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# MO-Calculations on the Stability of the $H_3O$-Radical in Water

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MO calculations by the INDO method are performed for the $H_3O$ free radical and some of its water complexes. Calculations on the corresponding $H_3O^+$ ion complexes are included for comparison.

It is found that the $H_3O$ radical is stable against bond dissociation to $H_2O$ and H, but unlike the ion it is destabilized by the surrounding water complexes.

Recent work on $\gamma$-radiolysis of water [1] indicates that the reaction of hydrated electrons with hydronium ions does not yield H-atoms as has earlier been assumed to be formed according to:

$$e^-_{aq} + H_3O^+_{aq} \longrightarrow H + H_2O \qquad (1a)$$

Instead the formation of $H_3O_{aq}$ radicals was postulated:

$$e^-_{aq} + H_3O^+_{aq} \longrightarrow H_3O\cdot_{aq} \qquad (1b)$$

The stability of this radical seems to be at least $10^{-5}$ sec at pH = 1, and more recent evidence indicates this to be so at all pH $\leq$ 7 (M. Kongshaug, to be published). If this hypothesis holds true it is of considerable importance, because the mechanism for the formation of H-atoms, as well as their reactions with solutes, plays a fundamental role in aqueous radiation chemistry. It should be observed, however, that there is indirect pulse radiolysis evidence (as well as direct ESR evidence [22]) that H-atoms are ultimately generated by the reaction $e^-_{aq} + H_3O^+_{aq}$. Thus it seems that the $H_3O_{aq}$ radicals decay to yield H-atoms:

$$H_3O_{aq} \longrightarrow H_{aq} + H_2O \qquad (2)$$

and that it is the reactions of the $H_3O_{aq}$ radicals and not those of H-atoms which have been extensively studied in aqueous radiation chemistry.

The main purpose of the present paper is to shed some light on this question by reporting molecular orbital calculations on the $H_3O$ radical and its complexes with water. This is done by studying:

1. The molecular stability of the $H_3O$ radical against bond dissociation.
2. The stabilization effect of surrounding water shells.
3. The potential curves obtained by moving a proton in the field of water molecules.

In addition a parallel series of calculations is performed for the experimentally better known cation $H_3O^+$ and its water complexes, as a basis for comparison.

No molecular orbital calculations have yet been performed on water complexes of the $H_3O$ radical. Gangi and Bader [2] have published *ab initio* calculations on the $H_3O$ radical. Grahn [4,5] and others [6,7,15] have made some calculations on $H_3O^+$ and its water complexes.

## METHOD OF CALCULATION

The calculations were performed according to the INDO (Intermediate Neglect of Differential Overlap) method introduced by Pople *et al.*[8–12] All parameter values were chosen according to the original scheme. INDO and the closely related CNDO/2 method include explicitly all valence electrons. INDO gives a better description than does CNDO/2, of spin densities in open shell systems. This is because it retains all one-center two-electron integrals. The calculations were performed on a CDC 3300 computor.

## RESULTS

(a) *Water (monomer and dimer)*. INDO optimalization of the water geometry gives a H – O – H angle of 104.8° and a bond distance of 1.03 Å (experimental: 104.5° and 0.96 Å). The calculated dipole moment is 2.1 D (experimental: 1.8 D). The dimer was optimized to give an O – O distance of 2.46 Å and a hydrogen bond energy of 14 kcal/mol. The experimental value is 6 kcal/mol. Kollman and Allen [13] found by CNDO/2 calculations the O – O distance to be 2.53 Å.

In all these cases the linear configuration of the dimer was considered (see Ref. 13).

(b) *The $H_3O$ radical (and the corresponding cation)*. The calculated equilibrium geometry of the radical is planar (see Tables 1 and 2). It is also *stable to bond dissociation*, giving a $\Delta H_1$ of the dissociation:

$$H_3O \longrightarrow H_2O + H \qquad (3)$$

of 40 kcal/mol, which is equivalent to a strong hydrogen bond.

No experimental data seem to have been reported. Gangi and Bader [2] found from *ab initio* calculations that the radical is not stable ($\Delta H_1 < 0$) but has a dissociation barrier of 6.6 kcal/mol. This means that though the total energy is in favour of dissociation, the $H_3O$-radical can exist because the dissociation curve at first rises, giving a barrier.

The planar equilibrium geometry calculated by INDO is in contrast to the results of Gangi and Bader who, with big-basis *ab initio* calculations find a pyramidal equilibrium geometry (inversion barrier 2 kcal/mol). Melton and

Joy [3] however, obtain from *ab initio* calculations (smaller basis) a planar configuration. This is also in accordance with the Walsh's rule [14] for the geometry of $AH_3$ type molecules.

For comparison the $H_3O^+$ equilibrium geometry was also calculated. It was found to have a planar equilibrium configuration with a bond distance of 1.03 Å. Experimental results are only available for ionic crystals and are slightly varying.[16] They naturally also deviate from those of the free ion. Richards and Smith [17] find a bond distance of 1.02 Å (NMR on $H_3O^+$ $ClO_4^-$).

Melton and Joy [3] and Grahn [4] find from *ab initio* calculations that the ion is planar, whereas Bishop [6] finds a non-planar configuration. Grahn also refers to experimental evidence for a nearly planar configuration.

It is therefore reasonable to assume that if $H_3O$ and its ion are not planar, they have a very low barrier of inversion and are easily bent according to the environment.[18]

The dissociation reaction for the ion corresponding to eqn. (3) also indicates that the ion is more than *six* times as stable against bond dissociation than is the radical (see Fig. 2).

The molecular orbitals obtained for $H_3O$ in the present work may be described as follows:

In order of increasing energy the filled radical orbitals are $(1a_{1g})^2(e_u)^4(a_{2u})^2(2a_{1g})^1$. The $a_{2u}$ orbital is the lone-pair $\pi$-orbital pointing out of the molecular plane.

The ion has essentially the same MO-arrangement except for an empty antibonding $2a_{1g}$ orbital.

Table 2 gives the charge and spin densities of the radical. In contrast to the water molecule, the radical has only slightly polarized bonds. The spin density is nearly completely located on the hydrogens.

Another characteristic of the radical, its ionization potential, is found from equilibrium geometries to be 7.45 eV. According to Melton and Joy [3] the experimental value lies between 9 and 11 eV, whereas their theoretical value is only 4.14 eV. Bishop reports 3.27 eV.[7]

(c) *The $H_3O.H_2O$ radical (and the corresponding cation).* For these and all the remaining systems included in this work, only planar configurations were considered. The reason for this is the planarity found for the $H_3O$ radical.

To investigate whether the $H_3O$ radical is stabilized by complex formation with water, the equilibrium configuration of $H_3O.H_2O$ was calculated. This configuration is given in Tables 1 and 2. It is symmetrical (single well potential for the central proton) with an O – O distance of 2.55 Å. Its energy relative to $H_3O$ and $H_2O$ separately is 13.4 kcal/mol, *i.e.* slightly *less* than the calculated hydrogen bond energy of the water dimer. Thus, there is no stabilizing effect in aqueous solution (see Table 4).

To test the validity of this result, the equilibrium configuration for the corresponding ion was calculated. The $H_3O^+$ ion is known to be stabilized by water complex formation.[4] Our calculations indeed confirms this (see Table 4).

The equilibrium configuration (see Table 1) of the ion was found to be symmetrical with an O – O distance of 2.35 Å.

Experimental O – O distance for the ion are only available from various crystalline compounds. An average of 2.45 Å was found, in agreement with the

*Table 1.* Bond distances and angles in the equilibrium configurations of the radicals and ions investigated (*cf.* Fig. 1).

| Compound | I | II | II$^+$ | III | III$^+$ | IV | IV$^+$ | V | V$^+$ | VI | VI$^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Angles (°) | | | | | | | | | | | |
| 3–1–2 | 104.8 | 120.0 | 120.0 | 106.0 | 112.0 | 120.0 | 120.0 | 108.0 | 112.0 | 108.0 | 120.0 |
| 2–1–4 | | 120.0 | 120.0 | 127.0 | 124.0 | 120.0 | 120.0 | 126.0 | 124.0 | 126.0 | 120.0 |
| 1–5–7 | | | | 127.0 | 124.0 | 127.6 | 126.5 | 126.0 | 124.0 | 126.0 | 120.0 |
| 5–1–9 | | | | | | 120.0 | 120.0 | 126.0 | 124.0 | 126.0 | 120.0 |
| 7–5–6 | | | | | | 105.0 | 107.0 | 108.0 | 112.0 | 108.0 | 107.0 |
| 12–9–13 | | | | | | 105.0 | 107.0 | 106.0 | 108.0 | 105.0 | 107.0 |
| Distances (Å) | | | | | | | | | | | |
| 1–2 | 1.03 | 1.08 | 1.04 | 1.045 | 1.035 | 1.11 | 1.09 | 1.09 | 1.09 | 1.08 | 1.07 |
| 1–3 | 1.03 | 1.08 | 1.04 | 1.045 | 1.035 | 1.11 | 1.09 | 1.09 | 1.09 | 1.08 | 1.07 |
| 1–4 | | 1.08 | 1.04 | 1.275 | 1.175 | 1.11 | 1.09 | 1.16 | 1.175 | 1.25 | 1.175 |
| 1–5 | | | | 2.55 | 2.35 | 2.50 | 2.35 | 2.45 | 2.35 | 2.50 | 2.35 |
| 1–9 | | | | | | 2.50 | 2.35 | 2.45 | 2.35 | 2.50 | 2.35 |
| 5–6 | | | | | | | | 1.09 | 1.09 | 1.08 | 1.07 |
| 8–10 | | | | | | | | 1.035 | 1.035 | 1.035 | 1.035 |

*Table 2.* Charges, *s*-orbital-, and total spin densities, and total energy (a.u.) (1*s*-orb. on O not included) of equilibrium configurations of the radicals studied.

| Compound | | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| Atom charge | 1 | −0.1211 | −0.2122 | −0.2869 | −0.2637 | −0.3305 |
| | 2 | 0.0404 | 0.1204 | 0.0639 | −0.0155 | 0.1303 |
| | 3 | 0.0404 | 0.1204 | 0.0639 | 0.1400 | 0.1303 |
| | 4 | 0.0404 | −0.0574 | 0.0639 | 0.0375 | −0.0304 |
| | 5 | | −0.2122 | −0.2651 | −0.3167 | −0.2799 |
| | 6 | | 0.1204 | 0.1484 | 0.1988 | 0.1303 |
| | 8 | | | −0.2651 | −0.2901 | −0.2799 |
| | 10 | | | 0.1484 | 0.1851 | 0.1635 |
| *s*-Orb. spin density | 1 | 0.2277 | 0.1181 | 0.1716 | 0.1614 | 0.1103 |
| | 2 | 0.3384 | 0.1148 | 0.3052 | 0.3118 | 0.1330 |
| | 3 | 0.3384 | 0.1148 | 0.3052 | 0.1755 | 0.1330 |
| | 4 | 0.3384 | 0.5941 | 0.3052 | 0.4118 | 0.5142 |
| | 5 | | 0.1181 | 0.0409 | 0.0756 | 0.1103 |
| | 6 | | 0.1148 | 0.0386 | 0.0696 | 0.1330 |
| | 8 | | | 0.0409 | 0.0101 | 0.0162 |
| | 10 | | | 0.0386 | 0.0078 | 0.0147 |
| Total spin density | 1 | −0.0153 | −0.0267 | −0.1042 | −0.0824 | −0.0714 |
| | 5 | | −0.0267 | −0.0144 | −0.0515 | −0.0714 |
| | 8 | | | −0.0144 | 0.0002 | −0.0048 |
| Total energy, $E_{tot}$ (a.u.) | | −19.741662 | −38.802334 | −76.916426 | −76.918850 | −115.034269 |

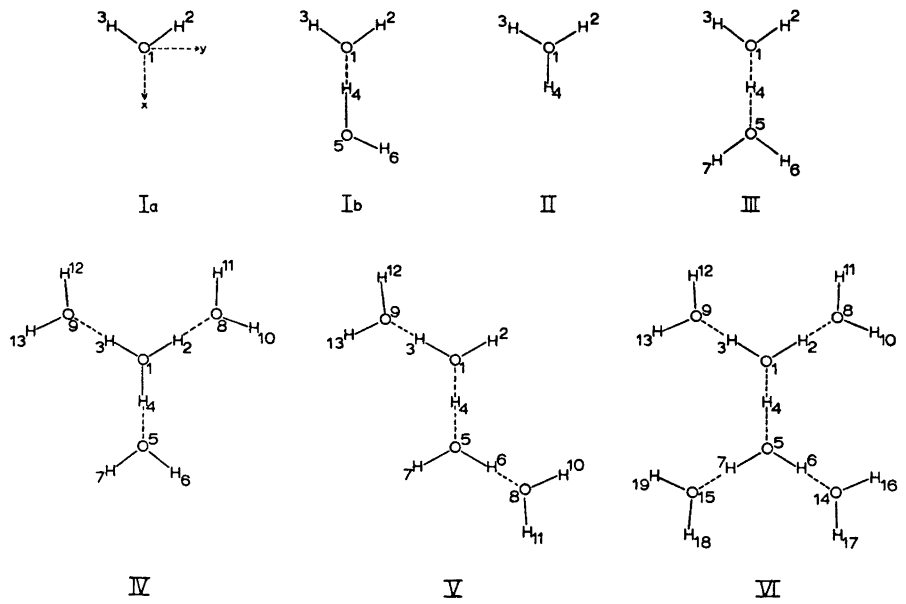


*Fig. 1.* Numbering of the atoms in the molecules investigated.

estimate of Conway.[16] The present value also agrees with two *ab initio* calculations giving an O – O distance of 2.38 [15] and 2.39 Å.[19]

Further INDO calculations on both systems were performed with three different O – O distances: 2.7 Å, 3.1 Å, and 10.0 Å. These distances represent a normal hydrogen bond distance, the average O – O distance in liquid water, and a very large distance. The water angle and outer OH-distances were first optimized keeping the central hydrogen fixed midway between the oxygens. Potential curves were then obtained by moving it, keeping the rest of the molecule fixed (see Fig. 2).

For the case of double-well potentials corrections were estimated by optimizing the water angles and distances at the energy minimum. The corrections were found to be of minor importance for the discussion here, and the position of the energy-minimum was found not to change. The curves in Fig. 2 are consequently giving a too high barrier compared to the fully optimized curves.

The shape of the potential curves changes from single-well to double-well at a certain O – O distance. In additional calculations this limit was found to be 2.85 Å for the radical and 2.60 Å for the ion.

(d) *$H_3O.3H_2O$ radical (and the corresponding cation).* The two configurations IV and V given in Fig. 1 were considered. Equilibrium configurations for the radicals are given in Tables 1 and 2.

As can be seen, the equilibrium O – O distance is slightly reduced by going from the IV to the V configuration (2.50 Å to 2.45 Å). V becomes a small

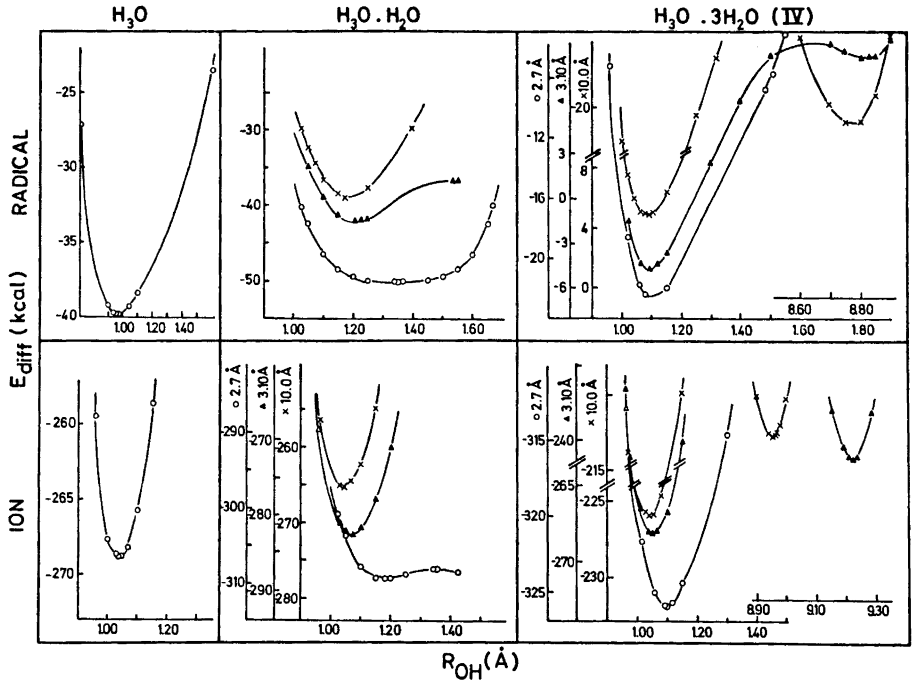


*Fig. 2.* Potential curves for the radicals and ions obtained by varying the position of the central proton, $R_{OH}$ (atom 4, Fig. 1). Curves are obtained for three different O – O distances (distance between atom 1 and atom 5, Fig. 1). The energy scale (kcal) is chosen relative to the energy of the separate $H_3O$ and water molecules.

double well potential. One explanation for this is that the unsymmetric potential of IV demands a stronger double well effect for actually giving a double well in the resulting potential. The symmetric potential can be said to be more sensitive to small energy changes.

To study this further, potential curves for IV were obtained for O – O distances of 2.7, 3.1, and 10.0 Å (see Fig. 2). A distance of 2.7 Å gives a single minimum and even 3.1 Å gives only a small double well. The curves were obtained for each O – O distance by keeping the central hydrogen midway between the oxygens and optimizing the remaining part of the molecule. The position of the central hydrogen was then varied, keeping all other angles and distances constant. For the case of double minima, the molecular geometry was reoptimized, assuring that the minimum positions did not change.

Similar calculations were performed for the cations. Equilibrium configurations are given in Table 3 and in Fig. 2. One finds an optimal O – O distance of 2.35 Å for both $IV^+$ and $V^+$.

(e) *$H_3O.5H_2O$ radical (and the corresponding cation).* The equilibrium configuration of the $H_3O.5H_2O$ radical is given in Table 2. This complex can be

*Table 3.* Charges and total energy (1*s* on O not included) for water and ion complexes of equilibrium configurations (*cf.* Fig. 1).

| Compound | | I | Ib | $II^+$ | $III^+$ | $IV^+$ | $V^+$ | $VI^+$ |
|---|---|---|---|---|---|---|---|---|
| Atom charge | 1 | −0.3136 | −0.3972 | −0.1528 | −0.2818 | −0.4479 | −0.3913 | −0.4861 |
| | 2 | 0.1568 | 0.1771 | 0.3843 | 0.2974 | 0.3180 | 0.2278 | 0.2850 |
| | 3 | 0.1568 | 0.1799 | 0.3843 | 0.2974 | 0.3180 | 0.3206 | 0.2850 |
| | 4 | | 0.2031 | 0.3843 | 0.3739 | 0.3180 | 0.3468 | 0.3249 |
| | | | −0.3875 | | −0.2818 | −0.3106 | −0.3913 | −0.4861 |
| | | | 0.1245 | | 0.2974 | 0.2376 | 0.3206 | 0.2850 |
| | | | | | | −0.3106 | −0.3014 | −0.3074 |
| | | | | | | 0.2376 | 0.2388 | 0.2145 |
| | | | | | | 0.2376 | 0.2421 | 0.2196 |
| $E_{tot}$ | | −19.039352 | −19.467855 | −38.625066 | −76.834302 | −76.825220 | −114.999445 | −38.101008 |

looked upon as an $H_3O.3H_2O$ with one of its water molecules hydrated by a second shell of water.

Similar calculations were performed for the cations (see Table 3).

The resulting hydration energy for the second shell ($\Delta H_5$) is 11.5 kcal/mol per hydrogen bond for the radical. This energy is less than the INDO-value for the water dimerization. As to the question of potential curves, one obtains a single well potential for both the radical and the ion.

## DISCUSSION

These calculations support the conclusion given by Melton and Joy [3] that the $H_3O$ radical is stable (energetically) relative to the ion. These authors, however, were unable to determine the stability with respect to bond dissociation. Furthermore, calculations have until now not been reported on the stabilization effect of the water surrounding the radical. To discuss this question it is convenient to consider the following reactions:

$$H_3O \longrightarrow H_3O + H \qquad \Delta H_1 \quad (3)$$

$$H_3O.H_2O \longrightarrow H_3O + H_2O \qquad \Delta H_2 \quad (4)$$

$$H_3O.3H_2O \longrightarrow H_3O + 3H_2O \qquad \text{configuration IV and V} \quad \Delta H_3 \quad (5)$$

$$H_3O.5H_2O \longrightarrow H_3O + 5H_2O \qquad \Delta H_4 \quad (6)$$

$$H_3O.5H_2O \xrightarrow{\Delta H_5} H_3O.3H_2O + 2H_2O$$

$$\xrightarrow{\Delta H_6} H_3O.H_2O + 4H_2O \quad (7)$$

The corresponding reactions are also considered for the ion.

Using the minimum energies in Tables 2 and 3 one obtains the reaction energies given in Table 4.

No direct experimental data on the stability of the $H_3O$ radical are available. As earlier mentioned a recent *ab initio* calculation by Gangi and Bader [2] indicates that the radical is *not* stable relative to water and hydrogen, but

*Table 4.* Reaction energy per hydrogen bond, in percentage of $\Delta H_1$ (40 kcal/mol for the radical). The energy with substript "diff." is the percentage of the first energy subtracted the calculated dimerization energy (14 kcal/mol).

For the calculations of $\Delta H_1$ the approximate hydrogen atom energy of INDO is used. The exact value is 0.5 a.u. but the standard method for INDO gives 0.638730 a.u. which must be used here to be consistent within the approximation (see eqns. 2.14 and 2.15 of Ref. 10). The $\Delta H_1$-value for the ion is 269 kcal/mol.

| | $\Delta H_1$ | $\Delta H_2$ | $\Delta H_3$ (IV) | $\Delta H_3$ (V) | $\Delta H_4$ | $\Delta H_5$ | $\Delta H_6$ |
|---|---|---|---|---|---|---|---|
| % $E$, rad. | 100 | 34 | 30 | 31 | 30 | 29 | 29 |
| % $E$, diff., rad. | 65 | −1.5 | −5.3 | −4.2 | −5.0 | −6.0 | −5.5 |
| % $E$, ion | 100 | 28 | 19 | 19 | 15 | 10 | 15 |
| % $E$, diff., ion | 95 | 22 | 14 | 13 | 10 | 5 | 10 |

has a local dissociation barrier of approximately 6 kcal/mol. In contrast, the present INDO calculation indicates that the radical is indeed stable ($\Delta H_1 > 0$). This stability, however, is reduced because the radical is *not* stabilized by complex formation in aqueous solutions as is the cation. In contrast the surrounding water has a destabilizing effect on the radicals; *i.e.*, it is not energetically favourable to break normal water hydrogen bonds and move into complex around the radical. This is seen by comparing $\Delta H_2$, $\Delta H_6$, and $\Delta H_5$ in Table 4 for the radical and for the ion, respectively, the $\Delta E$ diff. being negative for the radical.

Bishop [7] points out that the stability of the $H_3O$ radical can also be calculated indirectly. It is stable when the ionization potential of $H_3O$ is greater than the energy of hydrogen minus the proton affinity of water. Using the INDO values one obtains $0.27 > 0.64 - 0.43$ a.u., the difference between the two sides being $\Delta H_1$.

The experimental value of Melton and Joy [3] gives a $\Delta H_1$ of about 100 kcal/mol, supporting the qualitative conclusion that the radical is stable to bond dissociation.

The negative or non-stabilizing effect of complex formation of the radical can be further supported by the charge distributions obtained. From Table 2 it is seen that the outer free water hydrogens in the complexes III – VI are not significantly more positively polarized than in water (Ia) or dimer (Ib). Complexes V and VI also illustrate that the inner shell water hydrogens (atom 3, Table 2) have not a greater charge when bound than has water or water-dimer. In contrast, the ion has, in both cases mentioned above, a much higher charge on the hydrogens than in water, corresponding to an energy gain by complex formation (see Table 3).

Grahn [4] did similar reasoning for the ion complex VI. Total stabilization effect calculated here for the ion going from $H_3O^+$ to the full $H_3O^+.(H_2O)_9$ is about 70 % of the INDO proton affinity. This value is in reasonable agreement with the value of Grahn, reporting about 80 %, using experimental proton affinity and water hydrogen-bond energy.

As to the question of single or double minimum potential curves, it is necessary first to discuss the validity of the INDO method tested by calcula-

tions on the ion. Connected to the question of proton mobility in water, much speculation has been made about the proton energy barrier. A recent *ab initio* calculation [15] obtains an (extremely flat) single minimum. Even at an O – O distance of 2.49 Å they report an energy barrier less than the zero-point energy. Other authors [19] report a very shallow double minimum, stating that the energy difference is beyond the accuracy to be interpreted. Calculations of the corresponding properties of $HF_2^-$ also leads to a symmetrical potential for $H_5O_2^+$.[20] Thus, one can conclude that the predicted single-potential obtained by INDO is reasonable. The most essential difference is that the INDO-equilibrium configuration of $H_5O_2^+$ has an O – O distance of 0.25 Å below the double potential limit, whereas the *ab initio* calculations mentioned lie on the limit. INDO thus seems to overestimate the well depth. Relative trends comparing the different complexes are expected to be the most reliable.

Except for the configuration V of the $H_3O.3H_2O$ radical, none of the radical complexes calculated give double well potentials at their equilibrium configurations. $H_3O.3H_2O$, configuration V, has a double well barrier that is hardly significant.

Thus one can conclude that the primary stable $H_3O$ radical is probably not long-lived, and that the hydrogen atom is delocalized so that it cannot be said to be bound to any particular water molecule, but rather to be a solvated hydrogen atom. This is similar to the ion, the important difference between the two being the destabilizing effect of water molecules surrounding the radical.

Martin and Swift [21] describe a matrix-stabilized $H_3O$-radical which is stable relative to $H_2O$ and H. This does not, however, settle the question of unstabilized $H_3O$ in aqueous solutions.

Neta *et al.*[22] have shown that the solvated hydrogen atom, $H_{aq}$, exists. It is also distinguishable from a dry hydrogen radical (ESR *g*-factor: Neta *et al.*, unpublished).

Our calculation is not in disagreement with the hypothesis of Kongshaug *et al.*[1] stating that the primary irradiation product is $H_3O_{aq}$. The stability of $H_3O$ (without complex water) indicates that this can be the primary reaction product. One can, however, not predict the lifetime of $H_3O_{aq}$. The effect of pH is furthermore not considered here.

It is likely that since the hydrogens on the $H_3O$ radical are slightly positive (see Table 2) and are more easily charge inducible, the $OH^-$ ion will react faster than with a single H atom.

M. Kongshaug gives some experimental evidence that this is the case ($k_{(H_3O+OH^-)} \approx 10 \times k_{(H+OH^-)}$; to be published).

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