Chapter 4

The Structures of $CH_3NH_3^+$ and $CH_3PH_3^+$ in Water Clusters

Abstract

The structures of $CH_3NH_3^+(H_2O)_n$ (n = 0,1,2,3,4,5,6,9,10) and $(H_2O)_3CH_3NH_3^+(H_2O)_m$ (m = 0,1,2,3,6) clusters in the gas phase are determined by ab initio MINI-1 and 4-31G (for n = 0,1,2,3,4,5,6; m = 0,1,2,3) basis sets. Excellent correlations are found between the structural parameters and charge on the H of the outermost H_2O in $CH_3NH_3^+(H_2O)_n$. Based on these structures, the structure of $CH_3NH_3^+$ in aqueous solution is qualitatively predicted.

Also, I quantitatively determine the structure of $CH_3NH_3^+$ in aqueous solution considering the electron correlation based on the optimized structures of $CH_3NH_3^+(H_2O)_n$ (n = 0,1,2,3,4,5,6,9,21) using the 4-31G basis set and MP2/6-31G(d) (n = 0,1,2,3,4,5,6). The predicted structure of $CH_3NH_3^+$ in aqueous solution is as follow: 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.

Next I determine the structures of $CH_3PH_3^+(H_2O)_n$ (n = 0,1,2,3) using MP2/6-31+G(d,p). The structure of $CH_3PH_3^+$ moiety in $CH_3PH_3^+(H_2O)_n$ almost does not change with the n increment. Therefore, it is predicted that the structure of $CH_3PH_3^+$ in aqueous solution is almost equal to that in the gas phase.

1. Introduction

Since many biologically important species such as amino acids and peptides have -NH_3^+ groups, the structure of RNH_3^+ in aqueous solution is interesting. However, it is difficult to determine the structure of RNH_3^+ in aqueous solution at the present stage of experimentation and theory.

The purpose of this chapter is to predict the structure of $CH_3NH_3^+$ in aqueous solution, as the initial step in determining the structure of RNH_3^+ in aqueous solution. In Study (A), I qualitatively predicted the structure of $CH_3NH_3^+$ in aqueous solution at ten years ago. In Study (B), I quantitatively predicted the structure of $CH_3NH_3^+$ in aqueous solution, recently.

It is predicted that the structure of $CH_3PH_3^+$ in aqueous solution is almost equal to that in the gas phase.

2. Method

$CH_3NH_3^+$

Study (A)

The structures of $CH_3NH_3^+(H_2O)_n$ (n = 0,1,2,3,4,5,6,9,10) and $(H_2O)_3CH_3NH_3^+(H_2O)_m$ (m = 0,1,2,3,6) clusters in gas phase were determined by ab initio MINI-1 [1] and 4-31G [2] (for n = 0,1,2,3,4,5,6; m = 0,1,2,3) basis sets in Fig. 1 and 2. Based on these structures, the structure of $CH_3NH_3^+$ in aqueous solution was predicted. The MINI-1 is powerful tool for calculating molecular interactions [3]. The 4-31G works well for the protonated clusters [4].

All computations were carried out on a HITAC M-680 computer at the Computer Center of the Institute for Molecular Science (IMS). The GAUSSIAN 82 program was used. For H_2O, H_3O^+, CH_3NH_2, $(CH_3)_4N^+$ and $CH_3NH_3^+(H_2O)_n$ (n = 0, 1, 2, 3), all geometrical parameters were fully optimized by the energy gradient methods in GAUSSIAN 82. For $CH_3NH_3^+(H_2O)_n$ (n = 4,5,6,9,10), only a partial optimization was carried out in view of the negligible structural change in $CH_3NH_3^+$ and H_2O by $H_2O + CH_3NH_3^+(H_2O)_2 \longrightarrow CH_3NH_3^+(H_2O)_3$. The OH...O angles were fixed at 180°, and the OH...OH dihedral angles were fixed at ±90°. Because this assumption did not affect the geometry except for the OH...OH dihedral angle, electronic structures and total energy of $CH_3NH_3^+(H_2O)_4$, this assumption is acceptable. Similarly, the structures of $(H_2O)_3CH_3NH_3^+(H_2O)_m$ (m = 0,1,2,3,6), $(H_2O)_n$ (n = 2,3,7) and $(H_2O)(CH_3)_4N^+$ were partially optimized.

The total energies (E_T) obtained were then used to compute stabilization energies ($\triangle E_{n-1,n}$): $\triangle E_{n-1,n} = E_T(CH_3NH_3^+(H_2O)_n) - E_T(CH_3NH_3^+(H_2O)_{n-1}) - E_T(H_2O)$. In MINI-1, the stabilization energy corrected for basis set superposition error (BSSE) by the counterpoise method [5] was also computed. For the analysis of electronic structures, the Mulliken population analysis was used.

The proton affinity difference between solute and solvent is important [6]. For the evaluation of reliability of the MINI-1 and 4-31G basis sets, the proton affinity differences between CH_3NH_2 and H_2O by the MINI-1 and 4-31G basis sets were compared with that determined by experimental enthalpy. Also, for the evaluation of the reliability of the ab initio method in the hydrophobic bond ($H_2O...CH_3NH_3^+$), the interaction energies between H_2O and $(CH_3)_4N^+$ estimated by ab initio were compared with the experimental enthalpy. The conformation of $(CH_3)_4N^+$ was taken from Ref. [7]. For $(H_2O)(CH_3)_4N^+$, the 3-Me complex in Ref. [7] was used, only the N...O bond distance was optimized, the other parameters were identical with the values in H_2O and $(CH_3)_4N^+$, the C-N...O bond angle was fixed at 180° and the C-N...O-H dihedral angles were fixed at 0 and 180°.

Study (B)

Pudzianowski made the following statement [8]: Del Bene has established [9] that 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. Subsequent studies at higher levels of methodology [10—12] show that optimized geometries for 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, I essentially used MP2/6-31G(d) for the aqueous clusters in this study. For too large clusters which can not be optimized using MP2/6-31G(d), I used the 4-31G(d) basis set.

Using the ab initio closed-shell SCF method with the energy gradient technique, I carried out geometry optimization with the 4-31G basis set for $CH_3NH_3^+(H_2O)_n$ (n = 0,1,2,3), $CH_3NH_3^+(H_2O)_3(H_2O)_m$ (m = 1,2,3,6) (3 water molecules exist in first solvent shell and m water molecules exist in second solvent shell. As notation in this article, $CH_3NH_3^+(H_2O)_3(H_2O)_m$ is identical to $CH_3NH_3^+(H_2O)_{m+3}$.) and $CH_3NH_3^+(H_2O)_3(H_2O)_6(H_2O)_{12}$ (3 water molecules exist in first solvent shell, 6 in the second and 12 in the third. In this study, $CH_3NH_3^+(H_2O)_3(H_2O)_6(H_2O)_{12}$ is identical to $CH_3NH_3^+(H_2O)_{21}$) in Fig. 1. The 4-31G basis set works well for the protonated clusters [4]. 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), full optimizations were performed. For $CH_3NH_3^+(H_2O)_3(H_2O)_6(H_2O)_{12}$, partial optimization was performed. 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 of $CH_3NH_3^+(H_2O)_3(H_2O)_6(H_2O)$ with partial optimization. Therefore, this partial optimization was acceptable.

Also, the MP2/6-31G(d) calculations were performed 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). $CH_3NH_3^+(H_2O)_n$ ($n \geq 9$) cannot be optimized due to the limitation of program. For $CH_3NH_3^+(H_2O)_n$ (n = 0,1,2,3), full optimization was performed. For $CH_3NH_3^+(H_2O)_3(H_2O)_m$ (m = 1,2,3), only a partial optimization was carried out in view of the negligible structural changes in $CH_3NH_3^+$ and H_2O by $H_2O + CH_3NH_3^+(H_2O)_2 \longrightarrow CH_3NH_3^+(H_2O)_3$.

The orientation of the water molecules is as follow: There may be many conformations of water molecules around the $CH_3NH_3^+$ ion. However, it is expected that when the O-H...O angles are at almost 180°, the clusters are energically preferable. In fact, according to 4-31G results, the O-H...O angles are at almost 180°.

When the full optimizations were performed, I also carried out vibrational analysis at the optimized structures to confirm that all vibrational frequencies are real.

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

$$CH_3NH_3^+(H_2O)_{n-1} + H_2O \longrightarrow CH_3NH_3^+(H_2O)_n$$

were calculated by the following formula:

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

The enthalpy changes ($\Delta H^{298K}{}_{n-1,n}$) were also calculated by a similar formula.

$$\Delta H^{298K} = \Delta E_e^{O} + \Delta E_v^{O} + \Delta(\Delta E_v^{298K}) + \Delta E_r^{298K}$$
$$+ \Delta E_t^{298K} + \Delta(PV),$$

where ΔE_e^{O} is electronic energy change, ΔE_v^{O} is the change in the zero-point energy, $\Delta(\Delta E_v^{298K})$ is the change in the vibrational energy on going to 298K, and the remaining quantities are for the changes in rotational and translational energy and the work term which were treated classically.

Proton affinity difference between solute and solvent is important [13]. For the evaluation of reliability of the 4-31G basis set and MP2/6-31G(d), the proton affinity differences between CH_3NH_2 and H_2O by the 4-31G basis set and MP2/6-31G(d) were compared with the value determined by experimental enthalpy.

I used the Gaussian 94 [14] program and the SP2, HPC and HSP computers in the Institute for Molecular Science.

$CH_3PH_3^+$

I fully optimized the structures of $CH_3PH_3^+(H_2O)_n$ (n =

0,1,2,3) using MP2/6-31+G(d,p) in Fig. 3. I also performed vibrational analysis for all clusters at the optimized structures to confirm that all vibrational frequencies are real.

I used the Gaussian 94 program and the SX-5 computer in the Institute for Molecular Science.

3. Results and discussion

$CH_3NH_3^+$

Study (A)

The proton affinity differences estimated by the MINI-1 (47 kcal/mol) and 4-31G (48 kcal/mol) basis sets agree with that determined experimentally (48 kcal/mol) [15]. The interaction energies between H_2O and $(CH_3)_4N^+$ in the MINI-1 basis set (43 kJ/mol) and in the 4-31G basis set (54 kJ/mol) almost agree with the experimental enthalpy (38 kJ/mol) [7]. Table 1 shows the stabilization energy, that energy corrected for the BSSE and experimental $\triangle H^0_{n-1,n}$. Tables 2 and 3 show the changes of each optimized structural parameter, the charges on CH_3 (q_{CH_3}) and on the H (q_H) of the outermost H_2O, and the Mulliken population between C-N (P_{C-N}) in $CH_3NH_3^+(H_2O)_n$ with each n increment.

I felt that the MINI-1 and 4-31G results were reasonable, except that $-\triangle E_{n-1,n}$ are 1.5 times larger than $-\triangle H^0_{n-1,n}$ and MINI-1 overestimates the C-N, N-H and C-H bond distances by 0.03, 0.05 and 0.05 Å, respectively. Correcting for the overestimated C-N (-0.03 Å), N-H and C-H (-0.05 Å) bond distances, I obtain acceptable bond distances.

When n becomes larger, the following can be noted: (1) The charge on the H of the outermost H_2O and $-\triangle E_{n-1,n}$ in $CH_3NH_3^+(H_2O)_n$ are smaller, similarly to those in $H^+(H_2O)_n$ [17]. (2) The plus charge on CH_3 more strongly transfers to $(H_2O)_n$, and then the resonance structure $CH_3^+ \ldots NH_3$ contributes less to $CH_3NH_3^+$. As a result, the C-N bond distance, the charge on CH_3 and the population between C-N in $CH_3NH_3^+(H_2O)_n$ approach those in CH_3NH_2. (3) The N-H bond elongates more because $(H_2O)_n$ has a greater attraction for H in N-H. (4) These changes for n-1 ⟶ n are smaller: The first solvent shell greatly affects the structure of $CH_3NH_3^+$. The effect of the second solvent shell is about 1/3 of the effect of the first solvent shell. The effect of the tenth H_2O is very small.

From the results of $CH_3NH_3^+(H_2O)_n$, a least-squares fit yields

$$p = aq_H + b, \qquad (1)$$

where p are the structural parameters, the charge on CH_3 or the population between C-N in $CH_3NH_3^+(H_2O)_n$. The absolute correlation coefficients between p and q_H are over 0.99, except for the N-H bond distance in MINI-1 (0.908) and 4-31G (0.970), and the CNH bond angle in MINI-1 (0.975). Also, a similar equation with excellent correlation coefficients yields

$$p = c\triangle E_{n-1,n} + d. \qquad (2)$$

The charge on the H (q_H) of the outermost H_2O in $CH_3NH_3^+(H_2O)_n$ ($n \longrightarrow \infty$) is equal to that in $(H_2O)_n$ ($n \longrightarrow \infty$). That charge in $(H_2O)_n$ ($n \longrightarrow \infty$) must be nearly equal to that in

$(H_2O)_7$ because the difference between that in H_2O and in $(H_2O)_3$ is significant (-0.014 e in MINI-1 and -0.015 e in 4-31G) and the difference between that in $(H_2O)_3$ and in $(H_2O)_7$ is negligible (-0.003 e). Thus, when q_H in eq. (1) is equal to the charge on the outermost H in $(H_2O)_7$, each parameter of $CH_3NH_3{}^+(H_2O)_n$ ($n \longrightarrow \infty$) is predicted (Tables 2 and 3). Also, by eq. (2), I can predict each parameter of $CH_3NH_3{}^+(H_2O)_n$ ($n \longrightarrow \infty$): $\triangle E_{n-1,n}$ ($n \longrightarrow \infty$) is equal to the stabilization energy of $H_2O + (H_2O)_{j-1} \longrightarrow (H_2O)_j$ ($j \longrightarrow \infty$), which was approximated by the stabilization energy for $j = 3$. The structure of $CH_3NH_3{}^+(H_2O)_n$ ($n \longrightarrow \infty$) estimated by $\triangle E_{n-1,n}$ = the stabilization energy for $j = 3$ in eq. (2) agrees with that using eq. (1). The estimated structure of $CH_3NH_3{}^+$ in $CH_3NH_3{}^+(H_2O)_n$ ($n \longrightarrow \infty$) was nearly the same as that in $CH_3NH_3{}^+(H_2O)_{10}$.

Table 4 and 5 show the structural changes of $CH_3NH_3{}^+$ by $(H_2O)_3 + CH_3NH_3{}^+(H_2O)_n \longrightarrow (H_2O)_3CH_3NH_3{}^+(H_2O)_n$. When the plus charge on CH_3 (q_{CH_3}) in $CH_3NH_3{}^+(H_2O)_n$ is smaller, the structural changes ($\triangle p$) are smaller:

$$\triangle p = eq_{CH_3} + f \qquad \text{(high correlation coefficients)} \tag{3}$$

Also, the charge on H' ($q_{H'}$) in $(H_2O)'_3CH_3NH_3{}^+(H_2O)_n$ correlates with q_{CH_3}:

$$q_{H'} = gq_{CH_3} + h \tag{4}$$

The structure of $CH_3NH_3{}^+$ changes by $(H_2O)_k + CH_3NH_3{}^+(H_2O)_n \longrightarrow (H_2O)_kCH_3NH_3{}^+(H_2O)_n$ ($k = 3$) because the resonance structure $CH_3{}^+...NH_3$ is stabilized due to the hydrophobic bond ($(H_2O)'_3...CH_3NH_3{}^+(H_2O)_n$). Because the interaction $H_2O...(CH_3)_4N^+$ is primarily electrostatic [18], the bond must be primarily electrostatic. Thus, the structural changes of $CH_3NH_3^+$ by this reaction correlate with the charge on CH_3 in $CH_3NH_3^+(H_2O)_n$. Because the plus charge on CH_3 slightly transfers to H' by this reaction, the charge on H' in $(H_2O)'_3CH_3NH_3^+(H_2O)_n$ correlates with the charge on CH_3 in $CH_3NH_3^+(H_2O)_n$.

When q_{CH_3} in eqs. (3) and (4) is equal to the charge on CH_3 in $CH_3NH_3^+(H_2O)_n$ ($n \longrightarrow \infty$), the structural changes ($\triangle p$) of $CH_3NH_3^+$ by previous reaction and the charge on H' in $(H_2O)'_kCH_3NH_3^+(H_2O)_n$ ($k = 3$, $n \longrightarrow \infty$) can be predicted (Tables 4 and 5). Because the charge on H' ($k = 3$, $n \longrightarrow \infty$) is equal to that in H_2O, $\triangle p$ (k, $n \longrightarrow \infty$) must be equal to $\triangle p$ ($k = 3$, $n \longrightarrow \infty$), which was very small. When the structure of $CH_3NH_3^+(H_2O)_n$ ($n \longrightarrow \infty$) is corrected by $\triangle p$ (k, $n \longrightarrow \infty$), I can predict the structure of $CH_3NH_3^+$ in aqueous solution (Tables 2 and 3).

Differences between the plus charge on CH_3 in $CH_3NH_3^+$ in aqueous solution and in CH_3NH_2 in the gas phase were 0.12 e in the MINI-1 basis set and 0.07 e in the 4-31G basis set. It was predicted that the resonance structure of $CH_3^+...NH_3$ slightly contributed to $CH_3NH_3^+$ in aqueous solution.

Finally, from the results of $CH_3NH_3^+(H_2O)_n$ ($n = 1,2$), I can obtain eqs. (1') and (2') which are similar to (1) and (2). The estimated values of each parameter of $CH_3NH_3^+(H_2O)_n$ ($n \longrightarrow \infty$) by eqs. (1') and (2') agree with those in eqs. (1) and (2) (Tables 2 and 3). I may predict the structures of $RNH_3^+(H_2O)_n$ ($n \longrightarrow \infty$) based on $RNH_3^+(H_2O)_n$ ($n = 1,2$). If the interaction $(H_2O)_k...RNH_3^+(H_2O)_n$ ($k,n \longrightarrow \infty$) is negligible, this predicted structure may be the same as the structure of RNH_3^+ in aqueous solution.

Study (B)

The proton affinity differences estimated by the 4-31G basis set (48 kcal/mol) and MP2/6-31G(d) (52 kcal/mol) agree with the value determined by experimental enthalpy (48 kcal/mol) [15].

The clusters on which vibrational analysis was performed have all real vibrational frequencies and correspond to equilibrium structures. Table 6 and 7 show the enthalpy change ($-\triangle H^{298K}{}_{n-1,n}$) for $CH_3NH_3{}^+(H_2O)_n$ clusters. In the 4-31G basis set, $-\triangle H^{298K}{}_{n-1,n}$ are 1.5 times larger than experimental $-\triangle H^{0}{}_{n-1,n}$. In the MP2/6-31G(d), $-\triangle H^{298K}{}_{n-1,n}$ are slightly overestimated. Tables 8 and 9 show the changes of each optimized structural parameter and the charge on CH_3 (q_{CH_3}) with the n increment. The 4-31G optimized structural parameters are almost equal to the MP2/6-31G(d) optimized structural parameters. The trend for the changes of these values with the n increment is the same as the trend described in Study (A). Those changes result from the following phenomenon: Primary, the plus charge on CH_3 transfers more strongly to $(H_2O)_n$ and the resonance structure $CH_3{}^+...NH_3$ contributes less to $CH_3NH_3{}^+$ with the n increment. Secondary, the N-H bond elongates more because $(H_2O)_n$ has a greater attraction for H in N-H with the n increment.

In the 4-31G basis set for $CH_3NH_3{}^+$ moiety, the 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 the charge on

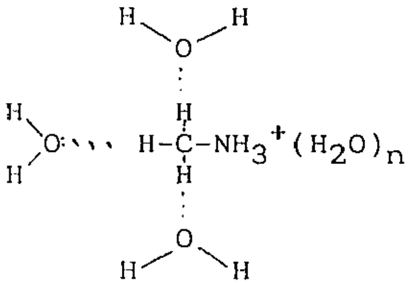
CH_3. Thus, the fourth solvent shell, fifth solvent shell and so forth are neglected. That is to say, the structure of $CH_3NH_3^+$ ion in $CH_3NH_3^+(H_2O)_{n \longrightarrow \infty}$ is predicted to be almost equal to the structure of $CH_3NH_3^+$ in $CH_3NH_3^+(H_2O)_3(H_2O)_6(H_2O)_{12}$.

From the results, a least-squares fit yields:

$$p = aq + b$$

where p are the structural parameters and 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) in the MP2/6-31G(d), and q are those in the 4-31G basis set. The correlation coefficients between p and q are over 0.98. When the q are equal to values in $CH_3NH_3^+(H_2O)_{n \longrightarrow \infty}$ in the 4-31G basis set (predicted above), each parameter of $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_{n \longrightarrow \infty}$ with MP2/6-31G(d) is predicted in Table 9. These predicted values for $CH_3NH_3^+(H_2O)_{n \longrightarrow \infty}$ with MP2/6-31G(d) are acceptable for the following reasons: The changes of the parameters of $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_n$ are very small with approaching n = 6. Therefore, the predicted values of $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_{n \longrightarrow \infty}$ are almost equal to those in $CH_3NH_3^+(H_2O)_6$.

The water molecules around CH_3 of $CH_3NH_3^+(H_2O)_{n \longrightarrow \infty}$ have a negligible impact on the structure of $CH_3NH_3^+$ in aqueous solution because the effect is very small using the oxygens of water molecules oriented toward H_3C (See Study (A)).



In aqueous solution, the O of H_2O is not oriented toward H_3C. Therefore, the effect of water molecules around CH_3 on the structure of $CH_3NH_3^+$ in aqueous solution is neglected. Thus, the structure of $CH_3NH_3^+$ in aqueous solution is predicted to be equal to the structure of $CH_3NH_3^+$ moiety in $CH_3NH_3^+(H_2O)_{n\longrightarrow\infty}$. In MP2/6-31G(d) results, the predicted structure of $CH_3NH_3^+$ in aqueous solution is as follow: 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 predicted structure of $CH_3NH_3^+$ using the MINI-1 basis set, 4-31G basis set and MP2/6-31G(d) in aqueous solution is in Table 10. The structural parameters using the three methods are predicted to have the same values. These values are almost equal to the values in Study (A). Thus, the procedure in Study (A) is useful. The C-N bond lengths of $CH_3NH_3^+$ in aqueous solution using the MINI-1 basis set, 4-31G basis set and MP2/6-31G(d) are 1.486, 1.478 and 1.479 Å, respectively. In general the MP2/6-31G(d) calculation has a ±0.005 Å error [19]. Therefore, I believe that the C-N bond length of $CH_3NH_3^+$ in aqueous solution is 1.479 ± 0.005 Å.

$CH_3PH_3^+$

All clusters have all real vibrational frequencies and correspond to equilibrium structures. Table 11 shows that the structure of $CH_3PH_3^+$ in $CH_3PH_3^+(H_2O)_n$ almost does not change with the n increment. It is predicted that (1) the contribution of resonance structure, $CH_3^+...PH_3$, does not change with the n increment and (2) $(H_2O)_n$ has not a attraction for H in P-H bond. Therefore, it is predicted that the structure of $CH_3PH_3^+$ in aqueous solution is almost equal to that in the gas phase.

Appendix

The optimized structural parameters will be provided upon request (free of charge).

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Table 1

The total energy (E_T, a.u.) and stabilization energy ($\triangle E_{n-1,n}$, kcal/mol) of $CH_3NH_3^+(H_2O)_n$ cluster in the gas phase

Cluster	$-E_T$		$-\triangle E_{n-1,n}$			$-\triangle H^0_{n-1,n}$ [a]
	MINI-1	4-31G	MINI-1	$-\triangle E_c$ [b]	4-31G	
H_2O	75.49557	75.90864				
$CH_3NH_3^+$	94.92466	95.44076				
$CH_3NH_3^+(H_2O)$	170.46391	171.38915	27.5	23.9	24.8	16.8
$CH_3NH_3^+(H_2O)_2$	245.99206	247.33099	20.5	17.2	20.8	14.6
$CH_3NH_3^+(H_2O)_3$	321.51403	323.26750	16.5	13.4	17.4	12.3
$CH_3NH_3^+(H_2O)_4$	397.03201	399.20204	14.1	11.2	16.2	10.3
$CH_3NH_3^+(H_2O)_5$	472.54853	475.13561	13.1	10.3	15.5	9.0
$CH_3NH_3^+(H_2O)_6$	548.06390	551.06826	12.4	9.6	15.0	8.5
$CH_3NH_3^+(H_2O)_9$	774.59248					
$CH_3NH_3^+(H_2O)_{10}$	850.10230		8.8			

[a] Ref. [16].

[b] Stabilization energy corrected for the BSSE in MINI-1.

Table 2

The MINI-1 optimized structure of $CH_3NH_3^+(H_2O)_n$ cluster in gas phase[a]

Cluster	C-N	N-H	C-H	NCH	CNH	q_{CH_3}[d]	P_{C-N}[e]	q_H[f]
n = 0	1.553	1.059	1.128	108.5	111.0	0.340	0.271	
1	1.537	1.077	1.125	109.2	110.6	0.272	0.284	0.338
2	1.529	1.079	1.123	109.6	110.3	0.236	0.289	0.318
3	1.525	1.079	1.122	109.8	109.9	0.210	0.291	0.306
4	1.523	1.083				0.195	0.293	0.296
5	1.521	1.085				0.184	0.294	0.293
6	1.519	1.086				0.175	0.295	0.291
9	1.516	1.091				0.152	0.297	0.280
10	1.516					0.146	0.297	0.281
CH_3NH_2	1.504	1.037	1.120	111.2	108.6	0.045	0.316	
$n \longrightarrow \infty$[b]	1.512	1.090	1.119	110.5	109.2	0.131	0.299	0.270
	(1.510)	(1.084)	(1.118)	(110.6)	(109.6)	(0.150)	(0.301)	
$CH_3NH_3^+{}_{aq}$[c]	1.486	1.035	1.073	110.1	109.2	0.161	0.297	0.270

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[a] Mean values. Bond distances in Å; angles in degrees.

[b] Based on the eq. (1). The values in parentheses are based on eq. (1').

[c] The C-N, N-H and C-H bond distances were corrected by -0.03, -0.05 and -0.05 Å, respectively.

[d] The charge on CH_3.

[e] The Mulliken population between C-N.

[f] The charge on H in outermost H_2O.

Table 3

The 4-31G optimized structure of $CH_3NH_3^+(H_2O)_n$ cluster in gas phase[a]

Cluster	C-N	N-H	C-H	NCH	CNH	q_{CH_3}	P_{C-N}	q_H
n = 0	1.526	1.010	1.076	108.2	111.0	0.487	0.059	
1	1.511	1.018	1.076	108.7	110.8	0.442	0.080	0.461
2	1.502	1.021	1.076	109.0	110.5	0.404	0.098	0.453
3	1.495	1.022	1.076	109.2	110.1	0.372	0.113	0.445
4	1.493	1.024				0.361	0.117	0.442
5	1.490	1.025				0.351	0.122	0.441
6	1.488	1.026				0.342	0.126	0.439
CH_3NH_2	1.450	0.994	1.084	111.1	116.4	0.219	0.211	
$n \longrightarrow oo$	1.469	1.032	1.076	110.0	109.0	0.260	0.164	0.420
	(1.465)	(1.033)	(1.076)	(110.2)	(109.3)	(0.247)	(0.172)	
$CH_3NH_3{}^+{}_{aq}$	1.471	1.027	1.077	109.6	109.0	(0.288)	0.139	0.420

[a] See Table 2.

Table 4

The structural changes ($\triangle$) of $CH_3NH_3^+$ by $(H_2O)'_3$ + $CH_3NH_3^+(H_2O)_n$ $\longrightarrow$ $(H_2O)'_3CH_3NH_3^+(H_2O)_n$, and the charge on H' ($q_{H'}$) of $(H_2O)'_3CH_3NH_3^+(H_2O)_n$ using MINI-1[a]

n	$\triangle$C-N	$\triangle$N-H	$\triangle$C-H	$\triangle$NCH	$\triangle q_{CH_3}$	$\triangle P_{C-N}$	$q_{H'}$
0	0.012	-0.004	0.007	-1.3	-0.003	-0.017	0.275
1	0.010	-0.009	0.006	-1.1	0.015	-0.014	0.270
2	0.009	-0.008	0.005	-0.9	0.021	-0.011	0.267
3	0.007	-0.007	0.005	-0.7	0.023	-0.009	0.265
6	0.005				0.016	-0.004	0.260
r[b]	0.975	0.996	0.979	0.975	0.812	0.969	0.989
∞[c]	0.004	-0.005	0.004	-0.4	0.030	-0.002	0.257
H_2O							0.253

[a] Mean values. Bond distances in Å; angles in deg. Because $\triangle$CNH (n = 0) is negligible (-0.1°), $\triangle$CNH (n $\longrightarrow$ ∞) is assumed to be 0.0°.

[b] Correlation coefficient with charge on CH_3 in $CH_3NH_3^+(H_2O)_n$. For N-H, observations for m = 1,2,3 were used.

[c] Based on eqs. (3) and (4).

Table 5

The structural changes ($\triangle$) of $CH_3NH_3^+$ in the reaction $(H_2O)'_3$ + $CH_3NH_3^+(H_2O)_n \longrightarrow (H_2O)'_3CH_3NH_3^+(H_2O)_n$, and the charge on H' ($q_{H'}$) of $(H_2O)'_3CH_3NH_3^+(H_2O)_n$ using 4-31G[a]

n	$\triangle$C-N	$\triangle$N-H	$\triangle$C-H	$\triangle$NCH	$\triangle q_{CH_3}$	$\triangle P_{C-N}$	$q_{H'}$
0	0.020	-0.004	0.001	-1.6	-0.015	-0.048	0.425
1	0.016	-0.005	0.001	-1.3	-0.004	-0.046	0.420
2	0.013	-0.005	0.001	-0.9	0.002	-0.041	0.417
3	0.011	-0.005	0.001	-0.6	0.006	-0.036	0.413
r	0.997	-	-	0.995	0.988	0.969	0.997
∞	0.002	-0.005	0.001	-0.4	0.028	-0.025	0.402
H_2O							0.402

[a] See Table 4. Because $\triangle$CNH (n = 0) is negligible (-0.6°), $\triangle$CNH (n $\longrightarrow \infty$) is assumed to be 0.0°.

Table 6

Enthalpy change ($-\Delta H^{298K}_{n-1,n}$) for $CH_3NH_3^+(H_2O)_n$ cluster with 4-31G basis set

n	4-31G			Experiment[a]
	E_t[b] (hartree)	$-\Delta E_{n-1,n}$ (kcal/mol)	$-\Delta H^{298k}_{n-1,n}$ (kcal/mol)	$-\Delta H^0_{n-1,n}$ (kcal/mol)
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. [16].

[b] $E(H_2O) = -75.88251$.

Table 7

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

n	MP2/6-31G(d)			Experiment[a]
	E_t[b] (hartree)	$-\Delta E_{n-1,n}$ (kcal/mol)	$-\Delta H^{298k}_{n-1,n}$ (kcal/mol)	$-\Delta H^0_{n-1,n}$ (kcal/mol)
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	-400.76945	13.7		10.3
5	-476.98725	13.1		9.0
6	-553.20418	12.6		8.5

[a] Ref. [16].

[b] $E(H_2O)$ = -76.19685.

Table 8

The 4-31G optimized structure of $CH_3NH_3^+(H_2O)_n$ cluster in gas phase[a]

n	C-N	N-H	C-H	NCH	CNH	q_{CH_3}[b]
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	1.592	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] Mean values. Bond distances in Å; angles in degrees. The values in parentheses are fixed values.

[b] The charge on CH_3.

Table 9

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

n	C-N	N-H	C-H	NCH	CNH	q_{CH_3}
0	1.510	1.029	1.088	108.2	111.6	0.400
1	1.502	1.035	1.088	108.5	111.0	0.365
2	1.495	1.037	1.088	108.7	110.5	0.333
3	1.491	1.038	1.088	108.9	110.0	0.305
4	1.488	1.040	(1.088)	(108.9)	(110.0)	0.295
5	1.487	1.041	(1.088)	(108.9)	(110.0)	0.288
6	1.485	1.041	(1.088)	(108.9)	(110.0)	0.280
$n \longrightarrow \infty$[b]	1.479	1.047	1.088	108.9	108.5	0.252
CH_3NH_2	1.466	1.018	1.095	111.0	109.5	0.137

[a] See Table 8. [b] See text.

Table 10

The structure of $CH_3NH_3^+$ in aqueous solution

Method	C-N	N-H	C-H	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] Study (A).

Table 11

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

n	C-P	P-H	C-H	PCH	CPH	q_{CH_3}
0	1.801	1.387	1.088	109.4	111.7	0.106
1	1.804	1.391	1.088	109.5	111.1	0.093
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	110.6	97.8	-0.100

[a] See Table 8.

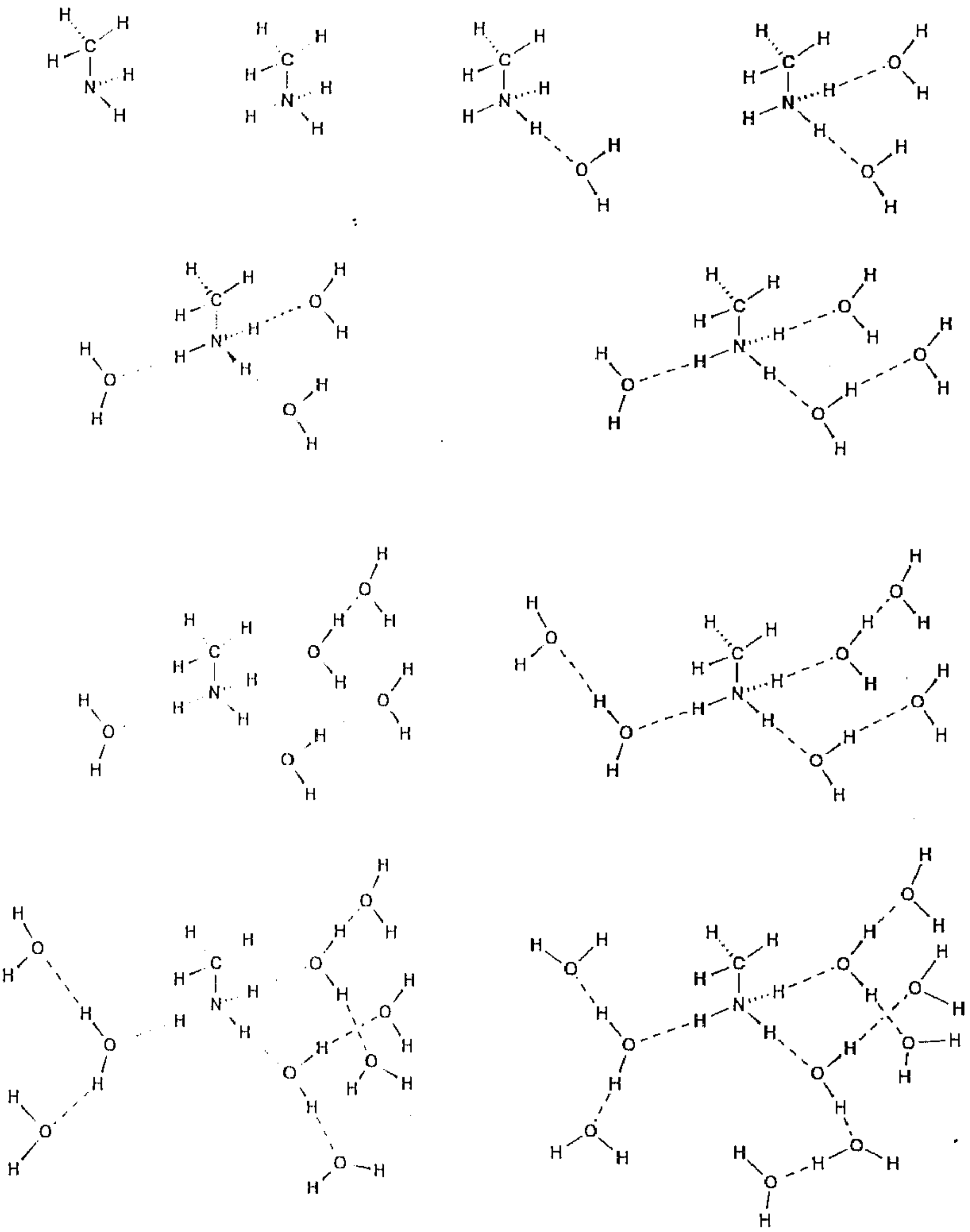

Fig. 1. The structures of $CH_3NH_3^+(H_2O)_n$ clusters and CH_3NH_2.

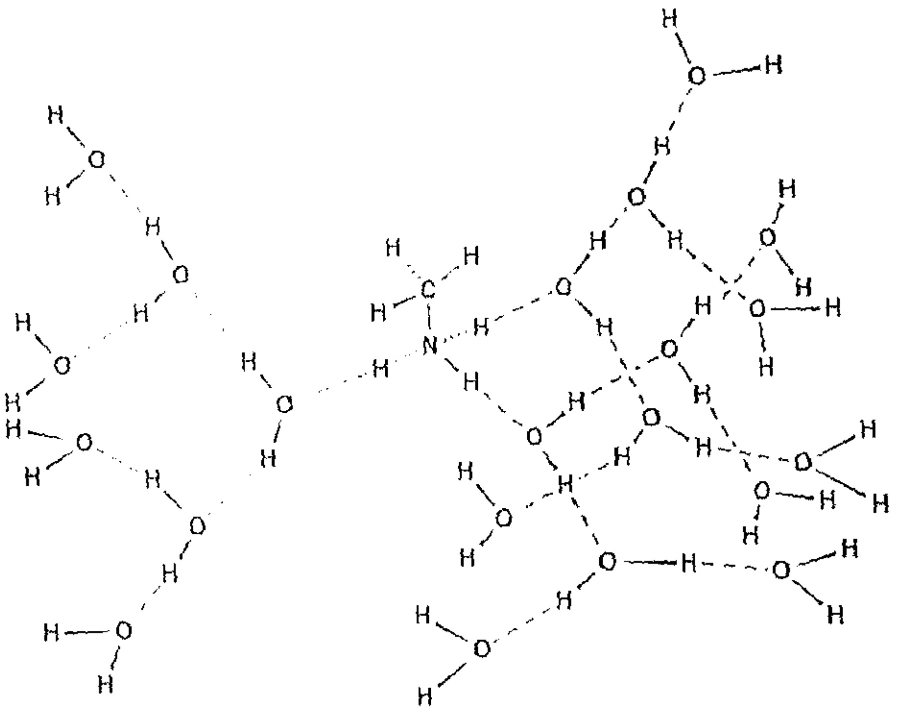

Fig. 1. Continued.

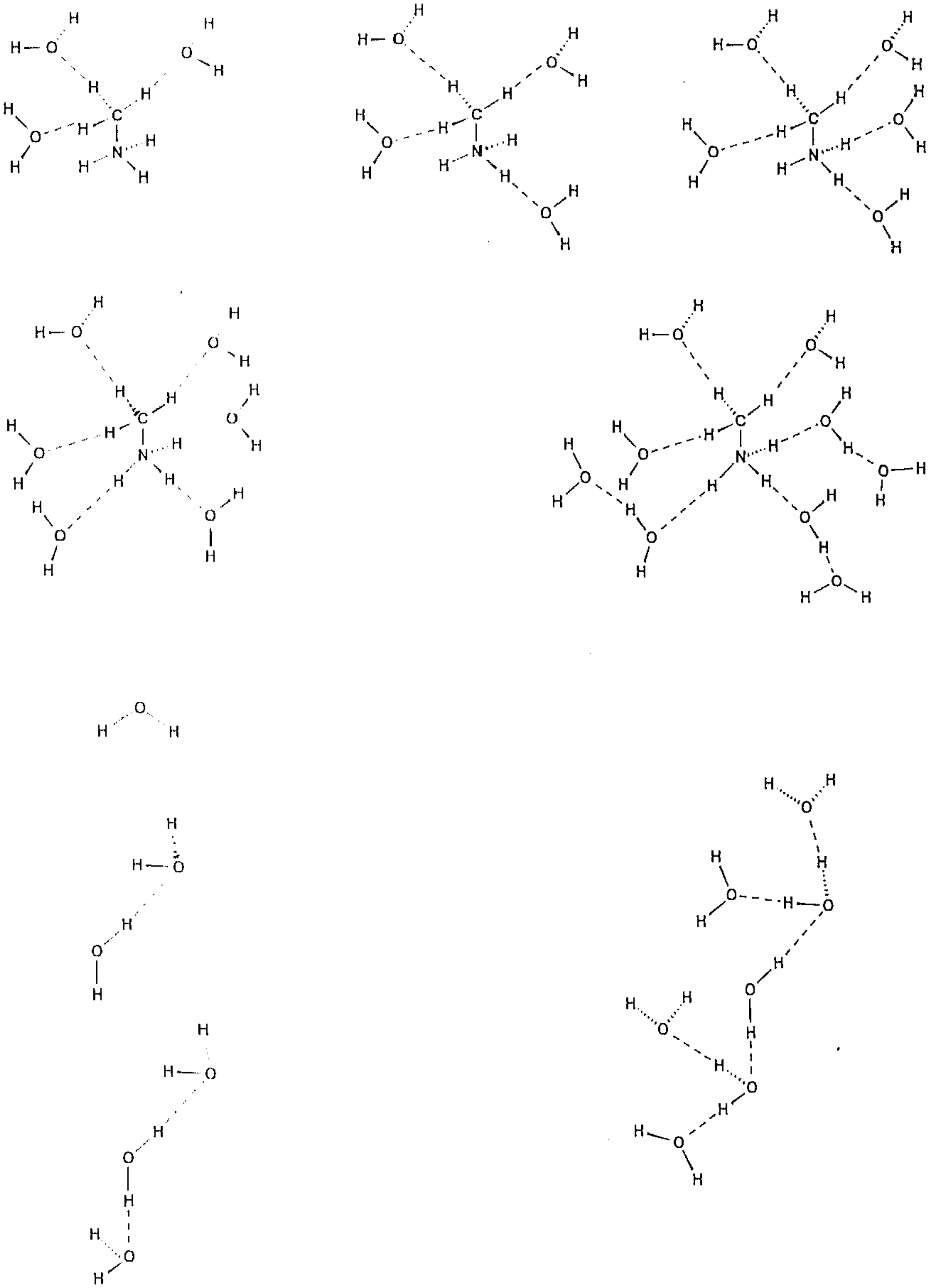

Fig. 2. The structures of $(H_2O)_3CH_3NH_3^+(H_2O)_n$ and $(H_2O)_n$ clusters.

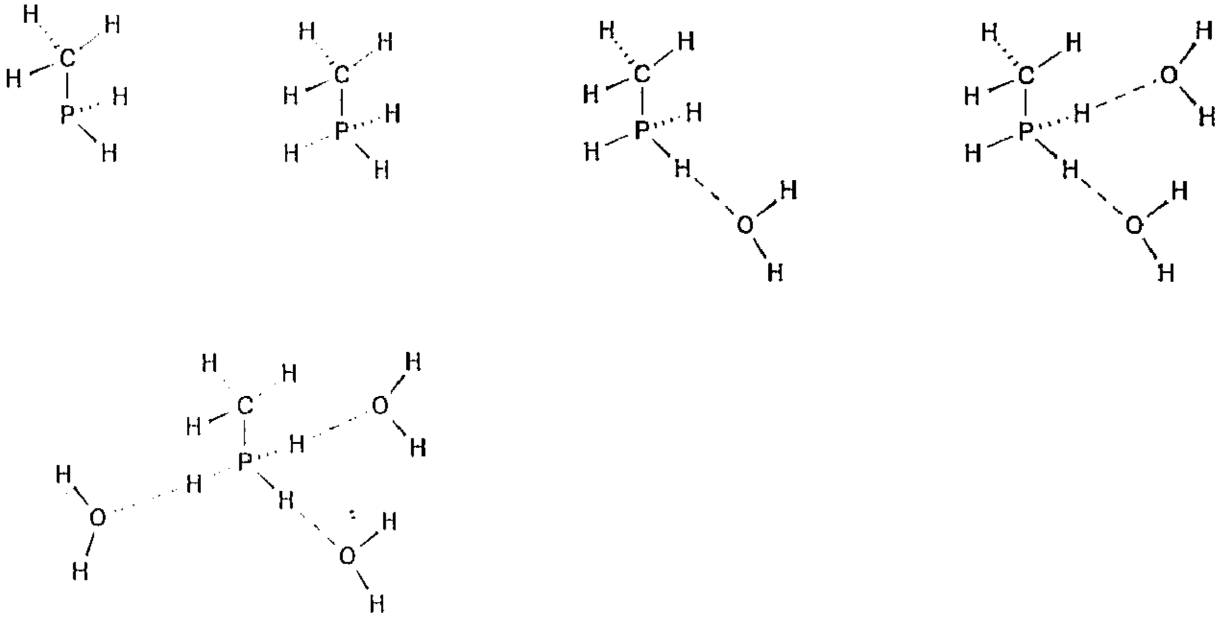

Fig. 3. The structures of $CH_3PH_3^+(H_2O)_n$ clusters and CH_3PH_2.