

Ammonia–Water Cation and Ammonia Dimer Cation

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We have investigated the structure, interaction energy, electronic properties, and IR spectra of the ammonia–water cation $(\text{NH}_3\text{H}_2\text{O})^+$ using density functional theory (DFT) and high-level ab initio theory. The ammonia–water cation has three minimum-energy structures of (a) $\text{H}_2\text{NH}^+\cdots\text{OH}_2$, (b) $\text{H}_3\text{N}^+\cdots\text{OH}_2$, and (c) $\text{H}_3\text{NH}^+\cdots\text{OH}$. The lowest-energy structure is (a), followed by (c) and (b). The ammonia dimer cation has two minimum-energy structures [the lowest $\text{H}_3\text{NH}^+\cdots\text{NH}_2$ structure and the second lowest $(\text{H}_3\text{N}\cdots\text{NH}_3)^+$ structure]. The minimum transition barrier for the interconversion between (a), (b), and (c) is ~ 6 kcal/mol. Most DFT calculations with various functionals, except a few cases, over stabilize the $\text{N}\cdots\text{O}$ and $\text{N}\cdots\text{N}$ binding, predicting different structures from Møller–Plesset second-order perturbation (MP2) theory and the most reliable complete basis set (CBS) limit of coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)]. Thus, the validity test of the DFT functionals for these ionized molecular systems would be of importance.

Introduction

Extensive studies of dissociation of acids, bases, and salts have been carried out to understand solvation phenomena.^{1–3} These phenomena are strongly involved in H-bonding and proton transfer. For a better understanding of H-bonding and proton transfer, it would be of interest to investigate such phenomena in the ionized state, which can be easily observable in the stratosphere. We are particularly interested in the hydration of the ammonia cation, namely, $(\text{NH}_3\cdots\text{H}_2\text{O})^+$.

Ammonium cluster cations $(\text{NH}_3)_n^+$ and their hydrated clusters $[(\text{NH}_3)_n(\text{H}_2\text{O})_m]^+$ were experimentally produced under special conditions in the gas phase.⁴ A few theoretical investigations for ammonia, water, and ammonia–water cluster cations were performed.^{5–8} The ammonia dimer cation and the ammonia–water cation were experimentally discussed.⁹ For the ammonia dimer cation, the disproportionated ionic structure $(\text{NH}_4^+\cdots\text{NH}_2)$ was predicted to be more stable than the hydrazine-like structure $(\text{H}_3\text{N}\cdots\text{NH}_3)$.⁶ In previous work, one of us reported that for the water dimer cation at high levels of ab initio theory, the $\text{H}_3\text{O}^+\cdots\text{OH}$ structure is much more stable than the $\text{H}_2\text{O}\cdots\text{OH}_2$ structure.¹⁰

Here, we investigate the structures, energetics, and spectra of the ammonia–water cation $(\text{NH}_3\text{H}_2\text{O})^+$ and the ammonia dimer cation $(\text{NH}_3)_2^+$ using high levels of ab initio theory. We compare the DFT, MP2, and CCSD(T) results. Serious failures for most DFT calculations are found, except for few functionals.

Calculation Methods

Before calculating the ionized structure of the ammonia–water cluster and the ammonia dimer, we need to calculate their neutral structure as the reference system. Since these structures are

already well-known,^{11,12} we calculated their structures and energies at the CCSD(T)/aVQZ//CCSD(T)/aVDZ level of theory. For the ionized structures, various structures of the ammonia–water cation and the ammonia dimer cation are optimized by using DFT methods with various functionals.

For the DFT calculations, we employ various functionals, Becke's exchange and Lee–Yang–Parr correlation functionals (BLYP),¹³ Becke's exchange and Perdew–Wang correlation functionals (BPW91),¹⁴ Handy's family functional including gradient-corrected correlation (HCTH407),¹⁵ the local spin density approximation, Vosko–Wilk–Nusair correlation and Slater exchange functionals (LSDA: SVWN),¹⁶ semiempirical-correction to BLYP for dispersion (BLYP-D),¹⁷ Tao–Perdew–Staroverov–Scuseria exchange and τ -dependent gradient-corrected functionals (TPSS),¹⁸ Becke's three-parameters for exchange and Lee–Yang–Parr correlation functionals (B3LYP),¹⁹ Zhao and Truhlar's parametrized exchange and correlation hybrid meta-GGA M05-2X,²⁰ Perdew–Burke–Ernzerhof hybrid functional (PBE1PBE),²¹ modified Perdew–Wang one-parameter model/modifed Perdew–Wang and Becke one-parameter model for kinetics (MPW1K/MPWB1K),^{22,23} Becke's half HF-LSDA (Hartree–Fock Local Spin Density Approximation) exchange and Lee–Yang–Parr correlation functionals (BH&H),²⁴ and Becke's half HF-LSDA-Becke exchange and Lee–Yang–Parr correlation functionals (BH&HLYP).²⁵ For these DFT calculations, we used the 6-311++G** basis set.²⁶ Then, as noted in the water dimer cation,¹⁰ we also find that in the ammonia–water cation and the ammonia dimer cation, DFT/MPW1K and DFT/ BH&HLYP are reliable, while others give seriously wrong energy values, as compared with the CCSD(T)/CBS values. Here, we compare the DFT, MP2, and CCSD(T) results using the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets²⁷ (which will be denoted as aVDZ, aVTZ, and aVQZ, respectively). The CBS limit interaction energies were obtained with the extrapolation

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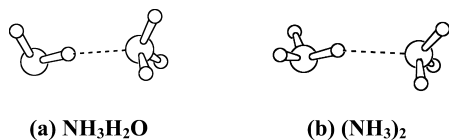


Figure 1. Structures for the neutral states of the ammonia–water cluster and the ammonia dimer at the CCSD(T)/aVDZ level of theory.

TABLE 1: Vertical/Adiabatic Ionization Energies (IP_v/IP_a in eV) and Protonation/Deprotonation Energies ($E_{\text{prot}}/E_{\text{deprot}}$ in kcal/mol) of NH_3 , H_2O , $\text{NH}_3\text{H}_2\text{O}$, and $(\text{NH}_3)_2$ at the CCSD(T)/aVQZ//CCSD(T)/aVDZ Level

	IP_v	IP_a	E_{prot}	E_{deprot}
NH_3	10.97	10.19	−9.19	17.92
H_2O	12.71	12.64	−7.44	17.23
$\text{NH}_3\text{H}_2\text{O}$	11.51	9.43	−9.79	16.83
$(\text{NH}_3)_2$	10.21	8.56	−10.19	17.42

scheme utilizing the fact that the electron correlation error is proportional to N^{-3} for the aug-cc-pVNZ basis set ($N = 2$: D; $N = 3$: T; $N = 4$: Q) [$\Delta E_{\text{CBS}} = (\Delta E_{\text{N}}N^3 - \Delta E_{\text{N-1}}(N-1)^3)/(N^3 - (N-1)^3)$].²⁸ Here, the CBS energies, which would give the most reliable values in these calculations, were obtained based on the aVTZ and aVQZ results. In this way, we could compare their CBS values and find the inherent errors in the DFT and MP2 results.

For the DFT and MP2 calculations using the aVDZ and aVTZ basis sets and the CCSD(T) calculations using the aVDZ basis set, the geometries were fully optimized, and frequency calculations were also carried out. A larger grid size (99, 974) than the ultrafine grid (99, 590) was employed to eliminate the imaginary frequencies for the DFT calculations. All of the optimizations were done by minimizing the total energy without any symmetry constraints. In the DFT and MP2 calculations using the aVQZ basis set, the corresponding aVTZ geometries were used, and the aVTZ frequencies were employed to obtain the zero-point energies (ZPEs) and thermal energies, while in the CCSD(T) calculations using the aVTZ and aVQZ basis sets, the corresponding aVDZ geometries were used, and the aVDZ frequencies were employed to obtain the ZPEs and

thermal energies. For the basis set, the 1s orbitals of oxygen atoms were frozen in the correlation calculations. All of the “d” and “f” orbitals used here are the spherical harmonic basis functions (5d and 7f).

For the ionic structure, the basis set superposition energy (BSSE) correction can be made. However, in the nonionic structure, the positive charge is almost equally distributed in two monomer species so that 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.

We calculated the ZPE’s 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 ($\Delta H_f/\Delta G_f$) at room temperature and 1 atm were obtained using the frequency calculations.

All of the calculations were carried out by using the Gaussian 03 suite of programs.²⁹ The BLYP-D calculations were done by using ORCA program³⁰ and the M05-2X calculations by Q-Chem program.³¹ The molecular structures were drawn using the POSMOL package.³²

Results and Discussion

Figure 1 shows the optimized neutral state structures of the ammonia–water cluster and the ammonia dimer at the CCSD(T)/aVDZ level. We calculated the vertical/adiabatic ionization energies (IP_v/IP_a) and protonation/deprotonation energies ($E_{\text{prot}}/E_{\text{deprot}}$) of NH_3 and H_2O at the CCSD(T)/aVQZ//CCSD(T)/aVDZ level (Table 1). For the ammonia monomer, the vertical/adiabatic IP (IP_v/IP_a) is 10.97/10.19 eV at the CCSD(T)/aVQZ//CCSD(T)/aVDZ level. These values are close to the experimental IP_v/IP_a (10.93/10.17 eV).³³ The N–H distance and HNH bond angle of the ammonia monomer cation are 1.031 Å and 120.0° at the CCSD(T)/aVDZ level, which shows 0.007 Å longer N–H distances and 14.1° wider bond angles than those of the neutral ammonia monomer (1.024 Å and 105.9° at the CCSD(T)/aVDZ level). The N–H bond strength becomes weaker, and the H–H repulsion is greater due to the ionization. Similarly, in case of the water monomer cation, the O–H distance and HOH bond

TABLE 2: DFT/6-311++G Interaction Energies^a (kcal/mol) for Various Structures of the Ammonia–Water Cation $(\text{NH}_3\text{H}_2\text{O})^+$ and the Ammonia Dimer Cation $(\text{NH}_3)_2^+$**

method	$(\text{NH}_3 \cdots \text{H}_2\text{O})^+$			$(\text{NH}_3 \cdots \text{NH}_3)^+$	
	$\text{H}_2\text{NH}^+ \cdots \text{OH}_2$	$\text{H}_3\text{N}^+ \cdots \text{OH}_2$	$\text{H}_3\text{NH}^+ \cdots \text{OH}$	$\text{H}_3\text{NH}^+ \cdots \text{NH}_2$	$(\text{H}_3\text{N} \cdots \text{NH}_3)^+$
	$-\Delta E_c (-\Delta E_0)$	$-\Delta E_c (-\Delta E_0)$	$-\Delta E_c (-\Delta E_0)$	$-\Delta E_c (-\Delta E_0)$	$-\Delta E_c (-\Delta E_0)$
BLYP	27.3(25.5)	28.4 (25.3)	22.9(19.2)	42.8(40.0)	47.6 (44.0)
BPW91	26.7(25.0)	27.3 (24.0)	22.3(18.6)	43.0(40.3)	46.7 (43.0)
HCTH407	26.0(24.2)	26.8 (23.6)	22.0(18.2)	42.1(39.2)	46.1 (42.4)
LSDA	35.8(34.2)	37.9 (34.2)	26.2(22.7)	50.6(48.0)	58.5 (54.7)
BLYP-D	27.8(26.3)	29.8 (26.6)	23.5(19.4)	43.9(40.9)	49.4 (45.6)
TPSS	26.9 (25.1)	26.6(23.4)	23.7(19.9)	43.3(40.4)	45.3 (41.6)
B3LYP	26.3 (24.5)	24.1(20.8)	24.1(20.9)	42.8(39.7)	43.6 (39.7)
M05-2X	26.3 (24.1)	24.1(20.6)	25.1(19.9)	42.4 (38.9)	41.4(37.8)
PBE1PBE	27.1 (25.3)	23.3(20.1)	24.6(20.9)	43.7 (40.7)	42.8(38.9)
BH&H	31.5 (29.6)	25.4(22.6)	27.8(24.1)	46.7 (43.6)	44.5(40.2)
BH&HLYP	26.1 (24.0)	20.2(17.9)	25.7(22.0)	42.2 (38.8)	37.0(32.9)
MPWB1K	26.0 (24.1)	21.4(18.7)	25.2(21.4)	42.5 (39.2)	40.4(36.3)
MPW1K	26.4 (24.5)	20.2(17.8)	24.9(21.1)	42.8 (39.6)	38.3(34.2)
CCSD(T) ^b	24.1 (22.3)	18.2(16.0)	21.4(17.7)	40.6 (37.5)	35.7(31.9)

^a The interaction energy between one neutral ammonia/water monomer and one ammonia monomer cation is reported. ΔE_c are the ZPE-uncorrected energies at the equilibrium point of the Born–Oppenheimer potential surfaces, and ΔE_0 are the ZPE-corrected energies. The minimum-energy structures in ΔE_c are denoted in bold. The italic interaction energies in $(-\Delta E_0)$ indicate that the calculated structure, although minimum, shows one imaginary frequency possibly due to the numerical instability. ^b CCSD(T)/CBS results.

TABLE 3: DFT, MP2, and CCSD(T) Interaction Energies (kcal/mol) of the Three Minimum-Energy Structures of the Ammonia–Water Cation [(NH₃H₂O)⁺]^a

method	H ₂ NH ⁺ ⋯OH ₂				H ₃ N ⁺ ⋯OH ₂				H ₃ NH ⁺ ⋯OH			
	−ΔE _c	−ΔE ₀	−ΔH _r	−ΔG _r	−ΔE _c	−ΔE ₀	−ΔH _r	−ΔG _r	−ΔE _c	−ΔE ₀	−ΔH _r	−ΔG _r
MPW1K/6-311++G**	26.43	24.45	25.36	17.43	20.18	17.78	18.36	11.08	24.92	21.10	21.86	14.49
MPW1K/aVTZ	24.97	23.25	24.05	16.39	18.70	16.06	16.77	9.30	23.76	20.01	20.78	13.99
MPW1K/aVQZ//	25.06	23.34	24.14	16.48	18.55	15.91	16.62	9.15	23.80	20.05	20.81	14.03
MPW1K/CBS	25.13	23.41	24.21	16.55	18.44	15.80	16.51	9.04	23.82	20.08	20.84	14.06
MP2/aVTZ	24.15	22.39	23.10	15.63	17.43	15.54	15.82	9.59	19.50	15.71	16.47	9.21
MP2/aVQZ//	24.19	22.42	23.14	15.66	17.49	15.60	15.88	9.65	19.14	15.35	16.11	8.84
MP2/CBS	24.21	22.45	23.16	15.69	17.54	15.65	15.92	9.70	18.87	15.09	15.84	8.58
CCSD(T)/aVTZ//	24.08	22.22	22.86	15.68	18.11	15.89	16.37	9.42	22.08	18.39	19.11	12.24
CCSD(T)/aVQZ//	24.11	22.25	22.90	15.71	18.18	15.96	16.43	9.49	21.66	17.97	18.70	11.82
CCSD(T)/CBS	24.14	22.27	22.92	15.73	18.23	16.01	16.48	9.54	21.36	17.67	18.39	11.52

^a At the MPW1K and MP2 levels, “aVQZ//” denotes the calculations done at the aVTZ geometry along with the aVTZ ZPE and thermal energy corrections. At the CCSD(T) level, “aVTZ//” and “aVQZ//” denote the calculations done at the aVDZ geometry along with the aVDZ ZPE and thermal energy corrections.

TABLE 4: DFT, MP2, and CCSD(T) Interaction Energies (kcal/mol) for the Two Minimum-Energy Structures of the Ammonia Dimer Cation [(NH₃)₂⁺]^a

method	H ₃ NH ⁺ ⋯NH ₂				(H ₃ N⋯NH ₃) ⁺			
	−ΔE _c	−ΔE ₀	−ΔH _r	−ΔG _r	−ΔE _c	−ΔE ₀	−ΔH _r	−ΔG _r
MPW1K/6-311++G**	42.77				38.33	34.21	35.30	26.94
MPW1K/aVTZ	41.57				37.08	32.98	34.06	25.60
MPW1K/aVQZ//	41.63				37.23	33.13	34.21	25.75
MPW1K/CBS	41.68				37.34	33.24	34.32	25.85
MP2/aVTZ	40.23	37.15	38.01	30.70	35.64	31.26	32.41	23.43
MP2/aVQZ//	40.16	37.07	37.94	30.62	35.79	31.40	32.55	23.57
MP2/CBS	40.10	37.02	37.88	30.57	35.89	31.51	32.66	23.68
CCSD(T)/aVTZ//	40.81	37.68	38.53	30.87	35.42	31.60	32.68	23.70
CCSD(T)/aVQZ//	40.71	37.58	38.43	30.77	35.57	31.75	32.83	23.85
CCSD(T)/CBS	40.64	37.51	38.36	30.70	35.68	31.86	32.94	23.96

^a At the MPW1K and MP2 levels, “aVQZ//” denotes the calculations done at the aVTZ geometry along with the aVTZ ZPE and thermal energy corrections. At the CCSD(T) level, “aVTZ//” and “aVQZ//” denote the calculations done at the aVDZ geometry along with the aVDZ ZPE and thermal energy corrections. The MPW1K thermal energies for H₃NH⁺⋯OH are not reported due to imaginary frequencies, which were raised due possibly to the numerical instability.

angle (1.002 Å and 109.1°) are 0.04 Å longer and 4.9° wider than those of the neutral water monomer (0.962 Å and 104.2°) at the CCSD(T)/aVTZ level.

Figure 2 shows the DFT/MPW1K optimized structures of the ammonia–water cation and the ammonia dimer cation. For the ammonia–water cation, the minimum-energy structures are (a) H₂NH⁺⋯OH₂, (b) H₃N⁺⋯OH₂, and (c) H₃NH⁺⋯OH, and the transition-state (TS) structures between (a) and (c) and between (b) and (c) are (d) [TS]/ab and (e) [TS]/bc, respectively. For the ammonia dimer cation, the minimum-energy structures are (f) H₃NH⁺⋯NH₂ and (g) (H₃N⋯NH₃)⁺, and the TS between the two structures is (h) [TS]/fg. These structures and energetics are found to be similar to those obtained at the CCSD(T)/CBS//CCSD(T)/aVDZ level, which will be discussed later.

We calculated the interaction energies for the dimerization between ammonia/water molecules, where the geometries for ammonia/water monomers were fully optimized in the dimer. For the ammonia–water cation, we may have two options for the interaction energies, ΔE_{NH₄⁺} = E(dimer cation) − E(H₂O) − E(NH₃⁺) or ΔE_{H₃O⁺} = E(dimer cation) − E(H₂O⁺) − E(NH₃). Since the protonation energy of NH₃ is smaller than that of H₂O, we report the interaction energy ΔE with ΔE_{NH₄⁺}. For the ammonia dimer cation, ΔE = E(dimer cation) − E(NH₃) − E(NH₃⁺).

In the case of (NH₃)₂⁺ (Table 2), the BLYP, BPW91, HCTH407, LSDA, BLYP-D, and TPSS calculations predict that

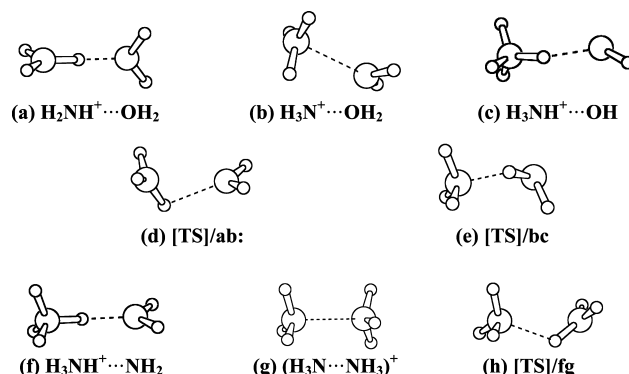


Figure 2. Minimum-energy and transition-state (TS) structures of the ammonia–water cation [(NH₃H₂O)⁺] (a–e) and ammonia dimer cation [(NH₃)₂⁺] (f–h). Notation “[TS]/ab” denotes the transition state between two minimum-energy structures (a) and (b). The minimum-energy structures are optimized at the CCSD(T)/aVDZ level, and the TS structures are optimized at the DFT/MPW1K level. The DFT/MPW1K structures and energies are similar to those at the CCSD(T)/aVQZ//CCSD(T)/aVDZ level.

the (H₃N⋯NH₃)⁺ structure is much more stable than the H₃NH⁺⋯NH₂ structure. The B3LYP, M05-2X, PBE1PBE, BH&H, and MPWB1K calculations predict that the two structures are compatible. On the other hand, the MPW1K and BH&HLYP calculations predict that the H₃NH⁺⋯NH₂ structure

TABLE 5: Geometrical Parameters [Distances ($r/\text{\AA}$)] of the Ammonia–Water Cluster $(\text{NH}_3\text{H}_2\text{O})^+$ and the Ammonia Dimer Cation $(\text{NH}_3)_2^+$ ^a

method	$\text{H}_2\text{NH}^+\cdots\text{OH}_2$					$\text{H}_3\text{N}^+\cdots\text{OH}_2$			$\text{H}_3\text{NH}^+\cdots\text{OH}$			
	$r_{\text{N}-\text{O}}$	$r_{\text{H}\cdots\text{O}}$	$r_{\text{N}-\text{H}^+}$	$r_{\text{N}-\text{H}}$	$r_{\text{O}-\text{H}}$	$r_{\text{N}-\text{O}}$	$r_{\text{N}-\text{H}}$	$r_{\text{O}-\text{H}}$	$r_{\text{N}-\text{O}}$	$r_{\text{N}-\text{H}^+}$	$r_{\text{N}-\text{H}}$	$r_{\text{O}-\text{H}}$
MPW1K/aVTZ	2.575	1.495	1.080	1.013	0.954	2.282	1.008	0.956	2.781	1.037	1.014	0.967
MP2/aVTZ	2.611	1.540	1.071	1.017	0.965	2.380	1.015	0.965	2.808	1.040	1.020	0.973
CCSD(T)/aVDZ	2.631	1.553	1.078	1.028	0.968	2.348	1.025	0.970	2.832	1.046	1.028	0.981

method	$\text{H}_3\text{NH}^+\cdots\text{NH}_2$				$(\text{H}_3\text{N}\cdots\text{NH}_3)^+$		NH_3	H_2O
	$r_{\text{N}-\text{N}}$	$r_{\text{H}\cdots\text{N}}$	$r_{\text{N}-\text{H}^+}$	$r_{\text{N}-\text{H}}$	$r_{\text{N}-\text{N}}$	$r_{\text{N}-\text{H}}$	$r_{\text{N}-\text{H}}$	$r_{\text{O}-\text{H}}$
MPW1K/aVTZ	2.739	1.665	1.074	1.014	2.197	1.005	1.005	0.951
MP2/aVTZ	2.768	1.695	1.073	1.019	2.164	1.013	1.012	0.961
CCSD(T)/aVDZ	2.794	1.719	1.075	1.029	2.198	1.022	1.024	0.967

^a The $r_{\text{N}-\text{H}}$ and $r_{\text{O}-\text{H}}$ report the average value for the non-hydrogen-bonded N–H and O–H distances, respectively. The data for the ammonia monomer and the water monomer are listed for comparison.

TABLE 6: MP2/aVQZ//MP2/aVTZ NBO Charges (q) of the Ammonia–Water Cation $(\text{NH}_3\text{H}_2\text{O})^+$ and the Ammonia Dimer Cation $(\text{NH}_3)_2^+$

structure	$\text{H}_2\text{NH}^+\cdots\text{OH}_2$	$\text{H}_3\text{N}^+\cdots\text{OH}_2$	$\text{H}_3\text{NH}^+\cdots\text{OH}$	$\text{H}_3\text{NH}^+\cdots\text{NH}_2$	$(\text{H}_3\text{N}\cdots\text{NH}_3)^+$
moiety	NH_3	NH_3	NH_4	NH_4	NH_3
$q(\text{NBO})$	0.909	0.956	0.948	0.885	0.500

is much more stable than the $(\text{H}_3\text{N}\cdots\text{NH}_3)^+$ structure. For these various DFT functionals, a similar trend is also noted in the case of $(\text{NH}_3\cdots\text{H}_2\text{O})^+$ (Table 2). Let us denote L/L' as a ligand representing NH_3 or OH_2 and denote L_d/L'_d as a deprotonated ligand representing NH_2 or OH . Then, the $\text{L}\cdots\text{L}'$ structure is favored over the $\text{LH}^+\cdots\text{L}'_d$ structure for BLYP, BPW91, HCTH407, LSDA, BLYP-D, and TPSS; the $\text{L}\cdots\text{L}'$ structure is compatible with the $\text{LH}^+\cdots\text{L}'_d$ structure for B3LYP, M05-2X, and PBE1PBE, despite that the $\text{LH}^+\cdots\text{L}'_d$ structure is more favored over the $\text{L}\cdots\text{L}'$ structure. Furthermore, $\text{L}\cdots\text{L}'$ structure is the most stable for BLYP, BPW91, HCTH407, LSDA, and BLYP-D, while the $\text{L}_d\text{H}^+\cdots\text{L}'$ structure is the most stable for the other functionals. We find that MPW1K and BH&HLYP results are the most consistent with the CCSD(T) results, while the MPW1K results are slightly better than BH&HLYP, which will be discussed later. Thus, we report the detailed computational results of DFT/MPW1K, MP2, and CCSD(T) using the aVNZ basis sets ($\text{N} = \text{D/T/Q}$) and their CBS limit values (Table 3 and 4). In Table 3, according to CCSD(T)/CBS values, the lowest-energy structure of $(\text{NH}_3\text{H}_2\text{O})^+$ is $\text{H}_2\text{NH}^+\cdots\text{OH}_2$, followed by $\text{H}_3\text{NH}^+\cdots\text{OH}$, and followed by $\text{H}_3\text{N}^+\cdots\text{OH}_2$. In Table 4, the lowest-energy structure of the ammonia dimer cation is $\text{H}_3\text{NH}^+\cdots\text{NH}_2$, followed by the $(\text{H}_3\text{N}\cdots\text{NH}_3)^+$.

The ammonia molecule is more easily ionized than the water molecule. On the unrestricted open-shell approach of the ammonia–water cluster, the calculated IP_v/IP_a of the lowest-energy structure $\text{H}_2\text{NH}^+\cdots\text{OH}_2$ is 11.51/9.43 eV at the CCSD(T)/aVQZ//CCSD(T)/aVDZ level. The calculated IP_v/IP_a of the ammonia dimer is 10.21/8.56 eV at the CCSD(T)/aVQZ//CCSD(T)/aVDZ level. The calculated IP_v , IP_a , protonation energy (negative value of the proton affinity), and deprotonation energies are listed in Table 1.

Table 5 lists the optimized geometrical parameters of the structures at the MPW1K and MP2 levels for the aVTZ basis set and those at the CCSD(T) level for the aVDZ basis set. The N–H⁺ distance ($r_{\text{N}-\text{H}^+}$) of the $\text{H}_2\text{NH}^+\cdots\text{OH}_2$ structure is longer than those of other ammonia–water cation structures. The N–H distance ($r_{\text{N}-\text{H}}$) of the $\text{L}_d\text{H}^+\cdots\text{L}'$ structure is longer than that of the $\text{L}\cdots\text{L}'$ structure, expectedly. Table 6 shows the natural bond orbital (NBO) charges of the ammonia or ammonium fragments in the ammonia–water cation and the ammonia dimer cation at the MP2/aVQZ//MP2/aVTZ level. Since the ammonia

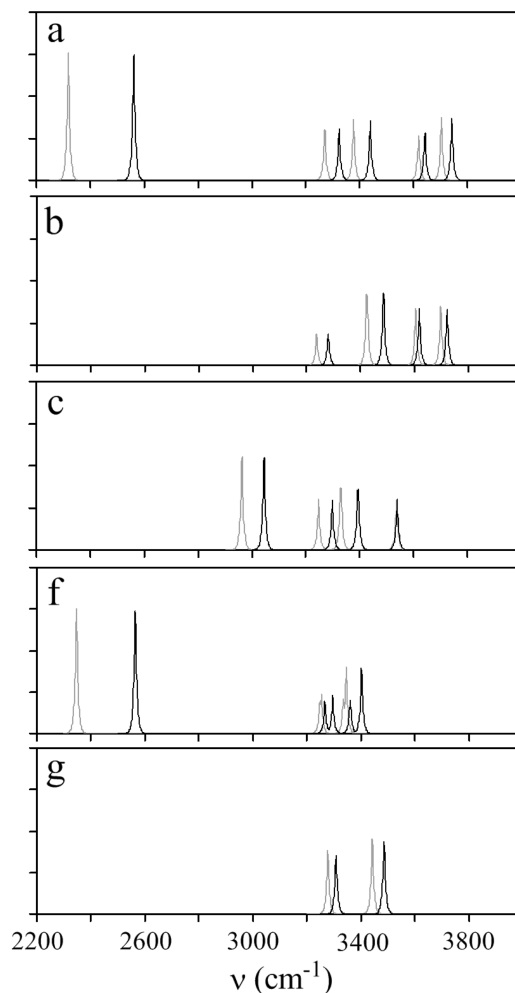


Figure 3. MPW1K/6-311++G** (gray) and CCSD(T)/aVDZ (black) predicted IR spectra for the N–H and O–H stretching frequencies of the ammonia–water cation [(a) $\text{H}_2\text{NH}^+\cdots\text{OH}_2$; (b) $\text{H}_3\text{N}^+\cdots\text{OH}_2$; (c) $\text{H}_3\text{NH}^+\cdots\text{OH}$] and ammonia dimer cation [(f) $\text{H}_3\text{NH}^+\cdots\text{NH}_2$; (g) $(\text{H}_3\text{N}\cdots\text{NH}_3)^+$]. For the CCSD(T) frequencies, the intensities are not available; therefore, the corresponding MPW1K intensities are employed.

TABLE 7: Scaled Frequencies [$\nu(\text{cm}^{-1})$] and the IR Intensities (in 10 km/mol in subscripts) of NH and OH Stretching Modes for $(\text{NH}_3\text{H}_2\text{O})^+$ and $(\text{NH}_3)_2^+$ at the DFT, MP2, and CCSD(T) Levels of Theory^a

method	scale factor ^b	H ₂ O	NH ₃	(NH ₃) ₂ ⁺	
				H ₃ NH ⁺ ⋯NH ₂	(H ₃ N⋯NH ₃) ⁺
MPW1K/6-311++G**	0.919	3764,3664	3438,3438,3311	3346 ₁₄ ,3346 ₁₄ ,3335 ₄ ,3254 ₅ ,3249 ₃ ,2347 ₂₁₀	3443 ₁₇ ,3443 ₁₉ ,3442 ₄ ,3442 ₇ ,3295 ₀ ,3278 ₅₃
MP2/aVTZ	0.950	3749,3630	3465,3464,3325	3394 ₄ ,3384 ₁₄ ,3384 ₁₄ ,3299 ₁ ,3280 ₈ ,2469 ₁₉₀	3476 ₁₇ ,3476 ₁₇ ,3474 ₃ ,3474 ₅ ,3317 ₀ ,3314 ₁
CCSD(T)/aVDZ	0.965	3765,3652	3445,3445,3312	3403,3403,3361,3296,3267,2564	3487,3487,3485,3485,3323,3308

method	(NH ₃ H ₂ O) ⁺		
	H ₂ NH ⁺ ⋯OH ₂	H ₃ N ⁺ ⋯OH ₂	H ₃ NH ⁺ ⋯OH
MPW1K/6-311++G**	3703 ₂₃ ,3618 ₁₀ ,3377 ₁₉ ,3270 ₁₄ ,2319 ₂₁₄	3697 ₁₉ ,3604 ₁₈ ,3424 ₂₃ ,3422 ₂₅ ,3237 ₃	3537 ₁₁ ,3331 ₁₇ ,3328 ₁₇ ,3247 ₁₂ ,2963 ₈₂
MP2/aVTZ	3697 ₂₀ ,3597 ₈ ,3448 ₂₀ ,3336 ₁₇ ,2505 ₁₉₁	3692 ₁₆ ,3588 ₉ ,3479 ₂₅ ,3479 ₂₅ ,3289 ₀	3561 ₁₀ ,3372 ₁₆ ,3370 ₁₆ ,3278 ₁₄ ,2999 ₈₀
CCSD(T)/aVDZ	3742,3642,3439,3324,2562	3721,3617,3485,3484,3280	3539,3395,3392,3298,3045

^a The frequencies of NH₃, NH₃⁺, H₂O, and H₂O⁺ are reported for comparison. ^b See the text.

molecule is more easily ionized than the water molecule, almost a full positive charge in the dimer cations is localized at the ammonia or ammonium moiety, except for the (H₃N⋯NH₃)⁺ structure for which the charge of the NH₃ moiety is obviously half of a unit.

The barrier heights for the interconversion between the L_dH⋯L', L⋯L', and LH⁺⋯L_d' structures are calculated at the MPW1K/6-311++G** level of theory. The CCSD(T)/aVDZ transition structures are closer to the MPW1K/6-311++G** ones than the MP2/aVDZ ones.¹⁰ For the ammonia dimer cation, the transition state [TS]/fg between (f) H₃NH⁺⋯NH₂ and (g) (H₃N⋯NH₃)⁺ in Figure 2 is higher in energy by 11.11/15.55 kcal/mol than the minimum-energy structure of (f)/(g) at the MPW1K/6-311++G** level and by 10.43/16.36 kcal/mol at the single-point CCSD(T)/aVDZ//MPW1K/6-311++G** level. This transition barrier is moderate. For the ammonia–water cation, the transition state [TS]/ab between (a) H₂NH⁺⋯OH₂ and (b) H₃N⁺⋯OH₂ is higher in energy by 6.58/0.33 kcal/mol than (a)/(b) at the MPW1K/6-311++G** level and by 6.16/0.24 kcal/mol at the CCSD(T)/aVDZ//MPW1K/6-311++G** level. This transition barrier is still considered to be not small. The transition state [TS]/bc between (c) H₃NH⁺⋯OH and (b) H₃N⁺⋯OH₂ is higher in energy by 23.25/27.99 kcal/mol than (c)/(b) at the MPW1K/6-311++G** level and by 23.93/27.96 kcal/mol at the CCSD(T)/aVDZ//MPW1K/6-311++G** level. This transition barrier is high.

The vibrational frequencies of the neutral water monomer and the water monomer cation were discussed in the previous study.¹⁰ The experimental asymmetric ν_3 and symmetric ν_1 frequencies of the ammonia monomer³⁴ are known to be 3444 and 3337 cm⁻¹, and those of the ammonia monomer cation³⁵ are 3388 and 3150 cm⁻¹, showing the red shifts by 56 and 187 cm⁻¹, respectively. This is because the strength of N–H bonds is weakened due to the ionization as compared with the neutral ammonia monomer. The calculated unscaled harmonic frequencies of the ammonia monomer are 3739 and 3601 cm⁻¹ at the MPW1K/6-311++G**, 3648 and 3501 cm⁻¹ at the MP2/aVTZ, and 3571 and 3434 cm⁻¹ at the CCSD(T)/aVDZ level. Those of the ammonia monomer cation are 3634 and 3449 cm⁻¹ at the MPW1K/6-311++G**, 3602 and 3411 cm⁻¹ at the MP2/aVTZ, and 3542 and 3340 cm⁻¹ at the CCSD(T)/aVDZ level. Then, the red shifts are 105 and 152 cm⁻¹ at the MPW1K/6-311++G**, 46 and 90 cm⁻¹ at the MP2/aVTZ, and 29 and 96 cm⁻¹ at the CCSD(T)/aVDZ level. Though the values are based on the harmonic frequencies, the red shifts seem to be better represented at the MPW1K/6-311++G** level than the other methods.

The calculated vibrational frequencies of the water monomer and the ammonia monomer show different deviations from the

experimental frequencies. Thus, we used the average scale factor to match both NH₃ and H₂O frequencies properly. The scale factors are 0.919 at the MPW1K/6-311++G**, 0.950 at the MP2/aVTZ, and 0.965 at the CCSD(T)/aVDZ level.

We have calculated the frequencies of the N–H and O–H stretching modes of the ammonia–water cation [(a) H₂NH⁺⋯OH₂, (b) H₃N⁺⋯OH₂, and (c) H₃NH⁺⋯OH] and the ammonia dimer cation [(f) H₃NH⁺⋯NH₂ and (g) (H₃N⋯NH₃)⁺] at the MPW1K, MP2, and CCSD(T) levels (Figure 3 and Table 7). At the CCSD(T)/aVDZ level, structure (g) (H₃N⋯NH₃)⁺ shows six weakly red-shifted N–H stretching frequencies of 3308, 3323, 3485, 3485, 3487, and 3487 cm⁻¹, while structure (f) H₃NH⁺⋯NH₂ shows one strongly red-shifted peak and five weakly red-shifted peaks at 2564, 3267, 3296, 3361, 3403, and 3403 cm⁻¹. One strongly red-shifted frequency (2564 cm⁻¹ at the CCSD(T)/aVDZ level) for (f) H₃NH⁺⋯NH₂ is of the ammonium moiety (H₃NH⁺) interacting with the •NH₂ radical. In the ammonia–water cation, structure (a) H₂NH⁺⋯OH₂ produces a more strongly red-shifted NH stretching frequency (2562 cm⁻¹) than (c) H₃NH⁺⋯OH (3045 cm⁻¹) at the CCSD(T)/aVDZ level. The five weakly red-shifted N–H and O–H stretching modes of structure (b) H₃N⁺⋯OH₂ appear at 3280, 3484, 3485, 3617, and 3721 cm⁻¹ at the CCSD(T)/aVDZ level of theory.

Concluding Remarks

At the CCSD(T)/CBS level of theory, for (NH₃⋯H₂O)⁺, the H₂NH⁺⋯OH₂ structure is the lowest, 2 kcal/mol more stable than the H₃NH⁺⋯OH structure and 4 kcal/mol more stable than the H₃NH⁺⋯OH structure. For (NH₃)₂⁺, the H₃NH⁺⋯NH₂ structure is the most stable, 5 kcal/mol more stable than the (H₃N⋯NH₃)⁺ structure. On the other hand, most DFT calculations with various functionals predict wrong structures in favor of the L⋯L' form. Nevertheless, the DFT results with MPW1K and BH&HLYP functionals provide the right structures and energetics, which are very close to the CCSD(T)/CBS results. In this regard, the energy comparison of these structures would be an important criterion for the validity test of the DFT functionals. The MP2 calculations give reasonable energies for most structures but unreasonable frequencies for the L⋯L' structures. Therefore, in order to obtain reliable stabilities and frequencies, the CCSD(T) calculations were necessary. However, the DFT (MPW1K) is an alternative approach to obtain reasonably reliable results for this system with much less computing time. The calculated spectra are provided to facilitate future experiments.

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- (25) Note that BH&HLYP means the $0.5E_X^{\text{HF}} + 0.5E_X^{\text{LSDA}} + 0.5\Delta E_X^{\text{Becke88}} + E_C^{\text{LYP}}$ functional.
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