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Ab initio study of the structures of $CH_3NH_3^+$ and $CH_3PH_3^+$ in aqueous solution

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ABSTRACT: The purpose of this work was to determine quantitatively the structures of $CH_3NH_3^+$ and $CH_3PH_3^+$ in aqueous solution. For this purpose, the structures of $CH_3NH_3^+$ $(H_2O)_n$ were optimized using MP2/6–31G(d) ($n = 0, 1, 2, 3, 4, 5, 6$) and RHF/4–31G ($n = 0, 1, 2, 3, 4, 5, 6, 9, 21$) and the structures of $CH_3PH_3^+$ $(H_2O)_n$ ($n = 0, 1, 2, 3$) were optimized using MP2/6–31+G(d,p). Based on these structures, the structure of $CH_3NH_3^+$ in aqueous solution was predicted as follows: C—N = 1.479 Å, N—H = 1.047 Å, C—H = 1.088 Å, NCH = 108.9° and CNH = 108.5°. The C—N bond length of $CH_3NH_3^+$ in aqueous solution is predicted to be smaller than that in the gas phase by 0.03 Å. The N—H bond lengths of $CH_3NH_3^+$ in aqueous solution are predicted to be longer than those in the gas phase by 0.02 Å. The structure of $CH_3PH_3^+$ in aqueous solution was predicted as follows: C—P = 1.808 Å, P—H = 1.394 Å, C—H = 1.087 Å, PCH = 109.5° and CPH = 109.9°. The structure of $CH_3PH_3^+$ in aqueous solution is predicted to be similar to that in the gas phase. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: *ab initio* calculations; structure; $CH_3NH_3^+$; $CH_3PH_3^+$; aqueous solution

INTRODUCTION

Many biologically important species, such as amino acids and peptides, possess —NH_3^+ groups. For this reason, the structure of RNH_3^+ in aqueous solution is of great interest. However, its experimental determination is still a difficult task. Ten years ago, the author qualitatively predicted the structure of $CH_3NH_3^+$ in aqueous solution without taking electron correlation into account.[1] The purpose of this work was to include this term in calculations. Also, the structure of $CH_3PH_3^+$ in aqueous solution is predicted.

EXPERIMENTAL

Computations were made using the program Gaussian 94[2] and the SP2, HPC, HSP and SX-5 computers at the Institute for Molecular Science.

According to Del Bene,[3] the optimized geometries of small, binary complexes with strong H-bonds essentially converge at the MP2/6–31+G(d,p) level of *ab initio* methodology. Later studies at higher levels of methodology[4–6] showed that the optimized geometries of a number of complexes change very little beyond the MP2/6–31+G(d,p) level, while the extra computational effort can increase dramatically.

Therefore, MP2/6–31G(d) was mainly used for the aqueous clusters studied here. For clusters too large to be optimized by MP2/6–31G(d), RHF/4–31G was used. In fact, the latter level as shown to be well suited for protonated clusters.[7]

A Monte Carlo simulation study of $CH_3NH_3^+$ in aqueous solution[8] showed that (1) the NH_3^+ group has an average coordination number of 3.5, corresponding to one water molecule closely associated with each H; (2) the water molecules in the first solvent shell have both lone pairs directed toward the NH_3^+ group, which implies that (3) only their hydrogen atoms are available for coordinating to bulk water; (4) the average number of H bonds to bulk water of each water molecule in the first solvent shell is 1.88; (5) the average angle O—H (in the first solvent shell)···H (in bulk water) is 158.5°; (6) for water molecules in the second solvent shell, the average coordination number is 4.70.

The cluster model used in this work (see Fig. 1) has the following features: (A) up to three water molecules are present in the first solvent shell, which agrees with the above result (1); (B) the optimized N—H···O bond angles obtained using RHF/4–31G and MP2/6–31G(d) levels are between 169.5° and 176.8°, in accordance with (2); (C) hydrogen atoms of water molecules in the first solvent shell are bonded to oxygen atoms of water molecules in the second solvent shell, but there are no relevant oxygen atom to water molecule bonds in either

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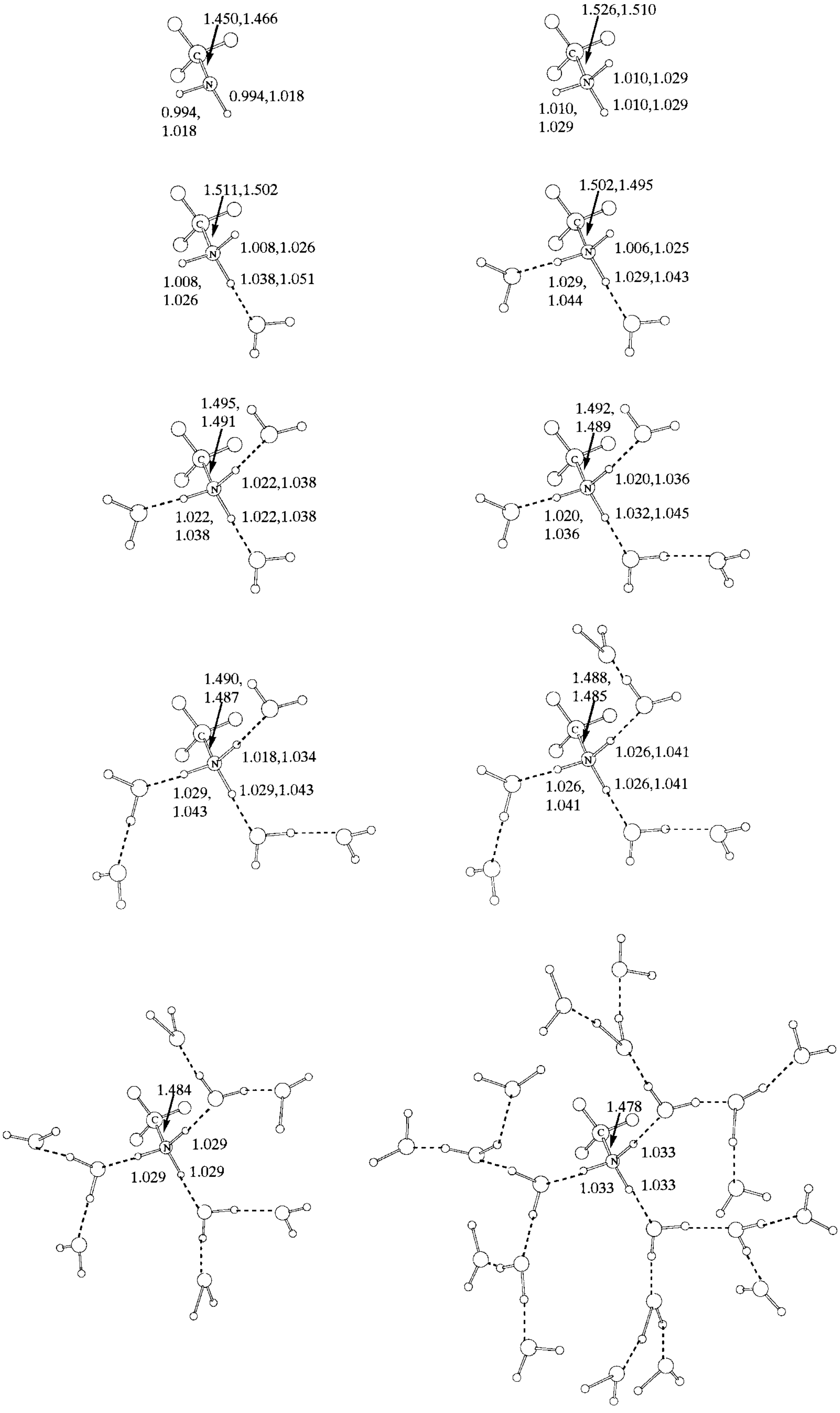


Figure 1. The structures of $CH_3NH_3^+(H_2O)_n$ clusters. The first number is the RHF/4–31G parameter and the second is the MP2/6–31G(d) parameter. The main optimized bond lengths (in Å) are included

the second or third solvent shells, in a agreement with (3) and (4); (D) the optimized angles O—H (in the first solvent shell)···O (in the second solvent shell) using RHF/4–31G and MP2/6–31G(d) levels are between 175.2° and 179.2°, which differs from (5), but, this difference is not expected to be important for predicting the geometry of $CH_3NH_3^+$ in aqueous solution; (E) up to six water molecules are present in the second solvent shell, which is consistent with (6); (F) as expected, the effect of water molecules in the third solvent shell on the geometry of $CH_3NH_3^+$ is very small; in fact, negligible changes in the result were obtained, even orienting water molecules in the third solvent shell so that their interaction with those in the second solvent shell is strong: bond angles O–H (in the second solvent shell)···O (in the third solvent shell) constrained at 180°; torsional angles of H (in the first solvent shell)···O—H (in the second solvent shell)···O—H (in the third solvent shell) constrained at ±90°; no explicit statement is made in Ref. 8 on this topic.

As far as the notation is concerned, $CH_3NH_3^+$ $(H_2O)_n$ ($n = 0, 1, 2, 3$) have n water molecules in the first solvent shell, $CH_3NH_3^+$ $(H_2O)_3(H_2O)_m$ have three water molecules in the first solvent shell and m water molecules in the second solvent shell, and are also denoted $CH_3NH_3^+(H_2O)_{m+3}$. $CH_3NH_3^+$ $(H_2O)_3(H_2O)_6(H_2O)_{12}$ has 3, 6 and 12 water molecules in the first, second and third solvent shells, respectively, and is identical with $CH_3NH_3^+(H_2O)_{21}$.

Geometry optimization at the MP2/6–31G(d) level was carried out for $CH_3NH_3^+(H_2O)_n$ ($n = 0$, 1, 2, 3) and $CH_3NH_3^+(H_2O)_3(H_2O)_m$ ($m = 1$, 2, 3). [$(CH_3NH_3^+(H_2O)_n$ ($n > 9$) cannot be optimized owing to the limitations of the program.] For the first set of clusters, full optimization was performed, whereas for the second set, only a partial optimization was carried out, considering the negligible structural changes in $CH_3NH_3^+$ and H_2O introduced by

$$H_2O + CH_3NH_3^+(H_2O)_2 \rightarrow CH_3NH_3^+(H_2O)_3 \qquad (1)$$

Full geometry optimization using RHF/4–31G was carried out for $CH_3NH_3^+(H_2O)_n$ ($n = 0$, 1, 2, 3) and $CH_3NH_3^+(H_2O)_3(H_2O)_m$ ($m = 1$, 2, 3, 6), but for $CH_3NH_3^+(H_2O)_3(H_2O)_6(H_2O)_{12}$ only partial optimization was performed. Since the C—N bond length of $CH_3NH_3^+(H_2O)_3(H_2O)_6(H_2O)$ with full optimization was only 0.0002 Å longer than that with partial optimization, the latter was considered to be acceptable for larger clusters.

When full optimization was carried out, vibrational analysis was performed, in order to check that all frequencies were real.

The energy changes ($\Delta E_{n-1,n}$) of

$$CH_3NH_3^+(H_2O)_{n-1} + H_2O \rightarrow CH_3NH_3^+(H_2O)_n \qquad (2)$$

were calculated with the equation

$$\Delta E_{n-1,n} = E[CH_3NH_3^+(H_2O)_n] - E[CH_3NH_3^+(H_2O)_{n-1}] - E(H_2O) \qquad (3)$$

The relevant enthalpy changes ($\Delta H^{298\,\mathrm{K}}{}_{n-1,n}$) were also calculated with a similar equation:

$$\Delta H^{298\,\mathrm{K}} = \Delta E_e^o + \Delta E_v^o + \Delta(\Delta E_v^{298\,\mathrm{K}}) + \Delta E_r^{298\,\mathrm{K}} + \Delta E_t^{298\,\mathrm{K}} + \Delta(\mathrm{PV}) \qquad (4)$$

where $\Delta E_e{}^o$ is the electronic energy change, ΔE_v^o is the change in the zero-point energy, $\Delta(\Delta E_v{}^{298\,\mathrm{K}})$ is the vibrational energy change for the thermodinamic path 0–298 K and the remaining quantities are for the changes in rotational and translational energy and for the work term, which were treated classically.

The proton affinity difference between the solute and solvent is important.[9] For reliability evaluation, the proton affinity differences between CH_3NH_2 and H_2O using MP2/6–31G(d) and RHF/4–31G were compared with experimental values of the enthalpy. Furthermore, the optimized structures obtained using MP2/6–31G(d) were compared with the fully optimized structures using MP2/aug-cc-pVDZ for $CH_3NH_3^+(H_2O)_n$ ($n = 0$, 1, 2) and CH_3NH_2.

Finally, the structures of $CH_3PH_3^+(H_2O)_n$ ($n = 0$, 1, 2, 3) were also fully optimized using MP2/6–31+G(d,p) (see Fig. 2). Vibrational analysis was carried out in order

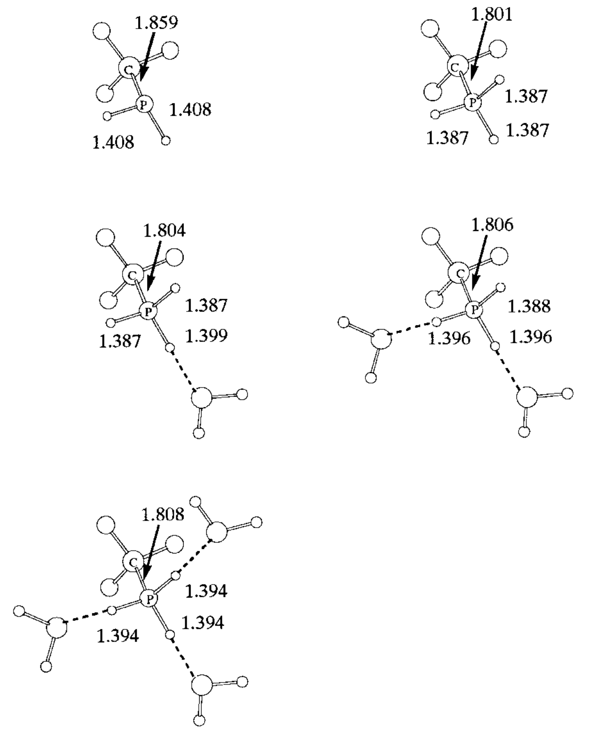


Figure 2. The structures of $CH_3PH_3^+(H_2O)_n$ clusters. The main optimized bond lengths (in Å) obtained using MP2/6–31+G(d,p) are included

Table 1. Enthalpy change ($-\Delta H^{298\text{ K}}_{n-1,n}$) for $CH_3NH_3^+(H_2O)_n$ cluster with RHF/4–31G

	4–31G			Experimental[a]
n	E_t[b] (hartree)	$-\Delta E_{n-1,n}$ (kcal mol^{-1})	$-\Delta H^{298K}_{n-1,n}$ (kcal mol^{-1})	$-\Delta H^{o}_{n-1,n}$ (kcal mol^{-1})
0	−95.44076			
1	−171.38915	24.9	23.1	16.8
2	−247.33112	20.9	19.0	14.6
3	−323.26797	17.7	15.9	12.3
4	−399.20279	16.4	14.4	10.3
5	−475.13648	15.7	13.7	9.0
6	−551.06916	15.1	13.0	8.5
9	−778.84679			
21	−1689.92835			

[a] Ref. 14.
[b] E (H_2O) = −75.88251 hartree.

Table 2. Enthalpy change ($-\Delta H^{298\text{ K}}_{n-1,n}$) for $CH_3NH_3^+(H_2O)_n$ cluster with MP2/6–31G(d)

	MP2/6–31G (d)			Experimental[a]
n	E_t[b] (hartree)	$-\Delta E_{n-1,n}$ (kcal mol^{-1})	$-\Delta H^{298K}_{n-1,n}$ (kcal mol^{-1})	$-\Delta H^{o}_{n-1,n}$ (kcal mol^{-1})
0	−95.86820			
1	−172.10043	22.2	20.8	16.8
2	−248.32756	19.0	17.4	14.6
3	−324.55069	16.5	14.9	12.3
4	−400.76946	13.8		10.3
5	−476.98727	13.2		9.0
6	−553.20421	12.6		8.5

[a] Ref. 14.
[b] E (H_2O) = −76.19685 hartree.

to confirm that all vibrational frequencies were real, and the optimized structures for $CH_3PH_3^+(H_2O)_n$ ($n = 0$, 1) and CH_3PH_2 were compared with the fully optimized structures obtained using MP2/6–31+G(2d,2p) for reliability evaluation.

RESULTS AND DISCUSSION

$CH_3NH_3^+$

The proton affinity differences estimated by MP2/6–31G(d) (52 kcal mol^{-1}) and RHF/4–31G (48 kcal mol^{-1}) are in good agreement with the experimental enthalpy (48 kcal mol^{-1}) (1 kcal = 4.184 kJ).[10]

The clusters on which vibrational analysis was performed all have real vibrational frequencies and correspond to equilibrium structures. Tables 1 and 2 show the enthalpy changes ($-\Delta H^{298K}_{n-1,n}$) for $CH_3NH_3^+(H_2O)_n$ clusters. Values of $-\Delta H^{298K}_{n-1,n}$ determined using RHF/4–31G are 1.5 times larger than the experimental $-\Delta H^{o}_{n-1,n}$, while those obtained using MP2/6–31G(d) are slightly overestimated. Since the structures for $CH_3NH_3^+(H_2O)_n$ ($n = 0$, 1, 2) and CH_3NH_2 optimized using MP2/6–31G(d) agree with those obtained using MP2/aug-cc-pVDZ, MP2/6–31G(d) optimization can be considered to be reliable.

Tables 3 and 4 show changes in the optimized structural parameters and of the charge on CH_3 (q_{CH_3}) with increasing n. The 4–31G optimized structural parameters are close to the MP2/6–31G(d) values, and the same trend as in Ref. 1 is found.

For the $CH_3NH_3^+$ moiety of $CH_3NH_3^+(H_2O)_n$, RHF/4–31G results show that changes in C—N bond length in the first, second and third solvent shells are 0.031 , 0.011 and 0.006 Å, respectively. A similar trend is observed for the other structural parameters and for the charge on CH_3. For this reason, contributions of shells larger than the third one were neglected, i.e. the structure of the $CH_3NH_3^+$ ion in $CH_3NH_3^+(H_2O)_{n\rightarrow\infty}$ is predicted to be similar to the structure of $CH_3NH_3^+$ in $CH_3NH_3^+$ $(H_2O)_3$ $(H_2O)_6$ $(H_2O)_{12}$.

The structural parameters and the charge on CH_3 of $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_n$ ($n = 0$, 1, 2, 3) and $CH_3NH_3^+$ $(H_2O)_3$ $(H_2O)_m$ ($m = 1$, 2, 3) obtained using MP2/6–31G(d) are found to be linearly related to those determined by RHF/4–31G. Least-squares fits yield correlation coefficients >0.98. These linear relations

Table 3. The 4–31G optimized structure of $CH_3NH_3^+(H_2O)_n$ cluster in the gas phase[a]

n	C—N (Å)	N—H[b] (Å)	C—H[c] (Å)	NCH[d] (°)	CNH[e] (°)	q_{CH_3}[f]
0	1.526	1.010	1.076	108.2	111.0	0.488
1	1.511	1.018	1.076	108.7	110.8	0.446
2	1.502	1.021	1.076	109.0	110.5	0.405
3	1.495	1.022	1.076	109.2	110.1	0.366
4	1.492	1.024	1.077	109.2	110.1	0.357
5	1.490	1.025	1.077	109.3	110.1	0.353
6	1.488	1.026	1.077	109.3	110.0	0.338
9	1.484	1.029	1.077	109.3	109.3	0.313
21	1.478	1.033	(1.077)	(109.3)	(109.3)	0.304
CH_3NH_2	1.450	0.994	1.084	111.1	116.4	0.219

[a] The values in parentheses are fixed values.
[b] Values are the means of three N—H bond lengths.
[c] Values are the means of three C—H bond lengths.
[d] Values are the means of three NCH bond angles.
[e] Values are the means of three CNH bond angles.
[f] The charge of CH_3.

Table 4. The MP2/6—31G(d) optimized structure of $CH_3NH_3^+(H_2O)_n$ cluster in the gas phase[a]

n	C—N (Å)	N—H (Å)	C—H (Å)	NCH (°)	CNH (°)	q_{CH_3}
0	1.510	1.029	1.088	108.2	111.6	0.400
	[1.512]	[1.028]	[1.095]	[108.0]	[111.5]	
1	1.502	1.035	1.088	108.5	111.0	0.365
	[1.504]	[1.033]	[1.095]	[108.4]	[111.1]	
2	1.495	1.037	1.088	108.7	110.5	0.333
	[1.498]	[1.036]	[1.096]	[108.7]	[110.7]	
3	1.491	1.038	1.088	108.9	110.0	0.305
4	1.489	1.039	(1.088)	(108.9)	(110.0)	0.296
5	1.487	1.040	(1.088)	(108.9)	(110.0)	0.288
6	1.485	1.041	(1.088)	(108.9)	(110.0)	0.282
$n \rightarrow \infty$[b]	1.479	1.046	1.088	108.9	108.5	0.256
CH_3NH_2	1.466	1.018	1.095	111.0	109.5	0.137
	[1.473]	[1.020]	[1.102]	[110.9]	[110.0]	

[a] See Table 3. Values in square brackets are MP2/aug-cc-pVDZ results.
[b] See text.

were used to predict parameters at the MP2/6–31G(d) level of the $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_{n\rightarrow\infty}$ from those obtained using RHF/4–31G (see Table 5). It can be seen that the predicted values of the $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_{n\rightarrow\infty}$ are close to those in $CH_3NH_3^+(H_2O)_6$. This is a reasonable result considering that in MP2/6–31G(d) calculations, the changes in the parameters of the $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_n$ become very small on approaching $n = 6$ (also in Table 5).

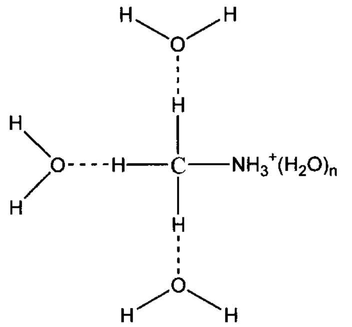
In previous work,[1] water molecules around the CH_3 of $CH_3NH_3^+(H_2O)_{n\rightarrow\infty}$ were found to have a negligible influence on the structure of $CH_3NH_3^+$ in aqueous solution, since very small changes in the results were

Table 5. The structure of $CH_3NH_3^+$ in aqueous solution

Method	C—N (Å)	N—H (Å)	C—H (Å)	NCH (°)	CNH (°)	q_{CH_3}
MINI-1[a]	1.486	1.035	1.073	110.1	109.2	0.161
4–31G	1.478	1.033	1.077	109.3	109.3	0.304
4–31G[a]	1.469	1.032	1.076	110.0	109.0	0.260
MP2/6–31(d)	1.479	1.047	1.088	108.9	108.5	0.252

[a] See Ref. 1.

obtained, even orienting the oxygen atoms of water molecules towards H_3C.



Since in aqueous solution these atoms are probably not oriented towards H_3C, the effect of water molecules around the CH_3 of the structure of $CH_3NH_3^+$ in aqueous solution was neglected in the present study, i.e. the structure of $CH_3NH_3^+$ in aqueous solution is predicted to be similar to the structure of the $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_{n\to\infty}$.

The following structure was obtained for $CH_3NH_3^+$ in aqueous solution using MP2/6–31G(d): C—N = 1.479 Å, N—H = 1.047 Å, C—H = 1.088 Å, NCH = 108.9° and CNH = 108.5°. The C—N bond length is found to be 0.03 Å smaller and the N—H bond length is longer 0.02 Å than in the gas phase. The predicted structure of $CH_3NH_3^+$ using MINI-1, [11] 4–31G and MP2/6–31G(d) calculations in aqueous solution is shown in Table 5. Structural parameters predicted by the three methods have similar values and are similar to those obtained in Ref. 1. Thus, it turns out that the procedure in Ref. 1, which does not take electron correlation into account, nevertheless yields reliable results. Since MP2/6–31G(d) calculations are usually affected by a 0.005 Å error,[12] it seemed sensible to assign the value 1.479 ± 0.005 Å to the C—N bond length of $CH_3NH_3^+$ in aqueous solution.

$CH_3PH_3^+$

All the studied clusters have real vibrational frequencies and correspond to equilibrium structures. Unfortunately, no experimental $\Delta H^{\circ}_{n-1,n}$ are available for comarison with $\Delta H^{298\,\mathrm{K}}_{n-1,n}$. Since the optimized structures for $CH_3PH_3^+(H_2O)_n$ ($n = 0$, 1) and CH_3PH_2 obtained using MP2/6–31+G(d,p) agree with those determined by MP2/6–31+G(2d,2p), MP2/6–31+G(d,p) can be considered sufficiently reliable.

Table 6 shows that the structure of $CH_3PH_3^+$ in $CH_3PH_3^+(H_2O)_n$ shows almost no change with increasing n. Therefore, it can be assumed that the structure of $CH_3PH_3^+$ in $CH_3PH_3^+(H_2O)_{n\to\infty}$ should be similar to that in $CH_3PH_3^+(H_2O)_3$. Since neither Monte Carlo nor molecular dynamics studies have been carried out on $CH_3PH_3^+$ in aqueous solution, the water structure around its PH_3^+ group is unknown. However, the fact that the geometry of $CH_3PH_3^+$ in aqueous solution can be expected to be independent of the water structure around its PH_3^+ group can be inferred from the following observation: although the interaction between $CH_3PH_3^+$ and $(H_2O)_n$ in $CH_3PH_3^+(H_2O)_n$ in Fig. 2 is the strongest one, the geometry of $CH_3PH_3^+$ in $CH_3PH_3^+(H_2O)_n$ does not change with increasing n.

Water molecules around CH_3 of $CH_3PH_3^+(H_2O)_{n\to\infty}$ have a negligible influence on the structure of $CH_3PH_3^+$ in aqueous solution, for the same reasons as for $CH_3NH_3^+$. In addition, since the charge on CH_3 of $CH_3PH_3^+(H_2O)_{n\to\infty}$ is considerably smaller than that of $CH_3NH_3^+(H_2O)_{n\to\infty}$ (see Tables 4 and 6), the interaction between CH_3 and water molecules around CH_3 in $CH_3PH_3^+(H_2O)_{n\to\infty}$ is weaker than that in $CH_3NH_3^+(H_2O)_{n\to\infty}$. Therefore, it can be expected that the structure of $CH_3PH_3^+$ in aqueous solution is similar to that in $CH_3PH_3^+(H_2O)_3$: C—P = 1.808 Å, P—H = 1.394 Å, C—H = 1.087 Å, PCH = 109.5° and CPH = 109.9°. Thus, the structure of $CH_3PH_3^+$ in aqueous solution is predicted to be similar to that in the gas phase (Table 6).

$CH_3NH_3^+$ vs $CH_3PH_3^+$

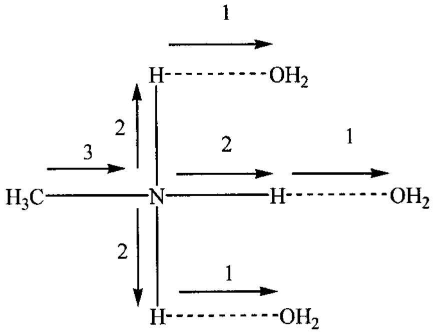
The C—N bond length of $CH_3NH_3^+$ obtained using MP2/6–31G(d) is longer than that of CH_3NH_2 in the gas phase by 0.044 Å (see Table 4). It can be argued that the cause of the elongation of the C—N bond of $CH_3NH_3^+$ in the

Table 6. The MP2/6—31+G(d,p) optimized structure of $CH_3PH_3^+(H_2O)_n$ cluster in the gas phase[a]

n	C—P (Å)	P—H (Å)	C—H (Å)	PCH (°)	CPH (°)	q_{CH_3}
0	1.801	1.387	1.088	109.4	111.7	0.106
	(1.799)	(1.391)	(1.089)	(108.9)	(111.8)	
1	1.804	1.391	1.088	109.5	111.1	0.093
	(1.802)	(1.395)	(1.088)	(109.1)	(111.2)	
2	1.806	1.393	1.087	109.5	110.5	0.084
3	1.808	1.394	1.087	109.5	109.9	0.077
CH_3PH_2	1.859	1.408	1.088	111.6	97.8	−0.100
	(1.865)	(1.413)	(1.088)	(110.3)	(97.4)	

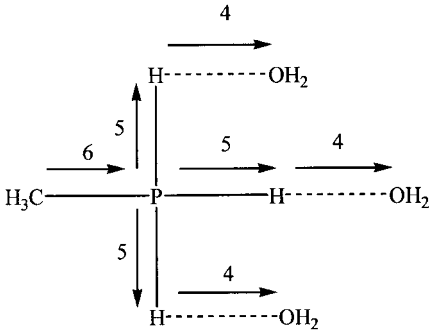
[a] Values in parentheses are MP2/6–31+G(2d,2p) results.

gas phase is the contribution of $CH_3^+\cdots NH_3$ as a resonance structure. The C—N bond length of $CH_3NH_3^+$ in aqueous solution was found to be smaller than that in the gas phase by 0.03 Å. In addition, the charge on CH_3 of $CH_3NH_3^+$ in aqueous solution was predicted to be less positive than that in the gas phase by 0.14. Therefore, it can be expected that the contribution of the resonance structure, $CH_3^+\cdots NH_3$, to $CH_3NH_3^+$ in aqueous solution is smaller than that in the gas phase. For $CH_3PH_3^+$, the resonance structure, $CH_3^+\cdots PH_3$, contributes to $CH_3PH_3^+$ in the gas phase.[13] The C—P bond length of $CH_3PH_3^+$ in aqueous solution was found to be similar to that in the gas phase. In addition, the charge on CH_3 of $CH_3PH_3^+$ in aqueous solution was predicted to be close to that in the gas phase. This means that the contribution of the resonance structure, $CH_3^+\cdots NH_3$, to $CH_3PH_3^+$ in aqueous solution is close to that in the gas phase. Why does the contribution of the resonance structure $CH_3^+\cdots NH_3$ in aqueous solution change in the gas phase? On the contrary, why does the contribution of the resonance structure $CH_3^+\cdots PH_3$ in aqueous solution not change in the gas phase? A possible explanation is depicted in the scheme shown.



Since the positive charge on the hydrogen of N—H in $CH_3NH_3^+$ is large (+0.41), the positive charge on the hydrogen atoms transfers to water molecules (step 1). As a result of step 1, the positive charge on the hydrogen atoms of NH_3 decreases, causing the charge on the nitrogen atom to be transfer to the hydrogen atoms of NH_3 (step 2). As a result of step 2, the negative charge on the nitrogen atom of NH_3 increases, causing the positive charge on CH_3 to be transferred to the nitrogen atom (step 3). As a result of step 3, the positive charge on CH_3 decreases. That is to say, it can be expected that the positive charge on CH_3 decreases because of the charge transfer (1 → 2 → 3). This idea is supported by the fact that for $CH_3NH_3^+(H_2O)_n$ with $n = 0 \rightarrow 6$, the changes of the charges on CH_3 and $(H_2O)_n$ are −0.12 and +0.14, respectively. Therefore, it can be predicted that the cause of the smaller contribution of the resonance structure $CH_3^+\cdots NH_3$ in aqueous solution than in the gas phase is due to the above phenomena.

In contrast, in $CH_3PH_3^+$ the positive charge on the hydrogen of P—H is very small (+0.07), so that the charge transfer from the hydrogen atoms to water molecules should be very small, and charge transfer (4 → 5 → 6) very unlikely.



Therefore, it can be expected that the positive charge on CH_3 barely changes. This idea is supported by the fact that for $CH_3PH_3^+(H_2O)_n$ with $n = 0 \rightarrow 3$, the change of charge on CH_3 is −0.03. Therefore, it can be predicted that, for the above reason, the contribution of the resonance structure $CH_3^+\cdots PH_3$ in aqueous solution is close to that in the gas phase.

The N—H bond lengths of $CH_3NH_3^+$ in aqueous solution were determined to be longer than those in the gas phase by 0.02 Å. In contrast, the P—H bond lengths of $CH_3PH_3^+$ in aqueous solution were found to be close to those in the gas phase. Since the positive charge on the hydrogen atoms of N—H in $CH_3NH_3^+$ is large (+0.41), water molecules exert a large attraction on the hydrogen of N—H. Hence the N—H bond lengths of $CH_3NH_3^+$ in aqueous solution can be expected to be longer than those in the gas phase by 0.02 Å. In contrast, in $CH_3PH_3^+$ the positive charge on the hydrogen of P—H was found to be very small (+0.07) and water molecules exert only a small attraction on the hydrogen of P—H. For this reason, the P—H bond lengths of $CH_3PH_3^+$ in aqueous solution can be predicted to be close to those in gas phase.

Full optimized structural parameters can be obtained from the authors on request.

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