Detailed Study of the Water Trimer Potential Energy Surface

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Abstract: The potential energy surface of the water trimer has been studied through the use of *ab initio* quantum mechanical methods. Five stationary points were located, including one minimum and two transition states. All geometries were optimized at levels up to the double-ζ plus polarization plus diffuse (DZP+diff) single and double excitation coupled cluster (CCSD) level of theory. CCSD single energy points were obtained for the minimum, two transition states, and the water monomer using the triple-ζ plus double polarization plus diffuse (TZ2P+diff) basis at the geometries predicted by the DZP+diff CCSD method. Reported are the following: geometrical parameters, total and relative energies, harmonic vibrational frequencies and infrared intensities for the minimum, and zero point vibrational energies for the minimum, two transition states, and three separated water molecules.

Introduction

For many years the interactions of water molecules have been a subject of great interest. As one of the simpler systems involving hydrogen bonding, the potential energy surface of the water dimer received *ab initio* treatment as early as 1968.[1] Investigations involving larger basis sets followed soon after,[2] and by 1970 *ab initio* methods had been applied to the trimer[3] and larger water polymers.[4] In 1972 molecular beam electric deflection experiments supported the cyclic structure of the water trimer proposed by Del Bene and Pople[4] in that no large dipole was found.[5] The following years saw many articles on the subject of water polymers[6] as various methods were applied in attempts to better characterize and understand such an important aspect of nature.

In 1980 the chain structure received support from experiments based on the vibrational spectroscopy of the trimer in low-temperature matrices.[7] Later experiments, however, showed strong support for a cyclic structure in both gas phase[8] and matrix isolation studies.[9] The recent paper by Pugliano and Saykally[10] provided much insight into the potential energy surface of the water trimer as they measured a vibration−rotation−tunneling band of the perdeuterated trimer. Their observations and analysis reveal a chiral six-membered ring in which enantiomers are quickly exchanged by quantum tunneling.

They described three possible tunneling motions: "flipping" corresponding to an external hydrogen moving from one side of the O−O−O plane to the other, "C_2" corresponding to internal rotation of a water subunit in such a way that it exchanges its external and hydrogen-bound protons, and "cw−ccw" which changes the sense of the hydrogen bonding from either clockwise to counterclockwise or *vice versa*.

Since the Pugliano−Saykally publication there has been a flurry of papers concerning the water trimer. Cooperative effects have been studied,[11] the intermolecular vibration spectrum has been simulated,[12] very recently density functional methods have been applied,[13] and the structure of the minimum has been determined at the MP2 level of theory. The latter work predicted a cyclic structure with the oxygens equidistant, two H···O interaction distances of 1.901 Å, and one H···O interaction distance of 1.920 Å.[14]

Since the original composition of this manuscript, several additional works on this subject have appeared. The OH vibrational shifts for the trimer have been computed by van Duijneveldt-van de Rijdt and van Duijneveldt at the counterpoise corrected SCF+MP2 level in the ESPB basis.[15] Their predictions are limited, though, by their constriction of the equilibrium geometry to pseudo-C_3 symmetry and the H$_2$O intramolecular coordinates to the observed monomer values. Schütz, Bürgi, Leutwyler, and Bürgi examined flipping coordinates in water trimer racemization, only one of which was a stationary point.[16] Wales has presented an excellent conceptual discussion of the water trimer rearrangements.[17] Most recently, an additional report from the group that unleashed this deluge of scientific inquiry provides significant additional data for the analysis of the water trimer structural rearrangement dynamics.[18] This recent measurement of one (H$_2$O)$_3$ intermolecular vibration at

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87.1 cm^{-1} and an additional $(D_2O)_3$ band at 98.1 cm^{-1} has allowed them to deduce characteristics of the water trimer in more detail than was possible in their earlier paper.

Lacking still in the literature, though, are a structural determination of the minimum and transition states at improved levels of correlation [single and double excitation configuration interaction (CISD) and single and double excitation coupled cluster (CCSD)] and a detailed description of the transition state structures for the motions described by Pugliano and Saykally, as well as energy differences between these structures. The purpose of this paper then is to fill that gap, providing structural data for the minimum, flipping transition state, internal rotation transition state (as we have labeled the C_2 motion of Pugliano and Saykally), and two other stationary points (a planar C_{3h} structure and a C_3 bowl structure) at high levels of theory [up to double-ζ plus polarization plus diffuse functions (DZP+diff) CCSD] and to provide information on the energetics of this system at even higher levels of theory [triple-ζ plus double polarization plus diffuse functions (TZ2P+diff) CCSD energies at the DZP+diff CCSD geometries)].

Theoretical Methods

This study was completed using the PSI program system.[19] Four different basis sets were used in the course of the investigation. The first and smallest basis, designated double-ζ plus polarization (DZP), was constructed from the Huzinaga–Dunning[20] set of contracted Gaussian functions to which was added a set of polarization functions. These polarization functions were a set of five pure angular momentum d-like functions on oxygen [$\alpha_d(O) = 0.85$] and a set of p functions on hydrogen [$\alpha_p(H) = 0.75$]. The contraction scheme consists of O(9s5p1d/4s2p1d) and H(4s1p/2s1p).

For the double-ζ plus polarization plus diffuse (DZP+diff) basis set, the DZP basis was augmented by a set of diffuse functions for the purpose of more properly describing this complex. Feller has shown that, for the water dimer, diffuse functions greatly reduce the effects of basis set superposition errors (BSSE) and, for correlated levels of theory, provide better interaction energies without the application of the counterpoise (CP) method.[21] To oxygen were added diffuse sets of s and p orbitals [$\alpha_s(O) = 0.0823$, $\alpha_p(O) = 0.0651$], and a diffuse s orbital was added to each hydrogen [$\alpha_s(H) = 0.0441$]. The procedure for the derivation of these coefficients was that recommended by Lee and Schaefer.[22]

For more flexibility of the basis set, the triple-ζ plus double polarization (TZ2P) basis set was utilized. This basis was formed by augmenting the Huzinaga–Dunning[23] triple-ζ basis with two sets of pure angular momentum d-like functions for oxygen [$\alpha_d(O) = 1.70$, $\alpha_d(O) = 0.425$] and two sets of p functions for hydrogen [$\alpha_p(H) = 1.50$, $\alpha_p(H) = 0.375$]. The contraction scheme for this basis consists of O(10s6p2d/5s3p2d) and H(5s2p/3s2p).

The largest basis set used for this study was the triple-ζ plus double polarization plus diffuse (TZ2P+diff) basis. This basis set was formed by adding sets of diffuse functions to the TZ2P basis described above. The diffuse exponents used were $\alpha_s(O) = 0.0899$, $\alpha_p(O) = 0.054$, and $\alpha_s(H) = 0.0302$ (these diffuse exponents, like those used in the DZP+diff case, were derived as recommended in ref 22). The hydrogen s functions were scaled by a factor of 1.2 in all basis sets.

All stationary points were fully optimized within the given symmetry utilizing closed shell self-consistent field (SCF),[24] single and double
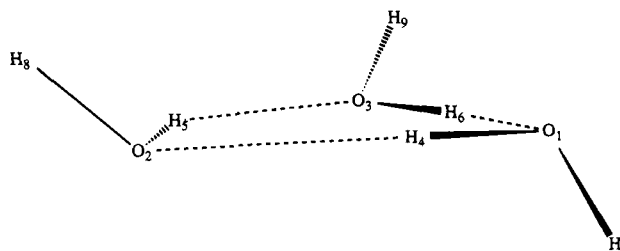

Figure 1. Water trimer minimum.

excitation configuration interaction (CISD),[25] and single and double excitation coupled cluster (CCSD)[26] analytic gradient techniques. Complete geometry optimizations were performed with all noted basis sets at the SCF level, but were limited to the DZP basis with the CISD method and to DZP and DZP+diff with the CCSD method. At the SCF level of theory, residual Cartesian and internal coordinates were less than 10^{-6} au, and at correlated levels less than 10^{-4} au. For each of the SCF stationary points harmonic vibrational frequencies were obtained using analytic second derivative techniques[27] in order to determine the nature of the stationary points. At the DZP+diff CCSD level of theory, the harmonic vibrational frequencies of the minimum were determined by the method of central finite differences. Single energy points were obtained using the larger basis sets (TZ2P and TZ2P+diff) with the CCSD method. The latter energies were computed at the optimized DZP+diff CCSD geometries.

At the correlated levels of theory (CISD and CCSD) only the valence electrons were correlated. Specifically, the three lowest doubly occupied molecular orbitals (O 1s-like) were kept doubly occupied (frozen core), and the three highest virtual orbitals (O 1s*-like) were deleted (frozen virtuals) in all cases. The numbers of walks (configurations) for the various basis sets were as follows: DZP, 234 955; DZP+diff, 406 351; TZ2P, 841 753; TZ2P+diff, 1 145 341. Note that, although the geometries of the planar and bowl structures were limited to C_{3h} and C_3 symmetries, respectively, the wave functions were obtained using C_s and C_1 symmetries. Thus, the C_3 bowl structure had in practice as many excitations in its CISD and CCSD wave functions as the C_1 stationary points, but the planar stationary point had only 124 291 walks in the DZP case and 217 207 walks in the DZP+diff case. In order to negate the lack of size consistency in the CISD case, the supermolecule technique was applied for comparison of monomer/trimer energies. In this case, the total energy of three separate water monomers was obtained by placing three optimized monomers 500 au apart.

Results

The five stationary points examined are depicted in Figures 1–5. The geometrical parameters for each structure at the various levels of theory applied are given in Tables 1 and 3–6. The harmonic vibrational frequencies and infrared intensities for the minimum as predicted by the SCF method with all basis sets are reported in Table 2 as are the harmonic vibrational frequencies predicted by the DZP+diff CCSD level of theory. For coordinate comparison, the geometrical parameters of the water molecule monomer as predicted by equivalent levels of theory are given in Table 7. Table 8 reports the total energy of

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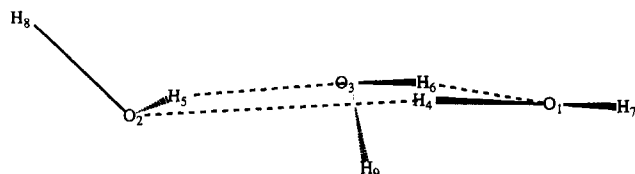
Figure 2. Water trimer flipping transition state.
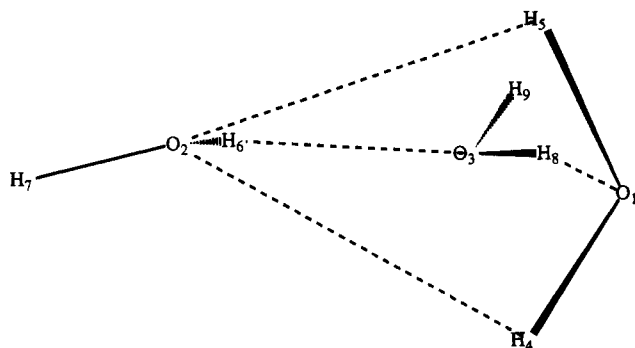
Figure 3. Water trimer internal rotation transition state.
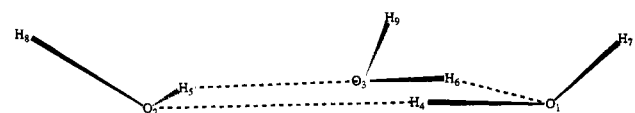
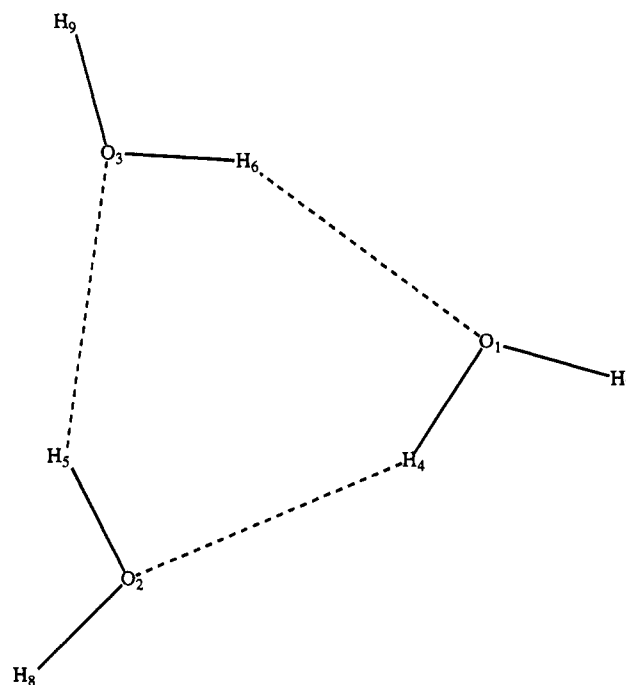**Figure 4.** Water trimer C_3 bowl structure.

Figure 5. Water trimer C_{3h} planar structure.

the stationary points and three separate water molecules. Table 9 reports relative energies. Zero point vibrational energies at various levels of theory for the minimum, the two transition states, and three separated water molecules are found in Table 10.

In the following discussion any reference to symmetry labeling of orbitals is meant to apply to the orbitals of the subunits as they would be labeled in the C_{2v} monomer case.

Discussion

Minimum. The minimum (equilibrium geometry) on the potential energy surface was found to be a ring structure of C_1 symmetry with two external hydrogens on one side of the

O—O—O plane and the third on the other side. Many other theoretical studies are in agreement with this prediction as are experimental results.[5,8-10]

None of the trimer H$\cdots$O distances are precisely equal, but two (H$_4\cdots$O$_2$ = 1.943 Å and H$_6\cdots$O$_1$ = 1.944 Å) are significantly shorter than the third (H$_5\cdots$O$_3$ = 1.970 Å). This difference is less pronounced in the O$\cdots$O distances where the difference between the largest and median O$\cdots$O distances is only 0.009 Å. Therefore the O$\cdots$O distance seems a poor guide in estimating relative hydrogen bond strengths, as the O—H$\cdots$O angle also plays a large part in determining this distance. Note that the O$_2$—H$_5\cdots$O$_3$ angle is the smallest of the three O—H$\cdots$O angles and serves to bring O$_2$ and O$_3$ atoms closer together. Note also that the difference in the two shortest distances (H$_4\cdots$O$_2$ and H$_6\cdots$O$_1$ vs O$_1\cdots$O$_2$ and O$_1\cdots$O$_3$) is slightly

Table 1. Geometrical Parameters for the Equilibrium Geometry of the Water Trimer[a]

	DZP SCF	DZP+diff SCF	TZ2P SCF	TZ2P+diff SCF	DZP CISD	DZP CCSD	DZP+diff CCSD
r(O$_1\cdots$O$_2$)	2.893	2.911	2.922	2.924	2.814	2.812	2.825
r(O$_1\cdots$O$_3$)	2.897	2.913	2.924	2.926	2.818	2.817	2.828
r(O$_2\cdots$O$_3$)	2.908	2.922	2.936	2.937	2.829	2.828	2.837
r(H$_4\cdots$O$_2$)	2.026	2.056	2.059	2.064	1.926	1.914	1.943
r(H$_5\cdots$O$_3$)	2.056	2.082	2.089	2.093	1.954	1.942	1.970
r(H$_6\cdots$O$_1$)	2.027	2.056	2.060	2.065	1.928	1.916	1.944
θ(O$_2$—H$_5$—O$_3$)	148.0	146.1	148.3	147.6	149.2	149.6	146.7
θ(O$_3$—H$_6$—O$_1$)	150.8	148.8	151.0	150.3	151.8	152.1	149.4
θ(O$_1$—H$_4$—O$_2$)	150.2	148.4	150.7	150.1	151.3	151.7	148.9
r(O$_1$—H$_4$)	0.953	0.953	0.947	0.947	0.968	0.977	0.976
r(O$_1$—H$_7$)	0.945	0.946	0.940	0.940	0.957	0.966	0.967
θ(H$_4$—O$_1$—H$_7$)	106.7	106.9	106.8	106.9	105.5	104.9	105.2
r(O$_2$—H$_5$)	0.953	0.953	0.947	0.947	0.967	0.976	0.976
r(O$_2$—H$_8$)	0.945	0.945	0.939	0.939	0.957	0.966	0.966
θ(H$_5$—O$_2$—H$_8$)	107.1	107.2	107.1	107.2	105.9	105.3	105.4
r(O$_3$—H$_6$)	0.953	0.953	0.947	0.947	0.968	0.977	0.977
r(O$_3$—H$_9$)	0.945	0.945	0.939	0.939	0.957	0.966	0.966
θ(H$_6$—O$_3$—H$_9$)	106.9	107.2	107.0	107.1	105.7	105.0	105.3
oop(H$_7$)	50.7	44.4	50.4	48.1	54.0	55.7	47.6
oop(H$_8$)	−41.5	−34.4	−42.2	−39.5	−47.1	−50.1	−41.0
oop(H$_9$)	−41.8	−33.5	−41.1	−38.0	−47.1	−49.7	−40.2

[a] Bond lengths in angstroms; bond angles in degrees. Atoms are numbered as in Figure 1.

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Table 2. Harmonic Vibrational Frequencies[a] and Infrared Intensities[b] in Parentheses for the Water Trimer Equilibrium Geometry (C_1 Symmetry)

DZP SCF	DZP+diff SCF	TZ2P SCF	TZ2P+diff SCF	DZP+diff CCSD
4235 (127)	4234 (130)	4212 (99)	4213 (103)	3957
4233 (125)	4233 (149)	4212 (130)	4212 (141)	3953
4229 (138)	4229 (156)	4207 (131)	4208 (134)	3951
4070 (301)	4072 (285)	4061 (276)	4062 (278)	3769
4066 (328)	4068 (315)	4056 (304)	4057 (307)	3762
4028 (7)	4038 (7)	4024 (7)	4027 (8)	3692
1793 (27)	1776 (8)	1799 (16)	1795 (11)	1720
1776 (181)	1754 (160)	1782 (155)	1775 (146)	1671
1768 (114)	1750 (131)	1777 (97)	1772 (102)	1667
810 (24)	741 (23)	766 (16)	742 (16)	941
635 (540)	614 (501)	598 (428)	592 (409)	664
515 (216)	481 (157)	492 (177)	480 (156)	536
415 (156)	392 (146)	393 (135)	386 (133)	443
325 (46)	314 (64)	312 (39)	309 (47)	356
314 (59)	305 (94)	300 (66)	298 (79)	331
222 (53)	207 (45)	214 (48)	208 (44)	264
194 (8)	184 (4)	179 (7)	176 (5)	208
169 (138)	166 (216)	167 (172)	165 (187)	195
162 (8)	151 (8)	148 (7)	145 (6)	186
154 (86)	144 (59)	145 (81)	142 (69)	177
133 (110)	122 (77)	136 (60)	132 (56)	170

[a] In cm^{-1}. [b] In km/mol.

accentuated by the fact that the $O_3-H_6\cdots O_1$ angle is a bit (0.5°) larger than the $O_1-H_4\cdots O_2$ angle.

The best explanation for these slight deviations from regularity lies simply in comparison between the dimer and the trimer. In the dimer, the $O-H\cdots O$ angle is close to linearity, and the optimum position for the free hydrogen of the proton-donating water is *trans* to the hydrogens of the proton acceptor. While the linearity is a factor of electrostatics *and* improved molecular orbital overlap, the *trans* conformation is driven mostly by electrostatics. In examination of the trimer we find two hydrogen bonds with approximate *trans* conformations ($H_4\cdots O_2$ and $H_6\cdots O_1$) and one with an approximate *cis* arrangement ($H_5\cdots O_3$). This explains the relative weakness of the $H_5\cdots O_3$ hydrogen bond. The external hydrogens of this particular interaction are in a position unfavorable for hydrogen bonding, thus this weaker bond is lengthened and the angle is lessened compared to the other bonds within the cyclic minimum.

Using these same criteria (bond length and bond angle) for comparison between the $H_4\cdots O_2$ and $H_6\cdots O_1$ bonds seems to bring a contradiction. The $H_4\cdots O_2$ bond is slightly shorter with the $O_3-H_6\cdots O_1$ angle is a bit wider. While no comment as to the relative strengths of the $H_4\cdots O_2$ and $H_6\cdots O_1$ linkages is intended, note that geometrical considerations easily explain the widening of the $O_3-H_6\cdots O_1$ angle. Widening of the $O_1-H_4\cdots O_2$ angle would involve stretching the $H_5\cdots O_3$ bond (if the $H_8-O_2-H_5$ orientation remains the same). However, it is seen that the $H_9-O_3-H_6$ subunit can rotate about the monomer axis, thereby improving the $O_3-H_6\cdots O_1$ bond angle while degrading only the $H_5\cdots O_3$ attack angle.

An earlier paper focused on the OH vibrational frequency shift,[15] but the symmetry and level of theory restrictions present severely limited the accuracy of that study. At the DZP+diff CCSD level of theory the predicted harmonic vibrational frequencies of the water monomer are as follows: $\nu_1 = 3864$ cm^{-1}, $\nu_2 = 1644$ cm^{-1}, and $\nu_3 = 3985$ cm^{-1}. By comparing these frequencies with those listed in Table 2, we find three different shifts for each harmonic: $\Delta\nu_1 = -95, -102$, and -172 cm^{-1}; $\Delta\nu_2 = 76, 27$, and 23 cm^{-1}; $\Delta\nu_3 = -28, -32$, and -34 cm^{-1}. These values stand in sharp contrast to the $\Delta\nu_{OH} = -230$ cm^{-1} as predicted by the earlier authors.[15]

Flipping Transition State. The next lowest energy stationary point identified on the potential energy surface is a C_1 structure with one external hydrogen atom above the O—O—O plane, one below, and one approximately coplanar. Through the use of analytic second derivatives at the SCF level this stationary point was shown to be a transition state corresponding to flipping motion of one external hydrogen across the O—O—O plane. No vibrational frequency analysis was completed at higher levels of theory, but the energy was maximized along the out-of-plane coordinate of H_7 and minimized along all other coordinates. Thus, with much confidence it is predicted that this stationary point continues to be the transition state for the flipping motion at higher levels of theory.

For the flipping transition state a marked difference is found between each of the $H\cdots O$ bond lengths. Again, comparison to the equilibrium dimer configuration provides helpful insight in explaining the differences. The only hydrogen bond for which the external hydrogens are in a *trans* arrangement is the

Table 3. Geometrical Parameters for the Flipping Transition State of the Water Trimer[a]

	DZP SCF	DZP+diff SCF	TZ2P SCF	TZ2P+diff SCF	DZP CISD	DZP CCSD	DZP+diff CCSD
$r(O_1\cdots O_2)$	2.889	2.910	2.920	2.922	2.808	2.805	2.820
$r(O_1\cdots O_3)$	2.887	2.908	2.918	2.922	2.804	2.802	2.820
$r(O_2\cdots O_3)$	2.906	2.920	2.933	2.934	2.831	2.832	2.841
$r(H_4\cdots O_2)$	2.042	2.073	2.079	2.084	1.944	1.932	1.963
$r(H_5\cdots O_3)$	2.025	2.051	2.056	2.060	1.927	1.916	1.938
$r(H_6\cdots O_1)$	2.047	2.075	2.081	2.088	1.951	1.942	1.975
$\theta(O_2-H_5-O_3)$	152.9	150.7	153.2	152.5	154.4	155.1	152.6
$\theta(O_3-H_6-O_1)$	146.2	145.2	146.6	146.2	146.0	145.8	143.7
$\theta(O_1-H_4-O_2)$	147.2	145.7	147.1	146.7	147.6	147.7	145.2
$r(O_1-H_4)$	0.953	0.953	0.946	0.946	0.967	0.975	0.975
$r(O_1-H_7)$	0.944	0.945	0.939	0.939	0.956	0.964	0.965
$\theta(H_4-O_1-H_7)$	107.8	107.8	107.8	107.8	107.1	106.6	106.5
$r(O_2-H_5)$	0.954	0.953	0.947	0.947	0.968	0.977	0.977
$r(O_2-H_8)$	0.945	0.945	0.940	0.940	0.957	0.966	0.967
$\theta(H_5-O_2-H_8)$	106.6	106.9	106.7	106.8	105.3	104.6	105.0
$r(O_3-H_6)$	0.952	0.952	0.946	0.946	0.966	0.974	0.975
$r(O_3-H_9)$	0.946	0.946	0.940	0.940	0.958	0.966	0.967
$\theta(H_6-O_3-H_9)$	106.6	106.9	106.7	106.8	105.3	104.6	105.0
oop(H_7)	1.8	0.3	0.6	0.1	2.2	2.3	0.7
oop(H_8)	−50.1	−42.4	−49.4	−46.4	−54.3	−56.5	−47.2
oop(H_9)	51.2	43.3	50.5	47.7	55.9	58.4	48.4

[a] Bond lengths in angstroms; bond angles in degrees. Atoms are numbered as in Figure 2.

Table 4. Geometrical Parameters for the Internal Rotation Transition State of the Water Trimer[a]

	DZP SCF	DZP+diff SCF	TZ2P SCF	TZ2P+diff SCF	DZP CISD	DZP CCSD	DZP+diff CCSD
$r(O_1\cdots O_2)$	2.979	3.019	3.054	3.074	2.878	2.867	2.909
$r(O_1\cdots O_3)$	2.920	2.930	2.945	2.942	2.851	2.854	2.860
$r(O_2\cdots O_3)$	2.913	2.934	2.945	2.948	2.834	2.833	2.850
$r(H_4\cdots O_2)$	2.600	2.653	2.686	2.711	2.483	2.464	2.534
$r(H_5\cdots O_2)$	2.643	2.694	2.723	2.756	2.519	2.494	2.555
$r(H_6\cdots O_3)$	2.034	2.069	2.070	2.077	1.941	1.931	1.964
$r(H_8\cdots O_1)$	2.055	2.080	2.080	2.079	1.961	1.952	1.973
$\theta(O_2-H_6\cdots O_3)$	152.6	150.3	153.1	152.5	152.8	152.8	150.0
$\theta(O_3-H_8\cdots O_1)$	150.2	147.9	151.1	150.8	152.1	152.8	149.9
$\theta(O_1-H_4\cdots O_2)$	104.3	103.5	104.0	103.7	104.5	104.7	102.9
$\theta(O_1-H_5\cdots O_2)$	101.4	100.8	101.5	100.7	102.2	102.7	101.5
$r(O_1-H_4)$	0.948	0.948	0.942	0.943	0.961	0.970	0.970
$r(O_1-H_5)$	0.948	0.948	0.942	0.942	0.960	0.969	0.970
$\theta(H_4-O_1-H_5)$	103.6	103.9	104.2	104.4	101.7	100.9	101.4
$r(O_2-H_6)$	0.952	0.952	0.946	0.946	0.966	0.974	0.975
$r(O_2-H_7)$	0.945	0.945	0.939	0.939	0.956	0.965	0.966
$\theta(H_6-O_2-H_7)$	106.9	106.9	106.9	107.0	105.9	105.4	105.2
$r(O_3-H_8)$	0.953	0.953	0.947	0.947	0.967	0.976	0.976
$r(O_3-H_9)$	0.945	0.945	0.939	0.939	0.957	0.966	0.966
$\theta(H_8-O_3-H_9)$	107.3	107.6	107.3	107.4	106.0	105.2	105.6
oop(H_7)	11.3	6.8	11.9	10.1	11.1	11.2	8.1
oop(H_9)	−35.6	−21.7	−35.0	−30.5	−44.3	−48.0	−36.4
$\tau(O_3H_8O_1H_4)$	49.8	48.3	47.1	46.3	48.1	47.7	44.3
$\tau(O_3H_8O_1H_5)$	−55.0	−57.5	−58.3	−59.6	−54.5	−53.9	−58.7

[a] Bond lengths in angstroms; bond angles in degrees. Atoms are numbered as in Figure 3.

Table 5. Geometrical Parameters for the C_3 Bowl Structure of the Water Trimer[a]

	DZP SCF	DZP+diff SCF	TZ2P SCF	TZ2P+diff SCF	DZP CISD	DZP CCSD	DZP+diff CCSD
$r(O_1\cdots O_3)$	2.898	2.911	2.928	2.928	2.825	2.826	2.833
$r(H_4\cdots O_3)$	2.044	2.072	2.079	2.084	1.950	1.940	1.964
$\theta(O_1-H_4\cdots O_3)$	148.3	146.0	148.5	147.7	149.7	150.2	147.0
oop(H_7)	32.4	22.2	33.2	29.3	41.1	45.0	34.8
$r(O_1-H_4)$	0.953	0.953	0.947	0.946	0.967	0.976	0.976
$r(O_1-H_7)$	0.945	0.945	0.939	0.939	0.957	0.965	0.966
$\theta(H_4-O_1-H_7)$	107.2	107.4	107.2	107.3	106.0	105.3	105.5

[a] Bond lengths in angstroms; bond angles in degrees. Atoms are numbered as in Figure 4.

Table 6. Geometrical Parameters for the C_{3h} Planar Structure of the Water Trimer[a]

	DZP SCF	DZP+diff SCF	TZ2P SCF	TZ2P+diff SCF	DZP CISD	DZP CCSD	DZP+diff CCSD
$r(O_1\cdots O_2)$	2.879	2.902	2.913	2.917	2.800	2.799	2.823
$r(H_4\cdots O_2)$	2.041	2.072	2.082	2.088	1.950	1.944	1.980
$\theta(O_1-H_4\cdots O_2)$	145.9	144.8	145.7	145.4	145.6	145.3	143.5
$r(O_1-H_4)$	0.952	0.952	0.946	0.946	0.965	0.973	0.974
$r(O_1-H_7)$	0.944	0.945	0.939	0.939	0.956	0.964	0.965
$\theta(H_4-O_1-H_7)$	107.6	107.6	107.6	107.6	106.8	106.2	106.2

[a] Bond lengths in angstroms; bond angles in degrees. Atoms are numbered as in Figure 5.

Table 7. Geometrical Parameters for the Water Monomer[a]

	DZP SCF	DZP+diff SCF	TZ2P SCF	TZ2P+diff SCF	DZP CCSD	DZP+diff CCSD
$r(O-H)$	0.946	0.946	0.940	0.940	0.966	0.967
$\theta(H-O-H)$	106.3	106.4	106.4	106.4	104.1	104.1

[a] Bond lengths in angstroms; bond angles in degrees.

$H_5\cdots O_3$ bond, thus explaining its short bond length and wide bond angle. Both of the other hydrogen bonds are intermediate between *cis* and *trans*. The significant difference in the two remaining hydrogen bonds lies in the attack angle of the hydrogens to the oxygens. H_6 must attack O_1 in approximately the same plane as H_4 and H_7. This eliminates essentially all the interaction between the b_2 bonding orbital of the $H_9-O_3-H_6$ monomer and the b_1 nonbonding orbital of the $H_7-O_1-H_4$ subunit, limiting the interaction to only the a_1 nonbonding orbital. H_4, however, is still capable of attacking both the b_1 and a_1 nonbonding orbitals of the $H_8-O_2-H_5$ subunit, and thus

a stronger bond exists between H_4 and O_2 than does between H_6 and O_1.

Internal Rotation Transition State. Also on the potential energy surface was found a stationary point geometrically arranged in such a way that two water subunits donate one hydrogen each for hydrogen bonding while the third donates both of its hydrogens in a bifurcated manner. This stationary point was identified as a transition state at the SCF level of theory by the analytic second derivative harmonic vibrational frequency analysis. The one imaginary vibrational frequency corresponds to rotation of the $H_5-O_1-H_4$ monomer about its

Table 8. Total Energies[a] for Each of the Stationary Points

level of theory	3 × H$_2$O	minimum	flipping	rotation	bowl	planar
DZP SCF	−228.139 652	−228.162 453	−228.162 242	−228.159 909	−228.161 152	−228.160 836
DZP+diff SCF	−228.149 732	−228.170 582	−228.170 459	−228.168 043	−228.169 747	−228.169 630
TZ2P SCF	−228.183 443	−228.202 460	−228.202 236	−228.200 033	−228.201 372	−228.200 990
TZ2P+diff SCF	−228.186 084	−228.204 233	−228.204 051	−228.201 798	−228.203 299	−228.203 039
DZP CISD	−228.675 203[b]	−228.703 149	−228.702 695	−228.700 052	−228.701 354	−228.700 302
DZP CISD+Q	−228.738 694[b]	−228.767 130	−228.766 567	−228.763 956	−228.765 203	−228.763 803
DZP CCSD	−228.750 730	−228.779 252	−228.778 646	−228.776 127	−228.777 296	−228.775 741
DZP+diff CCSD	−228.770 533	−228.797 191	−228.796 717	−228.793 909	−228.795 841	−228.794 522
TZ2P//DZP+diff CCSD	−228.909 905	−228.934 575	−228.934 118	−228.931 395		
TZ2P+diff//DZP+diff CCSD	−228.914 908	−228.938 492	−228.938 075	−228.935 246		

[a] In hartrees. [b] CISD results were obtained using the supermolecule approach.

Table 9. Water Trimer Relative Energies[a] with Respect to the Equilibrium Geometry

level of theory	flipping	rotation	bowl	planar	3 × H$_2$O
DZP SCF	0.13	1.60	0.82	1.01	14.31
DZP+diff SCF	0.08	1.59	0.52	0.60	13.08
TZ2P SCF	0.14	1.52	0.68	0.92	11.93
TZ2P+diff SCF	0.11	1.53	0.59	0.75	11.39
DZP CISD	0.28	1.94	1.13	1.79	17.54
DZP CISD+Q	0.35	1.99	1.21	2.09	17.84
DZP CCSD	0.38	1.96	1.23	2.20	17.90
DZP+diff CCSD	0.30	2.06	0.85	1.67	16.73
TZ2P//DZP+diff CCSD	0.29	2.00			15.48
TZ2P+diff//DZP+diff CCSD	0.26	2.04			14.80

[a] In kcal/mol.

Table 10. Zero Point Vibrational Energies[a,b]

	DZP SCF	DZP+diff SCF	TZ2P SCF	TZ2P+diff SCF
minimum	48.96	48.57	48.58	48.47
flipping TS[c]	48.71	48.36	48.31	48.21
(relative to min)	−0.25	−0.22	−0.27	−0.26
rotation TS	48.41	48.02	47.98	47.87
(relative to min)	−0.55	−0.55	−0.60	−0.60
3 × monomer	43.63	43.49	43.50	43.46
(relative to min)	−5.33	−5.08	−5.08	−5.01

[a] ZPVE at the DZP+diff CCSD level of theory: 46.63 kcal/mol. [b] In kcal/mol. [c] Transition state.

approximate C_2 axis. This then is the transition state for one monomer switching its internal and external hydrogens.

In this conformer of the trimer no pair of monomers has the optimum *trans* configuration. In order for the b$_2$ bonding orbital of the H$_5$−O$_1$−H$_4$ monomer to overlap properly with the b$_1$ nonbonding orbital of the H$_7$−O$_2$−H$_6$ monomer, H$_7$ must be approximately coplanar with the oxygens. This limits the interaction between H$_6$ and O$_3$ because the two water monomers are prevented from adopting a *trans* conformation.

C$_3$ Bowl Structure. Another stationary point on the trimer potential energy surface examined in this study was a structure in which all three external hydrogens were on the same side of the O−O−O plane. The geometry optimization for this stationary point was completed with a constraining C_3 axis of symmetry. The harmonic vibrational frequency analysis for this structure yielded a degenerate pair of imaginary frequencies (e symmetry) at the DZP, DZP+diff, and TZ2P+diff SCF levels of theory. However, at the TZ2P SCF level it was found to be a minimum. The degenerate pair of vibrations which are imaginary at most levels of theory for which frequencies were determined (DZP SCF, 73i; DZP+diff SCF, 95i; TZ2P+diff SCF, 37i) correspond to out-of-plane bend motions of the external hydrogens. At the TZ2P SCF level, this same degenerate mode has a very low but real frequency of 31 cm^{-1}.

The C_3 axis of this stationary point prevents all of the hydrogen bonds from adopting any kind of *trans* relationship. All three subunits must have the same orientation. This explains the hydrogen bond length of 1.964 (DZP+diff CCSD), which places the hydrogen bonds of this stationary point among the weaker hydrogen bonds of the stationary points already discussed.

Note that the effect of the diffuse functions on the optimal geometry is always to lessen the H−O−O−O out-of-plane angle. This is because with the addition of diffuse functions not only is the BSSE reduced, but also the b$_1$ nonbonding orbital of each subunit need not be rotated as far in order to interact significantly. The nuclear repulsion is also lessened when the external hydrogens are further away from each other (at smaller out-of-plane angles).

Because no vibrational frequency analysis was carried out for this structure at higher levels of theory, the nature of this stationary point is, at least slightly, in question. The fact that it is a minimum at the TZ2P SCF level of theory casts some doubt on the Hessian index as predicted by the other basis sets, but the agreement of the other basis sets (including one larger than TZ2P) argues that this structure is not a minimum.

C$_{3h}$ Planar Structure. The final stationary point studied in this work was of C_{3h} symmetry. All atoms were in the plane of symmetry. At all levels of theory for which vibrational frequencies were predicted this was a stationary point of Hessian index 3. The three imaginary modes all corresponded to external hydrogen out-of-plane motions. The a″ mode (115i at the TZ2P+diff SCF level) corresponded to all external hydrogens moving to the same side of the O−O−O plane, and the degenerate pair (181i at the TZ2P+diff SCF level) corresponded to the 2, −1, −1 combination of the external hydrogen out-of-plane bends and the 0, 1, −1 combination.

The hydrogen bond lengths of the C_{3h} planar stationary point are the longest of the hydrogen bonds found in this study except for the bifurcated bonds of the rotation transition state. Each bond is limited to interacting only with the a$_1$ nonbonding orbital of the proton acceptor, and because each bond is weaker, their cooperative effects are also smaller.

Potential Energy Hypersurface. The potential energy surface of the water trimer along all external hydrogen H−O−O−O out-of-plane coordinates is very flat. Note that at the least favorable orientation for the external hydrogens (planar) the energy difference with respect to the equilibrium at the highest level of theory applied (DZP+diff CCSD in this case) is only 1.67 kcal/mol. The bowl structure stationary point energy is only 0.85 kcal/mol above the minimum at the same level of theory. The flipping transition state was studied at higher levels of theory and was found to be only 0.26 kcal/mol above the minimum at the TZ2P+diff//DZP+diff CCSD level. From Table 10, it is obvious that ZPVE considerations place the minimum and the flipping transition state at approximately

the same energy (if 0.26 kcal/mol was not close enough already). As our frequency predictions are limited both by level of theory and the harmonic approximation, it must be conceded that these results are inconclusive as to whether the water trimer even has bound vibrational levels along this flipping coordinate. Certainly, we agree with Pugliano and Saykally[10] that enantiomers should be rapidly interconverted (note that their vibration–rotation–tunneling band was observed for the perdeuterated trimer $(D_2O)_3$, not $(H_2O)_3$ which we report on here).

Along the internal rotation coordinate the potential energy surface is steeper, but still far from mountainous. At the highest level of theory applied (TZ2P+diff//DZP+diff (CCSD) the internal rotation transition state lies 2.04 kcal/mol above the minimum. The ZPVE lowers this difference by 0.55–0.60 kcal/mol depending on the basis set used. It is possible that at higher levels of theory this ZPVE difference would change, but surely not so much that this coordinate would lack bound vibrational levels. The small energy separation between the minimum and the transition state along the rotation coordinate implies that quantum tunneling may be possible for this motion.

As one glances down the table of relative energies, it is hard not to notice the wide range of predicted classical binding energies (three waters relative to the minimum). The predicted values range from 11.39 kcal/mol at the TZ2P+diff SCF level to 17.90 kcal/mol at the DZP CCSD level of theory. In the end, it is a bit discouraging that for the classical binding energy the best agreement with the result from the highest level (TZ2P+diff//DZP+diff CCSD) of theory applied is that predicted by the lowest level (DZP SCF) of theory applied. If the sole purpose of this paper was to obtain the classical binding energy of the water trimer, then that observation would be disheartening indeed. But the relationship between the highest and lowest levels of theory does not hold through the rest of the relative energies, and the focus of this paper is the potential energy surface. Furthermore, the DZP SCF results for the classical binding energy should not be taken as correct, but rather as fortuitous. Results from the DZP basis are, in this case, replete with BSSE, and the SCF method is incapable of including dispersion forces. It is that these two rather large errors cancel at the DZP SCF level that causes the agreement with the TZ2P+diff//DZP+diff CCSD results to be good.

Conclusions

A detailed study of the potential energy surface of the water trimer at high levels of theory has been completed. Located on the potential energy surface were one minimum, two transition states, and two stationary points of higher Hessian index. The two transition states correspond to external hydrogen flipping from one side of the O–O–O plane to the other and to subunit rotation, exchanging hydrogen-bound and external protons. The other two stationary points are a bowl structure of C_3 symmetry and a planar structure of C_{3h} symmetry. The Hessian indices of these two stationary points are 2 and 3, respectively, although there is some doubt as to the Hessian index of the bowl structure.

The potential energy surface of the water trimer is quite flat. Without the inclusion of ZPVE corrections, the flipping transition state lies only 0.26 kcal/mol above the minimum at the highest level of theory applied (TZ2P+diff//DZP+diff CCSD). At this level of theory the internal rotation transition state lies 2.04 kcal/mol above the minimum. The other two stationary points were not studied at such a high level, but at the DZP+diff CCSD level the bowl structure lies 0.85 kcal/mol above the minimum, and the planar structure lies 1.67 kcal/mol above the minimum. The classical binding energy at the TZ2P+diff//DZP+diff CCSD level of theory is 14.80 kcal/mol.

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