

The structure of $(\text{H}_3\text{O}_2)^-$

Celeste McMichael Rohlfing, Leland C. Allen,^{a)} and Charles M. Cook^{b)}

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

H. Bernhard Schlegel

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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Global geometry optimizations of the hydroxide hydrate anion $(\text{H}_3\text{O}_2)^-$ are performed at the 4-31G, 6-31G*, and 6-31G** levels to determine its structure. Further geometry searches are carried out using configuration interaction with double substitutions, and Møller-Plesset perturbation theory to second and third order. An asymmetric hydrogen bond is found at the SCF level, while a symmetric structure results when correlation is included. Comparisons are made to previous theoretical studies of $(\text{H}_3\text{O}_2)^-$, and also to recent x-ray crystallography results. An analysis of the larger correlation energy in the symmetric case is given.

INTRODUCTION

Studies of anionic hydrogen bonds show that proton drift, the change in the A-H bond length from the monomer A-H to the dimer $(\text{A-H}\cdots\text{B})^-$, is considerably larger than that in normal neutral hydrogen bonds. In some cases, exceptionally strong, negatively charged hydrogen bonds may have the proton located midway between the donor and acceptor atoms $(\text{A}\cdots\text{H}\cdots\text{B})^-$. This has been demonstrated both experimentally^{1,2} and theoretically³⁻⁵ for the bifluoride ion $(\text{HF}_2)^-$. Hence, there has been much interest in the structure of hydroxide hydrate $(\text{H}_3\text{O}_2)^-$ (alternatively known as the bihydroxide anion and the hydrogen oxide ion), but the results of several theoretical studies⁵⁻⁹ have not been conclusive. In addition, the existence of this ion has only been recently demonstrated, and its geometry suggested by crystallographic methods.¹⁰⁻¹³

Previous theoretical work at the SCF level has shown the hydrogen bond in $(\text{H}_3\text{O}_2)^-$ to be asymmetric. Newton and Ehrenson,⁶ using a 4-31G basis, found a planar asymmetric geometry as the minimum energy conformation, with a nonplanar symmetric structure only 0.13 kcal/mol higher than this minimum. Roos, Kraemer, and Diercksen^{7,8} used an extended basis set with polarization functions on both the oxygen and hydrogen atoms. They found a planar asymmetric bond preferred over a planar symmetric one by 1.58 kcal/mol. Similar results were found by Støgaard *et al.*⁵ using a limited Gaussian basis, and Jorgensen and Ibrahim,⁹ using 4-31G and 6-31G* basis sets. Also, a partial optimization at 4-31G¹⁴ found a planar symmetric structure only slightly higher in energy than Newton and Ehrenson's asymmetric minimum. Unfortunately, none of the geometry optimizations in these investigations were complete.

Two of these studies also included correlation by using configuration interaction with single and double substitutions (CISD). The core electrons on the oxygen atoms were frozen in both treatments. Støgaard *et al.*⁵

and Roos, Kraemer, and Diercksen⁸ employed the same basis sets as in their respective SCF studies. Both investigations concluded that the asymmetric form of $(\text{H}_3\text{O}_2)^-$ was the lowest energy structure, but neither structure included a global geometry optimization.

Two recent x-ray crystallographic studies have demonstrated the existence of the $(\text{H}_3\text{O}_2)^-$ ion. A free anion hydrogen bonded to four water molecules was found with an O...O separation of 2.29 (2) Å.¹⁰ A correction for thermal motion (known to be an overestimate) yielded a distance of 2.377 (12) Å.¹¹ This very short distance, along with the fact that the proton in the hydrogen bond was at or near a crystallographic inversion center, led the authors to believe that $(\text{H}_3\text{O}_2)^-$ was symmetric. This ion has also been observed as a bridging ligand between two metal atoms.¹² In three such compounds O...O separations of 2.44 (1), 2.48 (1), and 2.52 (1) Å were found. Here also, the proton in the hydrogen bond was located at or near an inversion center in two of the compounds. The long distances found almost certainly arise from the nearby positively charged metal atoms withdrawing negative charge from the $(\text{H}_3\text{O}_2)^-$ system.¹³

These experimental studies have prompted us to extend the structure investigation of the hydroxide hydrate ion beyond that done previously. In all but one of the references cited above, external OH bond lengths and HOH bond angles were held fixed, and further optimization is clearly required to determine the true geometry. Likewise, the necessity of geometry searches using correlated wave functions is evident because of the conflicting results obtained at the SCF and CISD levels. Hence, we have undertaken a study of the structure of the $(\text{H}_3\text{O}_2)^-$ anion by performing global geometry optimizations at three basis set levels and by including correlations corrections in order to determine its minimum energy conformation.

COMPUTATIONAL PROCEDURE

Ab initio calculations were performed with the GAUSSIAN 80 program.¹⁵ The 4-31G split valence and the 6-31G* and 6-31G** split valence plus polarization basis sets were employed. SCF iterations were performed until the root-mean-square deviation between

^{a)}To whom any correspondence should be addressed.

^{b)}Present address: Department of Chemistry, Columbia University, New York, N.Y. 10027.

TABLE I. SCF optimized geometrical parameters and energies for $(\text{H}_3\text{O}_2)^-$, as shown in Fig. 1, at the basis set levels indicated.^a

Basis	r_1	r_2	r_3	r_4	θ_1	θ_2	ϕ	α	Energy	Reference
4-31G (sym)	1.212	1.212	0.958	0.958	109.2	109.2	180.0	150.0	-151.20325	This work
4-31G	1.097	1.361	0.955	0.962	108.1	110.0	176.1	135.0	-151.20358	This work
6-31G* (sym)	1.207	1.209	0.950	0.950	102.2	102.2	180.0	120.0	-151.39176	This work
6-31G*	1.040	1.488	0.948	0.953	100.8	101.8	173.2	115.0	-151.39340	This work
6-31G** (sym)	1.203	1.206	0.946	0.946	102.7	102.7	180.0	120.0	-151.41105	This work
6-31G**	1.044	1.457	0.944	0.949	101.4	102.5	174.3	115.0	-151.41228	This work
STO-3G	1.010	1.199	1.007	1.163	100.9	101.1	180.0	180.0	-149.14322	9
4-31G	1.106	1.348	0.955	0.962	108.8	108.8	180.0	180.0	-151.20343	9
6-31G*	1.095	1.384	0.949	0.951	102.6	101.7	180.0	180.0	-151.39246	9
{O(11,7,1/5,4,1) H(6,1/3,1)} (sym)	1.190	1.190	0.957	0.957	104.5	104.5	180.0	180.0	-151.49523	7
{O(11,7,1/5,4,1) H(6,1/3,1)}	1.022	1.524	0.957	0.957	104.5	104.5	180.0	180.0	-151.49774	8
{O(9,5/4,2) H(4,1/2,1)} (sym)	1.190	1.190	0.958	0.958	104.5	104.5	180.0	180.0	-151.45295	5
{O(9,5/4,2) H(4,1/2,1)}	1.064	1.427	0.958	0.958	104.5	104.5	180.0	180.0	-151.45341	5
4-31G (sym)	1.21	1.21	0.95	0.95	109.0	109.0	180.0	160.0	-151.2031	6
4-31G	1.11	1.34	0.95	0.95	111.2	111.2	180.0	180.0	-151.2033	6

^aBond lengths in Å; bond angles in degrees; energies in Hartrees.

consecutive density matrices was less than 1.0×10^{-7} . Full geometry optimizations at all basis set levels were done by the force relaxation method.¹⁶ The optimization criteria used were root-mean-square force less than 3.0×10^{-4} a.u., maximum force less than 4.5×10^{-4} a.u., root-mean-square displacement less than 1.2×10^{-3} a.u., and maximum displacement less than 1.8×10^{-3} a.u.

For each basis set, initial structures with both symmetric and asymmetric hydrogen bonds were chosen, and allowed to relax to fully optimized geometries. Linearity was not imposed and, as discussed in the next section, the asymmetric forms of $(\text{H}_3\text{O}_2)^-$ at each basis relaxed to nonlinear hydrogen bonds. The force optimization technique was found to be relatively insensitive to torsional changes in the dihedral angle so the degree of nonplanarity was determined in the following way: optimized planar structures were found, and the dihedral angle varied in increments of 5° until a minimum was reached. At this angle the rest of the geometry was reoptimized, with very little change observed in any of the parameters.

Inclusion of correlation effects was accomplished by

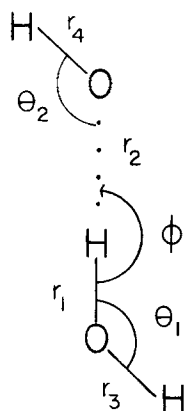


FIG. 1. Definition of geometrical parameters as they appear in Table I. The dihedral angle α is defined by the external hydrogens, and is equal to 180° for the planar *trans* structure.

using configuration interaction with double substitutions (CID) and Møller-Plesset perturbation theory to second (MP2) and third (MP3) order.^{17,18} The $1s$ core electrons on the oxygen atoms in $(\text{H}_3\text{O}_2)^-$ were frozen. The CID energies include a size-consistency correction, and the convergence criterion was a change of less than 2.0×10^{-6} a.u. in the total energy. Energy calculations using MP2, MP3, and CID were carried out on the 6-31G* optimized geometries using the 6-31G* basis, and on the 6-31G** optimized geometries using the 6-31G** basis.

A geometry optimization employing C_{2h} symmetry on the symmetric structure was performed at the MP2 6-31G** level,¹⁹ using all MO's instead of the frozen core approximation. The same optimization criteria were used as at the SCF level and nonplanarity was also tested. A similar optimization of the asymmetric structure, starting with the 6-31G** optimum geometry under C_s symmetry, proceeded directly toward the MP2 symmetric C_{2h} minimum. Further estimates of the most probable deviations from the SCF geometries were made using CID, MP2, and MP3 6-31G** calculations.

SCF RESULTS

Table I lists the optimized geometries found in this study as well as those from previous studies at the SCF level. The geometrical parameters are defined in Fig. 1. As noted above, in previous optimizations constraints were placed on some of the geometrical parameters. Newton and Ehrenson⁶ fixed both external OH bond lengths (r_3 and r_4) at 0.95 \AA and both HOH bond angles (θ_1 and θ_2) at 111.2° . They also imposed linearity on the hydrogen bond ($\phi = 180.0^\circ$). Roos, Kraemer, and Dierksen^{7,8} set r_3 and r_4 to 0.957 \AA and θ_1 and θ_2 to 104.5° . They only considered planar conformations of $(\text{H}_3\text{O}_2)^-$ and linear hydrogen bonds. Støgaard *et al.*⁵ used the same constraints as Roos, Kraemer, and Dierksen's study, but chose r_3 and r_4

TABLE II. SCF energy differences between symmetric and asymmetric forms of $(\text{H}_3\text{O}_2)^-$, at the basis set levels indicated.^a The asymmetric form is lower in energy in all cases.

Basis	Energy difference	Reference
4-31G	0.21	This work
6-31G*	1.03	This work
6-31G**	0.77	This work
{O(11, 7, 1/5, 4, 1)} {H(6, 1/3, 1)}	1.58	8
{O(9, 5/4, 2)} {H(4, 1/2, 1)}	0.29	5
4-31G	0.13	6

^aEnergies in kcal/mol, 1 Hartree = 627.50 kcal/mol.

equal to 0.958 Å. Jorgensen and Ibrahim⁹ restricted their search to planar structures with linear hydrogen bonds.

The fully optimized asymmetric form of $(\text{H}_3\text{O}_2)^-$ is lowest in energy for the 4-31G, 6-31G*, and 6-31G** basis sets, in agreement with all previous studies. Table II gives the energy difference in kcal/mol between the symmetric and asymmetric structures as found at the SCF level. These results indicate a quite flat potential for motion within the hydrogen bond as well as for torsional motion.

From Table I, it is also observed that the 4-31G basis correctly reproduces the geometry trends found at 6-31G* and 6-31G** in the asymmetric form. In particular, r_4 is greater than r_3 . Since the asymmetric

form more closely resembles $\text{H}_2\text{O} + \text{OH}^-$ than the symmetric form, this difference in bond lengths is expected. Both experimentally and theoretically,⁹ the OH^- bond length ($\cong r_4$) is larger than the H_2O bond length ($\cong r_3$). Also, the nonlinearity of the asymmetric hydrogen bond is shown at 4-31G, so this is not a polarization function effect. A Coulomb interaction calculation using net Mulliken charges shows that the asymmetric nonlinear optimum geometry is preferred over a linear geometry (with all other bond lengths and angles unaltered). Hence, it appears that this nonlinearity can be rationalized in terms of electrostatics and the asymmetry of the oxygen ligands. Lastly, θ_2 is slightly greater than θ_1 , probably as an electrostatic compensation for the nonlinearity of the hydrogen bond.

The 6-31G* molecular orbitals of $(\text{H}_3\text{O}_2)^-$ are shown in Fig. 2 for the 6-31G* optimized geometries of the symmetric and asymmetric forms. It is worth noting how remarkably different some of the MO's are in view of the very small difference in the $\text{O} \cdots \text{O}$ separation (0.1 Å). In the asymmetric case, the 3a, 5a, 6a, and 8a MO's resemble the $2a_1$, $1b_2$, $3a_1$, and $1b_1$ of water while the 4a, 7a, and 9a resemble the 2σ , 3σ , and out-of-plane 1π in the hydroxide ion.

POST SCF RESULTS

Table III gives the CISD results of Støgaard *et al.*⁵ and Roos, Kraemer, and Diercksen.⁸ Both employed the same geometrical constraints from their respective SCF studies given above. Also listed is the full MP2

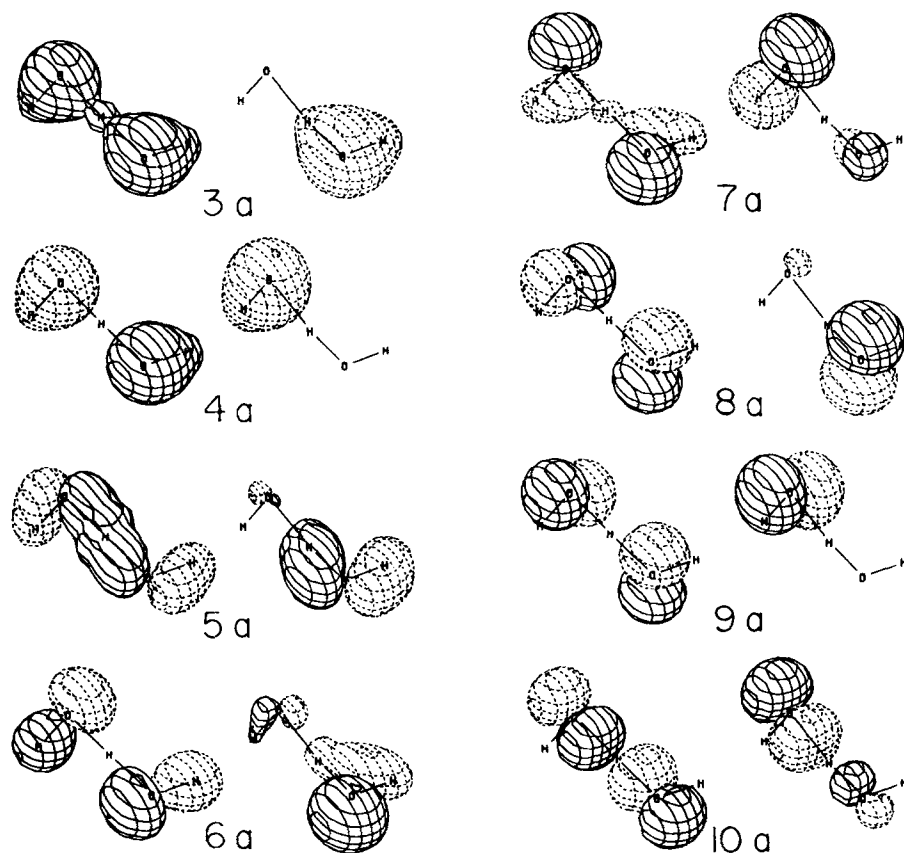


FIG. 2. 6-31G* molecular orbitals from the 6-31G* optimized geometries. In each pair, the symmetric structure is on the left and the asymmetric on the right. The hydroxyl hydrogen is bent below the plane of the molecule.

TABLE III. Post SCF optimized geometrical parameters and energies for $(\text{H}_3\text{O}_2)^-$ at the basis set levels indicated.^a

Basis	Method	r_1	r_2	r_3	r_4	θ_1	θ_2	ϕ	α	Energy	Reference
6-31G** (sym)	MP2(Full)	1.223	1.223	0.965	0.964	99.1	99.1	180.0	110.0	-151.82012	This work
$\left\{ \begin{array}{l} \text{O}(11, 7, 1/5, 4, 1) \\ \text{H}(6, 1/3, 1) \end{array} \right.$ (sym)	CISD	1.190	1.190	0.957	0.957	104.5	104.5	180.0	180.0	-151.91454	8
$\left\{ \begin{array}{l} \text{O}(11, 7, 1/5, 4, 1) \\ \text{H}(6, 1/3, 1) \end{array} \right.$	CISD	1.092	1.373	0.957	0.957	104.5	104.5	180.0	180.0	-151.91518	8
$\left\{ \begin{array}{l} \text{O}(9, 5/4, 2) \\ \text{H}(4, 1/2, 1) \end{array} \right.$ (sym)	CISD	1.200	1.200	0.958	0.958	104.5	104.5	180.0	180.0	-151.72689	5
$\left\{ \begin{array}{l} \text{O}(9, 5/4, 2) \\ \text{H}(4, 1/2, 1) \end{array} \right.$	CISD	1.112	1.268	0.958	0.958	104.5	104.5	180.0	180.0	-151.72642	5

^aSee the text for what parameters were actually varied. (Full) indicates the frozen core approximation was not used.

optimized symmetric structure found in this study. As noted previously, a stable asymmetric form could not be located. The MP2 treatment lengthens all of the bonds and decreases the θ_1 and θ_2 angles. The CISD studies show little change from the SCF level in the symmetric structures, but this is most likely due to the use of fixed values of r_3, r_4, θ_1 and θ_2 .

Table IV lists the energies obtained from our correlation study at the CID, MP2, and MP3 levels and Table V gives the energy differences (in kcal/mol) between the symmetric and asymmetric forms of $(\text{H}_3\text{O}_2)^-$ as found at the post SCF level. The geometries of the fully optimized 6-31G* and 6-31G** symmetric structures prove lowest in energy at the post SCF level, in agreement with the CISD studies. The lowest CISD energy in Table III obtained by Roos, Kraemer, and Diercksen⁸ shows an asymmetric hydrogen bond, but these authors state that they expect the remaining asymmetry in their structure to disappear if complete geometry optimization is performed. Table V indicates a quite flat potential for proton motion in the hydrogen bond of $(\text{H}_3\text{O}_2)^-$, and it is seen that our CID treatment lowers the barrier to this motion at the 6-31G* and 6-31G** optimized geometries. It may also be noted that energy differences calculated by the CID and MP3 methods are in excellent agreement with each other.

A test of how well the full MP2 geometry search can reproduce the CID (and MP3) potential surface was investigated in the following way. Several points on the CID potential surface near the 6-31G** optimum geometries of the symmetric and asymmetric forms were sampled. The points included changes in r_1 and

r_2 since these parameters are the important variables. Table VI summarizes the results for the symmetric case. The most significant feature of these numbers is the parallelism between the potential surfaces generated at the MP2 and CID (and MP3) levels. This observation strongly supports the MP2 optimization conclusion that the $(\text{H}_3\text{O}_2)^-$ anion is symmetric.

An exploration of the question of nonplanarity was performed at the 6-31G** full MP2 level for the symmetric structure. An energy lowering on the order of 0.2 kcal/mol was obtained for the nonplanar conformation. We conclude, as at the SCF level, that a very flat potential surface for out-of-plane bending exists. Zero point energies are larger than the energy differences calculated here, and in a crystal environment, packing forces will determine the observed conformation of the hydroxide hydrate ion.

DISCUSSION

The Hartree-Fock description of the formation and dissociation of hydrogen bonds is generally assumed to be adequate when such interactions are weak. However, for strong hydrogen bonds, e.g., $(\text{H}_3\text{O}_2)^-$, it is logical to make analogies to known results from covalent bonding. Thus the change from an asymmetric structure at the SCF level to a symmetric structure when correlation is included has led investigators^{5,8} to point out

TABLE IV. CID, MP2, and MP3 energies of $(\text{H}_3\text{O}_2)^-$ at the basis set levels indicated. The geometrical parameters used are the optimized 6-31G* and 6-31G** values in Table I.

Basis	E_{CID}	E_{MP2}	E_{MP3}
6-31G* (sym)	-151.78586	-151.77687	-151.78253
6-31G*	-151.78565	-151.77576	-151.78229
6-31G** (sym)	-151.82325	-151.81378	-151.82045
6-31G**	-151.82249	-151.81232	-151.81967

TABLE V. Post SCF energy differences between symmetric and asymmetric forms of $(\text{H}_3\text{O}_2)^-$, at the basis set levels indicated. The symmetric form is lower in all cases except Ref. 8, which is discussed in the text.

Basis	Method	Energy difference	Reference
6-31G*	CID	0.13	This work
6-31G*	MP2	0.69	This work
6-31G*	MP3	0.15	This work
6-31G**	CID	0.48	This work
6-31G**	MP2	0.91	This work
6-31G**	MP3	0.48	This work
$\left\{ \begin{array}{l} \text{O}(11, 7, 1/5, 4, 1) \\ \text{H}(6, 1/3, 1) \end{array} \right.$	CISD	0.40	8
$\left\{ \begin{array}{l} \text{O}(9, 5/4, 2) \\ \text{H}(4, 1/2, 1) \end{array} \right.$	CISD	0.29	5

TABLE VI. CID, MP2, and MP3 energies of the symmetric form of $(\text{H}_3\text{O}_2)^-$ using the 6-31G** basis of the geometries indicated.^a

r_1	r_2	E_{SCF}	E_{CID}	E_{MP2}	E_{MP3}
1.203	1.206	-151,411 05	-151,823 25	-151,813 78	-151,820 45
1.216	1.216	-151,410 92	-151,823 36	-151,813 98	-151,820 52
1.217	1.217	-151,410 90	-151,823 36	-151,813 98	-151,820 52
1.219	1.219	-151,410 85	-151,823 35	-151,813 99	-151,820 50

^aOther geometrical parameters fixed at the 6-31G** optimized values in Table I.

that the O-H bond in the symmetric case is longer than that in the asymmetric one and thereby rationalize the result on the basis of the known increase in correlation that occurs with bond stretching in most covalent bonds.

A complementary view is obtained from the informative charge density difference plot of the correlation contribution in $(\text{HF}_2)^-$ given by Støgaard *et al.*⁵ and reproduced here as Fig. 3. Except for the region immediately surrounding the hydrogen, the correlation correction is essentially identical in both cases, and there is no reason why an entirely similar result is not to be expected for $(\text{H}_3\text{O}_2)^-$. It is apparent from these two plots that correlation puts a larger negative charge around the proton in the symmetric case, thereby causing a differential lowering of the total energy. Since $(\text{HF}_2)^-$ is already strongly symmetric at the SCF level, the addition of a small correlation correction favoring the symmetric form does not change the predicted minimum energy geometry. In $(\text{H}_3\text{O}_2)^-$, the SCF potential surface for motion of the central hydrogen is very flat, however, and the small CI correction controls its minimum energy position.

The nature of the correlation correction is further suggested by comparing the SCF MO's for the asymmetric and symmetric geometries of $(\text{H}_3\text{O}_2)^-$. One can employ the working hypothesis that correlation corrections involve localized in-out, left-right, and angular separations in the orbitals of an α electron from those of its β partner. In $(\text{H}_3\text{O}_2)^-$, the pattern of occupied MO's in the asymmetric form is very close

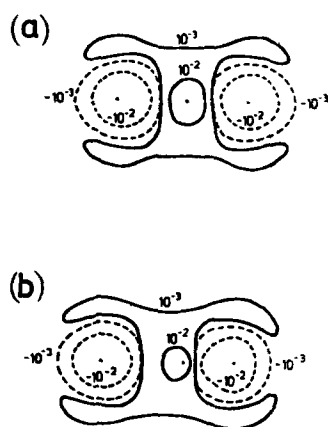


FIG. 3. Charge density difference plot ($\rho_{\text{SCF+CID}} - \rho_{\text{SCF}}$) of $(\text{HF}_2)^-$ — taken from Ref. 5: (a) $r_1 = 1.243 \text{ \AA}$, $r_2 = 1.296 \text{ \AA}$; (b) $r_1 = 0.952 \text{ \AA}$, $r_2 = 1.587 \text{ \AA}$.

to that in the symmetric form in the region around the central proton, except for the $6a$ and the $10a$ (HOMO). Table VII contains the MO coefficients of this hydrogen for the 6-31G* symmetric and asymmetric structures, since the magnitudes of these coefficients are not readily apparent from the plots depicted in Fig. 2. In both of these MO's, the coefficients of the central hydrogen AO's in the symmetric case are much smaller than those in the asymmetric case. These small hydrogen coefficients provide an opportunity for electrons to efficiently keep out of each other's way, thereby allowing the correlated part of the wave function to build up charge around the proton where it then contributes to a nuclear-electron energy lowering. The origin of the small hydrogen AO coefficients is largely a matter of symmetry. The $10a$ is dominated by a pair of antibonding oxygen $2p_\sigma$ AO's and the $6a$ by antibonding oxygen $2s$ AO's, thus eliminating significant coefficients for the centered proton AO's.

A final rationalization of the larger correlation in the symmetric case takes advantage of the result that its O...O separation is always smaller than that of the corresponding asymmetric structure. If one considers $(\text{H}_3\text{O}_2)^-$ as formed from H_2O and OH^- , two electron pairs (a water O-H bond pair and a hydroxide lone pair) will approach each other and overlap. The region of overlap is that volume in which the differential electron-electron correlation is occurring and it is clearly larger for the symmetric case.

SUMMARY

The flatness of the potential surface of the $(\text{H}_3\text{O}_2)^-$ anion is evident at both SCF and post SCF levels. The SCF geometry optimizations reported here show that an asymmetric, nonplanar form with a nonlinear hydrogen bond is the preferred structure. However, MP2 optimizations and a selected survey of the CID (and MP3) potential surface indicate that a nonplanar symmetric form with a linear hydrogen bond is the lowest energy gas phase structure. The potential energy

TABLE VII. 6-31G* molecular orbital coefficients of the central hydrogen from the 6-31G* optimized geometries.

Central hydrogen AO	Symmetric		Asymmetric	
	$6a$	$10a$	$6a$	$10a$
1s (inner)	0.00	0.00	-0.12	0.00
1s (outer)	0.00	0.00	-0.04	-0.13

surface is sufficiently flat so that the conformation will be completely determined by zero point energy effects and the nature of the anion's immediate environment. Several physical arguments and analogies are offered which explain why the correlation energy is larger for the symmetric structure.

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