

Water Dimer Cation: Density Functional Theory vs Ab Initio Theory

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Abstract: By using density functional theory (DFT) and high-level ab initio theory, the structure, interaction energy, electronic property, and IR spectra of the water dimer cation $[(\text{H}_2\text{O})_2]^+$ are investigated. Two previously reported structures of the water dimer cation [disproportionated ionic (Ion) structure and hydrazine-like (OO) structure] are compared. For the complete basis set (CBS) limit of coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)], the Ion structure is much more stable (by 11.7 kcal/mol). This indicates that the ionization of water clusters produce the hydronium cation moiety (H_3O^+) and the hydroxy radical. The transition barrier for the interconversion from the Ion/OO structure is $\sim 15/\sim 9$ kcal/mol. It is interesting to note that the calculation results of the water dimer cation vary seriously depending on calculation methods. Möller–Pleset second-order perturbation (MP2) theory gives reasonable relative energies in favor of the Ion structure but reports unreasonable frequencies for the OO structure. On the other hand, most DFT calculations with various functionals overstabilize the OO structure. However, the DFT results with MPW1K and BH&HLYP functionals are very close to the CCSD(T)/CBS results. Thus, as for the validity test of the DFT functionals for ionized molecular systems, the energy comparison of two water dimer cation structures would be a very important criterion.

I. Introduction

Numerous experimental and theoretical studies have been carried out on aqua clusters (neutral water clusters,¹ anion-water clusters,² and cation-water clusters³). The investigation of neutral water clusters has provided the information on neutral H-bonds. The studies of electron–water clusters have provided the information on the electron affinity (EA) of neutral water and the hydration of an electron.⁴ Through the study of the hydronium–water clusters,⁵ the hydration and coordination chemistry of hydronium cation or proton are understood. There have also been a number of studies on the hydration and dissociation phenomena of acids, bases, and salts,⁶ which are important in understanding the nature of water as a solvent. In addition, the studies of the ionization

and the ionized state of the water molecule are very useful for understanding the water cluster cations.^{7,8}

The ionization of water clusters is widely seen in neutron irradiation of the cooling water in a nuclear atomic plant, in the photoreaction of water, and in aqueous environments.⁹ The ionization energy of the water molecule is 12.61 eV.⁸ Water cluster cations $[(\text{H}_2\text{O})_n]^+$ were experimentally produced under special conditions in the gas phase.¹⁰ A few theoretical investigations for water cluster cations were performed.^{11–13} For the water dimer cation, the hydrazine-like (OO) structures and disproportionated ionic (Ion) structure were suggested.^{11,12} Therefore, we investigate the structures, energetics, spectra, and dynamics of the water dimer cations $[(\text{H}_2\text{O})_2]^+$ using high level ab initio calculations. Here, we note serious failures of most DFT calculations except for a few functionals. Thus, the comparison of the DFT and CCSD(T) results for the water dimer cation is also addressed.

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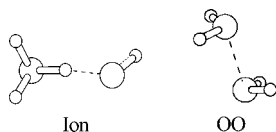


Figure 1. Disproportionated ionic (Ion) structure and hydrazine-like (OO) structure of the water dimer cation $(\text{H}_2\text{O})_2^+$.

II. Calculation Methods

The OO structure and the Ion structure of the water dimer cation are shown in Figure 1. We optimized the two structures and calculated their frequencies using various DFT methods of Becke's exchange and Lee–Yang–Parr correlation functionals (BLYP),¹⁴ Becke's exchange and Perdew–Wang correlation functionals (BPW91),¹⁵ Handy's family functional including gradient-corrected correlation (HCTH-407),¹⁶ Becke's three-parameters for exchange and Lee–Yang–Parr correlation functionals (B3LYP),¹⁷ Perdew–Burke–Ernzerhof hybrid functional (PBE1PBE),¹⁸ modified Perdew–Wang one-parameter model for kinetics (MPW-1K),¹⁹ Becke's half HF-LSDA (Hartree–Fock Local Spin Density Approximation) exchange and Lee–Yang–Parr correlation functionals (BH&H),²⁰ and Becke's half HF-LSDA–Becke exchange and Lee–Yang–Parr correlation functionals (BH&HLYP)²¹ with the 6-311++G** basis set.²² The MP2 optimizations and frequency calculations were also carried out using the aug-cc-pVDZ (abbreviated as aVDZ) and the aug-cc-pVTZ (aVTZ) basis sets.²³ The MP2 single-point calculations with the aug-cc-pVQZ (aVQZ) basis set were also done on the MP2/aVTZ geometries (MP2/aVQZ//MP2/aVTZ). To obtain more accurate results, the CCSD(T) optimizations and frequency calculations were performed using the aVDZ and aVTZ basis sets. The CCSD(T) single-point calculations using the aVQZ basis set were also done on the CCSD(T)/aVTZ geometries (CCSD(T)/aVQZ//CCSD(T)/aVTZ). The 1s orbitals of oxygen atoms were frozen in the correlation calculations. All the “d” and “f” orbitals used here are the spherical harmonic basis functions (5d and 7f).

For the Ion structure, which has the charged H-bonding between one hydronium cation and one neutral hydroxyl radical, the basis set superposition energy (BSSE) correction can be made. However, in the OO structure the positive charge is almost equally distributed in two water molecules, so the BSSE correction cannot be made properly. In order to compare the two structures at equal conditions, it is better not to make the BSSE corrections. Thus, the BSSE corrections are not considered in this system.

All the optimizations were done with the minimization of total energy without any symmetry constraints. We calculated the zero-point-energy (ZPE) uncorrected total energy (ΔE_c) at the equilibrium states of the Born–Oppenheimer potential surfaces and the ZPE-corrected total energy (ΔE_0). The enthalpy/free energy changes ($\Delta H_r/\Delta G_r$) at room temperature and 1 atm were obtained using the frequency calculations. The CBS limit interaction energies were obtained with the extrapolation scheme utilizing that the electron correlation error is proportional to N^{-3} for the aug-cc-pVNZ basis set [$\Delta E_{\text{CBS}} = (\Delta E_N N^{-3} \Delta E_{N-1} (N - 1)^3) / (N^3 - (N - 1)^3)$].²⁴ The

Table 1. Various DFT/6-311++** Interaction Energies (kcal/mol) of the Ion and OO Structures of the Water Dimer Cation, $(\text{H}_2\text{O})_2^+$ ^a

method	$-\Delta E_c (-\Delta E_0)$	
	Ion structure	OO structure
BLYP	49.3 (46.5)	58.4 (54.0)
BPW91	49.1 (46.4)	57.2 (52.8)
HCTH407	48.0 (45.2)	56.6 (52.1)
B3LYP	49.8 (46.8)	51.5 (46.7)
PBE1PBE	50.3 (47.4)	49.8 (45.0)
MPW1K	49.9 (46.9)	42.9 (37.9)
BH&H	55.5 (52.6)	48.9 (43.8)
BH&HLYP	49.9 (46.7)	41.4 (36.1)

^a Interaction energy between the neutral water monomer and the water monomer cation. ΔE_c is the ZPE-uncorrected energy at the equilibrium point of the Born–Oppenheimer potential surfaces, and ΔE_0 is the ZPE-corrected energy.

DFT and MP2 calculations were carried out by using the Gaussian 03 suite of programs,²⁵ and the CCSD(T) calculations were performed by using the Molpro2002.6 package.²⁶ The approximate resolution of the identity MP2 (RI-MP2) calculations²⁷ was also carried out by using the Turbomole5.6 package.²⁸ However, these results are essentially the same, with the MP2 values within 0.1 kcal/mol, so these results are not reported here.

III. Results and Discussion

For the water monomer, the vertical/adiabatic IP (IP_v/IP_a) calculated on the basis of the unrestricted open-shell approach is 12.70/12.61 eV at the MP2/aVDZ level of theory, 12.86/12.77 eV at the MP2/aVTZ level, 12.51/12.42 eV at the CCSD(T)/aVDZ level, 12.68/12.57 eV at the CCSD(T)/aVTZ level, and 12.74/12.64 eV at the CCSD(T)/aVQZ//CCSD(T)/aVTZ level. These values are close to the experimental IP (12.61 eV).⁸ The O–H distance and H–O–H bond angle of the water monomer cation are 1.002 Å and 109.1° at the CCSD(T)/aVTZ level, which shows 0.04 Å longer O–H distances and 4.9° wider bond angle than those of the neutral water monomer (0.962 Å and 104.2° at the CCSD(T)/aVTZ level). The O–H bond strength becomes weaker and the H–H repulsion is greater due to the ionization.

We calculated the interaction energy between the neutral water monomer and the water monomer cation [$\Delta E(\text{dimer cation}) = E(\text{dimer cation}) - E(\text{water monomer}) - E(\text{water monomer cation})$], where the geometries for water monomers are relaxed in the dimer. From the optimization of water dimer cation, the OO structure of the “anti” form has one imaginary frequency, while the asymmetric OO structure of the “gauche” form has all real frequencies. Thus, the asymmetric OO structure is shown in Figure 1. As in Table 1, the OO structure is much more stable than the Ion structure at the BLYP, BPW91, and HCTH407 levels of theory. The B3LYP and PBE1PBE calculations predict that both structures are compatible. On the other hand, MPW1K, BH&H, and BH&HLYP calculations predict that the Ion structure is much more stable than the OO structure. Table 2 lists the interaction energies of the two structures of the water dimer cation at the MPW1K, BH&HLYP, MP2/aVDZ,

Table 2. DFT, MP2, and CCSD(T) Interaction Energies (kcal/mol) of the Two Structures of the Water Dimer Cation, (H₂O)₂⁺^a

method	Ion structure				OO structure			
	−ΔE _e	−ΔE ₀	−ΔH _r	−ΔG _r	−ΔE _e	−ΔE ₀	−ΔH _r	−ΔG _r
MPW1K/6-311++G**	49.87	46.88	48.17	40.06	42.90	37.87	39.29	30.69
MPW1K/aVDZ	48.86	45.99	47.26	39.25	42.49	37.33	38.74	30.12
MPW1K/aVTZ	48.93	45.94	47.24	39.19	41.48	36.51	37.92	29.33
BH&HLYP/6-311++G**	49.88	46.74	47.99	39.94	41.12	36.08	37.50	29.30
BH&HLYP/aVDZ	48.83	45.82	47.07	39.09	40.45	35.46	36.88	28.64
BH&HLYP/aVTZ	48.84	45.73	46.99	38.97	39.73	34.75	36.18	27.90
MP2/aVDZ	45.92	42.91	44.15	36.25	40.68	30.17	31.71	23.23
MP2/aVTZ	46.48	43.47	44.73	36.80	40.40	30.69	32.18	24.00
MP2/aVQZ// ^b	46.47	43.45	44.72	36.78	40.48	30.77	32.26	24.08
CCSD(T)/aVDZ	45.96	46.11	47.81	38.07	39.49	34.75	36.66	26.46
CCSD(T)/aVTZ	46.68	46.48	47.81	38.79	39.51	34.76	36.67	26.49
CCSD(T)/aVQZ// ^c	46.69	46.49	47.82	38.81	39.52	34.77	36.68	26.50
CCSD(T)/CBS	46.70	46.50	47.83	38.82	39.53	34.78	36.69	26.51

^a The ZPE and thermal energy corrections at the MP2/aVQZ//MP2/aVTZ and CCSD(T)/aVQZ//CCSD(T)/aVTZ levels were made using the MP2/aVTZ and CCSD(T)/aVTZ values, respectively. ^b MP2/aVQZ//MP2/aVTZ. ^c CCSD(T)/aVQZ//CCSD(T)/aVTZ.

Table 3. Conformational Characteristics and Geometrical Parameters [Distances (*r*/Å) and Rotational Constants (*A* in GHz)] of the Two Structures of the Water Dimer Cation, (H₂O)₂⁺^a

method	Ion structure			OO structure			H ₂ O: <i>r</i> _{O–H}
	<i>r</i> _{O–H}	<i>r</i> _{O–O}	<i>A</i>	<i>r</i> _{O–H}	<i>r</i> _{O–O}	<i>A</i>	
B3LYP/6-311++G**	0.998	2.501	244.4	0.979	2.128	140.5	0.962
MPW1K/6-311++G**	0.986	2.470	252.1	0.968	2.052	143.9	0.951
MPW1K/aVDZ	0.989	2.481	242.3	0.970	2.046	142.4	0.954
MPW1K/aVTZ	0.987	2.476	243.4	0.968	2.040	143.4	0.951
BH&HLYP/6-311++G**	0.983	2.497	257.9	0.967	2.053	144.6	0.951
BH&HLYP/aVDZ	0.986	2.503	247.6	0.970	2.049	143.1	0.953
BH&HLYP/aVTZ	0.984	2.500	246.7	0.967	2.047	143.8	0.950
MP2/aVDZ	0.998	2.520	232.5	0.984	2.039	138.3	0.966
MP2/aVTZ	0.996	2.496	234.9	0.980	2.023	139.1	0.961
CCSD(T)/aVDZ	0.998	2.534	228.6	0.984	2.047	138.3	0.967
CCSD(T)/aVTZ	0.995	2.507	233.3	0.980	2.033	139.6	0.962

^a *r*_{O–H} is the average values for the O–H distances. The *r*_{O–H} of the water monomer is also listed for comparison.

MP2/aVTZ, MP2/aVQZ//MP2/aVTZ, CCSD(T)/aVDZ, CCSD(T)/aVTZ, CCSD(T)/aVQZ//CCSD(T)/aVTZ, and CCSD(T)/CBS levels of theory. Except for the MP2/aVQZ//MP2/aVTZ and CCSD(T)/aVQZ//CCSD(T)/aVTZ calculations, the two structures (OO and Ion) were fully optimized and their frequencies were calculated at each calculation level in Table 2. Although most DFT functionals predict that the OO structure is more stable than or at least comparable to the Ion structure, the most reliable CCSD(T)/CBS results show that the Ion structure is much more stable by 11.72 kcal/mol than the OO structure. Thus, only the MPW1K and BH&HLYP results among many DFT calculations are listed in Table 2 for comparison. The MPW1K and BH&HLYP results for the larger basis sets are closer to the CCSD(T)/CBS results. BH&H/6-311++G** predicts almost reasonable relative energy difference, but the interaction energy is overestimated. It is clear that most other functionals completely fail to predict the right energetics of the water dimer cation. We also note that the higher stability of the Ion structure over the OO structure retains even if the temperature rises to room temperature (298 K). Thus, the water dimer cation has the form of a hydronium cation and a hydroxyl radical. The experimental IP_v and IP_a of the water dimer are known to be 12.1 and 11.2 eV.^{29,30} On the unrestricted open-shell approach, the calculated IP_v of the water dimer is 11.9 eV at the CCSD(T)/aVQZ//CCSD(T)/aVTZ level. Using the

Ion structure, the calculated IP_a of the water dimer is 10.8 eV at the CCSD(T)/aVQZ//CCSD(T)/aVTZ level. These calculated IPs are in good agreement with the experimental data.

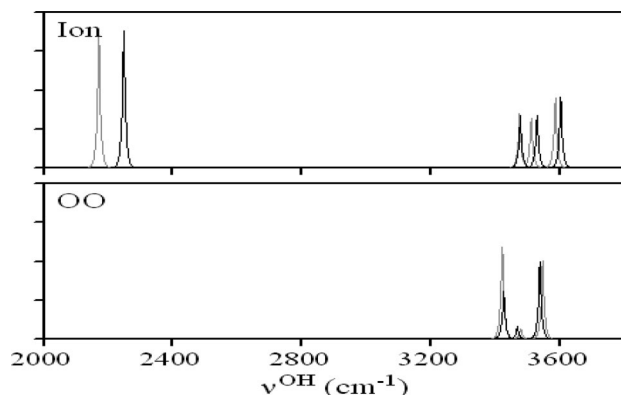
Table 3 lists the optimized geometrical parameters of Ion and OO structures at the B3LYP, MPW1K, BH&HLYP, MP2, and CCSD(T) levels. The Ion structure shows longer O–H distance and shorter O–O distance than the OO structure. The Ion structure has a larger rotational constant *A* than the OO structure. The optimized Cartesian coordinates of water dimer cations (OO and Ion structures) at the CCSD(T)/aVTZ level are listed in the Supporting Information.

The barrier height for the interconversion between the OO and Ion structures of the water dimer cation was calculated at the MPW1K/6-311++G** and MP2/aVDZ levels of theory. The transition state in the interconversion is higher in energy by 8.15 and 9.78 kcal/mol (15.11 and 15.02 kcal/mol) than the OO structure (Ion structure) at the MPW1K/6-311++G** and MP2/aVDZ levels. At the CCSD(T) single-point calculations, the transition state is higher in energy by 8.14 kcal/mol (14.59 kcal/mol) than the OO (Ion) structure with the MPW1K/6-311++G** geometries and is higher in energy by 9.69 kcal/mol (16.12 kcal/mol) than the OO (Ion) structure on the MP2/aVDZ geometries. These transition energy barriers are somewhat high.

Table 4. Scaled Frequencies [$\nu(\text{cm}^{-1})$] and the IR Intensities (as subscripts) (10 km/mol) of O–H Stretching Modes for H_2O , H_2O^+ , and $(\text{H}_2\text{O})_2^+$ (Ion and OO structures) at the DFT, MP2, and CCSD(T) Levels of Theory^a

method	scale ^b	H_2O	H_2O^+	Ion structure	OO structure
B3LYP/6-311++G**	0.956	3750, 3650	3246, 3196	3595 ₄₅ , 3523 ₁₄ , 3465 ₁₆ , 2157 ₄₅	3550 ₄₇ , 3549 ₀ , 3482 ₀ , 3434 ₇₀
MPW1K/6-311++G**	0.916	3750, 3650	3259, 3210	3585 ₄₁ , 3510 ₁₇ , 3474 ₁₈ , 2170 ₂₈₂	3546 ₅₁ , 3544 ₃ , 3478 ₀ , 3420 ₁₀₄
MPW1K/aVDZ	0.920	3752, 3648	3252, 3194	3582 ₃₇ , 3502 ₁₅ , 3468 ₁₇ , 2143 ₂₆₈	3546 ₄₉ , 3543 ₃ , 3472 ₀ , 3415 ₉₃
MPW1K/aVTZ	0.921	3749, 3651	3248, 3205	3583 ₃₈ , 3512 ₁₅ , 3476 ₁₆ , 2122 ₂₇₃	3545 ₅₀ , 3543 ₃ , 3479 ₀ , 3419 ₉₇
BH&HLYP ^c	0.917	3748, 3652	3252, 3207	3577 ₄₃ , 3506 ₁₅ , 3484 ₂₁ , 2346 ₂₆₂	3549 ₅₂ , 3547 ₅ , 3483 ₀ , 3419 ₁₂₄
BH&HLYP/aVDZ	0.920	3750, 3650	3243, 3188	3577 ₄₀ , 3500 ₁₅ , 3476 ₁₉ , 2297 ₂₅₄	3552 ₅₀ , 3549 ₅ , 3478 ₀ , 3415 ₁₁₂
BH&HLYP/aVTZ	0.922	3747, 3653	3241, 3200	3573 ₄₀ , 3506 ₁₄ , 3484 ₁₉ , 2282 ₂₅₇	3545 ₅₁ , 3543 ₄ , 3481 ₀ , 3414 ₁₁₇
MP2/aVDZ	0.957	3764, 3636	3308, 3232	3596 ₃₅ , 3519 ₇ , 3502 ₂₄ , 2221 ₂₆₁	6092 ₉₉₉₉ , 3537 ₃₇ , 3532 ₁₀ , 3442 ₀
MP2/aVTZ	0.952	3760, 3640	3304, 3245	3592 ₃₇ , 3520 ₆ , 3508 ₂₅ , 2157 ₂₇₂	5663 ₉₉₉₉ , 3528 ₄₇ , 3526 ₂ , 3447 ₀
CCSD(T)/aVDZ	0.962	3757, 3643	3277, 3207	3604 ₃₃ , 3522 ₁₅ , 3486 ₁₃ , 2288 ₂₄₇	3542 ₄₀ , 3540 ₄ , 3460 ₀ , 3419 ₁₁
CCSD(T)/aVTZ	0.958	3752, 3648	3279, 3225	3602 ₄₃ , 3528 ₁₉ , 3476 ₁₆ , 2248 ₃₁₅	3537 ₅₀ , 3536 ₅ , 3467 ₀ , 3424 ₁₄

^a The frequencies of H_2O and H_2O^+ are also reported for comparison. ^b Scale factors (see the text). ^c BH&HLYP/6-311++G**.

**Figure 2.** MPW1K/6-311++G** (gray) and CCSD(T)/aVTZ (black) predicted IR spectra for the O–H stretching frequencies of the water dimer cation.

The experimental ν_3 , ν_1 , and ν_2 frequencies of the water monomer cation are known to be 3259, 3213, and 1408 cm^{-1} .⁷ We employed the scale factors (0.956 at the B3LYP/6-311++G** level, 0.916 at the MPW1K/6-311++G** level, 0.952 at the MP2/aVTZ level, 0.962 at the CCSD(T)/aVDZ level, and 0.958 at the CCSD(T)/aVTZ level) to match the average value of calculated symmetric and asymmetric stretch frequencies (ν_1 and ν_3) of the neutral H_2O with the corresponding experimental value (3700 cm^{-1}).³¹ The calculated frequencies of the water monomer cation are 3246, 3196, and 1354 cm^{-1} at the B3LYP/6-311++G** level; 3259, 3210, and 1332 cm^{-1} at the MPW1K/6-311++G** level; 3304, 3245, and 1400 cm^{-1} at the MP2/aVTZ level; 3277, 3207, and 1413 cm^{-1} at the CCSD(T)/aVDZ level; and 3279, 3225, and 1413 cm^{-1} at the CCSD(T)/aVTZ level. In the water monomer cation, the strength of O–H bonds is weakened due to the ionization as compared with the neutral water monomer. The asymmetric and symmetric O–H stretching frequencies and bending frequency are red-shifted by 473, 422, and 163 cm^{-1} at the CCSD(T)/aVTZ level in comparison with those of pure neutral water monomer, respectively.

We have calculated the frequencies of the Ion and OO structures of the water dimer cation at the DFT, MP2, and CCSD(T) levels (Figure 2 and Table 4). For the OO structure, the MP2 calculations with aVDZ and aVTZ basis sets fail to produce reasonable frequencies, while DFT and CCSD(T) calculations give reasonable frequencies as shown in Table 4. At the CCSD(T)/aVTZ level, the OO structure shows four

weakly red-shifted O–H stretching frequencies of 3424, 3467, 3536, and 3537 cm^{-1} , while the Ion structure shows one strongly red-shifted peak and three weakly red-shifted peaks at 2248, 3476, 3528, and 3602 cm^{-1} . One strongly red-shifted frequency (2248 cm^{-1} at the CCSD(T)/aVTZ level) of the Ion structure is of the hydronium moiety (H_3O^+) interacting with the hydroxyl radical (OH).

IV. Concluding Remarks

At the CCSD(T)/CBS level of theory, the Ion structure is much more stable than the OO structure. The Ion structure is composed of a hydronium cation and a hydroxyl radical. On the other hand, most DFT calculations with various functionals favor the OO structure. Nevertheless, the DFT results with MPW1K and BH&HLYP functionals are very close to the CCSD(T)/CBS results. Thus, the energy comparison of the two structures of the water dimer cation would be an interesting example for the validity test of the DFT functionals. The MP2 calculations give reasonable relative energies but unreasonable frequencies for the OO structure. Therefore, in order to obtain reliable stabilities and frequencies of water dimer cation, the CCSD(T) calculations are required. However, the DFT(MPW1K) is an alternative to obtain reliable results for this system with much less computing time. The calculated spectra are provided to facilitate future experiments.

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Supporting Information Available: Optimized structures of water dimer cations (OO and Ion structures) at the CCSD(T)/aVTZ level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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