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Ab Initio Potential Energy and Dipole Moment Surfaces of $(H_2O)_2$[†]

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A full-dimensional ab initio potential energy surface (PES) and dipole moment surface (DMS) are reported for the water dimer, $(H_2O)_2$. The CCSD(T)-PES is a very precise fit to 19 805 ab initio energies obtained with the coupled-cluster (CCSD(T)) method, using an aug-cc-pVTZ basis. The standard counterpoise correction was applied to approximately eliminate basis set superposition errors. The fit is based on an approach that incorporates the permutational symmetry of identical atoms [Huang, X.; Braams, B.; Bowman, J. M. *J. Chem. Phys.* **2005**, *122*, 044308]. The DMS is a fit to the dipole moment obtained with Møller−Plesset (MP2) theory, using an aug-cc-pVTZ basis. The PES has an RMS fitting error of 31 cm^{-1} for energies below 20 000 cm^{-1}, relative to the global minimum. This surface can describe various internal floppy motions, including various monomer inversions, and isomerization pathways. Ten characteristic stationary points have been located on the surface, four of which are transition structures and the rest are higher order saddle points. Their geometrical and vibrational properties are presented and compared with available previous theoretical work. The CCSD(T)-PES and MP2-DMS dissociate correctly (and symmetrically) to two H_2O monomers, with $D_e = 1665.7$ cm^{-1} (19.93 kJ/mol). Accurate quantum calculations of the zero-point energy of the dimer (using diffusion Monte Carlo) and the monomers (using a vibrational configuration interaction approach) are reported, and these together with D_e give a value of D_0 of 1042 cm^{-1} (12.44 kJ/mol). A best estimated value is 1130 cm^{-1} (13.5 kJ/mol).

I. Introduction

Numerous theoretical[1−10] and experimental studies[11−23] have been devoted to the hydrogen bonding interactions and features of the potential energy surface of the simplest water cluster, $(H_2O)_2$. The global minimum has been determined to be a C_s structure formed between H-donor and H-acceptor monomers. The most exhaustive ab initio computational study of water dimer stationary points was reported in Smith et al.[7] and Tschumper et al.[8] Tschumper et al. characterized the 10 saddle points, structures on the water dimer surface with MP2 and coupled-cluster techniques, triple-ζ basis, polarization and diffuse functions. The one-particle limit was accessed by complete basis-set extrapolation (aug-cc-pVXZ, X = D − 6). The study also included the MP2-R12 method, core correlation and relativistic effects. The basis-set extrapolated dissociation energy D_e was given as 21.0 ± 0.3 kJ/mol,[8] which agrees well with the 21.0 ± 0.2 kJ/mol predicted by Klopper et al.[1] By including the harmonic zero-point vibrational energies, the most recent prediction of D_0 is 1165 ± 54 cm^{-1}.[1] The best experimentally estimated D_0 is 1256 and 1280 cm^{-1} for $(H_2O)_2$ and $(D_2O)_2$, respectively, with uncertainty of 175 cm^{-1}.[24]

There exist several possible rearrangement/self-isomerization pathways on the hyper surface of water dimer potential. Three mostly discussed pathways render acceptor tunneling, donor−acceptor-interchange tunneling and bifurcation tunneling. At the MP2/aug-cc-pVXZ (X = D, T, Q) level, Wales and co-workers[2,3] have carried out ab initio-based studies of these rearrangement pathways,[2] computed the tunneling splittings with the semiclassical WKB method,[3] and found good agreement with experiments.[14] Most other available model potentials of water dimer are intermolecular potential surfaces (IPSs) based on semirigid structures. Burnham and Xantheas have given a detailed comparison of several minimum energy paths of rearrangements on a few IPSs and ab initio calculations.[6] It was found that the family of anisotropic site potential (ASP) models has better agreement with the ab initio results. This family of surfaces was constructed by Leforestier, Saykally and co-workers. They have made significant contributions on the vibration−rotation−tunneling (VRT) spectra of both $(H_2O)_2$ and $(D_2O)_2$, and IPS constructions based on VRT data. The most recent ones are: VRT(ASP-W)III (the third fitting of the anisotropic site potential with Woermer dispersion to VRT data, $D_e = 1678$ cm^{-1}, $D_0 = 1080$ cm^{-1}),[13,14] SAPT-5st (five-site symmetry-adapted perturbation theory, tuned, $D_e = 1759$ cm^{-1}, $D_0 = 1077$ cm^{-1}),[25] and VRT(MCY-5f) (Matsuoka−Clementi−Yoshimine functions employed, flexible definition, $D_e = 1734.5$ cm^{-1}, $D_0 = 1231.6$ cm^{-1}).[15] The VRT(ASP-W)III has been confirmed as the best IPS for water dimer.[12,26] This empirical surface is an effective potential, averaged over the zero-point vibrations of the six monomer OH modes. Six-dimensional calculations have been carried out on these surfaces using the pseudospectral method,[14] trying to reproduce the $(H_2O)_2$ and $(D_2O)_2$ VRT spectra. Recently, full-dimensional calculations have been reported on the basis of adiabatic separation (6d+6d) between intermonomer modes and intramonomer modes.[15] Schofield and Kjiaergaard[9] have calculated OH stretches and monomer bending transitions up to 20 000 cm^{-1}, using the harmonically-coupled-anharmonic-oscillator local-mode model. Very recently, Crittenden and Jordan[4] reported a limited, but full-dimensional, ab initio potential based on B3LYP/6-31+G*

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calculations. However, the focus of that work was to investigate the level of accuracy needed in one aspect of the fitting method used to obtain a well converged zero-point wave function, obtained with the quantum diffusion Monte Carlo method.

A global ab initio-based potential energy surface that describes these various internal rearrangements and dissociates correctly to two H_2O monomers has not been reported. We do that in this paper. This potential is a fit to 19 805 ab initio energies, obtained at the CCSD(T) level of theory with an aug-cc-pVTZ basis. The approaches we take are quite similar to the ones described previously for full-dimensional potential and dipole moment surfaces for $H_5O_2^+$;[27] i.e., the fit is invariant with respect to permutation of like atoms. A global dipole moment surface and PES are also reported on the basis of MP2/aug-cc-pVTZ calculations. The details of the ab initio calculations and fitting are given in the next section. Section III gives many of the features of the two PESs, including fitting accuracies, characteristics of stationary points, and the dissociation energetics (based on quantum diffusion Monte Carlo calculations of zero-point energies), monomer properties and some properties of the dipole moment surface. A summary and conclusions are given are in section IV.

II. Fitting Algorithm and Ab Initio Calculations

A. Fitting Details. The methods applied for the current $(H_2O)_2$ potential and dipole fits have been described in detail in our recent paper describing a full-dimensional PES for $H_5O_2^+$,[27] so we will not go through details of the methods here. As before, the fifteen variables of the fit are $x_{ij} = e^{-r_{ij}/3}$ for the main polynomial, denoted p, and $y_{ij} = e^{-r_{ij}}/r_{ij}$ for the two-body short-range polynomial, denoted q, and where r_{ij} is the ijth internuclear distance. The polynomial p is complete to seventh order and q is a cubic. In total there are 5227 terms in the expression for the PES. The functional form, as in the case of $H_5O_2^+$, is capable of describing the two monomers in the dissociation limit, and doing so with complete permutational symmetry.

B. Ab Initio Calculations. Ab initio calculations of the energies were done using the CCSD(T) method with an aug-cc-pVTZ basis (MOLPRO 2002.6).[28] The selection of configurations for these calculations was done in several ways. First, to describe the dissociation 14 OO distances were selected from 4 to 100 bohr, with 8 distances between 4 and 6 bohr, 4 between 8 and 15 bohr and finally one at 50 and one at 100 bohr. At each OO distance the four r_{OH} distances, the two HOH angles and the two sets of monomer Euler angles were varied. For the latter the x axis is defined along OO bond axis and the angles were sampled over their full range. For r_{OH} and the monomer bond angles the ranges were restricted to avoid very high energies. At a given OO distance between 300 and 2000 monomer geometries were selected for a total of 15 000 configurations. Roughly 3000 additional grid points were generated at configurations where the energy is less than 2000 cm^{-1} (relative to the minimum on fit).

A fit was then done with these 18 000 configurations and then quantum diffusion Monte Carlo (DMC) calculations were run to locate regions where more ab initio points were needed. This process resulted in approximately 1800 additional configurations for a total of 19 805 configurations.

Given the relatively weak binding of the water dimer basis-set-superposition-error (BSSE) is a concern. This was approximately corrected by the standard counterpoise method[29] at each geometry.

$$\Delta E_{\mathrm{BSSE}} = E_{\mathrm{A}}{}^{*} + E_{\mathrm{B}}{}^{*} - E_{\mathrm{A}}{}^{!} - E_{\mathrm{B}}{}^{!}$$
$$E_{\mathrm{corrected}} = E_{\mathrm{ab\ initio}} - \Delta E_{\mathrm{BSSE}}$$

$E_{\mathrm{A,B}}{}^{*}$ are the energies of water monomer A or B in the basis set of the combined system and the geometry of the complex, $E_{\mathrm{A,B}}{}^{!}$ are the energies of water monomer A or B in their own basis at the geometry of complex.

Due to the high computational demands of counterpoise calculation, direct ab initio geometry optimizations with the CCSD(T) method and aug-cc-pVTZ basis were very time-consuming and so were not done. Instead we did structure optimizations at the MP2 level with an aug-cc-pVTZ basis with and without the correction. An MP2-level PES was also obtained and we give an energy comparison of the optimized structures from this PES and the direct ab initio MP2 calculations in the next section.

It should be noted that in ref 3 it was shown that the counterpoise-corrected and uncorrected binding energies D_e obtained with CCSD(T)/aug-cc-pVTZ calculations differed by approximately 0.25 kcal/mol, although in opposite directions, from an extrapolated result that could be estimated from DZ, and TZ CCSD(T) calculations and DZ, TZ and QZ MP2 ones. Thus, on the basis of that result, the differences between counterpoise corrected and uncorrected energies at the TZ level are small. This is not surprising as the TZ basis is fairly large and the differences should go to zero in the complete basis set limit. A further discussion of this point is given in part C of the next section.

III. Results and Discussions

A. Fitting Accuracy of the CCSD(T)-PES and MP2−PES. Figure 2 depicts the energy distribution of grid points and RMS errors of the CCSD(T)-PES with respect to increasing energy cutoffs relative to the global minimum. For the 9257 grid points between 0 and 10 000 cm^{-1}, the RMS fitting error is 10.5 cm^{-1}. At 20 000 and 40 000 cm^{-1}, the RMS error rises to 29.2 and 95.9 cm^{-1}, respectively. To check the quality, coverage, and extrapolation of this PES, four sets of additional geometries were chosen and independent ab initio calculations were carried out and compared with the PES values.

The first group of geometries starts from the global minimum found on the fit (Str 01), elongates or shortens the r_{OO} symmetrically but the 4 H atoms fixed at minimum position. r_{OO} was varied by ±1.5 bohr around the equilibrium value of 5.55 bohr, in a grid of 16 equally spaced values. Energy up to 20 000 cm^{-1} resulted from this (the large values at small r_{OO}) and the RMS error of the fit is 53 cm^{-1}.

In the second group of geometries each monomer OH stretch except the donor one was varied about the equilibrium value by ±0.5 bohr in 20 equally spaced steps. This was done independently with all other displacements at zero, relative to the global minimum. The ab initio energies vary by as much as 30 000 cm^{-1}. For the set of 60 new geometries the RMS of the fit is 42 cm^{-1}.

The third group of geometries contains 97 randomly selected geometries generated from long DMC runs. The RMS error on the fit is 17 cm^{-1} for 49 points below 8000 and 50 cm^{-1} for the rest 48 points between 8000 cm^{-1} and 25 000 cm^{-1}. The RMS error for this total dataset is 37 cm^{-1}.

The final group focuses on the 10 stationary points, denoted Str 01 to Str 10, we found on the fit. Direct ab initio calculations are carried out at the 10 geometries and results were compared to the fitted values (see Table 1 below). Excellent accuracy is achieved with an RMS error of 3 cm^{-1} (see below).

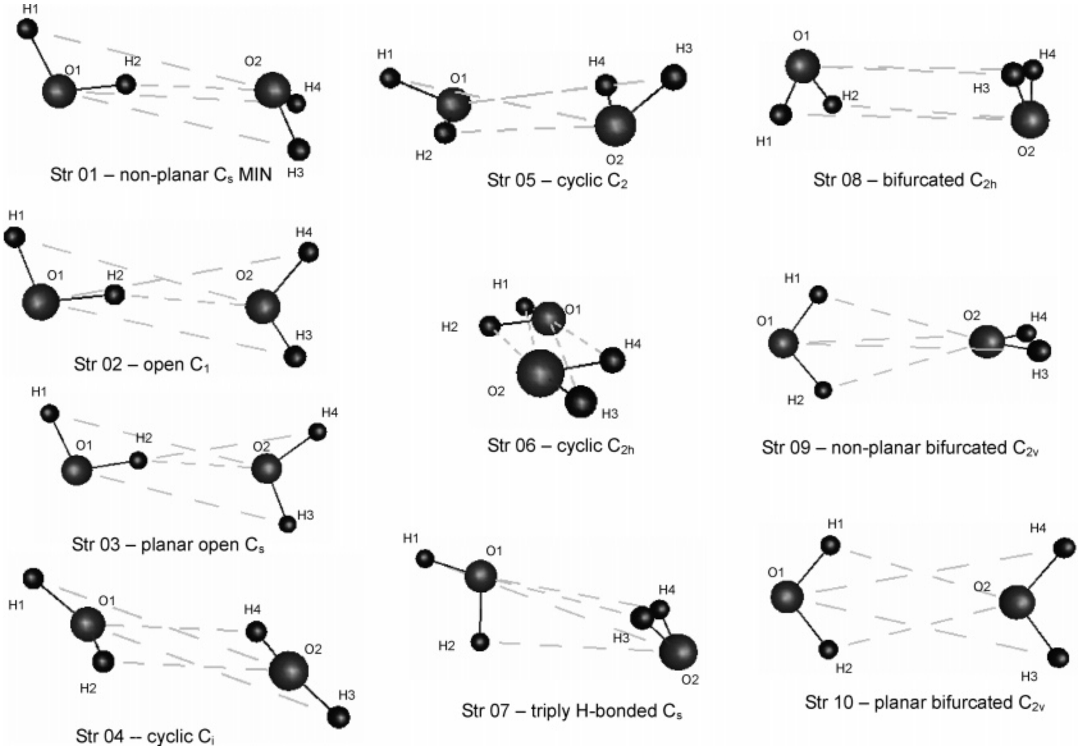

Figure 1. Geometries of 10 $(H_2O)_2$ stationary points. Notations follow the ones defined in ref 8.

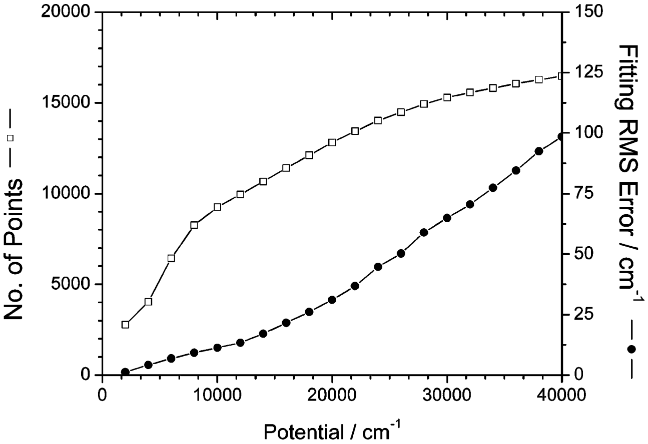

Figure 2. Fitting accuracy and data distribution with respect to the potential energy, related to minimum.

As noted above, we did not determine the stationary points at the CCSD(T) level with the counterpoise correction due to the large computational cost of doing so. Instead we did this at the MP2 level. We also did a PES fit, denoted “MP2-PES”, to MP2/aug-cc-pVTZ energies with the counterpoise correction using the same geometries and fitting method used in CCSD(T)-PES. Excellent agreement is found between optimized ab initio barrier heights and those optimized from the MP2-PES. Relative to the Str 01 energy, the barrier heights for Str 02−Str 09 are within 0−7 cm^{-1} relative to the direct MP2 results. We also have compared MP2 ab initio geometries at the optimized stationary points with fitted structures. Ranges of monomer geometry parameter deviations are ±0.0001 Å and ±0.06 ° (±0.001 Å/±0.20° for Str 02). For intermonomer parameters, ranges of deviations are ±0.04 Å and ±15°, which was basically caused by the nature of this dimer system and convergence limitation of ab initio optimization methods. The harmonic frequencies at the 10 structures on MP2-PES (not shown) are very similar to the frequencies we found on CCSD(T)-PES. These comparisons strongly support the accuracy of potential fits and reliabilities of fitting methods.

B. Stationary Points. As mentioned above, Str 01−Str 10 have been located on our CCSD(T)- and MP2-based PESs. The energies of these as well as the dipole moment from the MP2-DMS and direct MP2 calculations are given in Table 1 along with the benchmark CCSD(T)/TZ2P(f,d)+dif results of Tschumper et al. As seen, there is excellent agreement. Note that for convenience we also give a comparison of dipole moments in this table even though we defer a description of the fitting of the dipole moment to the next section. The monomer and intermonomer geometries of these 10 stationary points obtained from the CCSD(T)-PES are given in Tables 2 and 3, respectively, and compared with the benchmark results. As seen in Table 2, there is excellent agreement for the monomer geometries. As seen in Table 3, for the intermonomer distance $r(O_2\cdots H_2)$, the hydrogen bond length, differences with the ref 8 values range from −0.01 to +0.04 Å, with an average difference of 0.02 Å, except for Str 07 where this bond length is the longest and where the difference is 0.17 Å (5%). For other intermonomer parameters, bond angles and dihedral angles, differences range from −2.0 to +2.0° for 8 stationary points. Exceptions are for Str 2 and Str 7 where differences as large as 7° for Str 7 and −7 to +25° for Str 2. Thus, overall, the agreement with the benchmark calculations for these weakly interacting intermonomer configurations is good. The relatively larger differences compared to the monomer distances are basically caused by the floppy nature of this dimer system and also perhaps by differences in the ab initio basis used for the PES(aug-cc-pVTZ) and used for ref 8 (TZ2P(f,d)+dif).

The corresponding comparison of the normal-mode frequencies is given in Table 4, where again very good agreement is seen, except that the cyclic-C_2 geometry of Str 05 on the CCSD(T)-PES has one imaginary frequency, in disagreement with Tschumper et al., where it was classified as a second-order saddle point. The magnitude of the harmonic frequency of our first real mode, 47 cm^{-1}, is comparable to the reported imaginary

TABLE 1: Energy and Dipole Moment of 10 Stationary Points Found on the Present CCSD(T)-PES, the MP2-Based PES and MP2-Based Dipole Moment Surface (DMS)[a]

			energy (cm^{-1})				energy (kJ/mol)			dipole (Debye)		
str no.	sym	N_i	CCSD(T)-PES	ab initio	MP2-PES	MP2 ab initio	CCSD(T)-PES	ref 8	Δ	MP2	DMS	ref 8
1	C_s	0	0	0	0	0	0	0	0	2.5632	2.5602	2.6966
2	C_1	1	164.1	163.2	162.5	169.0	1.96	2.17	−0.20	3.3506	3.3460	3.7345
3	C_s	2	196.7	197.3	185.6	186.1	2.35	2.39	−0.04	3.3535	3.3554	3.4377
4	C_i	1	244.7	246.3	252.0	248.5	2.93	2.91	−0.00	0.0000	0.0000	0.0000
5	C_2	1[b]	328.6	328.7	322.2	325.7	3.93	3.97	−0.04	1.6541	1.6494	1.7183
6	C_{2h}	3	347.0	346.7	334.5	334.0	4.15	4.16	−0.01	0.0000	0.0000	0.0000
7	C_s	2	601.4	600.8	629.0	628.2	7.19	7.52	−0.33	3.6563	3.6571	3.4057
8	C_{2h}	3	1176.4	1186.0	1214.2	1219.8	14.07	14.82	−0.75	0.0000	0.0000	0.0000
9	C_{2v}	1	588.9	588.8	614.4	614.1	7.04	7.41	−0.37	4.1245	4.1110	4.1535
10	C_{2v}	2	897.1	898.6	918.9	919.0	10.73	11.26	−0.53	4.0603	4.0564	4.1121

[a] Structure No. 1 is the global minimum. N_i is the number of imaginary modes at saddle point. [b] It was classified as a second-order saddle point in ref 8.

TABLE 2: Monomer Geometry Parameters of 10 H_4O_2 Stationary Points Located on the Present Potential Energy Surface (CCSD(T)-PES)

	$R(O_1H_1)$	$R(O_1H_2)$	$R(O_2H_3)$	$R(O_2H_4)$	$\angle H_1O_1H_2$	$\angle H_3O_2H_4$
1	0.9608	0.9675	0.9623	0.9623	104.52	104.59
	(0.9581)	(0.9653)	(0.9597)	(0.9597)	(104.45)	(104.58)
2	0.9607	0.9668	0.9624	0.9616	104.52	104.66
	(0.9580)	(0.9645)	(0.9595)	(0.9589)	(104.47)	(104.84)
3	0.9606	0.9663	0.9616	0.9610	104.52	105.05
	(0.9579)	(0.9640)	(0.9590)	(0.9585)	(104.48)	(105.04)
4	0.9612	0.9644	0.9612	0.9644	104.82	104.82
	(0.9585)	(0.9616)	(0.9586)	(0.9616)	(104.84)	(104.84)
5	0.9609	0.9641	0.9609	0.9641	104.95	104.95
	(0.9583)	(0.9614)	(0.9583)	(0.9614)	(104.95)	(104.95)
6	0.9607	0.9636	0.9607	0.9636	105.08	105.08
	(0.9580)	(0.9611)	(0.9580)	(0.9611)	(105.14)	(105.14)
7	0.9618	0.9624	0.9624	0.9624	104.54	101.94
	(0.9591)	(0.9598)	(0.9598)	(0.9598)	(104.61)	(102.00)
8	0.9621	0.9621	0.9621	0.9621	103.20	103.20
	(0.9594)	(0.9594)	(0.9594)	(0.9594)	(103.15)	(103.15)
9	0.9623	0.9623	0.9619	0.9619	101.61	104.50
	(0.9596)	(0.9596)	(0.9593)	(0.9593)	(101.56)	(104.42)
10	0.9619	0.9619	0.9619	0.9619	101.91	104.07
	(0.9591)	(0.9591)	(0.9592)	(0.9592)	(101.91)	(104.09)

[a] The numbers in parentheses are the benchmark ab initio results from ref 8. Bond lengths are in Å and angles are in degrees. The atoms are numbered as in Figure 1.

frequency, 34i cm^{-1}, indicating that the real dimer potential is quite flat in this region. Thus, this deficiency of the present PES is not likely to be significant in any vibrational or dynamics calculation.

The effects of the counterpoise correction on the 9 barrier heights were investigated at MP2/aug-cc-pVTZ level. Direct ab initio optimizations without corrections result in barrier heights 7−15% higher than those computed with corrections. Relative to Str 01, the uncorrected ab initio barriers are 180, 213, 291, 378, 393, 678, 1332, 700, and 1023 cm^{-1}, for Str 02−Str 10, respectively.

C. Monomer Properties and Dissociation Energy (D_e and D_0). The CCSD(T)-PES dissociates correctly to two H_2O monomers as the O···O distance increases. The 1-D fully relaxed potential along this dissociation coordinate is shown in Figure 3. D_e is determined to be 1665.7 cm^{-1} (4.76 kcal/mol). This is very close to the D_e, 1678 cm^{-1} (4.80 kcal/mol), for the best water-dimer intermolecular potential surface, VRT(ASP-W)-III.[13,14] As noted earlier the effect of the counterpoise correction on D_e was reported in ref 3. In CCSD(T)/aug-cc-pVTZ calculations D_e equals 4.75 and 5.22 kcal/mol with and without the correction. Note the former value is gratifyingly very close to the PES value, as it should be for a precise fit. These values (with and without the counterpoise correction) differ from the benchmark value of 4.99−5.02 kcal/mol reported in ref 8 by roughly equal amounts, i.e., 0.25 kcal/mol (87 cm^{-1}).

Properties of the H_2O monomer from the CCSD(T)-PES are given in Table 5. Excellent agreement is seen with properties on the accurate H_2O Schwenke−Partridge surface.[30] The monomer properties on the CCSD(T)-PES are very similar to the ones obtained on our $H_5O_2^+$ PES.[27]

Diffusion Monte Carlo (DMC) calculations of the dimer zero-point properties were done using the CCSD(T)-PES, with 10 trials. Each trial contains 20 000 replicas and propagates nearly 9000 steps (1.33 ps imaginary time, in total). Following standard procedures initially the step size was 25 au to allow for rapid "equilibration" and the final step size was reduced to 5 au. The calculated zero-point energy is 9854 ± 3 cm^{-1}, which is 234 cm^{-1} lower than harmonic zero-point energy. Expectation values of distances have also been computed: the O···O distance is 3.02 (±0.02) Å; the two O−H bond lengths in H-donor monomer are 0.9852 and 0.9890 Å, and the two O−H bond lengths in H-receptor are both 0.9865 Å.

Combining the DMC zero-point energy and the ZPE of H_2O monomer beyond dissociation limit, we obtain $D_0 = 12.44$ kJ/mol, i.e., 1042 cm^{-1}. This agrees well with the D_0 on the VRT(ASP-W)III surface, 1080 cm^{-1}.[13,14] On the other hand, the harmonic ZPEs of the water monomer and dimer on the CCSD(T)-PES are 4686.5 and 10088 cm^{-1}, respectively and hence harmonic $D_0 = 951$ cm^{-1}, which is 91 cm^{-1} lower than anharmonic results. The DMC and variational calculations described above have been also carried out for the fully deuterated water dimer. The ZPE of the complex is 7239 ± 2 cm^{-1}, and the D_2O monomer ZPE is 3371 cm^{-1}. Three vibrational fundamentals of the monomer are 1177, 2657, and 2772 cm^{-1}. Combining these results with the D_e, the $(D_2O)_2$ D_0 is 1169 cm^{-1}, which is in the range of the experiments, 1280 ± 175 cm^{-1}.

As noted above, the PES D_e is roughly 85−90 cm^{-1} below the benchmark ab initio value. If we shift the D_0 values above by this amount, we obtain values of 1127−1132 cm^{-1} for H_2O_2 and 1254−1259 cm^{-1} for D_2O_2.

D. Dipole Moment Surface (DMS). The dipole moment was calculated at the MP2/aug-cc-pVTZ level at the same set of grid points used for the energies. The fit was done as described in detail previously.[27] In brief, the fit is based on the user's choice of Cartesian coordinates of the atoms because the fit uses effective nuclear charges that are located on each nucleus, and these parameters depend on the internuclear distances. The RMS fitting error is plotted in Figure 4, with respect to energy. Note we chose the *x*-axis is to be along the O···O bond and *y* and *z* are the remaining two perpendicular components. They

TABLE 3: Intermonomer Geometry Parameters of 10 $(H_2O)_2$ Stationary Points on the CCSD(T)-PES[a]

	$r(O_2\cdots H_2)$	$\angle O_1H_1O_2$	$\angle H_3O_2O_1$	$\angle H_4O_2O_1$	$\tau O_2H_2O_1H_1$	$\tau H_3O_2O_1H_2$	$\tau H_4O_2O_1H_2$
1	1.9775	171.23	109.29	109.29	180.00	123.05	−123.05
	(1.9485)	(172.92)	(110.50)	(110.50)	(180.00)	(122.37)	(−122.37)
2	2.0158	168.30	103.96	128.34	157.66	171.38	49.44
	(1.9724)	(168.94)	(107.33)	(135.00)	(144.61)	(159.63)	(25.88)
3	2.0040	166.25	109.79	145.16	180.00	180.00	0.00
	(1.9813)	(167.59)	(109.96)	(145.00)	(180.00)	(180.00)	(0.00)
4	2.2971	115.09	130.42	47.02	−132.08	109.54	180.00
	(2.2796)	(114.84)	(132.32)	(47.15)	(−134.78)	(111.86)	(180.00)
5	2.3047	112.18	145.51	49.32	−153.57	−118.56	−167.98
	(2.2810)	(112.52)	(145.10)	(48.95)	(−153.28)	(−118.27)	(−167.68)
6	2.3122	109.91	156.23	51.15	180.00	180.00	180.00
	(2.2756)	(110.27)	(155.80)	(50.66)	(180.00)	(180.00)	(180.00)
7	3.1718	69.72	53.30	53.30	180.00	−104.54	101.94
	(2.9997)	(77.32)	(55.16)	(55.16)	(180.00)	(−108.75)	(108.75)
8	3.1042	92.82	70.22	70.22	−63.02	180.00	67.22
	(3.1140)	(92.24)	(70.84)	(70.84)	(−64.02)	(180.00)	(67.93)
9	2.5260	112.02	127.75	127.75	0.00	−90.00	90.00
	(2.5154)	(112.03)	(127.79)	(127.79)	(0.00)	(−90.00)	(90.00)
10	2.6759	112.83	127.96	127.96	0.00	0.00	180.00
	(2.6830)	(112.92)	(127.95)	(127.95)	(0.00)	(0.00)	(180.00)

[a] The numbers in parentheses are the benchmark ab initio results from ref 8. Bond lengths are in Å and angles are in degrees. The atoms are numbered as in Figure 1.

TABLE 4: Harmonic Frequencies (cm^{-1}) and Symmetries of 12 Vibrational Normal Modes Analyzed at 10 Stationary Points on the CCSD(T)-PES

mode	Str 01	Str 02	Str 03	Str 04	Str 05	Str 06	Str 07	Str 08	Str 09	Str 10
1	120 A″	92i A	153i A″	139i A_u	128i B	128i B_g	206i A″	228i B_g	220i B_2	241i B_1
	(131)	(83i)	(177i)	(134i)	(120i)	(171i)	(204i)	(230i)	(221i)	(246i)
2	132 A″	119 A	60i A″	107 A_u	47 B	92i B_u	61i A′	157i A_u	51 B_1	178i A_2
	(155)	(133)	(90i)	(109)	(34i)	(91i)	(88i)	(159i)	(57)	(195i)
3	142 A′	153 A	105 A′	148 A_g	99 A	79i A_u	131 A′	124i B_u	123 A_1	94 B_2
	(158)	(140)	(118)	(148)	(102)	(104i)	(133)	(133i)	(123)	(9.2)
4	180 A′	167 A	164 A′	183 A_g	161 A	157 A_g	157 A″	82 A_g	161 B_2	96 A_1
	(191)	(177)	(169)	(190)	(165)	(161)	(175)	(81)	(175)	(95)
5	351 A′	371 A	353 A′	355 A_u	324 A	369 A_u	267 A″	246 A_u	204 A_2	162 B_1
	(369)	(340)	(370)	(374)	(339)	(385)	(294)	(248)	(213)	(156)
6	601 A″	486 A	437 A″	551 A_g	481 A	384 A_g	414 A′	356 A_g	417 B_1	330 B_2
	(640)	(550)	(454)	(551)	(506)	(410)	(422)	(363)	(427)	(318)
7	1646 A′	1647 A	1645 A′	1642 A_u	1632 B	1632 B_u	1641 A′	1651 A_g	1640 A_1	1641 A_1
	(1661)	(1660)	(1660)	(1654)	(1650)	(1648)	(1656)	(1669)	(1657)	(1661)
8	1661 A′	1670 A	1667 A′	1648 A_g	1658 A	1657 A_g	1654 A′	1652 B_u	1659 A_1	1659 A_1
	(1686)	(1688)	(1689)	(1667)	(1676)	(1674)	(1675)	(1670)	(1679)	(1677)
9	3734 A′	3750 A	3762 A′	3781 A_g	3791 A	3799 B_u	3803 A′	3807 A_g	3804 A_1	3801 A_1
	(3750)	(3768)	(3780)	(3805)	(3810)	(3822)	(3826)	(3833)	(3829)	(3831)
10	3805 A′	3807 A	3819 A′	3793 A_u	3794 B	3800 A_g	3816 A′	3812 B_u	3818 A_1	3828 A_1
	(3827)	(3832)	(3838)	(3816)	(3818)	(3817)	(3835)	(3830)	(3841)	(3846)
11	3894 A′	3898 A	3900 A′	3903 A_g	3910 B	3915 B_u	3906 A″	3905 A_u	3904 B_2	3915 B_1
	(3914)	(3918)	(3921)	(3928)	(3932)	(3939)	(3925)	(3934)	(3928)	(3936)
12	3911 A″	3914 A	3928 A′	3906 A_u	3913 A	3923 A_g	3913 A′	3910 B_g	3914 B_1	3915 B_1
	(3934)	(3941)	(3948)	(3929)	(3934)	(3938)	(3937)	(3933)	(3938)	(3938)

TABLE 5: Free Water Monomer Properties beyond the Dissociation Limit CCSD(T)-PES, Compared with the Results Acquired on the Schwenke−Partridge (SP) Surface

	r_{eq} (Å)	$\angle HOH_{eq}$ (deg)	r_{linear} (Å)	linear barrier (cm^{-1})	harmonic frequencies (cm^{-1})			vibrational fundamentals (cm^{-1})			
					ν_b	ν_{as}	ν_{ss}	ZPE	ν_b	ν_{as}	ν_{ss}
CCSD(T)-PES	0.9613	104.2	0.9377	11182	1642	3810	3921	4615	1595	3640	3737
SP-PES	0.9578	104.5	0.9335	11127	1649	3833	3944	4638	1595	3657	3756

are “user defined” and in the present case have some arbitrary but fixed orientation. The RMS errors for all the data points (up to 110 000 cm^{-1}) are 0.050, 0.028, and 0.028 D (D), for the *x*, *y*, and *z* components, respectively. The dipole magnitude varies from 0 to 4 D.

As given in Table 1, the magnitude from the DMS at the 10 stationary points differs from direct MP2/aug-cc-pVTZ dipole values by ±0.01 D, whereas the deviations from the ab initio dipoles given in Tschumper et al.[8] are as large as 10%.

As noted already, the DMS extends to the dimer dissociation limit. The water monomer dipole at the minimum given by the DMS is 1.8538 D, which agree excellently with the MP2 ab initio value of 1.8585 D. It is also very close to the benchmark dipole value given in ref 8, 1.9250 D.

To check the quality of present DMS, the global minimum structure on the potential surface has been chosen as reference, where the dipole magnitude is 2.5602 D, and the four O−H bonds and O⋯O bond are stretched to see how the dipole magnitude changes along these stretches. The variation of the dipole magnitude with these distances is shown in Figure 5.

As seen, the dipole magnitude changes most with the donor OH stretch suggesting large IR intensity associated with the

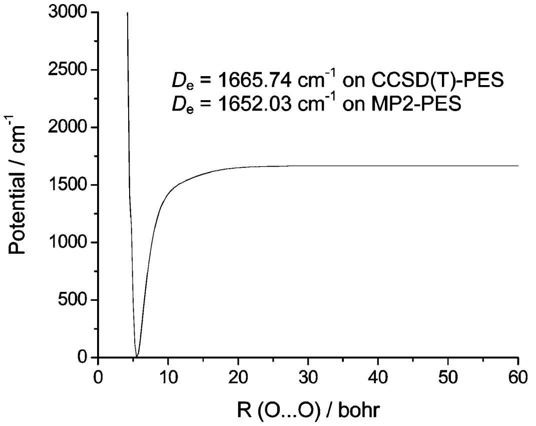

Figure 3. 1-D relaxed potential cut along the dissociation of water dimer.

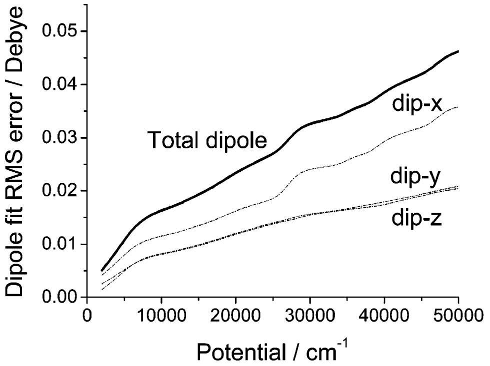

Figure 4. Fitting accuracy of $(H_2O)_2$ dipole moment surface. O···O is oriented along the *x* axis. The RMS errors for all the data points (up to 110 000 cm^{-1}) are 0.050, 0.028, and 0.028 D, respectively.

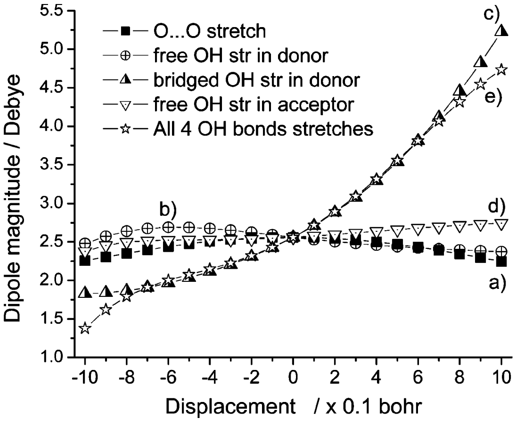

Figure 5. Dipole magnitude variations at the $(H_2O)_2$ global minimum on the reported CCSD(T)-PES and MP2-DMS: (a) O···O symmetric stretch; (b) free O−H stretch in donor; (c) hydrogen-bonded O−H stretch in donor; (d) free O−H stretch in acceptor; (e) synchronized stretches of all four O−H bonds. Each unit on displacement *x*-axis is 0.1 bohr. Both O atoms are fixed at minimum coordinates in (b)−(d) stretches. All dipole magnitudes are in Debye.

motions of shared H atom. This is consistent with the intensity calculation (in the double harmonic approximation) reported by Tschumper et al.[8]

IV. Summary

In this paper we presented a full-dimensional ab initio potential energy surface (CCSD(T)/aug-cc-pVTZ + BSSE correction) and dipole moment surface (MP2/aug-cc-pVTZ level) for the water dimer. Computational details and fitting accuracy checks were given. The surfaces can dissociate into two water molecules correctly, with equilibrium dissociation energy $D_e = 1665.74$ cm^{-1}. Ten characteristic stationary points have been located on the surface. Geometries, barrier heights, dipole moments, and harmonic frequencies of the 10 structures were reported in detail and compared with previous benchmark calculations at the stationary points. A lower level full-dimensional potential energy surface based on MP2 calculations was also reported and compared with the structures directly optimized from MP2-level ab initio calculations. All comparisons show that the potential surfaces faithfully represent the ab initio calculations. They are capable of describing the low-energy potential region of such a weakly bonded complex system. Water monomer properties beyond dissociation limit were presented. Diffusion Monte Carlo calculation gives a ZPE of water dimer of 9854 ± 3 cm^{-1}, which has been used to obtain the dissociation energy $D_0 = 12.44$ kJ/mol.

These surfaces can be obtained by contacting the author at jmbowma@emory.edu.

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References and Notes

(1) Klopper, W.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2227.

(2) Taketsugu, T.; Wales, D. J. *Mol. Phys.* **2002**, *100*, 2793.

(3) Watanabe, Y.; Taketsugu, T.; Wales, D. J. *J. Chem. Phys.* **2004**, *120*, 5993.

(4) Crittenden, D. L.; Jordan, M. J. T. *J. Chem. Phys.* **2005**, *122*.

(5) Wieczorek, R.; Haskamp, L.; Dannenberg, J. J. *J. Phys. Chem. A* **2004**, *108*, 6713.

(6) Burnham, C. J.; Xantheas, S. S. *J. Chem. Phys.* **2002**, *116*, 1479.

(7) Smith, B. J.; Swanton, D. J.; Pople, J. A.; Schaefer, H. F.; Radom, L. *J. Chem. Phys.* **1990**, *92*, 1240.

(8) Tschumper, G. S.; Leininger, M. L.; Hoffman, B. C.; Valeev, E. F.; Schaefer, H. F.; Quack, M. *J. Chem. Phys.* **2002**, *116*, 690.

(9) Schofield, D. P.; Kjaergaard, H. G. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3100.

(10) Xantheas, S. S.; Dunning, T. H. *J. Chem. Phys.* **1993**, *99*, 8774.

(11) Keutsch, F. N.; Braly, L. B.; Brown, M. G.; Harker, H. A.; Petersen, P. B.; Leforestier, C.; Saykally, R. J. *J. Chem. Phys.* **2003**, *119*, 8927.

(12) Goldman, N.; Leforestier, C.; Saykally, R. J. *J. Phys. Chem. A* **2004**, *108*, 787.

(13) Goldman, N.; Saykally, R. J. *J. Chem. Phys.* **2004**, *120*, 4777.

(14) Goldman, N.; Fellers, R. S.; Brown, M. G.; Braly, L. B.; Keoshian, C. J.; Leforestier, C.; Saykally, R. J. *J. Chem. Phys.* **2002**, *116*, 10148.

(15) Leforestier, C.; Gatti, F.; Fellers, R. S.; Saykally, R. J. *J. Chem. Phys.* **2002**, *117*, 8710.

(16) Bouteiller, Y.; Perchard, J. P. *Chem. Phys.* **2004**, *305*, 1.

(17) Forney, D.; Jacox, M. E.; Thompson, W. E. *J. Mol. Spectrosc.* **1993**, *157*, 479.

(18) Ceponkus, J.; Nelander, B. *J. Phys. Chem. A* **2004**, *108*, 6499.

(19) Huang, Z. S.; Miller, R. E. *J. Chem. Phys.* **1989**, *91*, 6613.

(20) Keutsch, F. N.; Goldman, N.; Karyakin, E. N.; Harker, H. A.; Sanz, M. E.; Leforestier, C.; Saykally, R. J. *Faraday Discuss.* **2001**, *118*, 79.

(21) Smit, M. J.; Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A.; Bukowski, R.; Szalewicz, K. *J. Phys. Chem. A* **2001**, *105*, 6212.

(22) Keutsch, F. N.; Goldman, N.; Harker, H. A.; Leforestier, C.; Saykally, R. J. *Mol. Phys.* **2003**, *101*, 3477.

(23) Mas, E. M.; Bukowski, R.; Szalewicz, K.; Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **2000**, *113*, 6687.

(24) Curtiss, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703.

(25) Groenenboom, G. C.; Mas, E. M.; Bukowski, R.; Szalewicz, K.; Wormer, P. E. S.; van der Avoird, A. *Phys. Rev. Lett.* **2000**, *84*, 4072.

(26) Goldman, N.; Leforestier, C.; Saykally, R. J. *Philos. Trans. R. Soc. A* **2005**, *363*, 493.

(27) Huang, X. C.; Braams, B. J.; Bowman, J. M. *J. Chem. Phys.* **2005**, *122*, 044308.

(28) MOLPRO, 2002.6, is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, M. Schütz, R. Lindh, P. Celani, T. Korona, G. Rauhut, F. R. Manby, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer,

A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone R. Tarroni, and T. Thorsteinsson.

(29) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(30) Partridge, H.; Schwenke, D. W. *J. Chem. Phys.* **1997**, *106*, 4618.