

Water trimer cation

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Received: 3 March 2011 / Accepted: 16 September 2011 / Published online: 1 October 2011
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Abstract By using density functional theory (DFT) and high-level ab initio theory, we have investigated the structure, interaction energy, electronic property, and IR spectra of the water trimer cation $[(\text{H}_2\text{O})_3]^+$. Two structures of the water trimer cation [the H_3O^+ containing linear (3Lp) structure versus the ring (3OO) structure] are compared. For the complete basis set (CBS) limit of coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)], the 3Lp structure is 11.9 kcal/mol more stable than the 3OO structure. This indicates that the ionization of water clusters produce the hydronium cation moiety (H_3O^+) and the hydroxyl radical. It is interesting to note that the calculation results of the water trimer cation vary seriously depending on the calculation level. At the level of Möller–Plesset second-order perturbation (MP2) theory, the stability of 3OO is underestimated due to the underestimated O...O hemibonding energy. This stability is also underestimated even for the CCSD(T) single point calculations on the MP2-optimized geometry. For the 3OO structure, the MP2 and CCSD(T) calculations give closed-ring structures with a hemi-bond between two O atoms, while the DFT calculations show open-ring structures due to the overestimated O...O hemibonding energy. Thus, in order to obtain reliable stabilities and frequencies of the

water trimer cation, the CCSD(T) geometry optimizations and frequency calculations are necessary. In this regard, the DFT functionals need to be improved to take into account the proper O...O hemibonding energy.

Keywords Water trimer · Ab initio calculations · Density functional theory · Water cluster · Energetics

1 Introduction

Numerous experimental and theoretical studies have been performed on aqua clusters (neutral water clusters [1–9], anion-water clusters [10–15], and cation-water clusters [16–23]). Through the investigation of neutral water clusters, we understand neutral H-bonds. From the studies of electron-water clusters, we have the information of the hydration of an electron [24–32]. Based on the study of the hydronium-water clusters [33–35], the hydration and coordination chemistry of hydronium cation or proton are understood. The hydration and dissociation phenomena of acids, bases, and salts have been widely studied [36], 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 [37–41], which can be easily observable in stratosphere. The ionization of water clusters is widely seen in neutron irradiation to the cooling water in a nuclear atomic plant, in the photoreaction of water, and in aqueous environments [42–44]. Water cluster cations $[(\text{H}_2\text{O})_n]^+$ were experimentally produced under special conditions in the gas phase [45]. A few theoretical investigations for water cluster cations were performed [46–55]. For the water dimer cation, the H_3O^+ -containing structure and the O...O structure were

Dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday and published as part of the Nagase Festschrift Issue.

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suggested [46–48]. However, the water polymer cations are hardly studied yet.

In previous works of the water dimer cation at high levels of ab initio theory, the $\text{H}_3\text{O}^+\dots\text{OH}$ structure is much more stable than the $\text{H}_2\text{O}\dots\text{OH}_2$ structure [56]. For $(\text{NH}_3)_2^+$, the $\text{H}_3\text{NH}^+\dots\text{NH}_2$ structure is the most stable, 5 kcal/mol more stable than the $(\text{H}_3\text{N}\dots\text{NH}_3)^+$ structure [57]. For $(\text{NH}_3\dots\text{H}_2\text{O})^+$, the $\text{H}_2\text{NH}^+\dots\text{OH}_2$ structure is the most stable, 2 kcal/mol more stable than the $\text{H}_3\text{NH}^+\dots\text{OH}$ structure and 4 kcal/mol more stable than the $\text{H}_3\text{NH}^+\dots\text{OH}$ structure [57]. Although the Becke's three-parameters for exchange and Lee–Yang–Parr correlation functionals (B3LYP) failed to give reliable energetics of the above systems, the modified Perdew–Wang 1-parameter model for kinetics (MPW1K) [58] and the Becke's half HF–LSDA–Becke exchange and Lee–Yang–Parr correlation functionals (BH&HLYP: $0.5 \times E_X^{\text{HF}} + 0.5 \times E_X^{\text{LSDA}} + 0.5 \times \Delta E_X^{\text{Becke88}} + E_C^{\text{LYP}}$) were reliable, very close to the CCSD(T)/CBS results.

The water trimer cation also shows two types of structure, as in the water dimer cation [56]. However, the calculated energies are not reliable even for the CCSD(T) single point calculations on the MP2 geometry-optimized structures. The density functional theory (DFT)-optimized structures are different from the MP2-/CCSD(T)-optimized ones. Therefore, we investigate the water trimer cation $[(\text{H}_2\text{O})_3^+]$ using the structures and spectra on the geometries optimized at the CCSD(T)/aug-cc-pVTZ level and the energies at the CCSD(T)/CBS level.

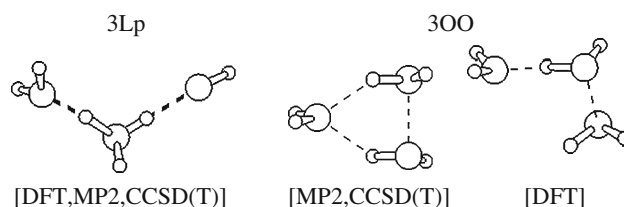


Fig. 1 Ionic (3Lp) structure and hydrazine-like (300) structure of the water trimer cation $(\text{H}_2\text{O})_3^+$

2 Calculation methods

The 3Lp structure and the 300 structure of the water trimer cation are shown in Fig. 1. We optimized the two types of structure of the water trimer cation and calculated their frequencies using B3LYP, MPW1K, and BH&HLYP with the 6-311++G**, aug-cc-pVDZ (abbreviated as aVDZ), and aug-cc-pVTZ (aVTZ) basis sets. The MP2 optimizations and frequency calculations were also carried out using the aVDZ and aVTZ basis sets. To obtain more accurate results, the CCSD(T) calculations at both MP2- and CCSD(T)-optimized geometries were performed using the aVDZ and aVTZ basis sets. The 1 s 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).

The 3Lp structure has two charged H-bond interactions [59, 60] of central hydronium cation with one neutral hydroxyl radical and one neutral water molecule. However,

Table 1 DFT, MP2, and CCSD(T) interaction energies (kcal/mol) of the two structures of the water trimer cation, $(\text{H}_2\text{O})_3^+$

Method	3Lp				300			
	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H_r$	$-\Delta G_r$	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H_r$	$-\Delta G_r$
B3LYP/6-311++G**	78.65	73.69	75.52	59.33	77.37	70.56	72.74	55.80
MPW1K/6-311++G**	79.17	74.21	76.07	59.88	69.78	62.92	65.17	48.11
MPW1K/aVDZ	76.64	71.86	73.72	57.57	67.80	61.05	63.31	46.21
MPW1K/aVTZ	76.47	71.50	73.45	57.08	66.81	60.11	62.35	45.30
BH&HLYP/6-311++G**	79.18	74.06	75.90	59.76	68.02	61.15	63.38	46.38
BH&HLYP/aVDZ	76.66	71.76	73.56	57.56	66.03	59.24	61.47	44.41
BH&HLYP/aVTZ	76.44	71.44	73.27	57.21	65.13	58.43	60.65	43.64
MP2/aVDZ	73.11	67.99	69.90	53.59	65.84	48.96	51.72	33.03
MP2/aVTZ	73.75	68.61	70.56	54.21	65.49	49.52	52.28	33.61
MP2/CBS	74.02	68.88	70.83	54.47	65.34	49.76	52.51	33.86
CCSD(T)//MP2/aVDZ ^a	65.33	60.20	62.12	45.80	64.68	47.79	50.56	31.86
CCSD(T)//MP2/aVTZ ^a	66.74	61.60	63.54	47.19	64.54	48.57	51.33	32.66
CCSD(T)/aVDZ	70.74	67.13	70.24	49.90	64.75	56.84	59.88	39.37
CCSD(T)/aVTZ ^b	71.65	68.03	71.15	50.81	64.53	56.62	59.66	39.15
CCSD(T)/CBS	72.03	68.41	71.53	51.19	64.43	56.52	59.57	39.06

^a The CCSD(T) single point calculations were carried out at the MP2-optimized geometries, and the MP2 ZPE and thermal energies were used

^b The geometries were fully optimized at the CCSD(T)/aVTZ, and the ZPE and thermal energy corrections were made using the CCSD(T)/aVDZ values

Table 2 Conformational characteristics and geometrical parameters [distances ($r/\text{\AA}$) and rotational constants (A in GHz)] of the two structures of the water trimer cation, $(\text{H}_2\text{O})_3^+$

Method	3Lp			3OO			H ₂ O
	$r_{\text{O-H}}$	$r_{\text{O-O}}$	A	$r_{\text{O-H}}$	$r_{\text{O-O}}$	A	$r_{\text{O-H}}$
B3LYP/6-311++G**	0.993	2.538	19.0	0.983	2.324	16.7	0.962
MPW1K/6-311++G**	0.981	2.509	19.5	0.973	2.272	16.9	0.951
MPW1K/aVDZ	0.984	2.510	19.2	0.975	2.274	16.4	0.954
MPW1K/aVTZ	0.982	2.510	19.6	0.973	2.270	16.6	0.951
BH&HLYP/6-311++G**	0.979	2.527	19.1	0.972	2.284	16.4	0.951
BH&HLYP/aVDZ	0.981	2.527	19.0	0.973	2.285	16.0	0.953
BH&HLYP/aVTZ	0.979	2.527	19.0	0.971	2.283	16.3	0.950
MP2/aVDZ	0.993	2.547	18.4	0.982	2.477	12.5	0.966
MP2/aVTZ	0.991	2.531	18.7	0.979	2.465	12.7	0.961
CCSD(T)/aVDZ	0.994	2.559	19.6	0.982	2.485	12.4	0.967
CCSD(T)/aVTZ	0.988	2.567	20.4	0.978	2.473	12.6	0.962

Distance reports the average values. The $r_{\text{O-H}}$ of the water monomer is also listed for comparison

in the 3OO structure, the positive charge is almost equally distributed in two water molecules, which are shared by an O–O hemi-bond interaction. 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 carried out 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 from 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 [$\Delta E_{\text{CBS}} = (\Delta E_{N^3} - \Delta E_{N-1}(N-1)^3)/(N^3 - (N-1)^3)$] [61–63]. The DFT and MP2 calculations were carried out by using the Gaussian 03 suite of programs [64], and the CCSD(T) calculations were carried out by using the Molpro2002.6 package [65].

3 Results and discussion

We calculated the interaction energies among two neutral water monomers and the water monomer cation [ΔE (trimer cation) = E (trimer cation) – $2 \times E$ (water monomer) – E (water monomer cation)], where the geometries for water monomers are relaxed in the trimer. Their interaction energies are listed in Table 1. For the geometry optimization of 3OO structure, the closed-ring structure was obtained at the MP2 and CCSD(T) levels, while the open-ring structure was obtained at the DFT (B3LYP,

MPW1K and BH&HLYP) level (Fig. 1). As shown in Table 1, the 3Lp structure is more stable by 1.3 kcal/mol in ΔE_c and by 3.1 kcal/mol in ΔE_0 than the 3OO structure at the B3LYP/6-311++G** level. At the MPW1K/aVTZ level, the 3Lp structure is 9.7 (11.4) kcal/mol more stable in ΔE_c (ΔE_0) than the 3OO structure, and at the BH&HLYP/aVTZ level, the 3Lp structure is 11.3 (13.0) kcal/mol more stable. At the MP2/CBS level, the 3Lp structure is 8.7 (19.1) kcal/mol more stable in ΔE_c (ΔE_0). For the water dimer cation [56], the MP2 calculations of O...O structure produced one absurd very large frequency, so the ZPE corrections of the O...O structure were over-estimated. We performed the CCSD(T) single point calculations using the MP2-optimized geometries [CCSD(T)//MP2/aVDZ and CCSD(T)//MP2/aVTZ]. The 3Lp structure is more stable in ΔE_c by only 0.7 and 2.2 kcal/mol at the CCSD(T)//MP2/aVDZ and CCSD(T)//MP2/aVTZ levels, respectively, similar to the B3LYP results. We optimized the geometries of the water trimer cation at the CCSD(T) level. The 3Lp structure is more stable in ΔE_c by 6.0 and 7.1 kcal/mol at the CCSD(T)/aVDZ and CCSD(T)/aVTZ levels, respectively. At the CCSD(T)/CBS level, the 3Lp structure is more stable by 7.6 (11.9) kcal/mol in ΔE_c (ΔE_0).

For the 3Lp structure of the water trimer cation, the contribution of three-body interaction is 34.1% at the B3LYP/6-311++G**, 30.9% at the MP2/aVDZ, and 31.3% at the CCSD(T)/aVDZ level of theory. For the neutral water trimer, the contribution of three-body interaction was estimated to be 15.5% at the B3LYP/6-311++G**, 16.1% at the MP2/aVDZ, and 15.6% at the CCSD(T)/aVDZ level of theory. Consequently, it is understood that the contribution of three-body interaction is increased by the extra positive charge possibly due to the

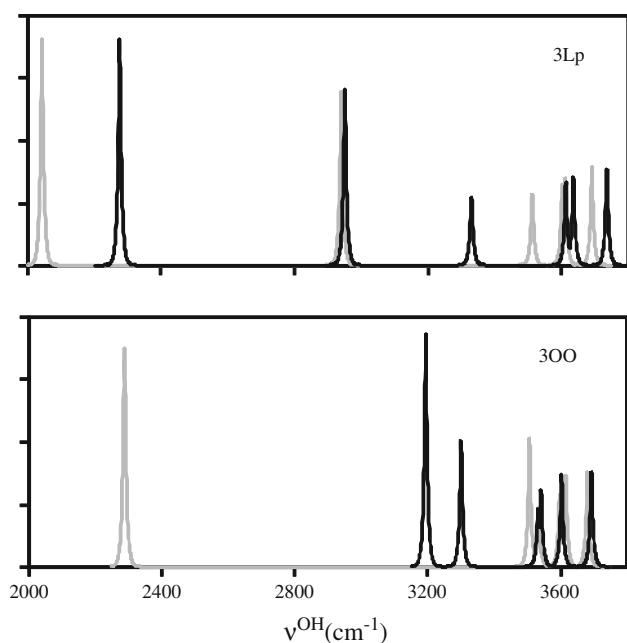


Fig. 2 MPW1K/6-311++G** (gray) and CCSD(T)/aVDZ (black) predicted IR spectra for the O–H stretching frequencies of the water trimer cation

large induction effect. The 300 structure has the charge distribution shared by two water monomers; then, the three-body interaction could not be calculated.

The calculated conformational characteristics and geometrical parameters of the two structures of the water trimer cation are shown in Table 2. The $r_{\text{O-H}}$ and $r_{\text{O-O}}$ distances of the 3Lp structure are longer than those of 300 structure, and the rotational constant A of 3Lp is larger than that of 300. The MP2-optimized geometries are closer to the CCSD(T)-optimized geometries, when compared with the DFT-optimized geometries. For the 300 structure, the DFT structure is quite different from the CCSD(T) structure. At the DFT level, the $r_{\text{O-O}}$ distances are small and the rotational constant A 's are large.

We have calculated the frequencies of the 3Lp and 300 structures of the water trimer cation at the DFT, MP2, and CCSD(T) levels (Fig. 2; Table 3). We employed the scale factors (0.956 at the B3LYP/6-311++G**, 0.916 at the MPW1K/6-311++G**, 0.920 at the MPW1K/aVDZ, 0.921 at the MPW1K/aVTZ, 0.917 at the BH&HLYP/6-311++G**, 0.920 at the BH&HLYP/aVDZ, 0.922 at the BH&HLYP/aVTZ, 0.957 at the MP2/aVDZ, 0.952 at the MP2/aVTZ, and 0.962 at the CCSD(T)/aVDZ 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 ($3,700\text{ cm}^{-1}$) [66]. The 3Lp structure has relatively strong H-bond interaction between the hydronium cation moiety and the neutral water monomer. Thus, it shows more red-shifted IR peak ($2,044\text{ cm}^{-1}$ at the BPW1K/6-311++G** level and

Table 3 Scaled frequencies [ν (cm^{-1})] and the IR intensities in subscripts (10 km/mol) of O–H stretching modes for H_2O , H_2O^+ and $(\text{H}_2\text{O})_3^+$ (3Lp and 300 structures) at the DFT, MP2, and CCSD(T) levels of theory (The frequencies of H_2O and H_2O^+ are also reported for comparison)

Method	Scale ^a	H_2O	H_2O^+	3Lp structure	300 structure
B3LYP ^b	0.956	3750, 3650	3246, 3196	3707 ₂₃ , 3628 ₁₉ , 3620 ₁₄ , 3508 ₉ , 2928 ₁₅₄ , 2055 ₃₂₃	3696 ₂₀ , 3613 ₈ , 3602 ₂₂ , 3542 ₂₁ , 3503 ₃₆ , 2420 ₂₇₅
MPW1K ^b	0.916	3750, 3650	3259, 3210	3693 ₂₆ , 3613 ₂₀ , 3605 ₁₇ , 3514 ₁₀ , 2941 ₁₅₆ , 2044 ₃₃₁	3683 ₂₃ , 3618 ₂₁ , 3600 ₁₂ , 3536 ₆ , 3509 ₅₆ , 2291 ₃₃₈
MPW1K/aVDZ	0.920	3752, 3648	3252, 3194	3700 ₂₃ , 3608 ₁₂ , 3604 ₂₁ , 3502 ₉ , 2867 ₁₅₇ , 2062 ₃₁₈	3686 ₂₁ , 3614 ₂₁ , 3597 ₁₀ , 3531 ₇ , 3502 ₄₉ , 2304 ₃₁₅
MPW1K/aVTZ	0.921	3749, 3651	3248, 3205	3693 ₂₃ , 3613 ₁₅ , 3606 ₁₈ , 3514 ₁₀ , 2883 ₁₅₅ , 2017 ₃₂₃	3683 ₂₁ , 3615 ₂₀ , 3602 ₁₁ , 3539 ₆ , 3509 ₅₁ , 2254 ₃₂₈
BH&HLYP ^b	0.917	3748, 3652	3252, 3207	3692 ₂₆ , 3612 ₁₁ , 3607 ₂₇ , 3520 ₁₁ , 3007 ₁₄₉ , 2142 ₃₂₂	3681 ₂₃ , 3623 ₂₂ , 3602 ₁₂ , 3538 ₁₀ , 3507 ₅₈ , 2351 ₃₃₅
BH&HLYP/aVDZ	0.920	3750, 3650	3243, 3188	3702 ₂₄ , 3611 ₆ , 3605 ₂₉ , 3507 ₁₀ , 2935 ₁₅₂ , 2179 ₃₀₈	3687 ₂₁ , 3622 ₂₁ , 3601 ₁₀ , 3533 ₇ , 3504 ₅₆ , 2376 ₃₁₄
BH&HLYP/aVTZ	0.922	3747, 3653	3241, 3200	3695 ₂₄ , 3613 ₆ , 3605 ₂₉ , 3516 ₁₀ , 2943 ₁₄₉ , 2151 ₃₁₂	3681 ₂₂ , 3620 ₂₁ , 3603 ₁₁ , 3538 ₇ , 3507 ₅₇ , 2325 ₃₂₈
MP2/aVDZ	0.957	3764, 3636	3308, 3232	3716 ₂₁ , 3614 ₂₁ , 3605 ₁₂ , 3553 ₉ , 2919 ₁₅₁ , 2146 ₃₀₇	8164 ₉₉₉₉ , 3686 ₁₈ , 3584 ₃ , 3534 ₂₉ , 3486 ₁₉₈ , 3277 ₉₀
MP2/aVTZ	0.952	3760, 3640	3304, 3245	3698 ₂₂ , 3609 ₂₁ , 3597 ₁₂ , 3556 ₁₀ , 2920 ₁₅₁ , 2078 ₃₁₉	7606 ₉₉₉₉ , 3670 ₁₉ , 3578 ₃ , 3528 ₂₉ , 3477 ₂₀₅ , 3274 ₉₆
CCSD(T)/aVDZ	0.962	3757, 3643	3277, 3207	3738 ₂₆ , 3637 ₂₀ , 3615 ₁₇ , 3331 ₁₀ , 2952 ₁₅₆ , 2276 ₃₃₁	3695 ₂₃ , 3605 ₂₁ , 3543 ₁₂ , 3533 ₆ , 3301 ₅₆ , 3194 ₃₃₈

^a Scale factors (see the text)

^b The 6-311++G** basis set was used

2,276 cm^{-1} at the CCSD(T)/aVDZ level), as shown in Fig. 2. Among the DFT-MPW1K, MP2 and CCSD(T) calculation results the MPW1K spectrum shows the most red-shifted IR peak and the CCSD(T) spectrum shows the least red-shifted peak. For the 3OO structure, the MP2 calculations with aVDZ and aVTZ basis sets fail to produce reasonable frequencies, while the CCSD(T) calculations give reasonable frequencies as shown in Table 3. However, for 3OO, the DFT calculations provide different structures from the MP2- and CCSD(T)-optimized ones, so the DFT IR spectra of 3OO structure are different from the CCSD(T) spectrum. The 3OO structure has stronger H-bond interaction in the DFT-optimized conformation than in the MP2-/CCSD(T)-optimized conformation. Thus, the DFT 3OO structure shows highly red-shifted peak of $\sim 2,300 \text{ cm}^{-1}$, while the CCSD(T) 3OO structure has slightly red-shifted peaks of $\sim 3,200$ and $\sim 3,300 \text{ cm}^{-1}$. The significant differences between the DFT and MP2 results from the CCSD(T) results need to be considered to improve the density functionals in the future.

4 Concluding remarks

At the CCSD(T)/CBS level of theory, the ionic 3Lp structure is much more stable than the 3OO structure. The 3Lp structure is composed of a hydronium cation, a hydroxyl radical and a neutral water molecule. From the geometry optimization of 3OO structure, the closed-ring structure was obtained with an O–O hemi-bond interaction at the MP2 and CCSD(T) levels, but the open-ring structure was obtained with the O–O hemi-bond at the DFT (B3LYP, MPW1K, and BH&HLYP) level. The MP2 calculations give significantly small binding energies and unreasonable frequencies for the 3OO structure. The CCSD(T) single point calculations at the MP2-optimized geometries also provide unreasonable relative energies. Therefore, in order to obtain reliable stabilities and frequencies of the water trimer cation, the CCSD(T) geometry optimization and frequency calculations are required. In this regard, the significant differences of the DFT results from the CCSD(T) ones should be considered for more reliable density functionals in the future.

Acknowledgments This work is dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday. We are grateful for the financial support by KISTI (KSC-2011-G3-02).

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