A Comparison of the Behavior of Functional/Basis Set Combinations for Hydrogen-Bonding in the Water Dimer with Emphasis on Basis Set Superposition Error

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Abstract

We evaluate the performance of nine functionals (B3LYP, M05, M05-2X, M06, M06-2X, B2PLYP, B2PLYPD, X3LYP, B97D and MPWB1K) in combination with 16 basis sets ranging in complexity from 6-31G(d) to aug-cc-pV5Z for the calculation of the H-bonded water dimer with the goal of defining which combinations of functionals and basis sets provide a combination of economy and accuracy for H-bonded systems. We have compared the results to the best non-DFT molecular orbital calculations and to experimental results. Several of the smaller basis sets lead to qualitatively incorrect geometries when optimized on a normal potential energy surface (PES). This problem disappears when the optimization is performed on a counterpoise corrected PES. The calculated ΔE's with the largest basis sets vary from -4.42 (B97D) to -5.19 (B2PLYPD) kcal/mol for the different functionals. Small basis sets generally predict stronger interactions than the large ones. We found that, due to error compensation, the smaller basis sets gave the best results (in comparison to experimental and high level non-DFT MO calculations) when combined with a functional that predicts a weak interaction with the largest basis set. Since many applications are complex systems and require economical calculations, we suggest the following functional/basis set combinations in order of increasing complexity and cost: 1) D95(d,p) with B3LYP, B97D, M06 or MPWB1k; 2) 6-311G(d,p) with B3LYP; 3) D95++(d,p) with B3LYP, B97D or MPWB1K; 4) 6-311++G(d,p) with B3LYP or B97D; and 5) aug-cc-pVDZ with M05-2X, M06-2X or X3LYP.

The hydrogen bond plays a fundamental role within chemistry and biochemistry. Many self-assembling systems such as nucleic acids, proteins and nanomaterials owe much of their stabilities to H-bonds. Consequently, many research groups that use quantum mechanical methods to study these systems (including our own) depend upon accurate, yet economical, molecular orbital (MO) methods to calculate hydrogen bonding properties. Density functional theory (DFT) has become the method of choice for studying large systems due to the balance of accuracy and efficiency. The B3LYP functional has generally been the method of choice for H-bonding interactions in self-assembling and biochemical materials such as peptides in studies by our laboratory[1-8] and several others (references are representative, but not exhaustive).[9-23] However, several recent reports have found fault with B3LYP as applied to many chemical problems,[24] most of which do not involve H-bonding. Also, many older functionals poorly describe non-bonding interactions but do describe H-bonds well.[25,26] In fact several reports have indicated that B3LYP and other similar functionals describe H-bonding systems reasonably well, particularly when properly corrected for basis set superposition error by performing geometric optimizations on a

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counterpoise (CP) corrected potential energy surface.ield25,27,28 Nevertheless, as new functionals are introduced, the choice of which to use becomes more complex, especially when combined with the many basis sets available and the CP-correction. In this paper, we shall focus on the calculation of the properties of the water dimer using a wide variety of functional/basis set combinations with and without CP-corrections (both single point and optimized on a CP-corrected surface). Our focus shall be upon which methods might provide acceptable accuracy for large systems without excessive computational burden. We note that one cannot assume that methods that work well for water dimer (or any specific models) will work equally well elsewhere. However, one should be suspicious of applying methods that do not properly describe the water dimer.

Among the several new functionals introduced in the last few years, we shall concentrate on those developed by Truhlar (M05, M05-2X, M06, M06-2X, and MPWB1K), Grimme (B2PLYP, B2PLYPDand B97D), and Goddard (X3LYP) in addition to B3LYP. Reports assessing the accuracy of these functionals for describing a wide variety of chemical phenomena, including some aspects of hydrogen bonding have appeared in the literature. [24,26,29] For example, Truhlar and coworkers evaluated the ability of various functionals to predict the properties of the possible isomeric $(H_2O)_6$ aggregates.[30] In general, these reports focus upon accuracies of functionals with basis sets too large to be practical for large systems. Consequently, these reports do not clarify which combinations of functional and basis set will yield reasonable accuracy for hydrogen bonding properties of large chemical systems (hundreds of atoms). We have previously tested a variety of levels of theory (methods and basis sets) for their ability to calculate H-bonding properties,[27,28] and another very recent report containing similar information has appeared. [31] Truhlar has tested many functionals for non-bonding properties, including many H-bonds.[32] We have shown that accurate H-bonding properties as calculated by high levels of theory can be reproduced by moderate to low levels of theory when structures were optimized on a CP corrected potential energy surface (PES). The advantage of the CP optimization procedure (CP-OPT) lies in its ability to obtain higher quality geometrically optimized structures using smaller basis sets than possible with an optimization on a PES not corrected for BSSE. As the basis set used becomes more complete, BSSE disappears, so the utility of the CP-OPT procedure becomes attenuated. We shall concentrate on the effects of BSSE and the CP correction upon the applicability of these functionals used with moderate basis sets to the prediction of the properties of H-bonds rather than repeat the analyses of others. While BSSE can affect the results of all DFT calculations,[33] it has a relatively large effect upon both the energies and geometries of H-bonding systems calculated with basis sets whose completeness become restricted due to the size and complexity of the chemical systems studied.

We have chosen the water dimer as our model system for several reasons. Firstly, it has been exhaustively studied by experimental and theoretical methods. Secondly, the potential energy surface is rather flat, so that its geometry will be very sensitive to the methods used. The larger water aggregates, such as the isomeric $(H_2O)_6$'s lie in much deeper minima on the PESs, making their geometries less sensitive to the methods of calculation used. We report the energies and geometrical features of the water dimer calculated by several DFT methods and basis sets, and compare these experimental and computational data. We compare and evaluate the H-bonding energies and geometries as calculated on the normal and CP corrected PESs, as well as those predicted by performing single point CP corrections on geometries optimized without the CP optimization procedure. Ultimately, we recommend a level of theory with an appropriate balance of accuracy and efficiency for the study of large H-bonding systems.

Computational Details

We performed molecular orbital (MO) calculations with the GAUSSIAN 09[34] suite of programs using the following functionals: B3LYP,[35-38] X3LYP,[39] M05,[40,41] M05-2X,[41] M06,[42] M06-2X,[42] MPWB1K, [43] B2PLYP,[44] B2PLYPD,[45] and B97D.[46] Two of these (B2PLYPD and B97D) contain an empirical correction designed to include dispersion interactions. We tested each functional with the following sixteen basis sets: 6-31G(d), 6-31G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311++G(3df,2p), D95(d,p), D95++(d,p), cc-pVnZ, and aug-cc-pVnZ a0 (n = D, T, Q, and 5). We optimized the geometries in all 12 internal degrees of freedom with every combination of functional and basis set used on both normal and counterpoise corrected (CP-OPT) potential energy surfaces,[47] followed by vibrational calculations using the harmonic method (the default in GAUSSIAN 09) to ascertain that the geometries correspond to true minima. In addition, we calculated the single point (a posteriori) CP corrections on the conventionally optimized structures (which are not minima on the CP-corrected surfaces).

Results

As expected, the energetic and geometric differences between the normally optimized dimers and those optimized on the CP-corrected PES generally become smaller as the basis set improves. These differences become smallest for the best basis sets (Table 1), but can still be substantial even for aug-cc-pV5Z (from 0.005 kcal/mol for MPWB1K and 0.008 kcal/mol for B3LYP and X3LYP to as much as 0.207 kcal/mol for M06). For moderate sized basis sets, this difference can be substantial and varies with the functional used, as well as, the basis set. The results for the CP-optimized dimers using moderate basis sets are always closer to those for the better basis sets than those for normal optimizations.

Interaction energies, ΔE's

For each combination of functional and basis set, we calculated the interaction energy three different ways: 1) optimization on the CP-corrected PES (CP-OPT); 2) optimization on the 'normal' (uncorrected) PES; and 3) optimization on the 'normal' PES followed by single point energy evaluation, a posteriori counterpoise correction (CP-SP). Table 1 collects the best interaction energies for the dimer using the most complete basis set with these three methods for each of the functionals considered. The data show a variation of about 0.8 kcal/mol (from -4.42 for B97D with CP-SP to -5.24 kcal/mol for uncorrected B2PLYPD) even for such a large basis set as aug-cc-pV5Z. Oddly, the two functionals tested that include the empirical dispersion corrections provide the extreme high and low values for the ΔE. Tables 2-4 displays the interaction energy for each combination of functional and basis set using each of these three methods.

Optimized geometries

Tables 5 and 6 displays the optimized O...O and O...H distances for the dimer calculated on the uncorrected PES's. Optimization with the larger basis sets gives the qualitatively correct water dimer geometry (figure 1A). However, some combinations of functional and basis sets yield geometries (figure 1B) containing two hydrogen bonds. Some of these optimizations converged to a transition-state (one imaginary frequency) resembling the 1A structure. Table entries in bold typeface indicate parameters for structures with these (1B) geometries. Only two of the functionals we studied (B2PLYP and MPWB1K) produce the figure 1A geometry for all basis sets used here. The 6-31G(d) basis leads to anomalous geometries with eight of the ten functionals used, the cc-pVDZ, and 6-31G(d,p) basis sets lead to such geometries with six and the 6-311G(d,p) basis sets with five different functionals. D95(d,p) is the smallest basis set to be free of this anomaly with all functionals tested. When optimized on a

CP-corrected surface (see Tables 7 and 8), all anomalous geometries encountered disappear, indicating that these anomalies are due to BSSE. We have previously reported similar situations.[48,49] For those combinations which give the qualitatively correct structure (A in figure 1) the O...O distance increases upon optimization on the CP-corrected PES, as expected.[27]

DISCUSSION

We shall compare the present results with both high level molecular orbital (MO) calculations that do not use DFT (Table 9) and experimental results (Table 10).

Comparison with high level MO calculations

Published calculated binding energies using various high level MO methods vary from -4.88 to -5.18 kcal/mol,[50-57] with -4.9 designated as the 'MP2 limit'. The interaction energies calculated with CP-OPT using five of the ten functionals considered with the largest basis set fall within the (approximately same) range of -4.92 to -5.19 kcal/mol. Without CP-OPT, only three fall within this range without CP and the same five with SP-CP. Xantheas reported -4.88 and -5.01 for the MP2/aug-cc-pV5Z (the largest basis set used here) with and without CP-OPT, respectively. The CP-OPT interaction energy calculated with X3LYP/aug-cc-pV5Z (-4.92 kcal/mol) comes closest to Xantheas's CP-OPT value.

The O...O distance for the optimized geometries vary from 2.886 to 2.925 Å for the same set of calculations (Table 9), while those calculated here with aug-cc-pV5Z vary from 2.893 to 2.922 Å when CP-OPT is used and from 2.883 to 2.919 when without CP-OPT. We do not see any correlation between the interaction energies and the O...O distances. While the functional with strongest interaction energy (B2PLYPD) does predict the shortest O...O distance, the O...O distance calculated with the other functionals present no correlation.

Comparison with experimental results

For a long time the generally accepted experimental value for the enthalpy of interaction for the water dimer was -3.59 ± 0.5 kcal/mol.[58] Several older and more recent reports suggest different values[59-67] (Table 10). However, the enthalpy of interaction cannot be directly determined by a MO or DFT calculation. The interaction *energy* determined from such a calculation must be converted to an *enthalpy* of interaction through a vibrational analysis performed on the calculated potential energy surface. Clearly, corrections can be made either to transform the experimental ΔH values to the anticipated theoretical ΔE's, or from the calculated theoretical ΔE values to the corresponding expected experimental ΔH's. Since some assumptions must be made to make these corrections which can affect them, we have chosen to present the theoretical results (i.e., ΔE rather than ΔH). Hence the experimentally measured ΔH's of interaction have been converted to ΔE's using some kind of vibrational analyses by the authors of the references cited (Table 10). The 'experimental' ΔE's range from -4.85 to -5.44 kcal/mol. The largest value comes from Curtis and Blander[58] but has a published uncertainty of +/- 0.7 kcal/mol. Klein, et al used the same enthalpy measurement to get a ΔE of -5.4 but reduced the uncertainty to +/-0.2 kcal/mol.[68] Only this last value does not agree with the 'MP2 limit' of -4.9 kcal/mol[56,69] within the limits of the published uncertainties. Thus, the best calculated and experimental values for ΔE agree reasonably well. Of the functionals that we tested, X3LYP gives the value closest to -4.9 kcal/mol, and three others (M06-2X, M05, and B2PLYP) predict values within 0.2 kcal/mol of this value.

Due to the relatively high anharmonicity of the water dimer vibrations, the measured O...O distance (which corresponds to the maximum amplitude of the zero-point vibration that separates the waters) does not correspond to the minimum O...O distance on the PES. In

order to obtain the O...O distance that corresponds to the minimum on a calculated PES, one needs once again to perform a vibrational analysis. Three of the four measured O...O distances[66,67,70] in Table 10 cluster around 2.98 Å. The fourth value is 2.94 +/- 0.03 Å. After correction for the anharmonicity, the three clustered values predict a minimum on the PES at about 2.95 Å, while the outlier predicts 2.924 Å. As seen from Table 9, all of the high level MO optimized structures predict O...O distances considerably shorter than the 2.95 Å value and only two agree with the 2.924 Å value. Similarly, one sees from Table 1 that the O...O distance calculated using CP-OPT and the aug-cc-pV5Z basis set with almost all functionals are considerably shorter than 2.95 Å (B97D predicts the largest value, 2.94), while only two functionals (M05 and B3LYP) predict O...O distances close to the 2.924 Å value. Without CP-OPT all of the calculated distances are shorter, thus, further in disagreement with the experimental reports.

The effect of basis sets

Many research groups, including our own, use DFT to calculate the energies and structures of large systems including those important to biochemical studies that involve H-bonding. The size of these systems precludes the use of basis sets approaching the complexity of aug-cc-pV5Z. How small a basis set can one use while still expecting reasonably accurate results for the H-bonds?

The qualitatively anomalous geometries (B in figure 1) that result from optimization on an uncorrected PES for certain functional/basis set combinations (see above) revert to the those of A in figure 1 when optimized on the CP-corrected PES. These data suggest that the functional/basis sets mentioned above might be inappropriate for calculations involving H-bonds. These combinations should certainly be used with caution. However, most H-bonds in large systems are more geometry constrained, and /or stronger than the H-bond in gas phase water dimer. Thus, their H-bonding PES's are not so flat as that of the water dimer, so their minima will be better defined.

The Effect of CP correction

The CP-OPT procedure greatly improves the performance of all basis sets relative to aug-cc-pV5Z for the calculation of interaction energies and geometries. The smaller basis sets, which have the most BSSE improve the most (and the geometrical anomalies disappear). One notes that CP-SP actually provides a closer match to the aug-cc-pV5Z value for many of the functional/smaller basis set combinations that overestimate the ΔE (and provide the qualitatively correct geometry) since the CP-SP procedure overestimates the BSSE correction, leading to a partial compensation of errors. For example, the CP-SP M06-2X/6-31G(d,p) interaction energy differs from the M06-2X/aug-cc-pV5Z CP-OPT value by only 0.11 kcal/mol despite the fact that without CP it overestimates the strength of the interaction by almost 50% (2.49 kcal/mol). However, the optimized O...O distance for M06-2X/6-31G(d,p) CP-SP is 0.045 Å shorter. For some basis sets, such as cc-pVDZ (where it provides the qualitatively correct geometry without CP-OPT), the over correction due to CP-SP reverses the sign of the difference with the large basis set (i. e. from -3.25 to +0.61 for B2PLYP).

The inclusion of the empirical dispersion correction in B2PLYPD has the effect of increasing the attraction between the waters by about 0.4 kcal/mol for those calculations that yield the correct dimer geometries and of converging to the incorrect geometry when used with four of the smaller basis sets, while B2PLYP converges to the qualitatively correct geometries for all basis sets used here. B97D unexpectedly gives the least stable dimer when used with every basis set considered when optimized with CP. It also converges to the incorrect geometry when used with the same four small basis sets.

Choosing the best combination of functional and basis set depends upon the criteria that one wishes to employ. As noted above, the interaction energies calculated with the best basis set vary from -4.54 to -5.19 kcal/mol and the O...O distances from 2.893 to 2.922. We estimate that the energy criterion to be more critical than the O...O distance as the flatness of water dimer PES will imply little change in energy for a small variation in this distance. If one chooses the experimental targets as -4.90 kcal/mol and 2.95 Å, one reasonable criterion would be to choose the smallest basis set that gives the qualitatively correct geometry together with the functional that gives the best interaction energy. That would be X3LYP/D95(d,p). However, this combination gives an interaction energy about 1.2 kcal/mol too strong (after either a CP-OPT or CP-SP correction). Using B3LYP, M06, B2PLYP, B97D or MPWB1K all lower the interaction energies to within 0.8-0.9 kcal/mol of -4.9 kcal/mol. This basis set predicts about the same O...O distance 2.892-2.893 with all of these functionals except B2PLYP (2.914) and B97D (2.903).

If one can afford to use a basis set as large as aug-cc-pVDZ, M05-2X, M06-2X, B2PLYPD and X3LYP all provide excellent results for the interaction energy after either CP correction. Of these functionals M05-2X and B97D produce the best O...O distances. D95++(d,p) produces ΔE's within about 0.3 of -4.9 kcal/mol with B3LYP, B2PLYP, B397D and MPWB1K, while the larger 6-311++(d,p) comes within 0.2 kcal/mol with B3LYP, B97D and B2PLYP. Another possible choice would be 6-311G(d,p), larger than D95(d,p) but smaller than aug-cc-pVDZ, either with B3LYP or B2PLYP, both of which predict to be with 0.2 of the target -4.9 kcal/mol, or B97D which yields the target value.. However, the corresponding CP-OPT O...O distances are 2.978, 2.989 and 3.018 Å, respectively. One should also note that this basis set yields qualitatively incorrect dimer structures with four of the other functionals.

Of the functionals studied here, only B2PLYP and B2PLYPD incorporate MP2-like exchange-correlation contribution, resulting in significantly longer computation times. If we eliminate these from consideration, the preferred choices become (in order of increasing size of the basis set) 1) D95(d,p) with B3LYP, B97D, M06 or MPWB1k; 2) 6-311G(d,p) with B3LYP; 3) D95++(d,p) with B3LYP, B97D or MPWB1K; 4)6-311++G(d,p) with B3LYP or B97D; and 5) aug-cc-pVDZ with M05-2X, M06-2X or X3LYP.

CONCLUSIONS

Our evaluation of these ten functionals shows that the interaction energies predicted for the optimized water dimer on a counterpoise corrected PES vary by 0.65 kcal/mol. While the CP corrections for these functionals combined with aug-cc-pV5Z become negligible for B3LYP, B97D, X3LYP and MPWB1K, they do not disappear for the other functionals and reach a high of 0.20 kcal/mol for M06. Some of the small basis sets cause the water dimer to optimize to a qualitatively incorrect geometry with most functionals. 6-31G(d) does this with all functionals except B2PLYP and MPWB1K, while cc-pVDZ, 6-31G(d,p) and 6-311G(d,p) do the same with some functionals. The smallest basis set that consistently provides the correct geometry with all functions is D95(d,p). As the best non-DFT MO calculations and the most recent experiments agree with a value of -4.9 kcal/mol, we choose this value as a target. The experimental O...O equilibrium distance exceed those calculated with any of these non-DFT MO methods, as well as, the values calculated with aug-cc-pV5Z and any of the functionals considered here (although B97D/aug-cc-pV5Z comes close).

With few exceptions, the interaction energies calculated with any basis set using fewer than 100 basis functions for the water dimer are more negative than that calculated using aug-cc-pV5Z with the same functional. Thus, calculated ΔE's using these functionals and small basis sets will be closer to the preferred experimental and non-DFT value when the

overestimation of the interaction caused by the small basis set is countered by a functional that underestimates the interaction. Thus, the best functionals to use with large basis sets appear to differ from those that produce the best results with smaller ones. Since many applications are complex systems and require economical calculations, we suggest the following functional/basis set combinations in order of increasing complexity and cost: 1) D95(d,p) with B3LYP, B97D, M06 or MPWB1k; 2) 6-311G(d,p) with B3LYP; 3) D95++ (d,p) with B3LYP, B97D or MPWB1K; 4)6-311++G(d,p) with B3LYP or B97D; and 5) aug-cc-pVDZ with M05-2X, M06-2X or X3LYP.

Acknowledgments

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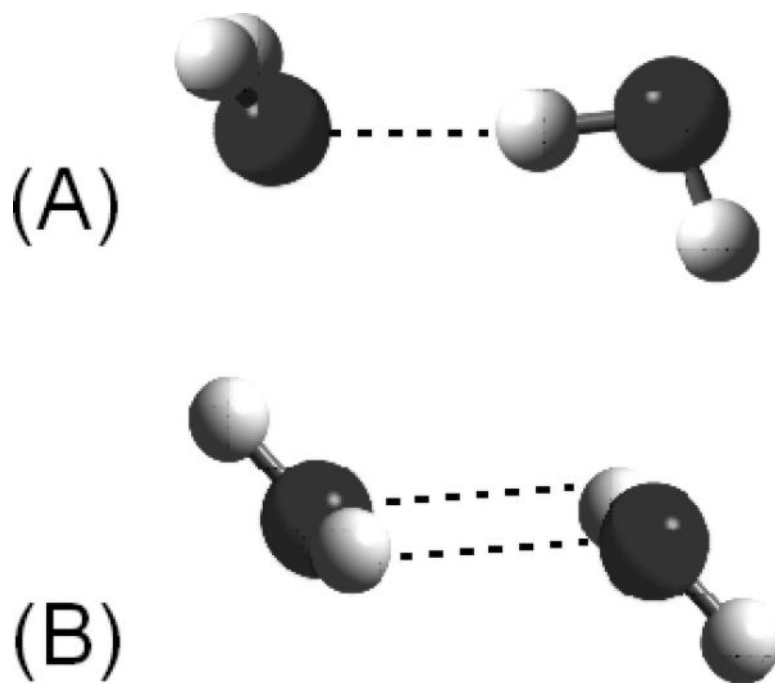
Figure 1.
Water Dimer Structures: (A) normal; (B) anomalous

Table 1

Calculated ΔE's (kcal/mol), O… H and (O…O) (Å) for the water dimer using the aug-cc-pV5Z basis set with different functionals.

	CP-OPT	CP-SP	Normal	CP-OPT	Normal	CP-OPT	Normal
	ΔE			Re(O—H)		Re(O—O)	
B2PLYPD	-5.19	-5.19	-5.24	1.936	1.926	2.893	2.883
M05-2X	-5.14	-5.14	-5.21	1.961	1.952	2.917	2.909
M06-2X	-5.07	-5.07	-5.12	1.943	1.940	2.900	2.894
M05	-4.98	-4.98	-5.05	1.965	1.961	2.922	2.918
X3LYP	-4.92	-4.93	-4.93	1.945	1.943	2.907	2.905
B2PLYP	-4.77	-4.77	-4.81	1.946	1.956	2.916	2.906
MPWB1K	-4.58	-4.59	-4.59	1.965	1.960	2.916	2.912
B3LYP	-4.55	-4.55	-4.55	1.959	1.957	2.921	2.919
M06	-4.54	-4.53	-4.74	1.953	1.943	2.912	2.902
B97D	-4.42	-4.42	-4.43	1.980	1.973	2.940	2.931

Table 2

Uncorrected calculated ΔE's (kcal/mol) for the water dimer.[a]

Basis Functions	B3LYP	M05	M05-2X	M06	M06-2X	B2PLYP	B2PLYPD	X3LYP	MPWB1K	B97D
aug-cc-pV5Z	574	-4.55	-5.05	-5.21	-4.74	-5.12	-4.81	-5.24	-4.93	-4.59	-4.43
cc-pV5Z	402	-4.78	-5.34	-5.30	-4.89	-5.25	-5.00	-5.43	-5.16	-4.76	-4.75
aug-cc-pVQZ	344	-4.58	-5.04	-5.22	-4.72	-5.15	-4.85	-5.27	-4.96	-4.62	-4.45
cc-pVQZ	230	-5.32	-5.71	-5.58	-5.16	-5.58	-5.48	-5.93	-5.72	-5.14	-5.36
aug-cc-pVTZ	184	-4.57	-5.15	-5.26	-4.79	-5.19	-4.88	-5.30	-4.96	-4.64	-4.48
6-311++G(3df,2p)	118	-4.83	-5.47	-5.40	-5.06	-5.42	-5.10	-5.54	-5.22	-4.90	-4.80
cc-pVTZ	116	-6.09	-6.48	-6.20	-5.96	-6.25	-6.20	-6.67	-6.50	-5.77	-6.17
aug-cc-pVDZ	82	-4.71	-5.44	-5.26	-4.86	-5.26	-5.00	-5.43	-5.11	-4.86	-4.62
6-311++G(d,p)	72	-5.83	-6.53	-6.49	-6.21	-6.47	-6.06	-6.46	-6.23	-5.93	-5.65
D95++(d,p)	64	-5.96	-6.46	-6.62	-6.10	-6.56	-6.25	-6.67	-6.36	-6.00	-5.77
6-31++G(d,p)	62	-6.03	-6.61	-6.61	-6.06	-6.67	-6.30	-6.72	-6.44	-6.16	-5.87
6-311G(d,p)	60	-7.65	**-8.29**	-7.62	**-7.78**	-7.66	-7.54	**-8.22**	**-8.26**	-7.22	**-8.17**
D95(d,p)	52	-6.61	-6.89	-6.84	-6.46	-6.80	-6.57	-7.03	-7.00	-6.36	-6.57
6-31G(d,p)	50	**-7.67**	**-8.08**	-7.60	**-7.49**	-7.61	-7.46	**-8.10**	**-8.15**	-7.17	**-8.01**
cc-pVDZ	48	**-8.60**	**-8.92**	-8.00	**-8.16**	-7.96	-8.06	**-8.84**	**-9.12**	-7.61	**-8.87**
6-31G(d)	38	**-7.80**	**-8.25**	**-8.11**	**-7.60**	**8.27**	-7.63	**-8.27**	**-8.28**	-7.30	**-8.12**

[a]Values in bold correspond to the cyclic water dimer (structure B of figure 1).

Table 3

CP-SP ΔE's(kcal/mol) for the water dimer.[a]

Basis	Functions	B3LYP	M05	M05-2X	M06	M06-2X	B2PLYP	B2PLYPD	X3LYP	MPWB1K	B97D
aug-cc-pV5Z	574	-4.55	-4.98	-5.14	-4.53	-5.07	-4.77	-5.19	-4.93	-4.59	-4.42
cc-pV5Z	402	-4.54	-5.01	-5.14	-4.54	-5.04	-4.75	-5.17	-4.92	-4.58	-4.41
aug-cc-pVQZ	344	-4.54	-4.96	-5.16	-4.47	-5.10	-4.76	-5.18	-4.92	-4.59	-4.42
cc-pVQZ	230	-4.51	-4.91	-5.10	-4.51	-5.03	-4.67	-5.08	-4.88	-4.56	-4.38
aug-cc-pVTZ	184	-4.52	-5.04	-5.17	-4.63	-5.11	-4.70	-5.12	-4.90	-4.57	-4.41
6-311++G(3df,2p)	118	-4.54	-5.16	-5.12	-4.80	-5.09	-4.68	-5.09	-4.88	-4.61	-4.43
cc-pVTZ	116	-4.47	-4.96	-5.10	-4.67	-5.04	-4.54	-4.93	-4.82	-4.55	-4.36
aug-cc-pVDZ	82	-4.48	-5.18	-5.05	-4.67	-5.05	-4.60	-5.01	-4.88	-4.64	-4.39
6-311++G(d,p)	72	-5.02	-5.70	-5.71	-5.36	-5.65	-4.95	-5.33	-5.41	-5.15	-4.84
D95++(d,p)	64	-5.21	-5.71	-5.88	-5.31	-5.77	-5.13	-5.53	-5.59	-5.25	-5.02
6-31++G(d,p)	62	-5.17	-5.78	-5.79	-5.25	-5.79	-5.16	-5.56	-5.57	-5.31	-5.03
6-311G(d,p)	60	-4.73	**-4.20**	-5.51	**-4.06**	-5.42	-4.65	**-4.05**	**-3.95**	-4.98	**-3.95**
D95(d,p)	52	-5.70	-6.05	-6.22	-5.74	-6.16	-5.57	-5.98	-6.08	-5.69	-5.51
6-31G(d,p)	50	**-3.64**	**-4.29**	-5.51	**-4.20**	-5.18	-5.03	**-4.42**	**-4.04**	-5.38	**-4.22**
cc-pVDZ	48	**-2.86**	**-3.51**	-4.81	**-3.35**	-4.85	-4.16	**-3.40**	**-3.26**	-4.56	**-3.39**
6-31G(d)	38	**-3.93**	**-4.60**	**-5.17**	**-4.53**	**-5.37**	**-5.40**	**-4.89**	**-4.46**	-5.70	**-4.63**

[a] Values in bold correspond to the cyclic water dimer (structure B of figure 1).

Table 4

CP-OPT calculated (kcal/mol) for the water dimer.

Basis	B3LYP	M05	M05-2X	M06	M06-2x	B2PLYP	B2PLYPD	X3LYP	MPWB1K	B97D
Functions										
aug-cc-pVQZ	574	-4.55	-4.98	-5.14	-4.54	-5.07	-4.77	-5.19	-4.92	-4.58	-4.42
cc-pV5Z	402	-4.55	-5.01	-5.14	-4.55	-5.06	-4.75	-5.17	-4.92	-4.59	-4.42
aug-cc-pVQZ	344	-4.54	-4.96	-5.16	-4.47	-5.10	-4.76	-5.18	-4.92	-4.59	-4.42
cc-pVQZ	230	-4.55	-4.94	-5.13	-4.52	-5.06	-4.71	-5.12	-4.91	-4.58	-4.41
aug-cc-pVTZ	184	-4.52	-5.05	-5.17	-4.63	-5.11	-4.70	-5.12	-4.90	-4.57	-4.41
6-311++G(3df,2p)	118	-4.54	-5.16	-5.15	-4.80	-5.11	-4.69	-5.10	-4.92	-4.62	-4.44
cc-pVTZ	116	-4.55	-5.03	-5.14	-4.73	-5.09	-4.62	-5.02	-4.90	-4.60	-4.44
aug-cc-pVDZ	82	-4.49	-5.18	-5.05	-4.67	-5.05	-4.60	-5.02	-4.88	-4.64	-4.39
6-311++G(d,p)	72	-5.05	-5.72	-5.74	-5.38	-5.68	-5.00	-5.38	-5.44	-5.18	-4.89
D95++(d,p)	64	-5.22	-5.72	-5.89	-5.33	-5.79	-5.17	-5.57	-5.61	-5.27	-5.07
6-31++G(d,p)	62	-5.20	-5.81	-5.82	-5.27	-5.82	-5.21	-5.61	-5.60	-5.36	-5.09
6-311G(d,p)	60	-5.09	-5.65	-5.74	-5.41	-5.64	-5.03	-5.39	-5.45	-5.23	-4.91
D95(d,p)	52	-5.74	-6.09	-6.25	-5.77	-6.19	-5.62	-6.03	-6.12	-5.72	-5.57
6-31G(d,p)	50	-5.48	-5.95	-6.00	-5.60	-6.03	-5.45	-5.85	-5.84	-5.66	-5.41
cc-pVDZ	48	-4.65	-5.20	-5.12	-4.91	-5.13	-4.61	-4.97	-5.00	-4.84	-4.53
6-31G(d)	38	-5.77	-6.18	-6.28	-5.76	-6.34	-5.74	-6.16	-6.15	-5.90	-5.70

Table 5

Uncorrected optimized O...O distances (Å) for water dimer.[a]

Basis	Functions	B3LYP	M05	M05-2X	M06	M06-2X	B2PLYP	B2PLYPD	X3LYP	MPWB1K	B97D
aug-cc-pV5Z	574	2.919	2.918	2.909	2.902	2.894	2.906	2.883	2.905	2.912	2.931
cc-pV5Z	402	2.915	2.916	2.914	2.904	2.898	2.909	2.887	2.901	2.911	2.930
aug-cc-pVQZ	344	2.919	2.919	2.908	2.901	2.894	2.906	2.883	2.905	2.912	2.931
cc-pVQZ	230	2.913	2.916	2.911	2.903	2.899	2.904	2.882	2.899	2.907	2.927
aug-cc-pVTZ	184	2.912	2.908	2.918	2.902	2.895	2.907	2.884	2.897	2.913	2.931
6-311++G(3df,2p)	118	2.918	2.919	2.912	2.900	2.890	2.911	2.888	2.904	2.911	2.929
cc-pVTZ	116	2.909	2.905	2.917	2.898	2.899	2.902	2.880	2.895	2.906	2.917
aug-cc-pVDZ	82	2.912	2.906	2.920	2.902	2.895	2.910	2.886	2.897	2.905	2.930
6-311++G(d,p)	72	2.899	2.891	2.895	2.882	2.883	2.899	2.881	2.887	2.892	2.917
D95++(d,p)	64	2.879	2.885	2.888	2.880	2.878	2.884	2.866	2.867	2.881	2.891
6-31++G(d,p)	62	2.886	2.890	2.895	2.886	2.877	2.888	2.871	2.874	2.880	2.894
6-311G(d,p)	60	2.886	**2.792**	2.872	**2.758**	2.869	2.886	**2.814**	**2.774**	2.874	**2.902**
D95(d,p)	52	2.869	2.883	2.877	2.876	2.871	2.878	2.859	2.858	2.868	2.875
6-31G(d,p)	50	**2.785**	**2.793**	2.856	**2.773**	2.855	2.882	**2.810**	**2.773**	2.868	**2.866**
cc-pVDZ	48	**2.771**	**2.778**	2.888	**2.757**	2.882	2.886	**2.802**	**2.759**	2.878	**2.878**
6-31G(d)	38	**2.777**	**2.788**	**2.746**	**2.768**	**2.734**	2.874	**2.805**	**2.767**	2.857	**2.849**

[a]Values in bold correspond structure B in figure 1.

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Table 6

Uncorrected optimized O---H (Å) for the water dimer.[a]

Basis	Functions	B3LYP	M05	M05-2X	M06	M06-2X	B2PLYP	B2PLYPD	X3LYP	MPWB1K	B97D
aug-cc-pV5Z	574	1.957	1.961	1.952	1.943	1.940	1.946	1.926	1.943	1.960	1.973
cc-pV5Z	402	1.954	1.958	1.956	1.944	1.944	1.948	1.928	1.940	1.960	1.972
aug-cc-pVQZ	344	1.957	1.963	1.952	1.942	1.940	1.946	1.926	1.943	1.960	1.973
cc-pVQZ	230	1.951	1.960	1.956	1.944	1.944	1.946	1.928	1.938	1.956	1.970
aug-cc-pVTZ	184	1.948	1.951	1.961	1.941	1.940	1.946	1.925	1.934	1.961	1.972
6-311++G(3df,2p)	118	1.956	1.952	1.961	1.940	1.943	1.951	1.931	1.942	1.960	1.972
cc-pVTZ	116	1.947	1.949	1.961	1.942	1.942	1.942	1.924	1.933	1.953	1.967
aug-cc-pVDZ	82	1.945	1.945	1.962	1.936	1.938	1.945	1.924	1.931	1.950	1.961
6-311++G(d,p)	72	1.932	1.929	1.932	1.916	1.920	1.934	1.916	1.920	1.935	1.948
D95++(d,p)	64	1.908	1.922	1.922	1.910	1.912	1.915	1.897	1.897	1.921	1.918
6-31++G(d,p)	62	1.917	1.926	1.933	1.919	1.914	1.922	1.905	1.906	1.923	1.925
6-311G(d,p)	60	1.925	**2.134**	1.910	**2.163**	1.911	1.927	**2.216**	**2.176**	1.922	**2.312**
D95(d,p)	52	1.897	1.919	1.911	1.909	1.905	1.909	1.894	1.886	1.908	1.913
6-31G(d,p)	50	**2.169**	**2.186**	1.949	**2.058**	1.971	1.940	**2.048**	**2.158**	1.929	**2.101**
cc-pVDZ	48	**2.147**	**2.160**	1.923	**2.142**	1.916	1.917	**2.096**	**2.135**	1.918	**2.228**
6-31G(d)	38	**2.162**	**2.158**	**2.073**	**2.037**	**2.144**	1.929	**2.010**	**2.058**	1.914	**2.045**

[a]Values in bold correspond figure 1 structure B.

Table 7

Optimized O…O distances using CP-OPT (Å) for water dimer

Basis	B3LYP	M05	M05-2X	M06	M06-2X	B2PLYP	B2PLYPD	X3LYP	MPWB1K	B97D
Functions										
aug-cc-pV5Z	574	2.921	2.922	2.917	2.912	2.900	2.916	2.893	2.907	2.916	2.940
cc-pV5Z	402	2.924	2.924	2.919	2.919	2.909	2.917	2.896	2.910	2.918	2.944
aug-cc-pVQZ	344	2.921	2.922	2.918	2.911	2.900	2.916	2.893	2.907	2.916	2.940
cc-pVQZ	230	2.935	2.933	2.926	2.920	2.910	2.930	2.908	2.920	2.926	2.957
aug-cc-pVTZ	184	2.923	2.915	2.920	2.913	2.907	2.918	2.895	2.909	2.918	2.942
6-311++G(3df,2p)	118	2.934	2.920	2.931	2.911	2.909	2.936	2.915	2.919	2.928	2.953
cc-pVTZ	116	2.950	2.934	2.947	2.930	2.929	2.950	2.929	2.935	2.939	2.971
aug-cc-pVDZ	82	2.927	2.919	2.935	2.913	2.913	2.938	2.914	2.913	2.922	2.942
6-311++G(d,p)	72	2.941	2.923	2.937	2.911	2.920	2.958	2.937	2.925	2.935	2.964
D95++(d,p)	64	2.910	2.911	2.920	2.903	2.909	2.933	2.908	2.895	2.913	2.924
6-31++G(d,p)	62	2.934	2.928	2.938	2.924	2.920	2.951	2.927	2.920	2.922	2.943
6-311G(d,p)	60	2.978	2.960	2.961	2.938	2.948	2.989	2.972	2.964	2.958	3.018
D95(d,p)	52	2.892	2.901	2.898	2.892	2.893	2.914	2.895	2.882	2.893	2.903
6-31G(d,p)	50	2.937	2.933	2.934	2.923	2.921	2.948	2.929	2.927	2.919	2.948
cc-pVDZ	48	2.982	2.967	2.977	2.952	2.965	2.996	2.978	2.968	2.963	3.011
6-31G(d)	38	2.912	2.915	2.909	2.912	2.893	2.926	2.905	2.900	2.896	2.914

Table 8

Optimized O...H distances using CP-OPT (Å) for water dimer

Basis	B3LYP	M05	M05-2X	M06	M06-2X	B2PLYP	B2PLYPD	X3LYP	MPWB1K	B97D
Functions										
aug-cc-pV5Z	574	1.959	1.965	1.961	1.953	1.943	1.956	1.936	1.945	1.965	1.980
cc-pV5Z	402	1.962	1.966	1.963	1.960	1.949	1.957	1.936	1.947	1.966	1.984
aug-cc-pVQZ	344	1.959	1.965	1.962	1.953	1.942	1.956	1.936	1.945	1.965	1.980
cc-pVQZ	230	1.971	1.976	1.968	1.961	1.950	1.968	1.949	1.956	1.973	1.997
aug-cc-pVTZ	184	1.960	1.958	1.963	1.953	1.953	1.957	1.936	1.946	1.966	1.981
6-311++G(3df,2p)	118	1.972	1.960	1.976	1.952	1.954	1.976	1.955	1.957	1.977	1.996
cc-pVTZ	116	1.985	1.973	1.988	1.968	1.968	1.988	1.967	1.970	1.985	2.009
aug-cc-pVDZ	82	1.961	1.958	1.976	1.947	1.957	1.974	1.952	1.947	1.967	1.974
6-311++G(d,p)	72	1.976	1.962	1.976	1.950	1.960	1.995	1.976	1.961	1.981	2.004
D95++(d,p)	64	1.941	1.948	1.956	1.938	1.945	1.968	1.946	1.928	1.956	1.959
6-31++G(d,p)	62	1.967	1.966	1.979	1.958	1.961	1.987	1.965	1.954	1.967	1.981
6-311G(d,p)	60	2.010	1.998	1.998	1.973	1.984	2.025	2.008	1.997	2.002	2.049
D95(d,p)	52	1.923	1.937	1.932	1.925	1.927	1.946	1.929	1.912	1.933	1.938
6-31G(d,p)	50	1.967	1.970	1.973	1.957	1.957	1.982	1.966	1.958	1.961	1.983
cc-pVDZ	48	2.008	1.998	2.009	1.981	1.994	2.026	2.008	1.994	2.001	2.037
6-31G(d)	38	1.939	1.949	1.941	1.942	1.924	1.956	1.935	1.927	1.935	1.944

Table 9

ΔE's (kcal/mol), optimized O...H, and O...O distances (Å) calculated using high level theory.

Authors	ΔE	O...H	O...O	Method	ref
Tschumper et. al.	-5.02 ± 0.07	1.9485[a]	2.9089[a]	FPA	50
Klopper et. al.	-5.02 ± 0.05	1.955 ± 0.005	2.912 ±	CCSD(T)(Full) limit	51
Szalewicz et. al.	-4.7 ± 0.2			SAPT	57
Xantheas	-4.88[b]		2.913[b]	MP2/aug-cc-pV5Z	54
	-5.01		2.905	MP2/aug-cc-pV5Z	54
	-4.9		2.905		54
Feller	-5.1	1.958[c]	2.911[c]	Estimate of the CI(Full)	52
Shields et. al.	-5.10	1.926	2.886	CBS-QB3	53
	-5.07	1.966	2.925	CBS-APNO	53
	-4.98	1.955	2.914	G2	53
	-5.14	1.955	2.914	G3	53
Schutz et. al.	-4.98 ± 0.05		2.925[b,d]	MP2 limit	56
Jordan et. al.	-5.18		2.908	MP2/aug-cc-pVTZ	55

[a] The CCSD(T)/TZ2P(f,d) + dif basis was employed

[b] CP-OPT

[c] Structure determined by Frisch et. al. with MP2/6-311++G(2d,2p) {Frisch, 1986 #873}

[d] Optimization performed with CCSD(T)/ANO-L

Table 10

Experimental ΔH's, and O…O distance and estimated ΔE's (kcal/mol) and O…O distances at the PES minimum for water dimer.

Authors	ΔE	ΔH (degrees K)	O…O (PES)	O…O (exper)	Method	ref
Curtiss et. al.	-5.44 ± 0.7	$-3.59 \pm 0.50a$ (353-393)	-	-	Thermal conductivity	58
	-5.40 ± 0.5^b	-3.66 ± 0.50^a	-	-		58
Kawasaki et. al.	-	-3.24 ± 0.94 (298)	-	-	Pressure Broadening	65
Gilbert et. al.	-	-5.2 ± 1.5	-	-	Infrared Absorption	59
Sizov et. al.	-	-4.55 (284-353)	-	-	Infrared Absorption	62
Gorbaty et. al.	-	-3.98 ± 0.90 (573-723)	-	-	Infrared Absorption	61
Ikawa et. al.	-	3.6 ± 0.7 (373-673)	-	-	Infrared Absorption	63
Cormier et. al.	-	-3.80 ± 0.07 (273-315)	-	-	Infrared Absorption	60
Saykally et. al.	-4.91^b	-3.46^a	2.924^b	2.94 ± 0.03^b	VRT(ASP-W)	66
Saykally et. al.	-4.85^b	-3.40^a	2.952^b	2.99 ± 0.20^b	VRT(ASP-W)II	67
	-4.92^b	-3.47^a	-	-	VRT(ASP-W)III	67
Saykally et. al.	-4.80	-3.74^k (375)	-	-	VRT(ASP-W)III	64
Dyke et. al.	-	-	2.952^b	2.976 (+0.000, -0.030)	Molecular beam electric resonance spectroscopy	69
Dyke et. al.	-	-	2.946^b	2.98 ± 0.01	Molecular beam electric resonance spectroscopy	58

[a] Deuterated water dimer

[b] Corrected for anharmonicity