Theoretical Study of Microscopic Solvation of Ammonia in Water Clusters: $NH_3(H_2O)_n$, $n = 3, 4$

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A number of significant structures of $NH_3(H_2O)_n$ ($n = 3, 4$) clusters have been identified by ab initio Monte Carlo simulated annealing, a procedure that efficiently samples minima on a potential energy surface. In this procedure, energies were computed ab initio at each Monte Carlo step by the B3-LYP density functional method with the 6-31G* basis set. All geometries of the isomers found for each cluster were refined in full conventional geometry optimizations, and frequency analyses were performed at both the B3-LYP and MP2 levels with the 6-311+G(d,p) basis set. The B3-LYP and MP2 energy orders were confirmed with single point QCISD(T) calculations with the 6-311+G(d,p) basis set performed on the MP2 optimized geometries. Only associated isomers were found for $NH_3(H_2O)_3$. However, for $NH_3(H_2O)_4$ both associated and dissociated structures were found.

1. Introduction

The study of the structure and properties of solvated ionic species is an active field of theoretical and experimental research. Solvation effects alter the chemical behavior of compounds. Knowledge of the interactions controlling the arrangement and the number of the solvent molecules necessary to stabilize the ions is prerequisite to the understanding of the solvation process. When a molecule of a compound more basic than water is dissolved in aqueous solution, a water molecule donates one of its protons and ions are formed. Solutions of ammonia in water have been used as a prototypical system for the study of this type of reactions. The formation of NH_4^+ and OH^- in solution has been established.[1] The equilibrium constant of the ammonia ionization in water at room temperature was determined experimentally to be 1.77×10^{-5}.[2]

NH_3 has recently attracted considerable interest for its possible role in atmospheric aerosol formation.[3] The results of this study can be valuable to understand the process of the partitioning of ammonia between the droplets and the gas phase in the troposphere. The $NH_3(H_2O)$ complex has been experimentally studied by microwave and far-infrared spectroscopy[4,5] and theoretically at the ab initio level.[6−8] Lee and co-workers[9] have shown the existence of a minimum energy structure in the potential energy surface of the $NH_3(H_2O)_4$ cluster, which is the result of one proton transfer from a water molecule to the ammonia molecule. They also postulated that with less than four molecules of water the formation of the double ionic cluster is not possible. Recently, Donaldson[10] reported an experimental and theoretical study of the structure, thermodynamics, and kinetics of the formation of $NH_3(H_2O)_n$, $n = 1, 2$, complexes. He found a global minimum for $NH_3(H_2O)$ and has determined its rotational and vibrational frequencies at the MP2 level. Also, he reported a cyclic structure for $NH_3(H_2O)_2$ where the molecules are attached by hydrogen bonds.

We report here the use of the ab initio Monte Carlo simulated annealing method (MCSA) to determine the structures of NH_3 with three and four water molecules.. For these clusters, the MCSA method was implemented with the density functional theory (DFT). This methodology has been applied successfully in the study of $HCl(H_2O)_n$, $n = 3, 4,$[11] and $LiCl(H_2O)_n$, $n = 1−4$ clusters.[12] It proved to be useful in locating a variety of low-lying isomers of that rather complex system.

2. Method

Ab initio MCSA was used to locate the minimum energy structures for the systems. MCSA energies were obtained from B3-LYP/6-31G* calculations. The B3-LYP functional consists of Becke's three parameters hybrid[13] plus the Lee, Yang, and Parr[14] correlation functional. All energies were evaluated using the GAUSSIAN 98 suite of programs.[15] Ab initio MCSA is a traditional Metropolis MC procedure[16] modified in two ways.[11,12] Energies are computed by ab initio electronic structure methods, and the temperature of the MC simulation is not held constant but gradually lowered to anneal the system. The details of the MCSA procedure have been given in previous work.[11,12] During the simulation the temperature is lowered slowly from a sufficiently high temperature to a "freezing" temperature, with a quenching factor determining the rate of decline.[17] The initial temperatures used in this study lie in the range 600−1000 K, with quenching factors ranging from 0.995 to 0.950. The Metropolis acceptance criterion permits both uphill and downhill movement on the potential energy surface; the magnitude of said motions are determined by the temperature. MCSA can, therefore, avoid becoming trapped in local minima but, with fast enough annealing, can also be used to find local minima.

A complication in the Monte Carlo simulation of NH_3−water clusters is that the procedure must describe aggregations in which NH_3 is both ionized and not ionized. For this reason the motions of N and H are treated independently. In addition, one or two of the water molecules are randomly selected to be moved atom-by-atom rather than as a whole molecule, potentially permitting it to dissociate as well. This approach is less time-consuming than a complete atom-by-atom treatment but has the flexibility to sample key significant configurations.

Structures obtained by simulated annealing were checked and refined using standard geometry optimizations at both the B3-
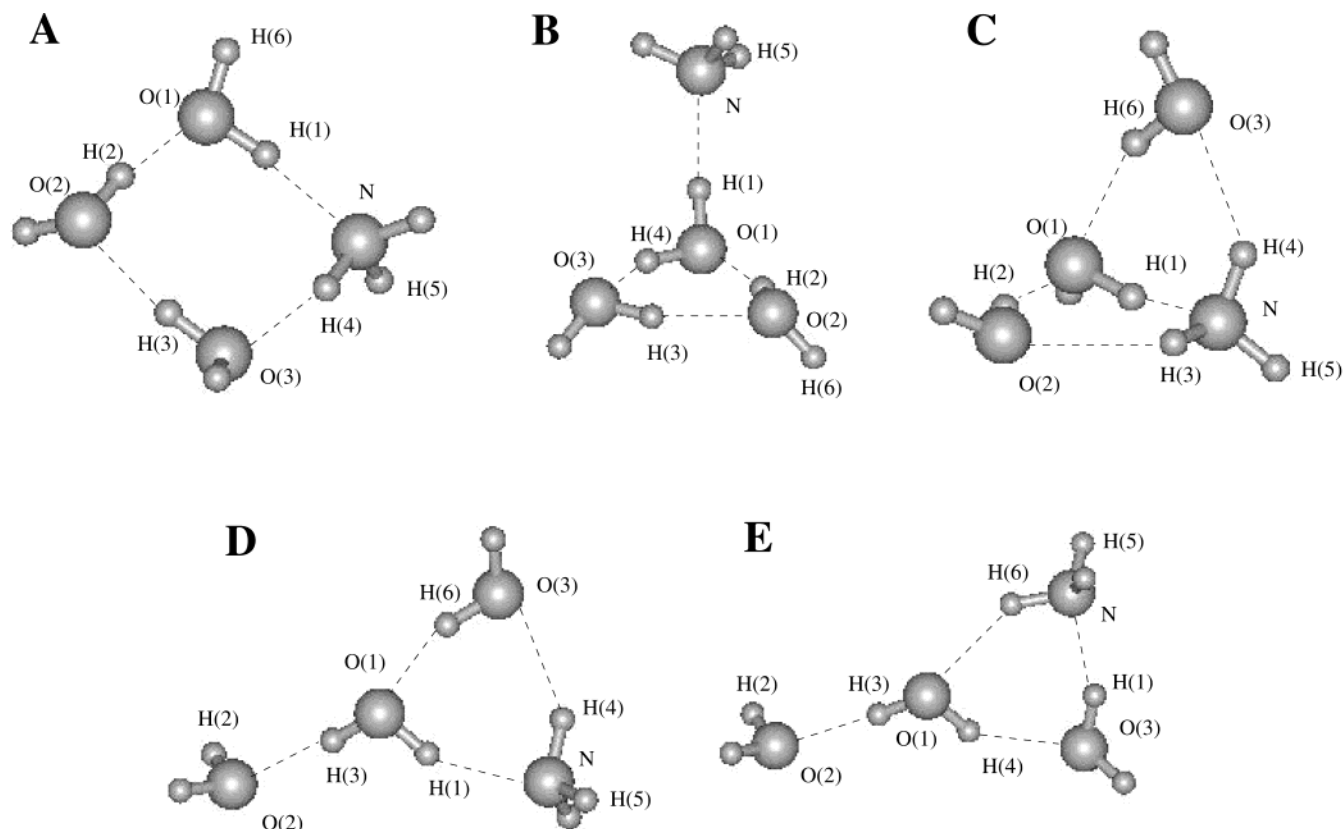
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J. Phys. Chem. A, Vol. 106, No. 46, 2002 **11191**

Figure 1. Structural isomers of NH₃(H₂O)₃.

TABLE 1: Selected Geometrical Parameters of Optimized Structures of NH₃(H₂O)₃[a]

parameter	A		B		C		D		E	
	B3-LYP	MP2	B3-LYP	MP2	B3-LYP	MP2	B3-LYP	MP2	B3-LYP	MP2
N−H(1)	1.8035	1.8154	1.9210	1.9243	1.7877	1.7754	1.9488	1.9637	1.8898	1.9013
O(1)−H(2)	1.7595	1.7727	1.7437	1.8038	1.9554	1.9668	3.4275	3.4529	3.4803	3.4923
O(2)−H(3)	1.8003	1.8144	1.9102	1.9293	2.2244	2.3569	1.9461	1.9550	1.9580	1.9672
O(3)−H(4)	2.0133	2.0265	2.0371	2.0594	4.3431	2.3569	2.2311	2.2227	1.9670	1.9832
N−H(4)	1.0247	1.0218	3.3257	3.2975	1.0156	1.0176	1.0206	1.0189	2.9439	2.9643
N−H(5)	1.0158	1.0152	1.0158	1.0152	1.0151	1.0141	1.0150	1.0147	1.0150	1.0146
O(1)−H(1)	0.9954	0.9873	0.9801	0.9749	0.9977	0.9924	0.9804	0.9744	2.8156	2.8143
O(1)−H(6)	0.9611	0.9592	3.2623	3.2452	1.9036	1.9674	1.8203	1.8321	2.1002	2.1124
N−H(1)−O(1)	168.701	168.514	177.134	176.203	161.873	156.391	153.283	152.577	75.884	75.920
O(1)−O(2)−O(3)	91.768	91.551	62.663	62.493	30.462	41.636	27.024	24.417	25.299	25.918
N−O(1)−O(2)	93.829	94.149	120.505	122.567	65.369	67.033	122.443	122.175	154.816	156.749
N−O(1)−O(2)−O(3)	1.613	0.420	105.922	104.086	94.736	61.542	−82.323	−84.674	95.913	95.052
N−H(1)−O(1)−O(2)	11.488	10.325	33.548	22.132	−20.170	−50.253	132.606	138.062	137.013	140.864

[a] Distances in angstroms, angles in degrees. All optimizations were performed with the 6-311+G** basis set. Atomic subscripts correspond to those in Figure 1.

LYP and MP2 levels of theory. The basis sets were progressively improved by adding diffusion and polarization functions. For each optimization, frequency calculations were performed to confirm that the structures were true minima at each theoretical level. Zero-point energies were obtained using the harmonic vibrational frequencies. A final energy ordering of the various minima was established in single-point quadratic singles and doubles configuration interaction plus perturbative triples (QCISD(T))[18] calculations on the MP2 optimized structures with the 6-311+G** basis set. Geometries of NH₃, H₂O, (H₂O)₂, (H₂O)₃, and (H₂O)₄ were also optimized at the MP2 and B3-LYP levels with the 6-311+G** basis set to permit the determination of the energetics of the clusters formation.

3. Results and Discussion

A number of DFT-MCSA calculations were performed on the potential energy surface of each cluster with different starting geometries. For NH₃(H₂O) just one structure was found in the potential energy surface. The MCSA procedure yielded two isomers for NH₃(H₂O)₂. One of these structures was found not to be a real minimum by using frequency analysis. Both global minima found for NH₃(H₂O) and NH₃(H₂O)₂ are in good agreement with the structures reported by Donaldson.[10]

In the NH₃(H₂O)₃ simulations, eight different geometries arose from the DFT-MCSA simulations which, after conventional optimization with 6-311+G** basis sets at both the B3-LYP and MP2 theoretical levels, converged to five distinct minima. The MP2 optimized structures of the five isomers are shown in Figure 1. Geometries are tabulated in Table 1. For NH₃(H₂O)₄ seven isomers were found, six at both the MP2 and B3-LYP levels and one only at the B3-LYP level. Figure 2 exhibits the structures for the NH₃(H₂O)₄ isomers. Six of them show only slight changes in the character of the NH₃ bond, and one displays the formation of the NH₄⁺ cation. The most
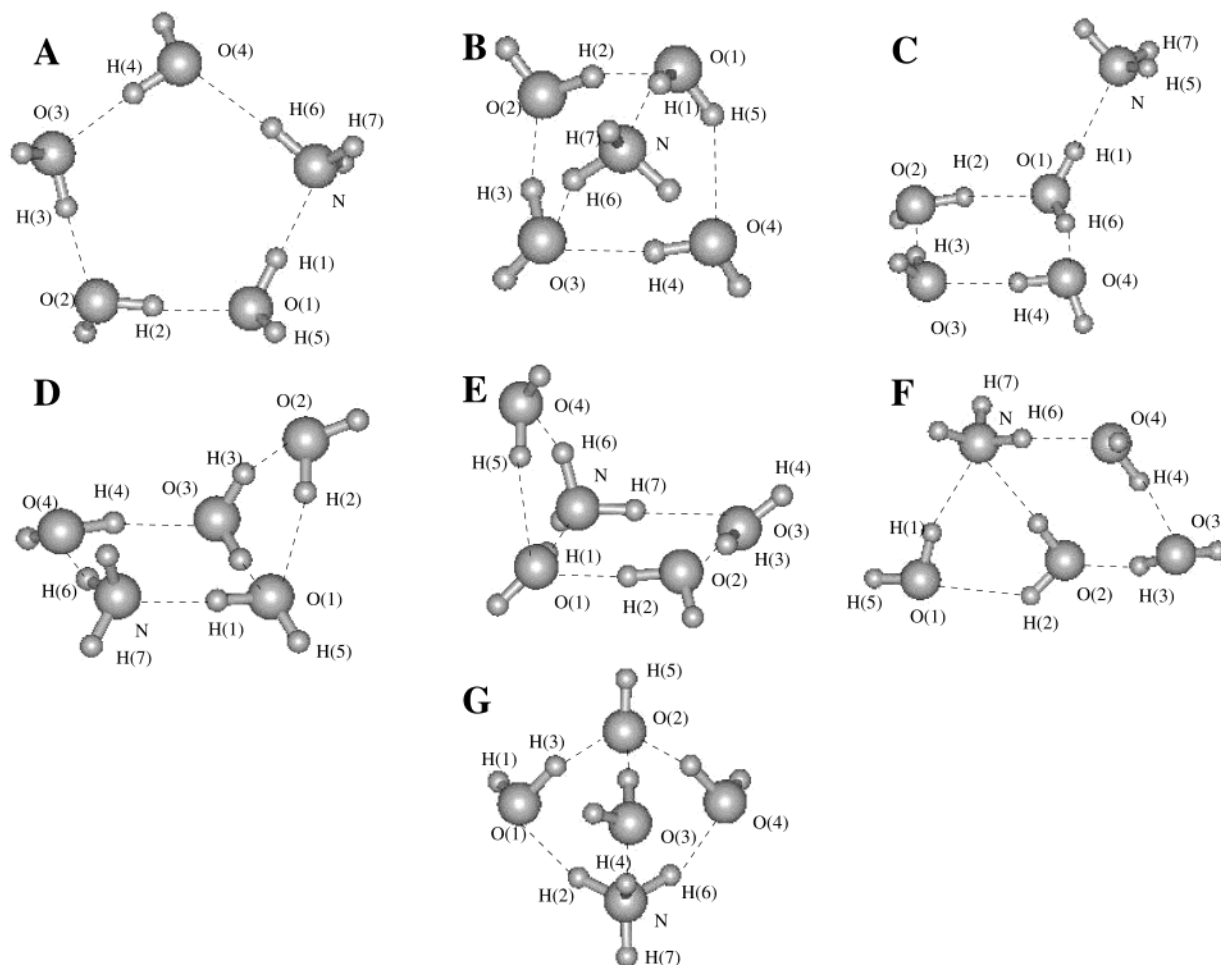
Figure 2. Structural isomers of $NH_3(H_2O)_4$.

TABLE 2: Selected Geometrical Parameters of Optimized Structures at B3-LYP Level of $NH_3(H_2O)_4$[a]

parameter	A	B	C	D	E	F	G
N–H(1)	1.7793	1.9260	1.9261	1.7555	1.6978	2.0651	3.3912
O(1)–H(2)	1.7256	1.7171	1.7041	1.8931	1.8129	2.2344	1.7487
O(2)–H(3)	1.7428	1.7454	1.7561	2.0360	1.8287	1.7781	1.5699
O(3)–H(4)	1.7741	1.8839	1.7917	1.7863	0.9610	1.7921	1.7033
O(4)–H(6)	1.9718	3.6968	1.8662	1.9751	2.4344	1.9901	1.7210
O(3)–H(7)	5.2845	2.2736	6.9006	4.7890	2.0461	4.9010	3.4110
N–H(6)	1.0259	1.0156	3.3207	1.0255	1.0184	1.0275	1.0507
N–H(7)	1.0161	1.0195	1.0156	1.0157	1.0233	1.0170	1.0150
O(1)–H(1)	0.9987	0.9833	0.9796	1,0037	1.0136	0.9758	0.9602
O(1)–H(5)	0.9613	0.9729	3.4044	0.9613	1.9638	0.9611	3.2317
N–H(1)–O(1)	175.304	161.254	178.647	171.014	163.557	166.259	31.152
O(1)–O(2)–O(3)	108.931	82.916	91.151	61.990	91.710	134.452	89.457
N–O(4)–O(3)	107.810	56.985	104.915	89.108	36.093	100.269	47.863
N–O(1)–O(2)–O(3)	−15.138	−42.161	−112.693	−80.033	−1.057	71.907	−47.093
O(1)–O(2)–O(3)–O(4)	15.834	−37.906	−2.467	77.811	34.482	−60.557	94.105

[a] Distances in angstroms, angles in degrees. All optimizations were performed with the 6-311+G** basis set. Atomic subscripts correspond to those in Figure 2.

important geometrical parameters of these isomers are tabulated in Tables 2 and 3.

Though we are confident that our investigation has revealed all, or nearly all, of the low-lying isomers of the $NH_3(H_2O)_3$ clusters, the complexity of the ammonia–four water surface makes it unlikely that we have found all possible structures for this cluster. However, we are confident in having located the global minimum structure for the $NH_3(H_2O)_4$. MCSA runs yielded this structure in the limit of the quenching factor approaching 1. In the following discussion we will restrict ourselves to the results obtained with 6-311+G** basis sets at both B3-LYP and MP2 levels of theory. The data in Tables

1–3 show that in general the B3-LYP N–H intramolecular interactions are underestimated in comparison with the MP2, whereas hydrogen bond interactions are overestimated.

3.1. $NH_3(H_2O)_3$. The most stable isomer, A in Figure 1, is an almost planar quadrilateral cyclic structure with the nitrogen and oxygens at the corners. The structure shows a strong intermolecular N- -H interaction with an atomic distance of 1.803 Å at the MP2 level (1.815 Å at B3-LYP). Each H_2O molecule acts as both a single hydrogen bond donor and a single acceptor. The free hydrogens of the water molecules lie alternately above and below the buckled plane. This isomer has torsional variants that are also minimum energy structures on

TABLE 3: Selected Geometrical Parameters of Optimized Structures at MP2 Level of $NH_3(H_2O)_4$[a]

parameter	A	B	C	D	E	F	G
N−H(1)	1.7914	1.9140	1.9268	1.7653	1.7163		3.4886
O(1)−H(2)	1.7355	1.7315	1.7128	1.9002	1.8123		1.7398
O(2)−H(3)	1.7538	1.7579	1.7696	2.0543	1.8457		1.5576
O(3)−H(4)	1.7867	1.8654	1.8051	1.7943	0.9589		1.6925
O(4)−H(6)	1.9877	2.6090	1.8785	1.9962	2.3923		1.7111
O(3)−H(7)	5.2953	2.4216	6.8836	4.7653	2.0640		3.3934
N−H(6)	1.0228	1.0164	3.2896	1.0229	1.0176		1.0459
N−H(7)	1.0155	1.0170	1.0151	1.0155	1.0210		1.0140
O(1)−H(1)	0.9903	0.9788	0.9746	0.9948	1.0022		0.9588
O(1)−H(5)	0.9593	0.9661	3.4114	0.9599	1.9830		3.2136
N−H(1)−O(1)	175.117	158.711	177.822	170.965	163.382		30.239
O(1)−O(2)−O(3)	108.713	83.473	90.934	61.982	92.090		89.754
N−O(4)−O(3)	107.538	65.120	105.384	87.273	39.235		47.778
N−O(1)−O(2)−O(3)	−17.213	−37.092	−110.218	−79.890	−6.739		−47.553
O(1)−O(2)−O(3)−O(4)	16.274	−29.976	−2.922	79.355	41.086		95.191

[a] Distances in angstroms, angles in degrees. All optimizations were performed with the 6-311+G** basis set. Atomic subscripts correspond to those in Figure 2.

the three-water potential surface, lying about 1−3 kcal/mol higher in energy than the global minimum A. The presence of the ammonia molecules renders the three free hydrogens nonequivalent, permitting torsional variants with the free hydrogens following different patterns than the up/down/up present in structure A.

Small water clusters have been intensely studied theoretically.[19−22] Structure A is similar to the most stable structure found for the isolated water tetramer in experimental and theoretical studies, but with NH_3 replacing a water molecule. The distortion of the cyclic structure caused by NH_3 is reflected in the hydrogen bond lengths. The optimum structure of $(H_2O)_4$ has a mean H-bond distance of 1.775 Å at the B3-LYP and 1.789 Å at the MP2 levels, with small deviations from the mean. Note the relatively wide range of hydrogen bond lengths in isomer A, presented in Table 1.

Following in stability is the isomer B in Figure 1. It is essentially a cyclic water trimer with the ammonia molecule resting on top, hydrogen bonded to one of the oxygens. The N- -H bond is slightly weaker than that present in isomer A, as is reflected in the calculated bond lengths of 1.924 Å (B3-LYP) and 1.921 Å (MP2). The water trimer moiety is similar to the most stable structure found experimentally and theoretically for isolated water trimer.[19−24] 6-311+G** B3-LYP and MP2 optimizations of water trimer yield geometries that agree with each other and with previously reported experimental[23,24] and theoretical[19−22] results. The geometric data in Table 1 reveal the slight distortion in the water cluster induced by interaction with NH_3. In isomer C the NH_3 molecule acts as a double donor and single acceptor of hydrogen bonds. This isomer has the shortest N- -H intermolecular distance for the $NH_3(H_2O)_3$ minima with a distance of 1.788 Å (B3-LYP) and 1.775 Å (MP2).

A central double donor water molecule forms structures D and E (Figure 1). One of the waters, single donor and single acceptor, is hydrogen bonded to NH_3. The only difference between these two isomers is the exchange position between water and ammonia molecules. Isomer D has the weakest N- -H interaction with distances of 1.950 Å (B3-LYP) and 1.964 Å (MP2). For isomer E, B3-LYP and MP2 predictions of the N- -H hydrogen bond length are 1.890 and 1.901 Å, respectively. The water−water interactions are weaker than in isomers A and B (see Table 1). Overall, for these last structures the B3-LYP geometries are more compact than those obtained by MP2 calculations.

3.2. $NH_3(H_2O)_4$. The most stable of the associated structures, indeed of all the four-water structures, is isomer A (Figure 2).

It is a pentagonal, nearly planar structure with nitrogen and the four oxygens at the apexes. One hydrogen of NH_3 is in the middle of a side of the pentagon and hydrogen bonded to a water molecule. The free hydrogens of the waters lie alternately above and below the plane. Three of the water subunits act as both H-bond donors and acceptors. The final water is a H-bond acceptor and one of its hydrogens interacts strongly with N at a distance of 1.779 Å (B3-LYP) and 1.791 Å (MP2). This isomer has also torsional variants, lying about two to four kcal higher than isomer A. This structure is similar to the global minimum cyclic ring structure determined for the $(H_2O)_5$ cluster[20−23,25] with NH_3 replacing a water molecule. Xantheas and Dunning[20] reported a HF/aug-cc-pVDZ optimized planar structure for $(H_2O)_5$ with oxygen−oxygen distances of 2.863, 2.862, 2.863, 2.865, and 2.882 Å. Recently, the energetics and a detailed study of the hydrogen bonding network of the water pentamer at the MP2 level have been reported.[21] The MP2 structure of our isomer A finds O(1)−O(2), O(2)−O(3), O(3)−O(4), O(4)−N, and N−O(1) distances of 2.714, 2.730, 2.761, 3.005, and 2.775 Å, respectively. The corresponding B3-LYP values are approximately 0.01 Å shorter.

Isomer B consists essentially of a square water tetramer with NH_3 sitting on top, hydrogen bonded to one water, and canted slightly from the perpendicular. It is reminiscent of structure B of the three-water isomers. The four water molecules are in the configuration, almost unperturbed, of isolated water tetramer in its minimum energy configuration.[21,24−26] Each H_2O of isomer A acts as a hydrogen bond single donor and single acceptor, except the water attached to the NH_3 in oxygen is a double acceptor. The free hydrogens lie alternately above and below the plane of the square formed by the oxygens. The N- -H hydrogen bond length is 1.803 Å (DFT), 1.815 Å (MP2). The O−O separation in the isolated water tetramer found by MP2/6-311+G** optimization is 2.747 Å, in substantial accord with the MP2/aug-cc-pVDZ distance of 2.785 Å reported by Xantheas and Dunning and with the experimental separations of 2.78−2.79 Å.[20] The O−O distances for the oxygen involved in the H-bond with NH_3 are slightly shortened on one side and lengthened on the other. Structure C is also a square water tetramer with NH_3 sitting on top, but the ammonia is situated in a more peripheral position. Again, the four-water moiety agrees well with the isolated water tetramer.

Isomers D and E are similar; both are composed of a square formed by the NH_3 and three water molecules. The difference between both structures is the role of the NH_3. In isomer D, the ammonia is the single donor and acceptor of hydrogen bond. In contrast, in isomer E the ammonia is a single acceptor and

TABLE 4: Energies of Low-Lying NH₃(H₂O)ₙ, n =3, 4, Structures[a]

cluster	isomer	B3-LYP		MP2		QCISD(T)	
		energy	Δ energy	energy	Δ energy	energy	Δ energy
NH₃		−56.5826354		−56.4153067		−56.4346268	
H₂O		−76.4620396		−76.2962947		−76.3084600	
(H₂O)₂		−152.9262246		−152.559068		−152.5827414	
(H₂O)₃		−229.4025332		−228.8514367		−228.8867493	
(H₂O)₄		−305.8820134		−305.1478632		−305.1945438	
NH₃(H₂O)₃	A	−286.0041190	0.00	−285.2865761	0.00	−285.3406079	0.00
	B	−285.9978175	3.97	−285.2801618	4.03	−285.3345641	3.79
	C	−285.9949486	5.75	−285.2790922	4.70	−285.3334093	4.52
	D	−285.9931138	6.91	−285.2760683	6.60	−285.3305413	6.32
	E	−285.9923853	7.36	−285.2754182	7.00	−285.3298626	6.74
NH₃(H₂O)₄	A	−362.4786947	0.00	−361.5775658	0.00	−361.6431680	0.00
	B	−362.4756027	1.94	−361.5763768	0.75	−361.6424965	0.42
	C	−362.4774603	0.77	−361.5762161	0.85	−361.6420694	0.69
	D	−362.4751062	2.25	−361.5750262	1.59	−361.6409795	1.37
	E	−362.4721335	4.12	−361.5722578	3.33	−361.6381041	3.18
	F	−362.4686325	6.31				
	G	−362.4574473	13.33	−361.5541413	14.70	−361.6171078	16.35

[a] Energies calculated with 6-311+G(d,p) basis sets. Isomers are indicated by the labels used in Figures 1and 2. Energies are in atomic units. Δ energy refers to the difference in energy (kcal/mol) with respect to isomer A.

TABLE 5: 6-311+G Energetics of Low-Lying NH₃(H₂O)ₙ, n =3, 4, Structures**

cluster	isomer	ΔE_{ZPE}[b]		ΔE_{B1}[c]		ΔE_{B2}[d]		ΔE_{B3}[e]	
		B3-LYP	MP2	B3-LYP	MP2	B3-LYP	MP2	B3-LYP	MP2
	A	0.00	0.00	9.66	10.02	17.32	17.69	20.84	21.35
	B	3.58	3.50	6.08	6.51	13.74	14.18	17.26	17.85
NH₃(H₂O)₃	C	4.84	3.71	4.82	6.30	12.48	13.97	16.00	17.63
	D	6.01	5.55	3.65	4.46	11.31	12.13	14.83	15.80
	E	6.33	5.85	3.33	4.17	10.99	11.84	14.51	15.50
	A	0.00	0.00	6.78	7.10	17.39	17.66	28.57	29.00
	B	2.25	0.92	4.53	6.17	15.14	16.73	26.32	28.07
NH₃(H₂O)₄	C	0.89	0.77	5.89	6.32	16.50	16.88	27.68	28.22
	D	2.23	1.36	4.55	5.73	15.16	16.29	26.34	27.63
	E	3.26	2.62	3.57	4.47	14.13	15.03	25.31	26.37
	F	7.39		0.61		10.00		−22.68	
	G	13.54	14.77	−6.76	−7.67	3.85	2.89	15.03	14.23

[a] All the energies are in kcal/mole. Isomers are indicated by the labels used in Figures 1 and 2 [b] ΔE_{ZPE} refers to the difference in the zero-point energy with respect to isomer A. [c-e] The binding energies were calculated as $E_{B1} = E_{NH_3}^{Opt} + E_{(H_2O)_n}^{Opt} - E_{NH_3(H_2O)_n}^{Opt}$, $E_{B2} = E1_{NH_3(H_2O)_{n-}}^{Opt} + E_{H_2O}^{Opt} - E_{NH_3(H_2O)_n}^{Opt}$, and $E_{B3} = E_{NH_3}^{Opt} + nE_{H_2O}^{Opt} - E_{NH_3(H_2O)_n}^{Opt}$, where the Opt superscript denotes the energy of the geometrical optimized structure.

a double donor of hydrogen bonds. Isomer F is a local minimum at B3-LYP level, but all the attempts to locate this structure at the MP2 level converged to one of the minima mentioned above. The introduction of spurious minima for the DFT approximation on complex potential energy surface had been reported previously.[27]

The only stable isomer in which H₂O is dissociated and where there is formation of the NH₄⁺ cation is labeled G in Figure 2. It is a structure in which three water molecules form the equatorial plane of a trigonal bipyramid, with a OH⁻ and an NH₄⁺ at the apexes. Isomer G agrees well with the structure determined by Lee et al.[9] in B-LYP/TZ94+P calculations. There are three hydrogens at distances of 1.57 Å (B3-LYP) or 1.56 Å (MP2) from the OH⁻ indicating a weak interaction. The NH₄⁺ shows strong H-bonds to the H₂O molecules, with separation distances of about 1.70 Å in DFT calculations and nearly the same in MP2. There are no hydrogen bonds between the water molecules. The OH⁻ and the NH₄⁺ are positioned in the opposite extremes of the structure, separated by the three water molecules. This arrangement maximizes the charge separation between the ions, creating a large dipole moment of 3.39 D in the isomer. This structural behavior in the formation of the dissociated species in the water cluster has been observed also in clusters of water with HCl,[11] LiCl,[12] and H₂SO₄[28] among others. The creation of this dipole will provide a totally different electrostatic

environment to which other water(s) may be added with associated new interactions. It therefore seems that the 3 to 4 number of water molecule transition marks a threshold beyond which there is a sufficient number of solvent molecules to stabilize the ions created by the dissociation. As expected, due to the weak basis character of the ammonia, the dissociated structures are much more unstable than the associated ones.

3.3. Energy Ordering and Frequency Analyses. The B3-LYP and MP2 predictions of the order stability and even the energy differences of the NH₃(H₂O)₃ clusters agree very well. The QCISD(T)/6-311+G** calculations confirm the order obtained with these methods. Results are presented in Table 4. Isomer A is the most stable structure on the potential surface. All isomers are within 8 kcal/mol in energy of each other. Table 5 shows the differences in stability of the isomers using the zero-point energies at both levels of theory. Also, these zero-point energies are used to calculate the binding energies of the isomers with respect to different pathways. It must be noted that those binding energies may have a significant basis set superposition error (BSSE).[29] Xantheas has reported that DFT predictions show reduced BSSE in comparison to MP2 calculations.[30] The structure A has a binding energy with respect to the isolated ammonia and the optimized water tetramer (see the caption of Table 5 for the equations used for the calculation of the binding energies) of approximately 10 kcal/mol.
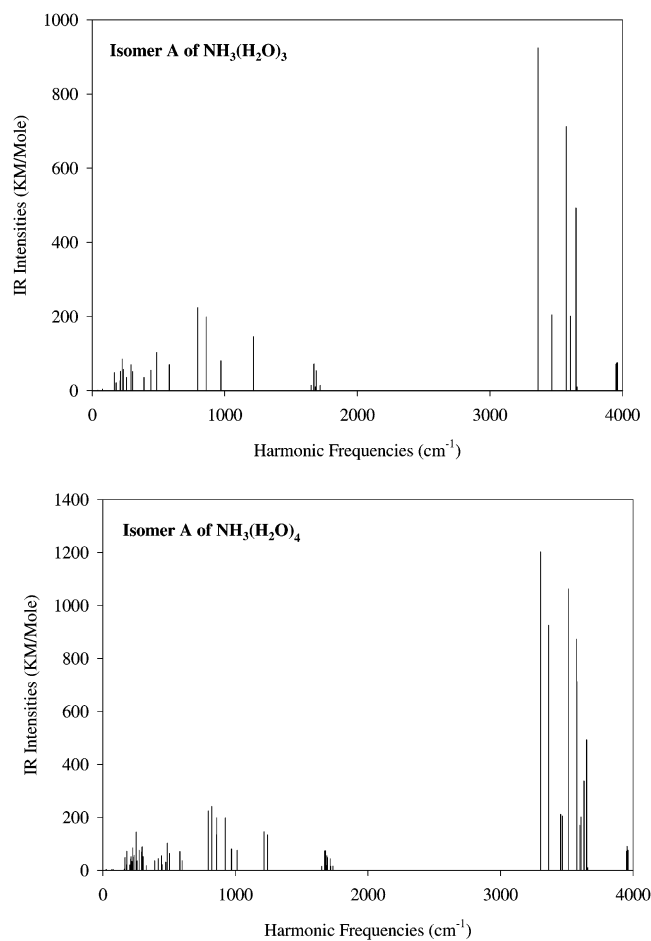
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Figure 3. Predicted IR (harmonic frequencies) spectra of the most stable isomers of $NH_3(H_2O)_3$ (above) and $NH_3(H_2O)_4$ (below).

The B3-LYP and MP2 harmonic frequencies for the three-water cluster agree well. The frequencies associated with the intramolecular modes of NH_3 show no significant red shifts with respect to the values of isolated ammonia. This is in agreement with the fact that there is no appreciable weakening of the bonds between the nitrogen and the hydrogen atoms in the ammonia molecule present in structure A.

For $NH_3(H_2O)_4$, the B3-LYP and MP2 energy orderings do not agree, but both methods establish isomer A as the global minimum in the potential surface. B3-LYP finds structure C to be more stable than B and also find the spurious minima F. MP2 establish the isomer B to be slightly more stable than C. However, after the zero point energy correction this order is reversed for a very small difference. The ordering predicted by the QCISD(T)/6-311+G** calculations agrees well with the order found with the MP2 approximation. The dissociated structure G is energetically unfavorable with respect to isolated ammonia and the optimized water tetramer. However, it is stable with respect to its formation via the addition of H_2O to NH_3-$(H_2O)_3$ and with respect to the ammonia and four isolated water molecules. The theoretical frequency synthesis from the MP2 calculations for the most stables isomers of $NH_3(H_2O)_4$ and NH_3-$(H_2O)_4$ are shown in Figure 3.

4. Conclusions

The MCSA-DFT method has proven to be capable of finding a number of low-lying minima on the potential hypersurfaces of $NH_3(H_2O)_n$, $n = 1-4$. As expected, hydrogen bonding was found to play the crucial role in the stability of the clusters,

and the several possible H-bond arrangements produced a number of isomers close in energy. Similar to other solvated species (HCl,[11] LiCl,[12] H_2SO_4,[28] HCOOH,[31] methylamines,[32] among others) the most stable conformation for both clusters are cyclic structures with geometries comparable to those reported for water clusters.[20–26] In each cluster of up to three water molecules, no isomers were found with water dissociation forming the NH_4^+ ion and OH^-. It appears that three water molecules are not sufficient to stabilize the ionic form. In NH_3-$(H_2O)_4$, on the other hand, NH_3 in both its ionized and nonionized structures are found. However, the dissociated structure is significantly higher in energy than the global minimum. The global minimum structure for $NH_3(H_2O)_4$ is an associated cyclic structure. It therefore seems that at least four water molecules are necessary to permit the formation of a stable ion pair.

All the isomers show an anticorrelation between intermolecular H-bond length (O- -H) and the intramolecular O–H distance; as a hydrogen bond shortens, the intermolecular O–H bond length increases. Such behavior is noted at both theoretical levels. This correlation has been observed in the water tetramer and in crystal structures of chemically related H-bonded molecules.[33] For the free hydrogens, the O–H bond length remains constant to within 0.001 Å at both levels of theory for all isomers.

We find in general that the structural complexity of the NH_3–water potential surface is well described by both the B3-LYP and the MP2 theoretical models with 6-311+G** basis sets. Both methods found the ionized structure and agree with its low stability compared with the rest of the isomers. Tables 1–3 exhibit two clear differences in the optimized geometrical parameters for all of the isomers discussed at both theoretical levels. The NH_3 intramolecular interactions are overestimated in the B3-LYP calculations when compared to the MP2, and all structures show an underestimation of H-bond interactions by MP2 as compared to B3-LYP. B3-LYP introduces an apparent spurious minimum into the $NH_3(H_2O)_4$ potential surface.

Supporting Information Available: Tables listing the vibrational frequencies, IR intensities, and spatial coordinates of all the isomers calculated at the MP2/6-311+G** level of theory. This material is available free via the internet at http://pubs.acs.org.

References and Notes

(1) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Chapman and Hall: London 1973.

(2) Perrin, D. B. *Ionization Constants of Inorganic Acid and Bases in Aqueous Solutions*, 2nd ed.; Pergamon: Oxford, U.K., 1982.

(3) (a) Weber, R. J.; Marti, J. J.; McMurry, P. H.; Eisele, F. L.; Tanner, D. J.; Jefferson A. *J. Geophys. Res. Atmos.* **1997**, *102*, 4375. (b) Weber, R. J.; McMurry, P. H.; Mauldin, L.; Tanner, D. J.; Eisele, F. L. *J. Atmos. Sci.* **1995**, *52*, 2242.

(4) (a) Dyke, T. R.; Herbine, P. *J. Chem. Phys.* **1985**, *83*, 3768. (b) Herbine, P.; Hu, T. A.; Johnson, G.; Dyke, T. R *J. Chem. Phys.* **1990**, *93*, 5485.

(5) Stockman, P. A.; Bumgarner, R. E.; Suzuki, S.; Blake, G. A. *J. Chem. Phys.* **1992**, *96*, 2496.

(6) Astrand, P.-O.; Karlstrom, G.; Engdahl, A.; Nelander, B. *J. Chem. Phys.* **1995**, *102*, 3534.

(7) Skurski, P.; Gutowski, M. *Chem. Phys.* **1998**, *108*, 6303.

(8) Sadlej, J.; Moszynski, R.; Dobrowolski, C. Cz.; Mazurek, A. P. *J. Phys. Chem. A* **1999**, *103*, 8528.

(9) Lee, C.; Fitzgerald, G.; Planas, M.; Novoa, J. J. *J. Phys. Chem.* **1996**, *100*, 7398.

(10) Donaldson, D. J. *J. Phys. Chem. A* **1999**, *103*, 62.

(11) Bacelo, D. E.; Binning, R. C., Jr.; Ishikawa, Y. *J. Phys. Chem. A* **1999**, *103*, 4631.

(12) Bacelo, D. E.; Ishikawa, Y. *Chem. Phys. Lett.* **2000**, *319*, 679.

(13) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 1053.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A;. Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; J. Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Head-Gordon, M.; Pople, J. A. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

(16) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.

(17) Kirkpatrick, S.; Gellat, C. D., Jr.; Vecchi, M. P. *Science* **1983**, *220*, 671.

(18) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys* **1987**, *87*, 5968.

(19) Kim, K. S.; Dupuis, M.; Lie, G. C.; Clementi, E. *Chem. Phys. Lett.* **1986**, *131*, 451.

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

(21) (a) Xantheas, S. S. *Chem. Phys.* **2000**, *258*, 225. (b) Xantheas, S. S.; Burnham, C. J.; Harrison, R. J. *J. Chem. Phys.* **2002**, *116*, 1493.

(22) Estrin, D. A.; Paglieri, L.; Corongiu, G.; Clementi, E. *J. Phys. Chem.* **1996**, *100*, 8701.

(23) Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929.

(24) Liu, K.; Loeser, J. G.; Elrod, M. J.; Host, B. C.; Rzepiela, J. A.; Pugliano, N.; Saykally, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 3507.

(25) Cruzan, J. D.; Braly, L. B.; Liu, K.; Brown, M. G.; Loeser, J. G.; Saykally, R. J. *Science* **1996**, *271*, 59.

(26) Xantheas, S. S. *J. Chem. Phys.* **1994**, *100*, 7523.

(27) Bacelo, D. E.; Ishikawa, Y. *J. Mol. Struct. (THEOCHEM)* **1998**, *425*, 87.

(28) Re, S.; Osamura, Y.; Morokuma, K. *J. Phys. Chem. A* **1999**, *103*, 3535.

(29) Kestner, N. R.; Combariza, J. E. Basis Set Superposition Errors: Theory and Practice. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 1999; Vol. 13, pp 99−132.

(30) Xantheas, S. S. *J. Chem. Phys.* **1995**, *102*, 4505.

(31) Aloisio, S.; Hintze, P. E.; Vaida, V. *J. Phys. Chem. A* **2002**, *106*, 363.

(32) Mmereki, B.; Donaldson, D. J. *J. Phys. Chem. A* **2002**, *106*, 3185.

(33) Schütz, M.; Klopper, W.; Lüthi, H. P.; Leutwyler, S. *J. Chem. Phys.* **1995**, *103*, 6114.