Chapter 5

The Structures of $CH_3OH_2^+$ and $CH_3SH_2^+$ in Water Clusters

Abstract

The purpose of this chapter is to predict the geometries and charges on atoms of $CH_3OH_2^+$ and $CH_3SH_2^+$ in aqueous solution. For this purpose, I carried out full geometry optimizations with the MP2/6-31+G(d,p) for $CH_3OH_2^+(H_2O)_n$ (n = 0,1,2,3,4,5) and $CH_3SH_2^+(H_2O)_n$ (n = 0,1,2,3,4). I also performed vibrational analysis for all clusters at the optimized structures to confirm that all vibrational frequencies are real. Those clusters have all real vibrational frequencies and correspond to equilibrium structures. For $CH_3OH_2^+(H_2O)_n$, when n becomes larger, (1) the C-O bond length becomes smaller, (2) the C-H bond lengths do not change, (3) the O-H bond lengths become larger, (4) the OCH bond angles become larger, (5) the COH bond angles become smaller, (6) the charge on CH_3 becomes less positive, (7) these predicted values except for the O-H bond lengths of $CH_3OH_2^+(H_2O)_n$ approach to the corresponding values of CH_3OH, with the n increment. The C-O bond length of $CH_3OH_2^+(H_2O)_5$ is smaller than that of $CH_3OH_2^+$ in the gas phase by 0.061 Å at the MP2/6-31+G(d,p) level of theory. Therefore, it is predicted that the structure of $CH_3OH_2^+$ in aqueous solution is considerably different from that in the gas phase. The structure of $CH_3SH_2^+$ moiety except for the S-H bond lengths in $CH_3SH_2^+(H_2O)_n$, however, does not change with the n increment. Thus, it is predicted that the structure of $CH_3SH_2^+$ except for the S-H bond lengths in aqueous solution is almost equal to that in the gas phase.

1. Introduction

In Chapter 3, I obtained an interesting prediction: (1) the geometry of CH_3O^- in aqueous solution differs from that in the gas phase; the discrepancy stems from a lower contribution of the resonance structure, $H^-...CH_2=O$, in aqueous solution than in the gas phase. (2) by way of contrast, the geometry of CH_3S^- in aqueous solution is almost equal to that in the gas phase. This means that the contribution of the resonance structure, $H^- ...CH_2=S$, in aqueous solution is almost equal to that in the gas phase. Therefore, the geometries of $CH_3OH_2^+$ and $Ch_3SH_2^+$ in aqueous solution are interesting.

However, the structures of $CH_3OH_2^+(H_2O)_n$ ($n \geq 1$) and $CH_3SH_2^+(H_2O)_n$ ($n \geq 1$) were not investigated, yet.

The purpose of this chapter is to predict the geometries and charges on atoms of $CH_3OH_2^+$ and $CH_3SH_2^+$ in aqueous solution.

2. Method

I carried out full geometry optimizations with the MP2/6-31+G(d,p) method for $CH_3OH_2^+(H_2O)_n$ ($n = 0,1,2,3,4,5$) and CH_3OH in Fig. 1. The core electrons were frozen. $CH_3OH_2^+(H_2O)_n$ ($n \geq 6$) was not fully optimized with MP2/6-31+G(d,p) due to the program limitation.

For $CH_3SH_2^+(H_2O)_n$, the structures were fully optimized using the MP2/6-31+G(d,p) level of theory (for $n = 0,1,2,3,4$). $CH_3SH_2^+(H_2O)_n$ ($n = 5$) can not be fully optimized using MP2/6-

31+G(d,p).

I also performed vibrational analysis for all clusters at the optimized structures to confirm that all vibrational frequencies are real.

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

$$CH_3OH_2^+(H_2O)_{n-1} + H_2O \longrightarrow CH_3OH_2^+(H_2O)_n$$
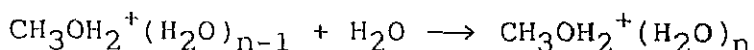
were calculated by the following formula:

$$\Delta E_{n-1,n} = E(CH_3OH_2^+(H_2O)_n) - E(CH_3OH_2^+(H_2O)_{n-1}) - E(H_2O)$$

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

$$\Delta H^{298K} = \Delta E_e^0 + \Delta E_v^0 + \Delta(\Delta E_v^{298K}) + \Delta E_r^{298K}$$
$$+ \Delta E_t^{298K} + \Delta(PV)$$

where ΔE_e^0 is electronic energy change, ΔE_v^0 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.

For the evaluation of the reliability of MP2/6-31+G(d,p), the following calculations were performed: (1) Because the proton affinity difference between CH_3OH and H_2O is important, the proton affinity difference evaluated at the MP2/6-31+G(d,p) level of theory was compared with the experimental one; (2) The enthalpy changes $(\Delta H^{298K}_{n-1,n})$ in MP2/6-31+G(d,p) were compared with the experimental $\Delta H^0_{n-1,n}$. For $CH_3SH_2^+(H_2O)_n$, similar comparisons were done.

In order to reproduce $\Delta H^0_{n-1,n}$, I performed MP4SDTQ/6-311++G(d,p)//MP2/6-31+G(d,p) energy calculations. Thermal

corrections were evaluated using the MP2/6-31+G(d,p) results.

I used the Gaussian 94 [1] program and the HPC and SX-5 computers in the Institute for Molecular Science.

3. Results

All the present clusters have all real vibrational frequencies and correspond to equilibrium structures. All O-H...O angles are nearly $180°$.
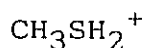
$CH_3OH_2^+$
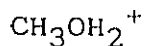
The proton affinity difference evaluated by the MP2/6-31+G(d,p) ($\Delta H = 15.4$ kcal/mol) is equal to the experimentally determined difference ($\Delta H = 15.4$ kcal/mol) [2].

Table 1 and 2 show that $-\Delta H^{298K}_{n-1,n}$ both at the MP2/6-31+G(d,p) and MP4/6-311++G(d,p) levels are close to the experimental $-\Delta H^0_{n-1,n}$ [3].

Table 3 shows the changes in the structural parameters and the gross charges on CH_3 in $CH_3OH_2^+(H_2O)_n$. When n becomes larger, (1) the C-O bond length becomes smaller, (2) the C-H bond lengths do not change, (3) the O-H bond lengths become larger, (4) the OCH bond angles become larger, (5) the COH bond angles become smaller, (6) the charge on CH_3 becomes less positive, (7) these values of $CH_3OH_2^+(H_2O)_n$ approach to the corresponding values of CH_3OH with the n increment. The C-O bond length of $CH_3OH_2^+(H_2O)_5$ is smaller than that of $CH_3OH_2^+$ in the gas phase by 0.061 Å at

the MP2/6-31+G(d,p) level of theory.

$CH_3SH_2^+$

The proton affinity difference evaluated at the MP2/6-31+G(d,p) ($\triangle H = 19.7$ kcal/mol) is nearly equal to the experimentally determined difference ($\triangle H = 20.9$ kcal/mol) [2].

Fig. 2 shows the schematic drawings of structures, and the optimized parameters are listed in Table 4. Table 4 shows that the structure of $CH_3SH_2^+$ moiety except for the S-H bond lengths in $CH_3SH_2^+(H_2O)_n$ clusters does not depend on the number of n. The S-H bond elongates more because $(H_2O)_n$ has a greater attraction for H in S-H bond with the n increment.

:

Discussion
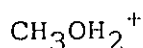
$CH_3OH_2^+$

It is predicted that the cause for the elongation of the C-O bond in $CH_3OH_2^+$ in the gas phase is the contibution of $H_3C^+\ldots OH_2$ as resonance structure. Since the C-O bond length of $CH_3OH_2^+(H_2O)_n$ becomes smaller with the increase of number n, the contibution of $H_3C^+\ldots OH_2$ decreases with the n increment. The C-O bond length of $CH_3OH_2^+(H_2O)_5$ is smaller than that of $CH_3OH_2^+$ in the gas phase by 0.061 Å. The O-H bond elongates more because $(H_2O)_n$ has a greater attraction for H in O-H bond with the n increment. Therefore, it is predicted that the structure of

124

$CH_3OH_2^+$ in aqueous solution is considerably different from that in the gas phase.

$CH_3SH_2^+$

The characteristic of $CH_3SH_2^+(H_2O)_n$ is different from that of $CH_3OH_2^+(H_2O)_n$: Because the C-S bond length of $CH_3SH_2^+(H_2O)_n$ is close to that of isolated CH_3SH, the contribution of $H_3C^+...SH_2$ does not exist in $CH_3SH_2^+$ moiety of $CH_3SH_2^+(H_2O)_n$. Because the structure of $CH_3SH_2^+$ moiety except for the S-H bond lengths in $CH_3SH_2^+(H_2O)_n$, however, does not change with the n increment, it is predicted that the structure of $CH_3SH_2^+$ except for the S-H bond lengths in aqueous solution is almost equal to that in the gas phase.

Appendix

Full optimized structural parameters are available from the author (free of charge).

References

[1] M.J.Frisch, G.W.Trucks, H.B.Schlegel, P.M.W.Gill,
    B.G.Johnson, H.A.Robb, J.R.Cheeseman, T. Keith,
    G.A.Petersson, J.A.Montgomery, K.Raghavachari,
    M.A.Al-Laham, V.G.Zakrzewski, J.W.Ortiz,
    J.B.Foresman, J.Cioslowski, B.B.Stefanov, A.Nanayakkara,
    M.Challacombe, C.Y. Peng, P.Y. Ayala, W.Chen,
    W.M.Wong, J.L.Andres, E.S.Replogle, R.Gomperts,
    R.L.Martin, D.J.Fox, J.S.Binkley, D.J.Defrees, J.Baker,
    J.P.Stewart, M.Head-Gordon, C.Gonzalez, and J.A.Pople
    Gaussian 94, Gaussian, Inc., Pittsburgh PA, 1995.

[2] S.G.Lias, J.F.Liebman and R.D.Levin, J.Phys.Chem.Ref.Data
    13(1984)695.

[3] M.Meot-Ner (Mautner), J.Am.Chem.Soc. 108(1986)6189.

Table 1

Enthalpy Change $(-\Delta H^{298K}_{n-1,n})$ for $CH_3OH_2^+(H_2O)_n$ Cluster with MP2/6-31+G(d,p)

n	MP2/6-31+G(d,p)			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)
CH_3OH	-115.39352			
0	-115.69318			
1	-191.97375	29.8	28.9	25.4
2	-268.24430	23.5	21.7	21.0
3	-344.50297	16.0	14.8	14.8
4	-420.75980	14.9	13.1	11.6
5	-497.01434	13.4	12.4	9.1

[a]Ref. [3].

[b]$E(H_2O) = -76.23311$.

Table 2

Enthalpy Change $(-\Delta H^{298K}_{n-1,n})$ for $CH_3OH_2^+(H_2O)_n$ Cluster with MP4/6-311++G(d,p)

n	MP4/6-311++G(d,p)			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	-115.77907			
1	-192.11244	29.0	28.1	25.4
2	-268.43646	23.1	21.3	21.0
3	-344.74827	15.5	14.2	14.8
4	-421.05851	14.5	12.7	11.6

[a]Ref. [3].

[b]$E(H_2O) = -76.28713$.

Table 3

The Structural Changes of $CH_3OH_2^+(H_2O)_n$ Clusters with the n

Increment in the Gas Phase[a]

n	C-O	C-H	O-H	OCH	COH	q_{CH_3}[b]
0	1.516	1.082	0.978	105.5	114.4	0.507
1	1.486	1.083	1.015	106.7	114.4	0.445
2	1.471	1.083	1.018	107.3	113.8	0.405
3	1.466	1.084	1.033	107.6	113.3	0.385
4	1.461	1.084	1.037	107.8	112.8	0.368
5	1.456	1.085	1.060	108.1	112.5	0.347
CH_3OH	1.429	1.090	0.964	109.9	108.6	0.224

[a]The values are mean values. Bond lengths are in angstroms, and the bond angles are in degrees.

[b]Charge on CH_3.

Table 4

The Structural Changes of $CH_3SH_2^+(H_2O)_n$ Clusters with the n Increment in the Gas Phase[a]

n	C-S	C-H	S-H	SCH	CSH	q_{CH_3}
0	1.820	1.085	1.339	108.0	100.2	0.182
1	1.818	1.085	1.357	108.2	100.0	0.159
2	1.815	1.085	1.361	108.4	99.7	0.151
3	1.815	1.085	1.374	108.5	99.1	0.126
4	1.815	1.085	1.379	108.5	98.7	0.114
CH_3SH	1.815	1.087	1.331	110.0	96.5	0.008

[a]See Table 3.
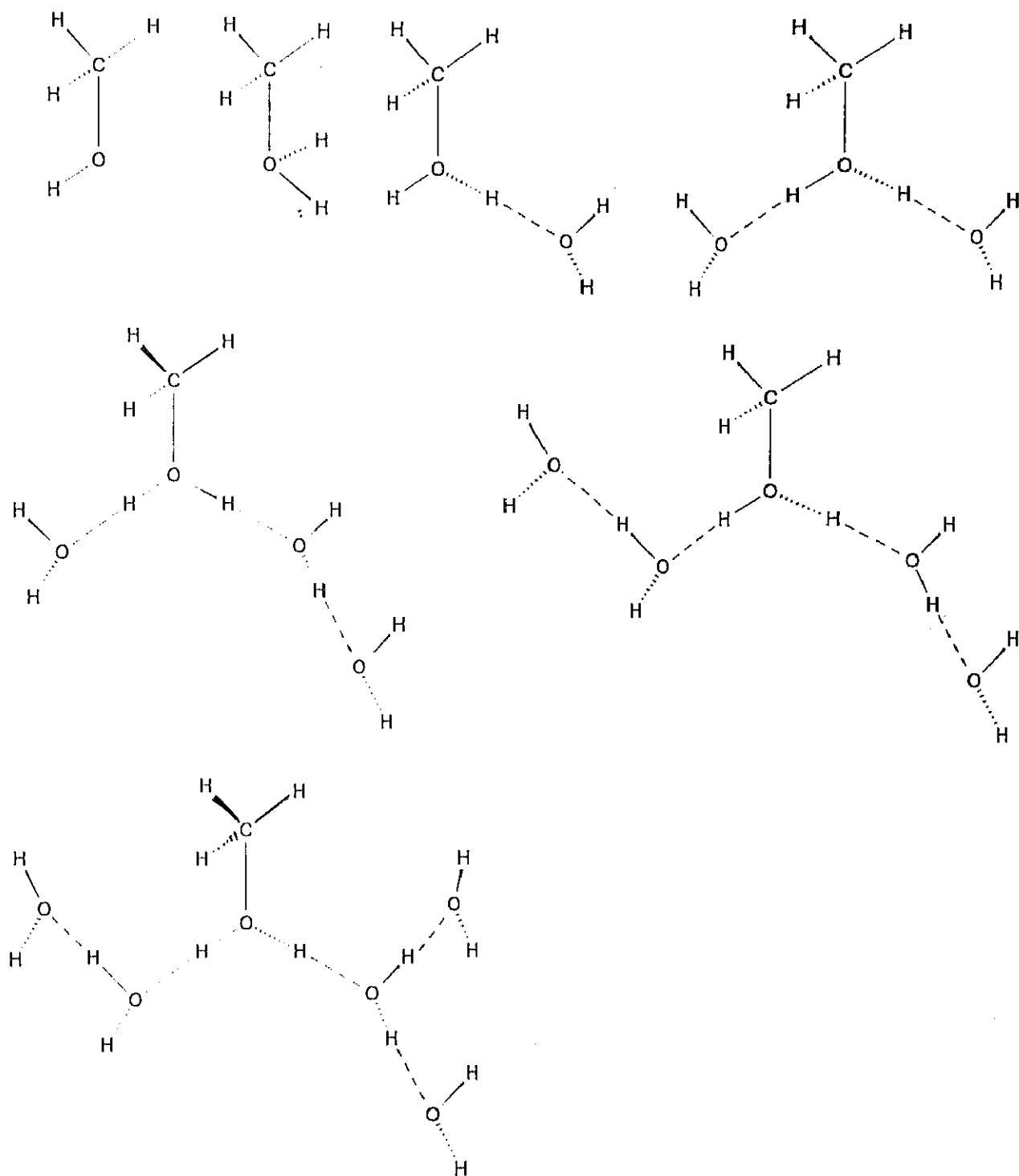
Fig. 1. The structures of $CH_3OH_2^+(H_2O)_n$ clusters and CH_3OH.
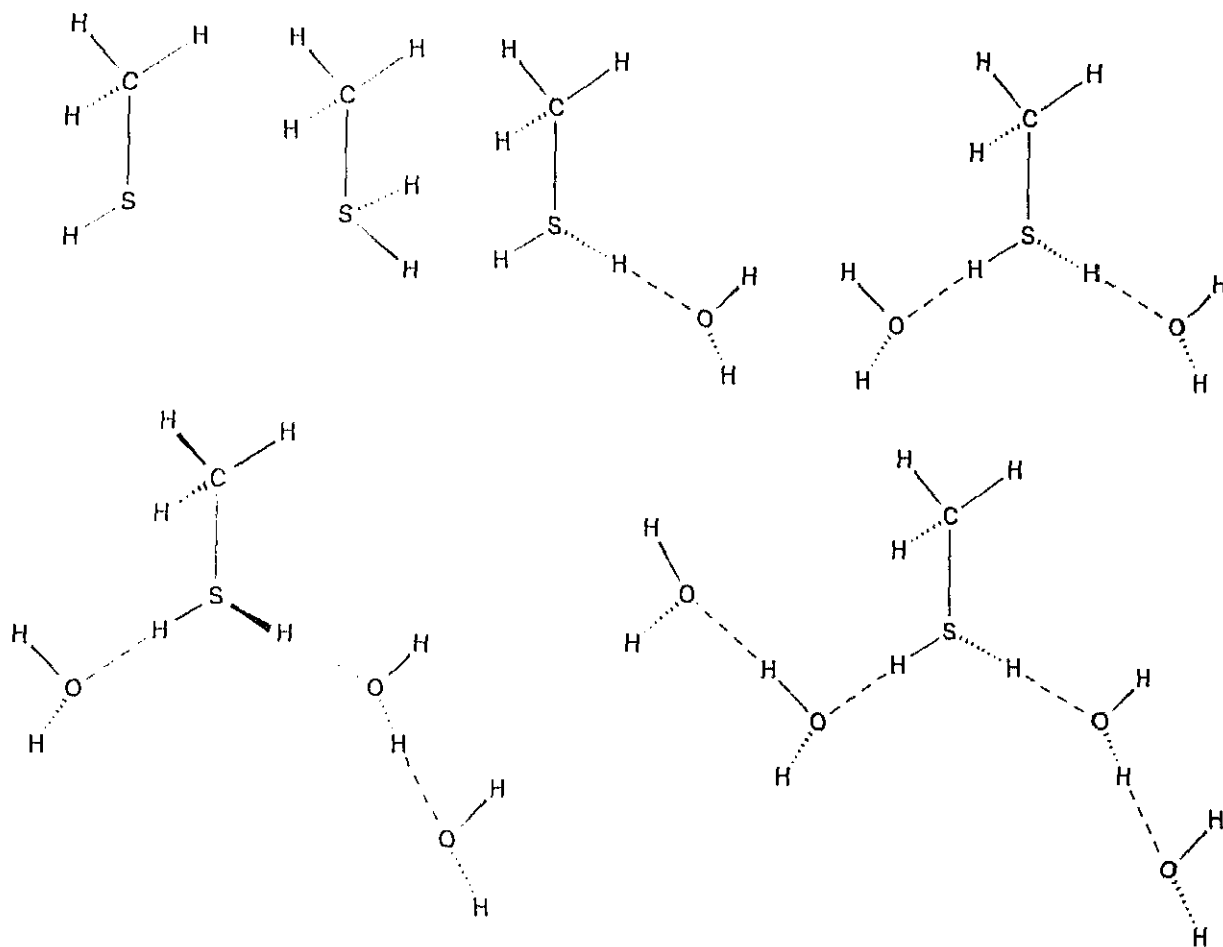
Fig. 2. The structures of $CH_3SH_2^+(H_2O)_n$ clusters and CH_3SH.