochim. Acta*, **18**, 1257 (1962)], for all H_2O modes and the bending mode of D_2O. The stretching modes for D_2O are estimated by assuming the same isotope effect as observed in gas phase and between the bending modes in the liquid (0.74). (c) C. C. Feriso and D. F. Hornig, *J. Chem. Phys.*, **23**, 1464 (1955).

(29) See discussion by V. McKoy, *ibid.*, 42, 2232 (1965), and correlation energies estimated by C. D. Ritchie and H. F. King, *ibid.*, 47, 564 (1967). The correlation energy of H_3O^+ is expected to be intermediate with respect to that of NH_3 and H_2O.

(30) (a) M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 2332 (1965); (b) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, 50, 2028 (1969).

most of the differences in the range 0.1–0.2 eV. Uniform agreement of such quality for this large group of complexes indicates that the basis set used for these calculations fulfills our criterion of providing reliable energetics while allowing computational efficiency. As mentioned above, the best structures for $H_{11}O_5^+$ and $H_9O_5^-$ were not optimized, having been formed by adding a water molecule to the O_4 structures IV-B1 and VIII-C2, respectively, without allowing for any readjustment of the latter species. We also note that compared to the acyclic structures, relatively little energy optimization was carried out for the cyclic O_4 structures. Since structures containing the O_4 ring are already nearly as stable as their acyclic isomers in the case of the O_4 anions and the O_5 cations, it is possible that further energy optimization would make the cyclic structures the most favored species in these two cases. The cyclic structure is already the favored $H_9O_5^-$ species. Clearly, further calculations are required for the O_4 and O_5 systems, including refinements of structures already considered and examination of alternative structures. In any case, we conclude that our calculations are in agreement with the experimental cation results in indicating that the decrease in solvation enthalpy is rather gradual and that the solvation energy associated with the outer solvation shell is considerably larger than the association energy of neutral liquid water.[3,4a] Our calculations also predict a similar situation for the anions.

IV. Population Analysis

The Mulliken population analysis[20] offers a convenient way of partitioning the total electron density of a molecular system into individual atomic contributions. This procedure has been extensively applied to minimal basis set molecular orbital wave functions, and the atomic charges so obtained provide useful models for molecular charge distributions.[31] Since the population analysis is explicitly dependent on the basis set, the latter must be well balanced with respect to the various types of atoms in a molecule, if a meaningful charge analysis is to be obtained. Experience has indicated that most atom-centered minimal basis sets are balanced in the above sense. It is by no means clear that extended basis sets are in general suitable for population analysis. Extended basis sets which include polarization functions appear in some cases to be balanced, leading to physically reasonable charge models.[32] However, the double-ζ level, in which the heavy first-row atoms are given an extra complement of s and p functions, while the hydrogen atom receives only a single extra s function, seems to lead to an exaggerated degree of ionic character in many bonds involving hydrogen. Thus in the present calculations with the 4-31G basis, the population analysis attributes formal charges of −0.81 and −0.75 to the oxygen atoms in H_2O and H_3O^+, respectively. Kollman and Allen obtained similar results with their double-ζ basis set.[14] They also found that supplementing the hydrogen atom basis set with three p orbitals led to an oxygen atom charge of −0.31 in H_3O^+, a considerably more plausible value. Thus, the absolute charges obtained from population analysis of a double-ζ wave function do not appear to be directly useful in many cases.[33] The formal charges for individual atoms may become more meaningful *per se* when they are lumped together to form effective overall charges for the various structural units present in the solvated complexes; *i.e.*, while the separation of charge for the short-range OH bond in H_2O, H_3O^+, or OH^- seems to be exaggerated by the population analysis, the net charge transfer (as inferred from the population analysis) between monomer groups held together by longer range forces (*e.g.*, the H_3O^+ and H_2O units of $H_7O_3^+$) appears to have more physically reasonable magnitudes. Accordingly, we have listed in Table XI the group charges for all energetically favorable structures.

In addition to atomic charges, the Mulliken population yields bond or overlap populations.[20] It is fair to say that the meaning of these quantities is even less well understood than that of the atomic populations, although they do appear to provide qualitative information about covalent bond strengths. Some trends in overlap population will be discussed in section VB.

V. Discussion

A. Comparison with Previous *Ab Initio* Calculations. In order to provide some basis for assessing the quality of the calculations reported here, we offer a brief comparison of some of our results (Table I) with those of previous *ab initio* calculations and consider the importance of polarization basis function. A survey of *ab initio* calculations on the first-row hydrides XH_n (n = 1–3) reveals that double-ζ basis sets without polarization functions generally yield exaggerated (relative to experiment) values of the dipole moment and equilibrium HXH angle.[11,34,35] Addition of d polarization functions leads to marked improvement. In molecules such as NH_3 or OH_3^+ it is clear that omission of d orbitals on the central atom would affect the energies of nonplanar configurations more than of the planar ones (the d orbitals are less important in the D_{3h} structure owing to symmetry constraints). Hence exaggeration of HXH bond angles is at least qualitatively understandable. The monomers of greatest relevance to the current study are, of course, H_2O, H_3O^+, and OH^-. The 4-31G basis leads to results

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(31) W. J. Hehre and J. A. Pople, *Chem. Phys. Lett.*, **2**, 379 (1968), and references therein. Note, however, the sensitivity to orbital exponents.

(32) *E.g.*, S. Rothenberg, R. H. Young, and H. F. Shaefer III, *J. Amer. Chem. Soc.*, **92**, 3243 (1970).

(33) Detailed examination suggests that there is enough systematic behavior in the 4-31G atomic charges to warrant their use, at least in qualitative comparisons of charge distributions in related systems; *e.g.*, comparison of the atomic charges obtained for the various "chain" cations and anions in the present *ab initio* study and the previous CNDO study[9] indicates that in the 4-31G basis framework the protons are 0.3 electron unit more positive and the oxygens ~0.6 electron unit more negative than corresponding CNDO values. Closer examination reveals that while a fairly good linear relationship may be constructed for the charges of all 23 types of protons found in the set consisting of H_2O, H_3O^+, OH^-, and all the chain cation and anion structures common to the CNDO and *ab initio* study, distinctions among the types of protons allow much better correlation. Thus, a least-squares analysis for all protons together leads to the relation $q_{4\text{-}31G} = 0.791q_{CNDO} + 0.314$ (standard deviation (SD) = 0.021, root-mean-square (rms) value of $q_{4-31G} = 0.487$), while segregating monovalent protons from the divalent or bridging protons in the above set produces the following results: $q_{4\text{-}31G} = 0.722q_{CNDO} + 0.317$ (SD = 0.012, rms value = 0.417) and for the bridging protons, $q_{4\text{-}31G} = 1.300q_{CNDO} + 0.158$ (SD = 0.007, rms value = 0.580).

(34) J. W. Moscowitz, D. Neumann, and M. C. Harrison, "Quantum Theory of Atoms, Molecules and the Solid State," P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1966, pp 227–230.

(35) A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, **52**, 4133 (1970).

Table XI. Charges of Component Water and Primary Ion Moieties in Energetically Favorable Positive and Negative Ion Hydrates[a,b]

		Positive ions			Negative ions	
Species	Table ref	$m\mathrm{H_2O}$	$\mathrm{H_{2m+1}O_m}^+$	Table ref	$m\mathrm{H_2O}$	$\mathrm{H_{2m-1}O_m}^-$
O_2 chain	II-A1	0.17 (2)	0.66 (0)	VI-A1	−0.21 (1)	−0.79 (1)
O_3 Chain	III-A1	0.08 (2)	0.84 (1)	VII-A1	−0.13 (2)	−0.74 (1)
O_4 straight chain	IV-A1	0.06 (2)	0.88 (2)	VIII-A1	−0.09 (2)	−0.82 (2)
O_4 branched chain	IV-B1	0.07 (3)	0.79 (1)	VIII-B	−0.10 (3)	−0.70 (1)
O_4 ring	IV-C2	0.04 (2) 0.08 (1)	0.84 (1)	VIII-C2	−0.09 (2) −0.10 (1)	−0.73 (1)
O_5 from O_4 straight chain	V-A	0.06 ± 0.01 (3)	0.83 (2)			
O_5 from O_4 branched chain	V-B	0.06 (2) 0.05 (1)[c] 0.03 (1, int)[d]	0.80 (1)	IX-A	−0.10 (2) −0.06 (1)[c] −0.05 (1, int)[d]	−0.69 (1)
O_5 from O_4 ring	V-C	0.03 (2) 0.08 (1) 0.06 (1, ext)[e]	0.80 (1)	IX-B	−0.08 ± 0.01 (4)	−0.68 (1)

[a] Charges are defined by Mulliken population analysis, as discussed in Section IV. [b] The integers in parentheses (*m*) are used either to indicate the number of H_2O moieties which have a given charge or to define the ionic moiety appropriate to each species. The identities of the various H_2O moieties referred to can be inferred from the symmetry of the complexes (as reflected by the values of *m*), except as noted. [c] Refers to the H_2O molecule in the outer solvation sphere. [d] Refers to the internal H_2O, to which the outer sphere H_2O is complexed. [e] Refers to the exocyclic H_2O group.

typical of double-ζ basis sets: the equilibrium angle and dipole moment of H_2O are respectively 111.3° (experimental, 104.2[36a]) and 2.48 D (experimental, 1.85[36b]); a planar equilibrium geometry for H_3O^+ is predicted, with $R_{\mathrm{OH}} = 0.964$. Although H_3O^+ is apparently slightly nonplanar in some crystal environments,[36c] the geometry of the isolated species is still somewhat uncertain.[11a,13] Most of the discrepancy between the calculated and observed ($R_{\mathrm{OH}} \sim 1.01$ Å)[36c] bond length is presumably explained by the fact that the hydronium ion is hydrogen bonded in the solid. The 4-31G basis predicts a proton affinity of 183 kcal for H_2O, within 1 kcal of the double-ζ result of Kollman and Allen.[14] A more extensive basis set including a set of d functions on oxygen leads to a somewhat smaller value ($\sim$175 kcal).[12b] The proton affinity of OH^- is calculated to be 18.5 eV in the 4-31G basis, compared to the estimated Hartree–Fock limit of 17.8 eV.[10]

Our principal interest lies in the various complexes among the three monomers just discussed. Comparisons with previous calculations are possible for $(H_2O)_2$, $(H_2O)_3$, and $H_5O_2^+$. Extended basis sets including polarization functions have led to H_2O dimerization energies of $\sim$5 kcal ($R_{\mathrm{OO}} \sim 3.0$ Å),[12a,17] in good agreement with a recent statistical mechanical treatment.[37] Kollman and Allen obtained a value of 5.3 kcal with an LCAO basis,[16a] while their double-ζ basis led to a value of 7.9 kcal,[16b] quite similar to the present 4-31G value of 8.1 kcal. Del Bene and Pople have calculated the stabilization energy (relative to $3H_2O$) of both linear and cyclic $(H_2O)_3$ trimers obtaining respectively 14.6 and 17.1 kcal.[19] Moscowitz[17] has obtained a value of 8.3 kcal for the linear trimer while the 4-31G basis predicts a value of $\sim$24 kcal for the symmetric (C_3) cyclic trimer. As in the case of the dimer, the 4-31G basis appears to exaggerate the stabilization energy; the ratio of the cyclic trimer stabilization to dimer stabilization is about the same ($\sim$3:1) for the 4-31G basis and the minimal STO basis.[19] For $H_5O_2^+$, the 4-31G solvation energy of 44 kcal is to be compared with the Kollman–Allen double-ζ value of 37 kcal[14] and a value of 32 kcal from Kraemer and Diercksen.[12b] A 4-31G calculation using the Kollman–Allen geometry (not completely optimized) gives a value of 40 kcal, showing once again that the 4-31G and other double-ζ bases lead to very similar molecular properties.

To the extent that the dipole moment of monomeric H_2O is important in determining stabilization energies, the exaggerated stabilities noted above might well be expected from a double-ζ basis. This would be especially true for $H_5O_2^+$ where the two H_2O moieties are oriented favorably (in the sense of charge–dipole interaction) with respect to the central proton. Dipole–dipole interactions are clearly not dominant in the neutral H_2O polymer calculations, and the LCAO basis of Kollman and Allen gives a reasonable dimerization energy (5.3 kcal) in spite of a monomer dipole moment of 2.52 D.[16a] In the case of the 4-31G basis, the off-center calculations mentioned in section I indicate that overestimates on the order of a few kilocalories can be partially accounted for by the difference in quality of the basis sets used for the monomers and complexes. One may wonder if the above-noted exaggeration of stabilization energy is accompanied by any significant distortion of the potential energy surface (relative, say, to the potential in the Hartree–Fock limit). The equilibrium geometries calculated for $(H_2O)_2$ and $H_5O_2^+$ in the 4-31G framework are found to be quite similar to those obtained with more accurate calculations: *e.g.*, the optimal interoxygen distance for $H_5O_2^+$ from Diercksen's calculation[12b] was 2.39 Å, while the 4-31G value is 2.37 Å. In both $H_5O_2^+$ calculations, the potential for asymmetric motion of the central proton is very flat, over a range of $\sim$0.2 Å. To summarize, we find that omission of polarization functions does lead to certain systematic errors, but we nevertheless feel that the 4-31G basis (or other double-ζ bases) provides an efficient and adequate framework for analyzing the structure and potential surfaces of the systems under consideration.

B. General Discussion of Structures and Energetics. Energetically Favorable Species and Their Deformations.

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(36) (a) A. Kutchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2460 (1962); (b) G. Birnbaum and S. K. Chatterjee, *J. Appl. Phys.*, **23**, 220 (1952); (c) D. E. O'Reilly, E. M. Peterson, and J. M. Williams, *J. Chem. Phys.*, **54**, 96 (1971).

(37) R. W. Bolander, J. L. Kassner, Jr., and J. T. Zung, *ibid.*, **50**, 4402 (1969).

We begin our discussion of structural results with a summary of the principal features of the most favorable structures, as determined by the minimum-energy criterion. Although some ring structures were found to be favorable, especially in the four- and five-oxygen systems, we shall defer our discussion of them to a later section. For the present, we shall consider only the straight-chain structures and (in the case of the O_4 and O_5 systems) their branched isomers. In order to make the structural results more meaningful, we shall include data on the sensitivity of the potential energy surfaces to certain deformations of the optimal structures. Comparison with available experimental structural data is also provided.

Looking first at the cations, we find for the series $H_5O_2^+$ (II-A1), $H_7O_3^+$ (III-A1), and $H_9O_4^+$ (IV-A1 and IV-B1) an appreciable lengthening of the H-bonded O–O distance (outer O–O bond in the case of IV-A1 as the main structural variant). Although the $H_{11}O_5^+$ structure (V-B) was not optimized, further lengthening is predicted. Preliminary calculations indicate that its outer O–O bond length is intermediate between that of $H_9O_4^+$ (IV-B1) and the neutral dimer $(H_2O)_2$. The values 2.36, 2.46, and 2.54 Å for $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$, respectively, are in fair agreement, both in trend and in magnitude with recent crystallographic data. These data have been summarized and discussed by Beecham, *et al.*[38] For several hydrated acid salts, an $H_5O_2^+$ moiety has been detected with an interoxygen distance in the range 2.44–2.45 Å.[5] Neutron diffraction studies of two heavy-metal complexes have revealed $H_5O_2^+$ groups with somewhat larger interoxygen distances (2.50 ± 0.03 and 2.57 Å).[6] Crystalline HBr·$4H_2O$ has been shown by X-ray diffraction to contain $H_7O_3^+$ and $H_9O_4^+$ (branched structure) moieties, with interoxygen distances of 2.46–2.50 and 2.50–2.59 Å, respectively.[5c] More than one value was obtained for each species because the crystal environment destroyed the expected symmetries of the oxygen frameworks (C_{2v} for $H_7O_3^+$, C_{3v} for $H_9O_4^+$). It should be emphasized that because of the effect of the crystal environment, no more than rough correspondence can be expected between our calculated geometries for the isolated species and the experimental quantities. Probably the most important environmental perturbation is the incorporation of the terminal OH bonds into H-bond linkages. This effect might account for the fact that the experimental interoxygen distances tend to be somewhat greater than the calculated values, and it certainly accounts for the great variety of experimentally observed configurations of the $H_2O\cdots H$ grouping[5,6] and its conformation with respect to the rest of the ionic complex. Our calculations on the isolated species $H_5O_2^+$ led to an optimal staggered structure of D_{2d} symmetry, whereas pyramidal $H_2O\cdots H$ groups in trans conformations are generally found in the solid phase. The calculated barrier to rotation is $\sim 2 \times 10^{-3}$ au. As mentioned in section II, all attempts to optimize a trans staggered structure of C_{2h} symmetry led to the planar D_{2h} structure. However, a typical C_{2h} structure, with terminal HOH angles of 112° and terminal HOH planes forming angles of 170° with the OO bond, has an energy only 2×10^{-3} au above the energy of the stable D_{2d} structure. Such an energy deficit could easily be overcome by formation of external H bonds (*cf.* section III, where estimates are made of the crystal effects on the zero-point energy differences accompanying hydration of H_3O^+).

The branched $H_9O_4^+$ structure, calculated to be 0.007 au more stable than the chain isomer, is worthy of special comment, since this is the structure which was postulated by Eigen to account for the properties of the proton in aqueous solution.[1] This complex, consisting of H_3O^+ surrounded by three strongly bound water molecules, can be referred to as the inner solvation shell. Eigen suggested that it would have a flat pyramidal structure. Although we calculate a planar oxygen framework (IV-B1) for the isolated species, the above-noted exaggeration of angles in XH_n systems with the 4-31G basis set suggests that the inclusion of polarization functions might lead to a slightly nonplanar equilibrium geometry. The calculated energy change accompanying out-of-plane distortion, as reflected by structure IV-B2, is quite small. The CNDO method, which generally gives reliable HXH bond angles, predicts an apical interoxygen angle of ~116°. The $H_9O_4^+$ moiety in crystalline HBr·$4H_2O$ possesses a pyramidal structure, characterized by OOO angles of 116, 116, and 105°.[5c] The most stable structure (V-B) for the incipient outer solvation shell ($H_{11}O_5^+$) is obtained by H bonding an additional H_2O molecule to one of the peripheral H_2O groups of $H_9O_4^+$ (IV-B1). Complexing of another H_2O directly to the H_3O^+ oxygen atom is expected (see below) to lead either to an unbound structure (based on II-B2), or a structure less strongly bound (based on II-B3) than V-B.

The strength of the $O\cdots H\cdots O$ bond in $H_5O_2^+$ is reflected in the calculated symmetric O–O stretching force constant of ~4.5 mdyn/Å[39] (*cf.* the calculated value of ~4.8 mdyn/Å for H_2O_2 with the same basis set). Of course, the symmetric stretch would lead eventually to $2H_2O + H^+$ as dissociation products. The antisymmetric motion of the central proton, a mode relevant to the asymmetric dissociation into H_2O and H_3O^+, corresponds to a calculated harmonic force constant of only ~0.3 mdyn/Å.[39] For appreciable displacements, a quartic force constant would be expected to become important.[40] Although the central proton is found to be symmetric, we emphasize the softness of the antisymmetric mode. For a distance of ~0.2 Å, the energy changes less than 0.5 kcal; *i.e.*, we have essentially a particle in a one-dimensional box. The particle-in-a-box model has also been invoked by Hamilton in a discussion of strong H bonds.[41] The absence of a symmetric double-well potential for the central proton seems especially significant, since much previous discussion of the $H_5O_2^+$ grouping in connection with proton mobility in aqueous solution has depended on a model of proton tunneling through the barrier of such a potential.[1,42,43] Conway, Bockris,

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[38] A. F. Beecham, A. C. Hurley, M. F. Mackay, V. W. Maslen, and A. McL. Mathieson, *J. Chem. Phys.*, **49**, 3312 (1968).

[39] The values quoted for the symmetric and antisymmetric force constants in ref 14 are based on different definitions of symmetry coordinates [we employ the normalized coordinates, $Q = 1/\sqrt{2}\,(R_{OH} \pm R_{O'H})$] and should be multiplied by 2 and 0.5, respectively, for comparison with the values given here.

[40] J. A. Ibers, *J. Chem. Phys.*, **41**, 25 (1964).

[41] W. C. Hamilton, *Nat. Bur. Stand.* (*U. S.*), *Spec. Publ.*, **No. 301**, 193 (1969).

[42] (a) B. E. Conway, J. O'M. Bockris, and H. Linton, *J. Chem. Phys.*, 24, 834 (1956); (b) I. Kampschulte-Scheuing, and G. Zundel, *J. Phys. Chem.*, 74, 2363 (1970).

and Linton[42a] arrived at a double-well potential by superimposing two Morse potentials, corresponding to the two internal OH bonds, with a small correction for resonance interactions. The more accurate calculation by Kraemer and Diercksen[12b] on the $H_5O_2^+$ potential revealed a very slight degree of double-well character, but these authors emphasized the essential flatness of the potential for a wide range of proton motion.[44] The present calculations indicate a similar situation for the short, central interoxygen bond in "chain" $H_9O_4^+$. This bond is like the $H_5O_2^+$ bond, with respect to both length and sensitivity to distortion. Thus the flat potential for the central proton in $H_5O_2^+$ appears to be largely unaffected by the additional symmetric solvation represented by the chain $H_9O_4^+$ structure.

Aside from the two relatively short central interoxygen bonds just discussed, all equilibrium OO bonds are characterized by decidedy asymmetric H bonds, *e.g.*, distorting $H_7O_3^+$ from its optimal H-bonded distances (1.04, 1.42 Å) to symmetric distances (1.23, 1.23 Å) costs ~0.02 au. Conversely, distorting the symmetric $H_5O_2^+$ distances to asymmetric $H_7O_3^+$-like distances costs only $\sim 2 \times 10^{-3}$ au. Therefore, in none of the cations under consideration is there a *strong* tendency for symmetric H bonds, even when the oxygen framework might suggest it. The H bonds in $H_9O_4^+$ are even more asymmetric than those in $H_7O_3^+$, with the short bonds (R_{OH} = 1.00 Å) only slightly longer than the optimal monomer OH bond, and the long bonds (R_{OH} = 1.50 Å) halfway between the corresponding distances in $H_5O_2^+$ and $(H_2O)_2$. The asymmetry of the H bonds suggests that the various building blocks of the complexes (H_2O, H_3O^+, and $H_5O_2^+$) tend to maintain their identity. This picture is strengthened by an examination of the overall Mulliken populations of the various subunits (Table XI). We can view $H_5O_2^+$ either as two water molecules bound to a proton which retains 66% of the positive charge, or as a single H_2O molecule bound to an H_3O^+ moiety with 83% of the positive charge. The $H_5O_2^+$ moieties of chain $H_9O_4^+$ (IV-A1) and $H_{11}O_5^+$ (V-A) possess overall positive charges of 0.88 and 0.83, respectively, and the H_3O^+ unit accounts for 84, 79, and 80% of the positive charge in $H_7O_3^+$, branched $H_9O_4^+$ (IV-B1), and $H_{11}O_5^+$ (V-B), respectively. In spite of the rather high degree of central charge localization, there is nevertheless a significant amount of charge transfer to the outer H_2O units. Not surprisingly, the charge transfer to each H_2O decreases with the degree of hydration, varying from +0.17 for the H_2O groups of $H_5O_2^+$ to 0.03–0.07 for the H_2O groups in the linear and branched-chain structures of $H_9O_4^+$ and $H_{11}O_5^+$.

The emergence of a well-defined H_3O^+ moiety in the series of cations is also indicated by the force constant associated with symmetric stretching of all the "short" OH bonds involving bridging protons. The appropriate symmetric force constants for $H_7O_3^+$ and $H_9O_4^+$ (IV-B1) are calculated to be ~5.1 and ~6.6 mdyn/Å, respectively, compared to a calculated symmetric stretching force constant of ~8.3 mdyn/Å for H_3O^+; *i.e.*, the central H_3O^+ in $H_9O_4^+$ has OH bonds with ~80% of the strength of the OH bonds in H_3O^+ itself, as measured by these force constants. The relative magnitudes of these force constants are in rough agreement with experimental values based on ir spectra.[28b]

From solvation energies (Table X), bond lengths, group charges (Table XI), and force constants, we have arrived at a picture of the solvated proton in terms strong $O \cdots H \cdots O$ bonds which become increasingly weaker and asymmetric as successive water molecules are added, thereby making the complexes more and more recognizable in terms of their component parts. The important point to note is that these changes are all gradual. No discontinuities are observed in the transition from the inner solvation sphere ($H_9O_4^+$) to the outer sphere ($H_{11}O_5^+$). It seems likely that the successive solvation shells about a central H_3O^+ may approach the weak H bonding present in neutral liquid water in a gradual and continuous way; *i.e.*, there do not appear to be unique features associated with systems containing multiple strong H bonds. In trying to understand this weakening process, it is important to note that in the isolated species being considered here there is no indication of extensive spreading or leveling of the positive charge over the entire complex. Indeed, as suggested by the group population analyses, the positive charge in $H_7O_3^+$, $H_9O_4^+$, and $H_{11}O_5^+$ is found to be at least 80% localized on the central ionic moiety (H_3O^+ or $H_5O_2^+$).[45]

The falloff in solvation energy associated with successive solvation arises to some extent from the fact that participation of a proton in bridging is accompanied by weakening and lengthening of its original OH bond. Thus, in $H_7O_3^+$, the two OH bonds of H_3O^+ which are involved in bridging are extended to ~1.04 Å, with overall bridged O–O distances of ~2.46 Å, while the bridging demands on all three of the H_3O^+ bonds in branched $H_9O_4^+$ (IV-B1) result in a compromise whereby the three OH bonds are only stretched out to ~1.00 Å, with correspondingly longer interoxygen

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(43) M. Eigen and L. De Maeyer, *Proc. Roy. Soc., Ser. A*, 247, 505 (1958).

(44) Conway, *et al.*,[42a] assumed an interoxygen distance of 2.45 Å. *Ab initio* calculations for the proton potential with similar (nonequilibrium) values of the interoxygen distance, both in the present study and elsewhere,[14] do lead to double wells. They are, however, shallow, with central barriers <1 kcal (*i.e.*, well below the zero-point level) as opposed to the barrier of ~5 kcal (above the zero-point level) obtained by Conway, *et al.* As discussed below, the proton potential is sensitive not only to the interoxygen potential, but also to the environment of the $H_5O_2^+$ moiety.

(45) In connection with our discussion of overall group charges, it is also of interest to examine the trends in the populations of the individual oxygen atoms, proceeding through the series from the smaller to the larger cations. The oxygens in all complexes exhibit substantial electron excesses and, with the exception of H_3O^+, all are predicted to have greater excesses than the oxygen in H_2O. Equally striking is the observation that the population on a given oxygen increases with the number of bridges formed to other oxygens (waters), a phenomenon similar to the theoretically predicted buildup of negative π-electron charge at junction positions in certain cationic hydrocarbons: A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, 50, 901 (1954). Analogous to the situation for hydrocarbon ions, we find the most stable hydrated proton isomers to be those with the greatest amount of bridging to central sites. While drawing analogies, however, we should not overlook a major difference in these systems, which may be related to the substantial leveling of stabilization energies (Table X) associated with successive hydration. Unlike the situation in the formation of C–C bonds in hydrocarbons, strong repulsions can be expected to exist between adjacent, electron-rich oxygen atoms. The repulsion is offset to some extent by the interposition of electron-deficient bridging protons, whose partial positive charge is significantly greater than that for nonbridging protons. Thus, complexing an additional H_2O to an H_3O^+ unit causes little overall modification of the H_3O^+ charge, since the increased population of the H_3O^+ oxygen is nearly balanced by the increased positive character of the H_3O^+ proton in the newly formed H bond.

distances (~2.54 Å). In other words, the leveling noted in the energetics of complexing within the inner solvation shell may be partially rationalized in terms of the greater distances by which successive waters of hydration find themselves separated from the centers of positive charge, or *vice versa.* Water molecules in the outer solvation shell are, of course, still further removed. As shall be seen below, isomeric preferences in larger hydrated systems also appear to correlate satisfactorily with this rationalization.

To pursue the "weakening" process in more detail, one should consider the actual nature of the bonds involved. By "hydrogen bond," one generally is referring to a divalent hydrogen atom whose valence orbital (1s) is involved in two covalent bonds, either by resonance, in valence-bond language, or perhaps by three-center bond orbitals, in molecular orbital language. Since we are dealing with ions in the present study, however, we must consider the possibility that the H-bond configurations may to a large extent simply correspond to electrostatic stabilization resulting from various ionic and dipolar interactions. In a later section we shall examine some charge–dipole models. In the present discussion, we investigate the covalent character of the H bonds by looking at the appropriate OH overlap populations.[20] Overlap populations are at best only a rough guide to covalent bond strengths, but the trends in values for a series of similar bonds are certainly qualitatively useful. For the outer O—H···O bonds in the series $H_5O_2^+$ through $H_{11}O_5^+$ (with the entry for the long-range H···O bond given in parentheses), the OH overlap populations form the following monotonic sequence: 0.22 (0.22), 0.34 (0.14), 0.40 (0.11), and 0.46 (0.08); the corresponding values for $(H_2O)_2$ are 0.51 (0.05); the OH overlap population for H_3O^+ is 0.51, and for H_2O, 0.53. Thus the overlap populations reinforce the picture of gradual strengthening and weakening respectively of the short-range and long-range components of the O—H···H bond as one passes from the "strong" to the "weak" H-bond limit. Covalent bonding appears to play an important, although not necessarily dominant, role in the solvation of the proton. We have already seen that charge transfer is another significant factor.

The discussion just given for the series of solvated proton complexes is generally applicable to the analogous series of solvated OH^- complexes. We therefore offer an abbreviated discussion of the anions, referring back to the relevant cation discussion and emphasizing only the salient features and any differences between cation and anion structures. As noted also for the cations, the interoxygen distances increase with successive solvation, going from 2.45 Å for $H_3O_2^-$ to 2.61 Å for $H_7O_4^-$ (outer OO bond for chain $H_7O_4^-$). It is interesting to note that the same optimal H-bonded distances are found for both the chain and branched $H_7O_4^-$ structures, a result also found for the $H_9O_4^+$ isomers. Beecham, *et al.*, have pointed out that an interoxygen distance of 2.44–2.46 Å is characteristic of many different O···H···O⁻ groupings, including the crystal salts of several different carboxylic acids.[38] The calculated interoxygen distance for $H_3O_2^-$ is seen to lie within this range. The present calculations predict that the interoxygen bond of an anion, OH^--$(H_2O)_n$, is appreciably longer (by ~0.07 ± 0.01 Å) than the corresponding bond of the cation, H_3O^+-$(H_2O)_n$. Experimental attenuation cross sections indicated a similarity in the molecular volumes of corresponding anions and cations.[4b] The crystal data cited by Beecham[38] suggest that the value for the interoxygen bond in many ionic O_2 systems is roughly constant, irrespective of charge.

The potential for the motion of the central proton in $H_3O_2^-$ and chain $H_7O_4^-$ is found to be even softer than was the case for the corresponding cations. For a range of ~0.25 Å, the change in energy is $<10^{-4}$ au. An asymmetric location of the central proton is slightly more favorable than the symmetric position, as is also the case for chain $H_7O_4^-$ (VII-A1). Nevertheless, the central barrier is <1 kcal, and once again (as for $H_5O_2^+$ and chain $H_9O_4^+$), the particle-in-a-box model seems preferable to the double-wall-tunneling model. Analysis of neutron diffraction data has led to similar conclusions.[41] A stronger tendency against symmetric H bonds is found for $H_5O_3^-$, where 0.0224 au is required to distort the optimal bonds to $H_3O_2^-$-like symmetric H bonds. The optimal dihedral angle for $H_3O_2^-$ was found to be ~160°, with calculated cis and trans barriers of $\sim 2 \times 10^{-3}$ and $\sim 10^{-5}$ au, respectively.

The most stable $H_7O_4^-$ isomer is calculated to be the branched chain (VIII-B), characterized by pyramidal geometry. A cyclic isomer (VIII-C2), whose energy is calculated to be within 0.1 eV of that for VIII-B, will be discussed below. The pyramidal structure VIII-B is of interest, since it offers an example of an energetically favorable four-coordinate oxygen. Ackermann,[46] apparently proceeding by analogy with Eigen's postulated structure for the inner solvation sphere of the proton,[1] has proposed a structure for the OH^- inner solvation sphere quite different from our most stable structure (VIII-B). The most significant difference between Ackermann's $H_7O_4^-$ species and VIII-B is that the former involves the hydroxyl ion as a proton donor as well as a double acceptor. In later discussion of alternatives to chain structures, we shall find that proton donation by OH^- is extremely unfavorable energetically. Hence we feel that as long as a given proton can be said to belong to a hydroxyl ion, it will not participate in H bonding. Of course, proton transfer accompanying isomerization may convert OH^- into H_2O, whereupon the same proton becomes available for H bonding. The calculated $H_7O_4^-$ structure (VIII-B) is actually more analogous to Eigen's $H_9O_4^+$ structure than is Ackermann's proposed structure. In both IV-B1 and VIII-B, the central ionic moiety is surrounded by three equivalently oriented H_2O molecules, while additional H-bonded solvation along the threefold axis is very unfavorable because of the reluctance of the H_3O^+ lone pair to be involved in an H bond (see II-B2) in the case of $H_9O_4^+$, and because of the reluctance of the OH^- proton to form an H bond in the case of $H_7O_4^-$. The possibility of a fourth, *non-H-bonded* ligand, to H_3O^+ has been mentioned above. Further discussion of Ackermann's structure will be given below.

The analysis of cations in terms of clearly recognizable fragments, and the analysis of the bonding in terms of a gradual transition from strong to weak H bonds, applies equally well to the solvated hydroxyl ion. In

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(46) Th. Ackermann, *Discuss. Faraday Soc.*, 24, 180 (1957).

all species the negative charge is at least 70% localized on a central OH^- or $H_3O_2^-$ group. As in the case of the cations,[45] the bridging protons are appreciably more positive than the terminal protons, and the internal oxygen atoms are more negative than the peripheral ones. For the series of molecules $H_3O_2^-$, $H_5O_3^-$, $H_7O_4^-$, and $(H_2O)_2$, the following trend in overlap population is found for the outer O···H—O bonds (long-range O···H bond entries are in parentheses): 0.30 (0.30); 0.38 (0.21); 0.44 (0.15); and 0.51 (0.05). In the case of $H_9O_5^-$, the H bonds adjacent to the OH^- group in structures IX-A and IX-B have overlap populations in the range 0.37 (0.19)–0.43 (0.16), while for the H bonds once removed from the OH^-, we find the values 0.50 (0.08), Thus the H-bond overlap populations associated with the formation of the outer solvation shell are intermediate in value between those for $H_7O_4^-$ and the neutral dimer, a result similar to that found for the cations. The limiting OH overlap population for monomeric H_2O is 0.53. One may conclude that charge transfer and covalent bonding play important roles in the solvation of both hydroxyl and hydronium ions.

Having completed the general discussion of the most favorable cation and anion structures, we turn in the next section to a more detailed examination of the potential energy surfaces in order to illustrate some general points concerning energetics of proton jumps and the related matters of complex formation and isomerization.

Energetics of Complex Formation and Proton Jumps. Of particular interest in the current study are those features of the potential surfaces which are relevant to mechanisms of complex formation and proton jumps. This interest arises because of recent gas-phase data on the kinetics[2] and thermodynamics[3,4] of proton and hydroxyl ion solvation and the long-known rapid mobilities of protons and hydroxyl ions in water and ice.[1,43,46] As discussed by Eigen and De Maeyer,[43] these mobilities may depend both on rates of proton jumping within existing H bonds and rates of breaking and forming other H bonds. One must, of course, be cautious in attempting to relate calculations on isolated species to experimental data obtained from solutions or solids. Nevertheless, we feel that the current *ab initio* calculations provide a useful reference for examining previous models invoked to account for H^+ and OH^- mobilities.

Although it is not feasible to carry out a thorough investigation of all important pathways, the sample calculations included in Tables II–IX suggest that many ion-solvation and proton-jump processes occur with little or no activation energy. For example, we have already noted the absence of a double-well potential for the central proton in $H_5O_2^+$ and linear $H_9O_4^+$ (IV-A1). As another example, we consider the $H_7O_3^+$ system. The formation of the optimal chain $H_7O_3^+$ by the addition of H_2O to $H_5O_2^+$ may be pictured as occurring by the following steps: (1) an H_2O molecule is brought up to an $H_5O_2^+$ molecule until the new interoxygen bond length is 2.46 Å (III-A4), with an energy decrease of 0.0411 au, presumably monotonic; (2) H bonds of the $H_5O_2^+$ moiety readjust to the optimal asymmetric H-bond distances for $H_7O_3^+$ (III-A5), with a further energy drop of 0.0049 au; (3) the proton in the newly formed H bond relaxes from its original OH bond length of 0.95 Å to the optimal length of 1.04 Å, with a final energy drop of 0.0033 au. It is quite likely that the continuous energy change for the entire process is monotonic. Other mechanisms of $H_7O_3^+$ formation might involve the reaction $H_3O^+ + (H_2O)_2$ (*via* intermediates III-A6, III-A7, and III-A2) and $H_3O^+ + 2H_2O$ (*via* the intermediate III-A8). In spite of expected monotonic potential energy drops for these pathways also, the latter mechanism would not be kinetically favorable as a one-step process, since it involves the formation of two bonds, and the former mechanism would not be expected to be important in the gas phase, owing to the predominance of monomeric H_2O. The results just quoted for the positive ion, $H_7O_3^+$, are similar to what one would find for the corresponding anion, $H_5O_3^-$.

Let us now turn to the general question of proton jumps between adjacent oxygen atoms in the various species associated with the solvated proton and hydroxyl ion. Our studies of potential energy surfaces for $H_7O_3^+$, $H_9O_4^+$, $H_5O_3^-$, and $H_7O_4^-$ clearly show that the equilibrium geometries of the isolated species correspond roughly to inner or central ionic moieties surrounded by outer water molecules. A proton jump is then equivalent to an effective transfer of the ionic moiety from an inner to an outer position. The current calculations reveal that such a process in the *isolated* species is strongly endothermic. For example, an endothermicity of ~13 kcal is found for the conversion of chain $H_7O_3^+$ (III-A1) to the isomer with a terminal H_3O^+ group (III-A7). The corresponding process in $H_9O_4^+$ (IV-B) is even more endothermic. Similar magnitudes are found for the analogous processes in $H_5O_3^-$ and $H_7O_4^-$. For the anions, of course, the endothermic process involves transfer of a proton from an outer to an inner oxygen atom, with the hydroxide appearing to move in the opposite direction. The endothermicities just referred to are easily understandable to the extent that the bonding arises from charge–dipole interactions, since the electrostatic stabilization is clearly much greater if the ionic moiety is at the center of the complex rather than on the periphery. We conclude that rapid proton jumping is not an intrinsic property of the isolated O_3 and O_4 cations and anions. The endothermicities just described would be somewhat reduced if the proton jumps were accompanied by readjustments of the various interoxygen distances. Further reduction would be expected with the introduction of outer-shell solvation. As a test of this possibility, we have noted the effect of moving a proton from the central oxygen atom to the oxygen atom which is H bonded to the outer-shell H_2O in $H_{11}O_5^+$ (V-B), and find the endothermicity still >10 kcal. The endothermicity just discussed never arose in the treatment of Conway, *et al.*,[42a] since the two oxygen atoms in their model were assumed to be in a symmetric environment.

Let us now examine the bearing of the above results on previous condensed-phase studies of H^+ and OH^-. Various properties of H^+ and OH^- in aqueous solution, such as dielectric constant,[47] heat capacity,[46] and dependence of activity coefficient on concentration,[48] have

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(47) J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

(48) E. Glueckauf, *Trans. Faraday Soc.*, **51**, 1235 (1955).

led[1] to the model of a strongly bound inner solvation shell ($H_9O_4^+$ and $H_7O_4^-$), weakly bound to an outer shell of water molecules by H bonds. As noted above, the structure for $H_7O_4^-$ proposed by Ackermann[46] differs significantly from the branched structure obtained from the present calculations. Eigen and De Maeyer have assumed rapid fluctuations[43] (*i.e.*, transfer between inner and outer oxygen atoms) of the excess proton in aqueous $H_9O_4^+$, suggesting a rate of $\geq 10^{13}$ jumps/sec as being consistent with the difficulty in detecting an H_3O^+ vibrational spectrum in sufficiently dilute aqueous acid. Similar rapid fluctuations of the "defect proton" in $H_7O_4^-$ have been postulated by Ackermann.[46] Since the rate of proton fluctuation just described is much too rapid to serve as the rate-determining step for effective proton mobility in water, Eigen and De Maeyer concluded that the latter process depended on the rate of forming and breaking H bonds between the inner and outer solvation shells.[43]

Our calculations strongly suggest that any rapid proton fluctuations (as defined above) associated with $H_9O_4^+$ or $H_7O_4^-$ require a considerable degree of outer solvation and would not occur to any significant degree in the isolated species; *i.e.*, there must be a sufficient number of outer water molecules, appropriately oriented so as to reduce or eliminate the endothermicity which pertains to proton jumps in the isolated or partially solvated species.[49] Thus, even in the solid phase, we might expect the excess proton to be localized in the central H_3O^+ moiety of $H_9O_4^+$ if the proper electrostatic or H-bonding environment were not present. Indeed, Rudolph and Zimmermann claim to have observed the H_3O^+ vibrational spectrum, albeit strongly perturbed, in solid $HBr \cdot 4H_2O$.[8] They concluded that they were observing $Br^-H_9O_4^+$. Presumably as a result of the absence of an outer hydration sphere, the excess proton was largely localized on the central H_3O^+ moiety. This result is consistent with our claim that rapid proton fluctuation is not an intrinsic property of $H_9O_4^+$, but probably depends in a rather complicated manner on the environment. Subsequent crystallographic work on $HBr \cdot 4H_2O$ has indicated that in reality the situation is somewhat more complicated in that the solid appears to exist as $(H_7O_3)^+(H_9O_4)^+2Br^- \cdot H_2O$.[5c] We are not aware of a revised analysis of the spectrum in view of the structural data. Both $H_7O_3^+$ and $H_9O_4^+$ are expected on the basis of our calculations to have central H_3O^+ moieties, and apparently the spectral study did not distinguish the two types of H_3O^+ present in the solid. At any rate, our calculations for the isolated species, and the spectral properties of solvated H_3O^+ in the solid phase, suggest certain constraints on the model for proton (or hydroxyl ion) solvation in aqueous solution. The correct model must allow sufficient tertiary (outer shell) solvation, if it is to be consistent with rapid proton fluctuations in dilute aqueous solution,[50] while at the same time allowing sufficient disorder and defects in the H-bond network to account for the greatly reduced mobility of protons in water relative to ice.[51]

Thus far we have referred only to single proton jumps. Many concerted processes can also be envisioned. For example, assuming the configuration $H_3O^+ \cdots H_2O \cdots H_2O$ as a model, we infer from the energies of structures III-A7 and III-A3 that a concerted double proton jump would be essentially thermoneutral at all stages. Such a process would also avoid the possibility of trapping the proton at the central oxygen in the stable chain form of $H_7O_3^+$. A similar situation would apply to solvated hydroxyl ions. For instance, the concerted double proton jump just outlined might be employed as a model for hydroxyl mobility, using structures VII-A4 and VII-A3. A barrier of 1–5 kcal would be expected, depending on how much motion of the oxygen atoms was allowed during the proton jumps, and the stable $H_5O_3^-$ configuration (VII-A1) would be avoided.

In our brief examination of the energetics associated with complex formation and proton jumps, we have encountered a variety of situations ranging from strongly exothermic and endothermic processes to essentially thermoneutral transformations. The expected reluctance of a central proton in isolated $H_9O_4^+$ to jump to an outer oxygen atom is in strong contrast to the ease of motion of the bridging proton in $H_5O_2^+$. This and other examples underscore the sensitivity of the various transformations to the degree and nature of ion hydration.

Alternatives to Chain Structures. The discussion so far has dealt with chain structures and their branched isomers; the various structural units in these complexes are held together by linear H bonds of varying degrees of strength and asymmetry. In this section we attempt to round out our understanding of the structural principles involved by considering alternative, energetically less favorable structures. First let us examine some examples of nonlinear H bonds. The energies of the bifurcated $H_5O_2^+$ (II-B1) and $H_3O_2^-$ (VI-B) structures indicate that two strongly bent H bonds are not as favorable as a single linear one. These ring structures are $\sim$15 and $\sim$10 kcal less stable than the chain structures for $H_5O_2^+$ and $H_3O_2^-$, respectively; however, both species are bound with respect to H_2O and the appropriate ion (H_3O^+ or OH^-). In the following discussion, a "bound" species $X^{\pm}(H_2O)_n$ is one whose total energy is lower than the combined total energy of H_2O and $X^{+}(H_2O)_{n-1}$ (in its most stable structure).

Nonlinear H bonds also arise in cyclic structures. For $H_7O_3^+$, $H_9O_4^+$, $H_5O_3^-$, and $H_7O_4^-$ we have considered several types of cyclic structure. The first type is obtained by removing a proton from, or adding a proton to, the corresponding cyclic neutral structure. Since calculations indicate that the cyclic neutral species may be significant in liquid water,[19] it is of interest to investigate the related cations and anions. As the tables indicate, all cyclic ions obtained in this way from the parent neutral cyclic are unbound. While the geometries of these cyclic ions have not been completely optimized, it nevertheless seems unlikely that

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(49) Eigen recognized that there would be some electrostatic differentiation between "inner" and "outer" H_3O^+ groups (footnote 35a, ref 1). Our preliminary results for $H_{11}O_5^+$, quoted above, suggest a rather strong degree of differentiation.

(50) While the inference of rapid proton fluctuations in aqueous solution is a *plausible* explanation of the failure to observe H_3O^+ or OH^- spectra, one must recognize that there could be many other explanations.

(51) Of course, the mechanisms for effective proton mobility are not necessarily the same in water and ice; *e.g.*, see A. von Hippel, *et al.*, *J. Chem. Phys.*, **54**, 145 (1971).

structures of this type will be competitive with the chain structures. The instability of these structures is not primarily the result of bent H bonds. In the case of the cyclic cations, addition of a proton to the cyclic polymer creates an unfavorable four-coordinate oxygen (three short OH bonds and one long one). Formation of the anion by removing an external proton from the neutral cycle creates an OH^- moiety which donates its proton to the neighboring water molecule, also an unfavorable situation. These two features—the four-coordinate hydronium oxygen and the proton-donating OH^-—can be studied in the prototype situations represented by the $H_5O_2^+$ structure II-B2[52] and the $H_3O_2^-$ structure VI-C. Both of these structures are unbound, and their energies drop monotonically with increasing interoxygen distance. Another example of an unbound species with a bridging hydroxyl proton is provided by structure VII-A6. More favorable cyclic structures were found, whose energies after partial geometry optimization are within 16, 11, 11, and 2 kcal of the energies for the most stable $H_7O_3^+$, $H_9O_4^+$, $H_5O_3^-$, and $H_7O_4^-$ species, respectively. These cyclic structures are illustrated in Figures 7, 10, 13, and 16. In the cyclic cations, the H_3O^+ moiety serves as a double proton donor, while one H_2O unit serves as a double proton acceptor. The corresponding anions are characterized by a double-proton-acceptor hydroxyl moiety and a double-proton-donor H_2O molecule. All four of these cyclic ions can be viewed as distorted linear-chain structures whose terminal HOH groups are twisted in such a way as to allow the formation of an additional bent H bond. The fact that the O_4 rings are more strongly bound than the O_3 rings for the most part probably reflects the effect of greater nonlinearity in the H bonds of the latter systems. We also note that the cyclic anions are more strongly bound than the corresponding cations, presumably because the latter species contain four-coordinate oxygen atoms, which are less favorable than the two- and three-coordinate oxygens found in the cyclic anions. The four-coordinate oxygen atom associated with the double-proton-acceptor water molecules must, of course, be distinguished from the much less favorable four-coordinate hydronium oxygen atom referred to above. The cyclic $H_7O_4^-$ structure VIII-C2 is essentially as stable as the optimal structure VIII-B1 and, with more extensive optimization of geometrical parameters, it could very well become the favored structure. An important feature of the O_4 cyclic ions is that the ionic moiety still has a site available for complexing with an additional water molecule. Thus, whereas the O_4 ring cation IV-C2 is 0.0182 au less stable than the Eigen structure, the $H_{11}O_5^+$ obtained by adding an H_2O molecule to IV-C2 is only 0.0061 au less stable than the species obtained by adding H_2O to one of the peripheral H_2O groups in IV-B1. In the case of the anions, however, the ring structure is already essentially as favorable as the acyclic structures at the O_4 level, and the $H_9O_5^-$ structure IX-B, which results from adding another H_2O to the cyclic structure VIII-C2, is 0.0076 au *more stable* than the branched chain $H_9O_5^-$ isomer IX-A. This predicted difference in preference for cyclic and acyclic structures constitutes the principal departure from the otherwise close parallel between the calculated structural properties of isoelectronic cations and anions.

As a final comment on the ring structures, it is worth pointing out that although the ionic ring structures obtained from the neutral cyclic polymers by proton abstraction or addition are energetically unfavorable, they may nevertheless be important intermediates in the formation of the stable ring structures from the neutral polymers; *i.e.*, the unfavorable ring structures can be converted into the favorable, bound structures by appropriate rotation of the monomeric units or by proton jumps within the hydrogen bridges.

At this point it is useful to summarize our structural results in terms of the various degrees of coordination about the oxygen and hydrogen atoms. The oxygen atoms in the linear-chain structures are all either two- or three-coordinate. In view of the stability of the branched $H_7O_4^-$ structure VIII-B, we conclude that the hydroxyl oxygen can easily accommodate as many as three long-range ligands. Another type of four-coordinate oxygen atom is found in the double-proton-acceptor water molecules of bifurcated $H_5O_2^+$ (II-B1) and the cyclic cation structures III-B2 and IV-C2. We have seen that the four-coordination arising from donation of a proton to an H_3O^+ lone pair is energetically quite unfavorable. Hence, the four-coordinate oxygen atom becomes an increasingly less favorable complexing unit as the number of short-range ligands increases from one to three. We have examined one case of a three-coordinate bridging proton—the central proton $H_7O_3^+$ structure III-C. Although an energy minimum was found for the symmetric stretching of the three central OH bonds, the structure is unbound with respect to $H_5O_2^+$ and H_2O, and we considered no further examples of three-coordinate hydrogen.

An interesting energetic relationship is found among three of the chain $H_5O_3^-$ structures—the optimal chain VII-A1, the terminal OH^- variant VII-A4, and the central double-donor H_2O isomer VII-A5—and the ring structure VII-B2. The terminal OH^- structure VII-A4 is bound, while structure VII-A5, also a terminal OH^- species, is unbound. Modest distortions of the latter structure convert it into the much more favorable cyclic structure VII-B2. The reason for the sharp increase in stability which attends the ring closure may be understood as follows. The open structure VI-A5 is most likely unstable because the central H_2O has acquired a partial negative charge (~ -0.14) from the terminal OH^-, and thus is not a suitable proton donor to the oxygen of the other terminal group (H_2O). Distortion of VII-A5 to form the ring VII-B2, however, allows the terminal H_2O to interact directly with the OH^- as a proton donor, while the original interaction with the central H_2O changes from mildly antibonding to mildly bonding (as inferred from overlap populations).

Models for the $H_5O_2^+$ Bonding Energy. We have attempted to further our understanding of the bonding involved in the present set of ionic complexes by studying various simplified models. We shall consider only

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[52] The unbound nature of the four-coordinate-oxygen $H_5O_2^+$ structure II-B2 is perhaps of some relevance to the reaction $(EtOH)_2H^+ \rightarrow (Et_2OH)^+ \cdot HOH$, reported by K. M. Bansal and G. R. Freeman, *J. Amer. Chem. Soc.*, **92**, 4173 (1970). These authors felt that the initial product of this reaction would be expected to have a structure similar to II-B2. Expecting such a structure to be energetically unfavorable, they then suggested that the reaction might better be described as $(EtOH)_2H^- \rightarrow Et_2OH^+ + H_2O$. This suggestion is consistent with our failure to observe a bound state of II-B2 with respect to H_2O and H_3O^+.

$H_5O_2^+$, although our conclusions should be relevant to the higher hydrates as well. The optimal chain structure for $H_5O_2^+$ (II-A1) suggests that a fair portion of the $H_5O_2^+$ stabilization might arise from electrostatic charge–dipole interaction. The binding relative to H_2O and H_3O^+ can be viewed (model I) as the interaction between the H_2O dipole and the H_3O^+ positive charge. An alternative viewpoint (model II), appropriate for the process $H_5O_2^+ \rightarrow 2H_2O + H^+$, would involve two H_2O dipoles interacting with the central point charge of the proton. The interaction energy for either model could be accurately evaluated by constructing an antisymmetrized product of all the occupied molecular orbitals of the various component monomers, placed in the appropriate relative positions, and evaluating the energy without allowing polarization or charge transfer. For the present discussion we simply quote the results of crude estimates, based on point charges and point dipole moments, with origins taken at the appropriate oxygen atoms. For model I, we obtain a stabilization energy of 1.35 eV using the calculated H_2O dipole moment, approximately 70% of the total calculated stabilization energy (without zero-point corrections). Use of the experimental H_2O dipole accounts for a similar percentage of the experimentally observed stabilization energy. We conclude that a substantial portion of the stabilization energy can be understood in terms of the simple electrostatic model. Nevertheless, there still remains a significant portion which must be accounted for by a combination of polarization of the monomers, charge transfer between the monomers, and covalent bonding involving the bridge proton. Overlap populations have suggested that the covalent bonding is an important factor. To give more insight into the relative importance of these various contributions, we can consider two additional models. A refinement of Model II which allows polarization of the H_2O molecules but no charge transfer or covalent H bonding is provided by structure II-A5, in which the central hydrogen is constrained to be a bare proton. The structure is unbound with respect to H_2O and H_3O^+ by a few kilocalories, although it accounts for ~80% of the stabilization with respect to $2H_2O + H^+$. Structure II-B3 offers a refinement of model I in which the two monomers are still favorably oriented with respect to charge–dipole interaction, but there is no internal proton. Both monomer polarization and charge transfer are possible in this structure, which nevertheless possesses only ~40% of the stabilization energy calculated for the optimal H-bonded structure (II-A1).

Although the discussion just given for $H_5O_2^+$ is undoubtedly relevant to the larger cations in the series, it is presumably of less relevance to the anions, since the H_2O units in the latter species are not oriented favorably for charge–dipole interactions. If charge–dipole interactions were very important for the anion, one might expect structures like bifurcated $H_3O_2^-$ (VI-B) to be more competitive with the chain structures.

VI. Conclusions

The extended valence shell basis set calculations reported in this study have led to the following general results and conclusions. Solvation enthalpies based on energy-optimized structures are within a few kilocalories of experimental values, and the experimentally observed similarity in solvation energies for isoelectronic cations and anions is reproduced. The calculated solvation energies associated with the outer solvation shell, though smaller than inner-shell energies, are still appreciably larger than association energies for neutral water. Chain structures, with branching when possible, are generally favored over cyclic structures, although the latter structures become increasingly competitive in the higher hydrates. A cyclic structure is found to be the most stable $H_9O_5^-$ species. The interoxygen distances of the chain species increase significantly and regularly with increasing degree of hydration, paralleling the regular decrease noted in hydrogen-bond energies, with the distances for the anions somewhat larger than those for the corresponding cations. Our calculations are in basic agreement with Eigen's model[1] for $H_9O_4^+$, and have led us to propose an analogous structure for the inner shell of the hydrated hydroxyl ion, $H_7O_4^-$. Most of the bridging protons in the chain structures are found to prefer asymmetric equilibrium positions, and are associated with potentials characterized by a single, asymmetrically located minimum, rather than a double-well type. The potential for motion of the central protons in the linear O_2 and O_4 chains is extremely flat for a range of ~0.2–0.3 Å. Thus the model of a double-well potential does not appear to be appropriate for any of the bridging protons in the isolated chain species considered in this study.

Analysis of equilibrium geometries, force constants, gross atomic and group charges, and overlap populations of the optimal structures, and consideration of the energies of alternative structures, leads to a picture of complexes composed of recognizable units (H_2O and various ionic moieties) which are held together by a combination of ionic, charge–dipole and covalent interactions. For mainly electrostatic reasons, the ionic moieties strongly prefer central or internal locations in the complexes. This result implies that rapid fluctuations of protons between central and outer oxygen atoms of the inner solvation shell would be facile only in the presence of a significant degree of outer-shell solvation.

The calculations reveal distinct preferences of the various monomers for different types of coordination. The most favorable structures involve water in a two- or three-coordinate environment. The four-coordinate, double-proton-acceptor water molecule is found in the less favorable bifurcated and cyclic cations, while the four-coordinate proton-acceptor H_3O^+ is associated with unbound structures. The hydroxyl ion will accept anywhere from one to three bridging protons, while attempts to involve the hydroxyl proton in bridging lead to unbound structures in all cases considered.

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