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The nature of the hydrated proton

Part Two: Theoretical studies; the liquid state

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In Part One [1] the *raison d'être* for this review was given as follows: 'To what extent can one "see" that most important of all the cations – the hydrated proton?' In Part One our search for an answer encompassed a review of studies of the proton, in association with H_2O, in the solid state and the gaseous state by a variety of techniques: X-ray and neutron scattering, vibrational spectroscopy, NMR studies, proton conduction and mass spectrometry. This search is continued here. We shall deal with a review of theoretical studies and with the more difficult liquid state. The literature relating to Part One has also been brought up to date.

1.1 Theoretical studies

The major part of this section will be concerned with molecular orbital (MO) calculations, though other kinds of model calculations will be described where appropriate. There is now a large body of literature concerned with semi-empirical and *ab initio* MO calculations applied to numerous and diverse aspects of the hydrated proton:

(1) Molecular energies of the ground and excited states.
(2) Molecular geometry.
(3) Charge distribution.
(4) Inversion barriers.
(5) Proton affinities.
(6) Force constants, vibrational frequencies and IR intensities.
(7) NMR chemical shift tensors and isotropic shifts, and quadrupole coupling constants of ^{17}O and ^2H.
(8) Heats of reaction with other small molecules and equilibrium constants.
(9) Proton transfer and the shape of the potential of the central strong hydrogen bond of $H_5O_2^+$.
(10) Relative stabilities of the higher hydrates in different configurations.

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We will not go into a lengthy discussion of the accuracy and merits of the different methods of calculation, but rather attempt to relate the contribution of these results to our understanding of the hydrated proton. The majority of the calculations apply most directly to the gas phase, since they concern isolated H_3O^+, $H_5O_2^+$ or higher hydrated clusters, though the results can to a certain extent be extrapolated to the liquid phase. In a few cases, which were mentioned in Part One [2–4] and will not be discussed further here, calculations have been applied to specific crystal environments.

1.1.1 H_3O^+

The list of calculations on the oxonium ion is lengthy [5–93, 166–9], and, no doubt, not exhaustive. The interested reader may find useful the bibliographies of *ab initio* calculations by Richards, Scott, Sackwild & Robins [91] and Ohno & Morokuma [92, 93]. Hund, in 1925, was really the first to attempt theoretical calculations on H_3O^+. [5, 6] Using a semi-empirical method, in which the system was treated as interacting O^{2-} and $3H^+$, he calculated the proton affinity of H_2O to be $-753 \pm 167\,kJ\,mol^{-1}$. *Ab initio* MO studies did not begin until 1961 with the work of Grahn [8], but there were also a few other semi-empirical quantum mechanical calculations prior to and around this time. [7, 9, 11] In those early years the calculations centred mainly on obtaining the equilibrium configuration of atoms which gave an energy minimum, and the proton affinity of H_2O. Interest in these parameters has continued up to the present, through numerous approaches and refinements, as indicated in table 1.1. The early calculations nearly always arrived at a planar minimum energy configuration for H_3O^+, which confounded experimental evidence from solids for a pyramidal form. It was found in 1973 that the inclusion of polarisation functions reduced the minimum energy and gave pyramidal equilibrium configurations [21, 22]; i.e. studies which included only s and p functions on oxygen and s on hydrogen all gave planar H_3O^+, whereas introduction of p polarisation functions on hydrogen gave slightly non-planar structures, and introduction of d functions on oxygen proved to be even more important in stabilising the C_{3v} form relative to the planar D_{3h} form. Further improvements in energy minimisation were then realised with the inclusion of configuration interaction (CI) to take account of electron correlation effects.

As can be seen from table 1.1 the geometrical parameters determined in more recent years (since 1980) nearly all fall within small ranges of values: $O–H = 96.2–98.0\,pm$, $\angle\,HOH = 111.6–114.4°$ (see figure 1.1). The lowest minimum energies were obtained by Lischka & Dyczmons [22], Rodwell & Radom [44], and followed most recently by Botschwina [90], whose optimised equilibrium geometry was $O–H = 97.45\,pm$ and $\angle\,HOH = 111.9°$. The bond length is significantly shorter than is found for H_3O^+ in solids (average values from neutron diffraction studies in Table 3 of Part One are
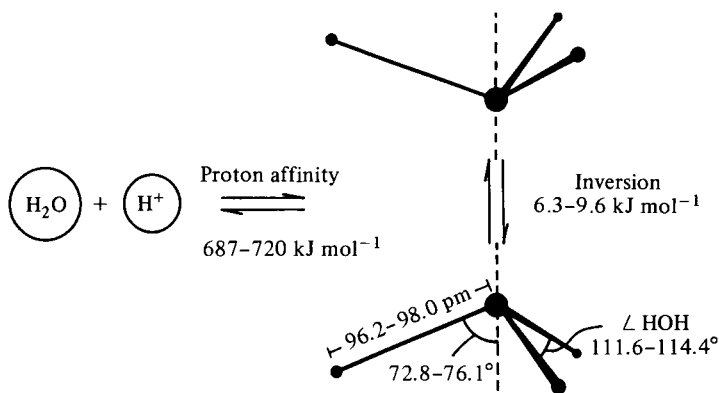
Fig. 1.1. The structure of H_3O^+, inversion barrier and proton affinity of water from *ab initio* calculations. The ranges of values given are from the more accurate calculations. (The range of inversion barriers are from the five lowest total energy calculations.)

$O-H = 101.7$ pm and $\angle HOH = 111.8°$) as might be expected in the absence of hydrogen bonding. Unfortunately there are only a few values of the geometrical parameters available from gas phase experiments, and these are derived from fits of the vibration–rotation spectra and are thus dependent on the details of the model inversion potential. These experimental values fall in the range $O-H = 97.6$–98.6 pm, $\angle HOH = 110.7$–$115.3°$. [94–7] The *ab initio* values are, therefore, in quite good agreement.

Once a pyramidal equilibrium geometry had been established, it was possible to calculate the inversion barrier from the difference in energy between the C_{3v} pyramid and the D_{3h} planar transitional configuration. Since this is a very small difference between two very large energies, one might expect appreciable differences in the values obtained using different basis sets. In fact an inversion barrier of 10 kJ mol^{-1} is of the order of 0.005 % of the total electronic energy of H_3O^+. Over the years the calculated values have fallen in the range 2.6–14.6 kJ mol^{-1} (table 1.1). Rodwell & Radom's [44] value was 9.6 kJ mol^{-1}, and Botschwina's [90] value was 8.13 kJ mol^{-1}. Again, experimental results are few; two values have been obtained from gas phase IR, namely 10.82 and 8.04 kJ mol^{-1}. [94, 95]

The proton affinity (PA) or ΔH for the reaction $H_2O + H^+ \rightarrow H_3O^+$ was, in the early estimates, taken as the difference (ΔE) in the total energies of H_2O and H_3O^+. The minimised energies are for the rigid ground states and hence really apply to zero degrees Kelvin. Before any meaningful comparison can be made with experimental values the calculated values should be corrected for zero point energy (ZPE) and thermal differences [e.g. 50, 57]:

$$PA = \Delta E - \Delta ZPE + \tfrac{5}{2}RT$$

Values which have had a correction applied are indicated in table 1.1 by the letter C preceding the value. The most recent experimental values of the PA of

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Table 1.1. *Selected results of molecular orbital calculations on* H_3O^+ *by year*

Method	Total energy (au)^a	O–H^b (pm)	∠HOH^b (deg)	Inversion barrier (kJ mol^{-1})	Proton affinity^c ($-$kJ ,ol^{-1})	Year	Ref.
STO (SE)	−76.182	94.7	(104.5)			1959	7
SCF LCAO	−75.412	95.81	120		1104	1961	8
United atom (SE)	−76.174	90.5	120		782	1962	9
Valence bond		95.8	120		1054	1962	11
SCF LCAO OCE CI	−76.0184	95.0	114.4			1965	13
SCF LCAO Gaussian	−76.3213	95.3	120		753	1965	12
SCF OCE	−76.2330	96.3	110.9			1967	14
SCF LCAO large Gaussian set	−76.3066				C728	1968	15
CNDO/2 (SE)		105.0	111			1970	17
SCF GTO DZ	−76.2006	95.8	120		C745	1970	16
SCF 4-31G	−75.33044	96.4	120		C740	1971	18
SCF STO-3G	−76.20060	99.0	113.9	4.2		1971	19
SCF 4-31G		96.4				1971	19
Near HF SCF	−76.3386	97.9	113.5	3.93	739	1973	23
+IEPA-PNO	−76.6015				728	1973	23
SCF (several bases)	−76.34042	96.5	113.5	2.6–6.3		1973	22
+IEPA-PNO	−76.60166	98.3	111.6	14.2–14.6		1973	22
SCF LCAO	−76.3326	96.3	112.5	7.9	C701	1973	21
SCF STO-DZ	−76.30141	97.0	120		776	1973	24
SCF	−76.32436	(96.3)	114.3			1974	25
6-31G*	−76.28656	96.9	113.2			1974	28
SCF LCAO	−76.329776	95.9	113.5	5.4	C707	1975	30
+CI	−76.541803	97.2	111.6	8.6	C701	1975	30
SCF PNO-CI	−76.54453	(97.9)	(111.4)	3.3		1975	31
CEPA-PNO	−76.55526			6.3		1975	31
SCF LCAO large Gaussian set	−76.3233	96.3	114.2	6.3		1977	33
SCF CI	−76.33822	96.4	113	5.0		1977	34
MBRSPT+CP					C712	1978	37
SCF DZ+P	−76.329995				C687	1978	38
CI	−76.579539	97.8	111.8	6.3		1980	40

Method/basis	Energy (au)				Ref.	Year	
SCF large basis	−76.58579	97.3	111.6	9.6		1981	44
Near HF/MP3					736–57	1981	42
SCF various basis sets						1981	42
6-311G**/MP4	−76.58079					1982	50
STO-6G, 4-31G*		98.9	113.9		C733	1982	49
6-31G**, MP4					C720	1983	57
STO-3G, DZ + D	−76.31231	96.7	113.2		C695	1983	56
HF MP4/SDTQ	−76.57585				C689	1983	53
SCF CI	−76.32970	97.8	111.6	8.5		1983	65
SCF DZ + P	−76.33808	96.3	114.4	4.5		1983	65
SCF extended	−76.28934	96.2	114.1			1983	59
6-31G*		96.9	113.1		C711	1983	55
SCEP-CEPA		98.0	111.6	9.4		1984	68
SCF CI	−76.563579	97.5	111.8	9.2		1986	90
SCF-CEPA-1	−76.621730	97.45	111.9	8.13	C687		

[a] $1\ \mathrm{au} = 2625.15\ \mathrm{kJ\ mol^{-1}}$.
[b] Values in brackets were held fixed.
[c] Proton affinity for H_2O (i.e. $H_2O + H^+ \rightarrow H_3O^+$), values corrected for ZPE and thermal effects are preceded by C.

Key to table 1.1

CEPA   Coupled electron pair approximation
CI   Configuration interaction
CNDO   Complete neglect of differential overlap
CP   Counter-poise correction
DZ   Double-zeta
GTO   Gaussian type orbitals
HF   Hartree–Fock
IEPA   Independent electron pair approximation
LCAO   Linear combination of atomic orbitals
MBRSPT Many-body Rayleigh–Schrödinger perturbation theory

MP3   Möller–Plesset perturbation theory to third order
OCE   One-centre expansion
P   Polarisation
PNO   Pair-natural orbitals
SCEP   Self-consistent electron pairs
SCF   Self-consistent field
SDTQ   Single, double, triple and quadruple excitation
SE   Semi-empirical
STO   Slater type orbitals

For explanations of the notations for such basis sets as 6-31G** the reader is referred either to the reference given or to two modern texts on *ab initio* calculations. [366, 367]

H_2O (since 1980) all fall in the small range -691 to -697 kJ mol^{-1} [98–101], though going back to 1977 one can find values ranging up to -713 kJ mol^{-1}. [102] The values obtained from reasonably accurate *ab initio* calculations agree quite well, falling in the range -687 to -720 kJ mol^{-1}. Values are portrayed on figure 1.1.

It is appropriate at this point to mention the polarisation model developed by Stillinger & David [36], which treats O^{2-} and H^+ particles as the structural and dynamic elements. The results of calculations for H_3O^+ were surprisingly good (cf. *ab initio* results in table 1.1). They found a C_{3v} pyramidal structure with O–H $= 104.1$ pm and $\angle$ HOH $= 107.9°$, a PA of H_2O of -692 kJ mol^{-1}, and an inversion barrier of 16.6 kJ mol^{-1}.

The MO calculations can also be used to give an idea of the charge distribution in H_3O^+. The most recent evaluation of this [58] found $q_H = +0.518$ au and $q_O = -0.555$ au for a calculation using a 6-31G** basis.

There have been numerous reports of calculated vibrational force constants or frequencies. [12, 13, 25, 30, 32, 38, 47, 53, 55–7, 65, 68, 86] The most recent of these have been summarised in [86]. In general, because of inadequacies in the theory and neglect of anharmonicity, the calculated harmonic frequencies are too high. However, scaling factors have been proposed for particular basis sets, based on comparison of experimental versus theoretical results for many molecular species. DeFrees & McLean [86] give harmonic frequencies (MP2/6-31G* calculations) $v_1 = 3519$, $v_2 = 963$, $v_3 = 3632$ and $v_4 = 1731$ cm^{-1} respectively, which when uniformly scaled (by 0.96) give $v_1 = 3378$, $v_2 = 924$, $v_3 = 3487$ and $v_4 = 1662$ cm^{-1} as the predicted frequencies. Some authors have also attempted to predict the doubled mode frequencies caused by inversion; their results for the inversion mode v_2 are in reasonable agreement with experiment for the $v_2(1- \leftarrow 0+)$ transition (observed $= 954.4$ cm^{-1}, calculated $= 992$, 961 and 985 cm^{-1} [53, 55, 68]). Since there is not, as yet, a complete set of experimental frequencies for H_3O^+ in the gas phase, a full comparison cannot be made, though the calculated results are obviously quite reasonable (see gas phase section, Part One). They also compare reasonably well with the solid phase frequencies for H_3OSbCl_6 (see solids section, Part One), with the exception of the v_2 mode, which might be expected to be most affected by external interactions. Colvin, Raine, Schaefer & Dupuis [65] also calculated the IR intensities for the vibrational modes of H_3O^+, H_2DO^+, HD_2O^+ and D_3O^+. They predicted intensities for H_3O^+ roughly in the ratios 1:13.9:13.5:3.2 for v_1, v_2, v_3, and v_4 respectively (i.e. $v_3 > v_1$ and $v_2 > v_4$). In connection with Raman vibrational mode intensities Lopez Bote & Montero [79] have calculated the Raman tensor of H_3O^+ based on bond polarisability parameters.

A few papers have dealt with calculations of NMR or NQR properties of H_3O^+. [10, 27, 52, 63, 84, 85, 87] The majority [10, 52, 63, 84, 87] concerned the ^1H chemical shielding tensor and isotropic chemical shift; σ_{iso} values range from 19.8 to 26.0 ppm. In general these reproduce the ^1H shifts relative to

H_2O moderately well; the observed values fall 2–3 ppm further downfield, but this may be due in part to medium effects (i.e. the experimental shifts are for solids and liquids whereas the calculations are for isolated ions). The calculated ^{17}O shifts [52, 63, 87] fall in the range $\sigma = 294$–330 ppm. The observed line falls 21.6 ppm downfield from molecular H_2O (and 9 ppm downfield from bulk water). [103] This is contrary to the predictions of Galasso [63] (57 ppm upfield from H_2O) and Fukui, Miura & Tada [52] (34.6 ppm upfield). Fukui, Miura, Yamazaki & Nosaka [87] later predicted a value 27.6 ppm downfield from H_2O, in much better agreement. Galasso [63] has also calculated spin–spin coupling constants; $1J(O–H) = -161$ Hz (observed = 106 Hz) and $2J(H–H) = -9.7$ Hz and more recently Fronzoni & Galasso [85] studied the effects of electron correlation on J couplings.

Dixon, Overill & Claxton [27] have studied the effects of varying bond length and angle on the calculated ^2H and ^{17}O quadrupole coupling constants (QCC) of D_3O^+. The ^2H QCC is quite sensitive to bond length (QCC decreases, and η, the asymmetry parameter, increases as O–H distance increases) but is almost independent of bond angle; the QCC, which is 288 kHz for the optimum geometry ($\eta = 0.128$), is reduced by only 2 kHz from $\angle$ HOH = 100° to 120° (η increases significantly). For ^{17}O the QCC is relatively insensitive to bond length and more sensitive to angle ($\eta = 0$ because of the C_{3v} symmetry). At the optimum geometry QCC = -10 MHz, whereas experiment gives QCC = $+7.513$ MHz, which is opposite in sign to that calculated, with $\eta = 0.104$ (values for $H_3O^+HSO_4^-$ where H_3O^+ is not C_{3v} [45]).

Apart from the calculations for the protonation of H_2O a number of *ab initio* calculations have dealt with protonation reactions of H_3O^+ with other simple molecules or ions including NH_3, NH_2, OH^-, HF, HCl, PH_3, H_2S, C_2H_2, C_2H_4, N_2, O_2, CO, HCN, N_2H_2, HCOOH, CH_4^{2+}, H^+ [29, 35, 38, 39, 41, 46, 51, 59, 60, 64, 66, 67, 69, 71, 73, 80–3, 89, 167–9], with the general aim of determining energies or heats of reaction, and in some cases the equilibrium constant. (Again, as with PA, one must take account of ZPE and thermal parameters before reasonable comparison with experiment can be made.) The equilibria usually favour the stability of the reaction products over H_3O^+ and reactant: e.g.

$$NH_3 + H_3O^+ \rightleftarrows H_2O + NH_4^+ \qquad \Delta E = -171.3 \text{ kJ mol}^{-1} \qquad [38]$$

$$H_3O^+ + OH^- \rightleftarrows 2H_2O \qquad \Delta E = -1023.7 \text{ kJ mol}^{-1} \qquad [35]$$

$$(H_2O)_2^+ \rightleftarrows H_3O^+ + OH \qquad \Delta E = +93.6 \text{ kJ mol}^{-1} \qquad [64]$$

However, one should note that these reactions apply to isolated reactant and product species. The calculations on $(H_2O)_2^+$ also show that although the dimer cation is more stable than dissociated H_3O^+/OH its minimum energy structure is actually $H_3O^+ \cdot OH$. [64, 67] On the other hand $H_2O + HX$ (X = F, Cl) is slightly less stable than the associated hydrogen-bonded species

$H_2O \cdot HX$, which is much more stable than the separated ions H_3O^+/X^-. [39] *Ab initio* calculations on the interesting H_4O^{2+} ion (i.e. protonated H_3O^+ [89]) show that the tetrahedral form of this species is at an energy minimum, although it is $248 \, kJ \, mol^{-1}$ less stable than separate H_3O^+ and H^+, but the barrier to dissociation is considerable; $184 \, kJ \, mol^{-1}$. The reaction of $H_3O^+ + H_2O$ will be considered in the next section.

Attention has also been paid to the processes involving H_3O^+ occurring at electrodes [61, 62 and references therein, 77, 78], though we will only briefly mention this here. Knowles [61] used a quantum mechanical model to study the charge transfer reaction

$$M^- + H_3O^+(aq) \rightarrow MH + H_2O$$
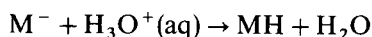
which occurs in the electrochemical generation of H_2 from acid solution, and compared the activation energy for this process with that for

$$MH^- + H_3O^+(aq) \rightarrow MH_2 + H_2O$$
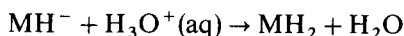
as a function of the M–H coupling. (MH represents H chemisorbed on the metal electrode.) The model accounted for M–H and H–H interactions and solvation effects. Pataki *et al.* [77] used *ab initio* calculations to study 12 possible reaction mechanisms which might explain the simplified process $H_2 \rightarrow 2H^+ + 2e^-$ at the anode of the hydrogen/oxygen acidic fuel cell. They concluded that the following reaction steps provided the most likely mechanism, though several other schemes were not excluded:

$$H_2 + 2H_2O + 2H_3O^+ \rightarrow 2H + 2H_2O + 2H_3O^+ \rightarrow H + H_2O + H_3O + 2H_3O^+$$
$$\rightarrow H + H_2O + 3H_3O^+ + e^- \rightarrow H_3O + 3H_3O^+ + e^-$$
$$\rightarrow 4H_3O^+ + 2e^-$$
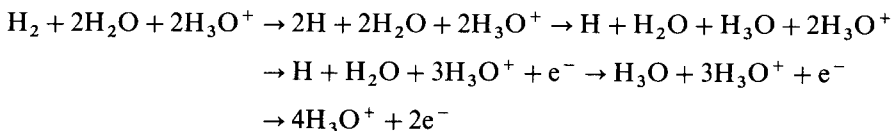
They also investigated some reaction schemes involving H_3O^+ in the hydrogen/oxygen alkaline fuel cell. [78]

1.1.2 $H_5O_2^+$

There have been a number of semi-empirical MO calculations on $H_5O_2^+$, [17, 26, 104–6], but since this type of calculation is notoriously poor in modelling hydrogen bonds we will concentrate on the more rigorous *ab initio* MO calculations. [16, 18, 24, 26, 41, 59, 80, 83, 84, 106–27] *Ab initio* studies have been particularly useful in looking at $H_5O_2^+$, beginning in 1970 with the work of Kollman & Allen [16] and Kraemer & Diercksen [107], since they help in understanding properties which arise because of the presence of the strong central hydrogen bond.

Relative to H_3O^+ it is much more costly and time consuming to do a complete geometry search for an energy minimum of $H_5O_2^+$, because of the increased number of atoms and internal degrees of freedom. Many of the earlier calculations optimised the geometries within certain symmetry

constraints. Symmetries were favoured where each oxygen atom had a planar configuration of three hydrogen atoms [e.g. 16, 24, 107, 109, 112, 115, 120]. However, more recent calculations have shown that for some properties, such as the hydration energy and the central hydrogen-bonded proton potential, this is not a serious drawback. Newton & Ehrenson [18] also investigated several unconventional structures for $H_5O_2^+$ using the 4-31G basis set: (*a*) a bifurcated ring structure in which an H_2O accepts two hydrogen bonds from an H_3O^+; (*b*) a structure in which an H_2O donates a proton to hydrogen bond with the lone pair of H_3O^+; (*c*) a charge dipole structure in which the oxygen of H_2O sits below the base of the H_3O^+ pyramid. However, these were all found to be substantially higher in energy than the normal central hydrogen-bonded structure, by 65, 222 and 106 kJ mol^{-1} respectively. (Note that the H_2O proton donor (case (*b*)) is even less stable than separate $H_3O^+ + H_2O$.)

Only in recent years have structures been calculated which have optimised to non-planar coordination of the oxygens, i.e. more in keeping with most of the unambiguous solid structures (see Part One). Note here particularly [83, 118, 119, 122, 126] which are the most accurate to date. Yamabe, Minato & Hirao [118] obtained an asymmetric system in which the central hydrogen bond has $O \cdots O = 240.92$ pm, $O–H' = 106.7$ pm and $\angle OH'O = 177.0°$ where H' is the proton involved in the central strong hydrogen bond of $H_5O_2^+$. (Note that on the basis of our earlier criteria (Part One) these distances would make this an $H_3O^+H_2O$ system rather than $H_5O_2^+$. We would remark, however, that it seems odd that this is the only calculation which has minimised to such an asymmetric but short hydrogen bond. Nor does this geometry fit the well known O–H vs. $O \cdots O$ correlation [128–30] from which an O–H distance of 106.7 pm would correspond to $O \cdots O = 250$ pm.) Potier, Leclercq & Allavena [119] did a very careful study of the effects of variations in the angular conformations. Their lowest energy structure (see figure 1.2) has $O \cdots O = 238.7$ pm with the protons placed slightly off the centre of the $O \cdots O$ line ($\angle OH'O = 178.4°$). The terminal H_2O groups have $\angle HOH = 110.5°$ and the bisector of this angle is at 30° to the $O \cdots O$ direction. However, the energy needed to make the coordinations of the oxygens planar is only 5 kJ mol^{-1}. Rotation of the two end H_2O groups (dihedral angle ϕ) with respect to each other shows that the least favourable conformation is *cis* ($\phi = 0°$) which is about 5.3 kJ mol^{-1} above the lowest energy conformation which is *gauche* ($\phi = 105°$). However, the *gauche* form is only about 2.5 kJ mol^{-1} more stable than the *trans* form ($\phi = 180°$). A recent study [122] reported on a geometry search carried out using a gradient optimisation technique with the 6-31G(d) and 6-31+G(d) basis sets. The optimised structures were then used in calculations which included fully polarised basis sets, 6-31G(d, p) and 6-31+G(d, p), and electron correlation. All the minimum energy structures calculated (with different symmetry constraints) gave non-planar coordination of the oxygen atoms. The lowest energy was obtained using 6-31+G(d, p)/MP4SDQ for a C_2 structure with a
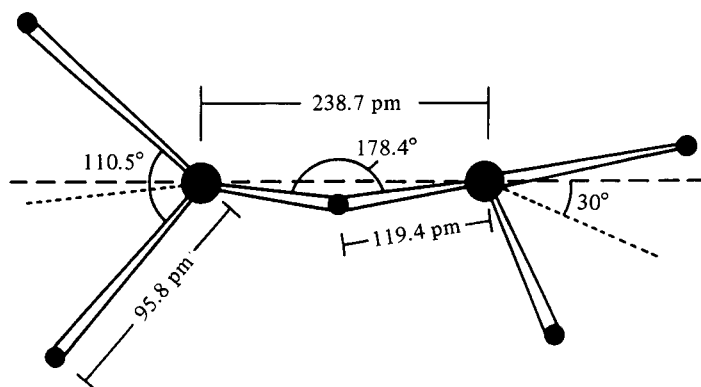
Fig. 1.2. The structure of $H_5O_2^+$ from the lowest energy conformation calculated by Potier *et al.* [119] The structure is C_2, and *gauche* (viewed down the $O \cdots O$ axis the bisectors of the two terminal H_2O units are rotated 105° with respect to each other). The pyramidal geometry around the oxygen atoms is indicated by the 30° angle between the $O \cdots O$ axis and the bisector of the H_2O group.

symmetrical $O \cdot \cdot H' \cdot \cdot O = 238.2$ pm and $\angle OH'O = 177.5°$. What is perhaps of more interest, however, is the remarkably small energy difference of 4.2 kJ mol^{-1} between this and a C_s structure with $O-H' \cdot \cdot O = 248.2$ pm and $O-H' = 103.9$ pm calculated at the same level of theory. (At lower levels of theory without correlation this C_s structure is actually more stable by 0.9 kJ mol^{-1}.)

In the most recent study [126] the calculations have been taken to yet another level of theory to obtain an even lower energy. Unfortunately few geometrical parameters were given in this last paper, but it is included in table 1.2 to indicate that the search for the minimum is not yet over. Once again we may consider for comparison the results of Stillinger & David's non-*ab initio* polarisation model. [36] As might be expected, this does not appear to model the strong hydrogen bond very well (symmetrical $O \cdot \cdot H' \cdot \cdot O = 256.5$ pm), though it does produce pyramidal coordination for the oxygens and a hydration energy for H_3O^+ of -151 kJ mol^{-1}. Their minimised structure has C_{2h} symmetry.

What clearly emerges from all these calculations is that the potential energy surface around the minimum energy configuration must be rather flat; many different configurations appear to have only very small energy differences. This helps to explain the great variety of conformations observed for $H_5O_2^+$ ions in different solids; the configuration must readily adjust to the requirements of the lattice, since the external barriers formed by hydrogen bonding to anions in a lattice are likely to be much larger than the small internal conformational barriers. Most of the calculations obtain lowest energy $O \cdots O$ distances of about 239 ppm, which is a little less than the range of 241–244 pm observed in crystals (from neutron diffraction, see Part One).