

Chapter 2

The Structures of RCOO^- in Water Clusters

Abstract

The purpose of this chapter is to predict the structure of the HCOO^- anion in aqueous solution. For this purpose, the following effects of water molecules on the structure of HCOO^- in aqueous solution are considered: (A) the effect of the first solvent shell; (B) the effect of water molecules around the O' of $\text{HCOO}^-(\text{H}_2\text{O}')_6$; (C) the effect of water molecules around the H' of $\text{H}'\text{COO}^-(\text{H}_2\text{O})_6$; (D) the effect of water molecules around H' of $\text{HCOO}^-(\text{HOH}')_6$. In order to estimate these effects, geometry optimization with the 3-21+G and 6-31++G(d) basis sets is carried out for $\text{HCOO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4, 5, 6$), $\text{HCOO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$ ($m = 1, 2$), $\text{HCOO}^-(\text{HOH})_6(\text{OH}_2)_m$ ($m = 1, 2$), $\text{H}_2\text{O}\dots\text{HCOO}^-(\text{H}_2\text{O})_6$. The effect of the first solvent shell is significant. The other effects are small. Thus, the structure of HCOO^- in aqueous solution is nearly the same as the structure of HCOO^- in $\text{HCOO}^-(\text{H}_2\text{O})_6$. The C-H bond length of HCOO^- in aqueous solution is smaller than the C-H bond length of HCOO^- in the gas phase by 0.017 \AA .

Next the structure of the CH_3COO^- anion in aqueous solution is predicted, considering the effects of the water molecules in the same manner as the HCOO^- . In order to estimate these effects, geometry optimization with the 6-31++G(d) basis set is carried out for $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4, 5, 6, 7$), $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$ ($m = 1, 2$), $\text{CH}_3\text{COO}^-(\text{HOH})_6(\text{OH}_2)_m$ ($m = 1, 2$), and $\text{H}_2\text{O}\dots\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_6$. The vibrational analysis for $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4, 5, 6$) with the 6-31++G(d) basis set was performed at the optimized structures to confirm that all vibrational frequencies

are real. The effect of the first solvent shell is significant. The other effects are predicted to be small. Thus, the structure of CH_3COO^- in aqueous solution is nearly the same as the structure of CH_3COO^- in $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_6$. The C-C bond length of CH_3COO^- in aqueous solution is predicted to be smaller than the C-C bond length of CH_3COO^- in the gas phase by 0.022 \AA .

Finally, the structure of the FCOO^- anion in aqueous solution is predicted, considering the effects of the water molecules in the same manner as the HCOO^- . Also, we consider the bulk effect. In order to estimate these effects, geometry optimization with B3LYP/6-311++G(2d,p) is carried out for $\text{FCOO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4, 5, 6, 7$), $\text{FCOO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$ ($m = 1, 2$) and $\text{HOH} \dots \text{FCOO}^-(\text{H}_2\text{O})_6$ are optimized with the 6-31++G(d) basis set. Also, in order to estimate the bulk effect, SCRF calculation (Onsager model) with the 6-31++G(d) basis set is performed for $\text{HOH} \dots \text{FCOO}^-(\text{H}_2\text{O})_6$. The effect of the first solvent shell is significant. The effect of water molecules around the O' of $\text{FCOO}^-(\text{H}_2\text{O}')_6$ is negligible. The effect of water molecules around the F of $\text{FCOO}^-(\text{H}_2\text{O})_6$ is significant. The effect of water molecules around the H' of $\text{FCOO}^-(\text{HOH}')_6$ is negligible. The bulk effect is very small. Considering these effects, the structure of FCOO^- in aqueous solution is predicted. The C-F bond length of FCOO^- in aqueous solution is predicted to be smaller than that in the gas phase by 0.09 \AA .

In R= CH_3 and F, I predict by these calculations that the maximum number of water molecules which can directly interact with carboxylate oxygen is six.

1. Introduction

The structure of RCOO^- in aqueous solution is interesting because many chemically and biologically important species such as amino acids and peptides have carboxylate groups in aqueous solution. However, at the present stage of experimentation, it is impossible to determine the structure of RCOO^- in aqueous solution.

The purpose of this chapter is to predict (1) first the structure of the HCOO^- anion in aqueous solution as the initial step in determining the structure of RCOO^- in aqueous solution, (2) next the structure of the CH_3COO^- anion in aqueous solution because the CH_3COO^- anion is an important substance and (3) finally the structure of the FCOO^- anion in aqueous solution for the following reasons: (i) the contribution of resonance structure, $\text{R}^-\dots\text{CO}_2$, to RCOO^- is important. The resonance structure is much more stable in $\text{R} = \text{F}$ than in $\text{R} = \text{H}$ and CH_3 ; (ii) when R is H or CH_3 , the effect of water molecules around R on the structure of RCOO^- in aqueous solution is negligible. However, it is predicted that the effect of water molecules around F on the structure of FCOO^- in aqueous solution is significant. For these two reasons, the structure of FCOO^- in aqueous solution is interesting.

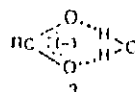
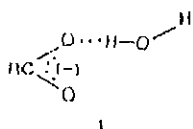
Markham et al. [1] stated that possibly the maximum number of water molecules that can directly interact with carboxylate oxygen in RCOO^- structures may be sensitive to the R substituent. When R is CH_3SCH_2 , the above maximum number of water molecules is

four. Therefore, I examined the sensitivity of R (R = CH₃ and F) to the maximum number of water molecules.

2. Method

I used the Gaussian 82 [2], Gaussian 86 [3], Gaussian 94 [4], Gaussian 98 [5], and NBO [6] programs and the M-680, S-820, HSP, SP2, HPC and SX-5 computers at the Institute for Molecular Science. I also used the Gaussian 94 and the SP2 computer in the Computer Center of Tokyo Metropolitan University.

I concluded that RCOO⁻(H₂O)_n complex are singly bonded between O⁻ and water molecules for the following reasons: (1) According to Michael Meot-Ner (Mautner) et al., these observations suggest that the RCOO⁻(H₂O) complexes are singly bonded as in ion 1 and the double hydrogen bonded structure 3 is not formed [7].



(2) Monte Carlo simulation studies show that acetate has six tightly bound waters around the COO⁻ group in aqueous solution [8].

For the analysis of atomic electron populations, the natural population analysis [9] was used.

HCOO⁻

In order to predict the structure of HCOO^- in aqueous solution, I must consider the following effects of water molecules on the structure of HCOO^- in aqueous solution: (A) the effect of water molecules in the first solvent shell. (We assume six water molecules in the first solvent shell, although a Monte Carlo calculation predicted that seven water molecules exist in the first solvent shell [10]); (B) the effect of water molecules around the O' of $\text{HCOO}^-(\text{H}_2\text{O}')_6$; (C) the effect of water molecules around the H' of $\text{H}'\text{COO}^-(\text{H}_2\text{O})_6$; (D) the effect of water molecules around the H' of $\text{HCOO}^-(\text{HOH}')_6$.

In order to estimate these effects by the ab initio closed-shell SCF method, I carried out geometry optimization with the 3-21+G [11] and 6-31++G(d) basis sets for $\text{HCOO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4, 5, 6$), $\text{HCOO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$ ($m = 1, 2$), $\text{HCOO}^-(\text{HOH})_6(\text{OH}_2)_m$ ($m = 1, 2$), $\text{H}_2\text{O} \dots \text{HCOO}^-(\text{H}_2\text{O})_6$, $(\text{H}_2\text{O})_n$ ($n = 1, 2$), and OH^- in Fig. 1.

The vibrational analysis for $\text{HCOO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4$) with the 3-21+G basis set was performed at the optimized structures to confirm all real vibrational frequencies.

For the evaluation of reliability of the 3-21+G basis set, the following calculations were performed: (1) because the proton affinity difference between HCOO^- and OH^- is important [12], the proton affinity difference evaluated by the 3-21+G basis set was compared with the proton affinity difference determined by experimental enthalpy; (2) the structural changes of $\text{HCOO}^-(\text{H}_2\text{O})_n$ with the n increment ($n = 0-4$) evaluated using the 3-21+G basis set were compared with the structural changes by the 6-31++G(d) basis set; (3) the 3-21+G optimized structure of HCOO^- was

compared with the optimized structure of HCOO^- by MP3/6-31++G(d) without frozen core; (4) stabilization energy $(-\Delta E_{n-1,n})$ was compared with experimental $-\Delta H_{n-1,n}^{298\text{K}}$.

CH_3COO^-

Jorgensen et al. used the 6-31+G(d) basis set for several anions [13]. The dimerization energy of H_2O evaluated by the 6-31++G(d) basis set is equal to the experimental dimerization energy of H_2O [14]. Therefore, I use the 6-31++G(d) basis set for this anion.

The structure of the CH_3COO^- anion in aqueous solution is predicted, considering the effects of the water molecules in the same manner as the HCOO^- .

In order to estimate these effects by the ab initio closed-shell SCF method, I carried out geometry optimization with the 6-31++G(d) basis set for $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ ($n = 0 - 7$), $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$ ($m = 1, 2$), $\text{CH}_3\text{COO}^-(\text{HOH})_6(\text{OH}_2)_m$ ($m = 1, 2$), $\text{H}_2\text{O} \dots \text{CH}_3\text{COO}^-(\text{H}_2\text{O})_6$, $(\text{H}_2\text{O})_n$ ($n = 1, 2$) and OH^- in Fig. 2.

The vibrational analysis for $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4, 5, 6$) was performed with the 6-31++G(d) basis set at the optimized structures to confirm that all vibrational frequencies are real.

For CH_3COO^- , structure 1 in Fig. 2 is more stable than structure 2 in Fig. 1 by 0.006 kcal/mol. In more accurate calculations, structure 2 must be more stable than the structure 1.

The enthalpy changes ($\Delta H^{298K}_{n-1,n}$) of $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ were calculated with the 6-31++G(d) basis set by the following formula:

$$\Delta H^{298K}_{n-1,n} = H^{298K}(\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n) - H^{298K}(\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_{n-1}) - H^{298K}(\text{H}_2\text{O})$$

For the evaluation of reliability of the 6-31++G(d) basis set, the following calculations were performed: (1) because the proton affinity difference between HCOO^- and OH^- is important, the proton affinity difference between CH_3COO^- and OH^- evaluated by the 6-31++G(d) basis set was compared with the proton affinity difference determined by experimental enthalpy; (2) the 6-31++G(d) optimized structure of CH_3COO^- was compared with the optimized structure of CH_3COO^- by MP3/6-31++G(d) with frozen core; and (3) the enthalpy changes ($-\Delta H^{298K}_{n-1,n}$) in the 6-31++G(d) basis set was compared with experimental $-\Delta H^0_{n-1,n}$ [15].

FCOO^-

The structure of the FCOO^- anion in aqueous solution is predicted, considering the effects of the water molecules in the same manner as the HCOO^- . Also, we consider the bulk effect.

In order to estimate these effects, I carried out geometry optimization with B3LYP/6-311++G(2d,p) for $\text{FCOO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4, 5, 6, 7$) in Fig. 3. $\text{FCOO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$ ($m = 1, 2$) and $\text{HOH}\dots\text{FCOO}^-(\text{H}_2\text{O})_6$ are optimized with the 6-31++G(d) basis set in

Fig. 3. Also, in order to estimate the bulk effect, SCRF calculation [16] (Onsager model) with the 6-31++G(d) basis set is performed for $\text{HOH}\dots\text{FCOO}^-(\text{H}_2\text{O})_6$, employing the dielectric constant of 80.

Vibrational analysis for $\text{FCOO}^-(\text{H}_2\text{O})_n$ ($n = 0, 1, 2, 3, 4, 5, 6$) was performed with the 6-31++G(d) basis set at the optimized structures to confirm that all vibrational frequencies are real.

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3. Results and Discussion

HCOO^-

1. The Reliability of the 3-21+G basis set.

The proton affinity difference evaluated by the 3-21+G basis set ($\Delta E = -47.0$ kcal/mol) agrees with the proton affinity difference determined using an experimental enthalpy ($\Delta H = -45.6$ kcal/mol) [17]. The changes in structural parameters with the n increment in the 3-21+G basis set agree with the changes in structural parameters in the 6-31++G(d) basis set. The optimized C-H bond length of HCOO^- with the 3-21+G basis set is shorter than the optimized C-H bond length of HCOO^- with MP3/6-31++G(d) by -0.026 \AA . The optimized C-O bond length of HCOO^- with the 3-21+G basis set is longer than the optimized C-O bond length of HCOO^- with MP3/6-31++G(d) by 0.010 \AA . With the corrections for the C-H ($+0.026 \text{ \AA}$) and C-O (-0.010 \AA) bond lengths optimized with the 3-21+G basis set, I can obtain acceptable bond lengths for C-H and C-O in this study. Table 1 shows $-\Delta E_{n-1,n}$ in the 3-21+G basis set is slightly overestimated.

2. Effect of Water Molecules in the First Solvent Shell.

Tables 2 and 3 show the changes in structural parameters and charges on atoms in $\text{HCOO}^-(\text{H}_2\text{O})_n$ with each n increment. When n becomes larger, (1) the C-H bond length becomes smaller, (2) the charge on the H' of $\text{H}'\text{COO}^-(\text{H}_2\text{O})_n$ becomes larger, (3) the charge on the C is larger, (4) the C-O bond length and HCO bond angle are nearly unchanged, and (5) the charge on the O of HCOO^- becomes slightly more negative.

I showed the cause for the elongation of the H-C bond in HCOO^- in the gas phase [18]. This elongation results from the contribution of $\text{H}^-\dots\text{CO}_2$ as resonance structure to the HCOO^- [18]. When more water molecules attach HCOO^- , more minus charge withdraws from HCOO^- to water molecules. Consequently, it is predicted that the resonance structure, $\text{H}^-\dots\text{CO}_2$, contributes less to HCOO^- with each n increment. Due to less contribution of the resonance structure $\text{H}^-\dots\text{CO}_2$ with each n increment, the C-H bond length becomes shorter with the n increment.

$\text{HCOO}^-(\text{H}_2\text{O})_n$ ($n = 1, 2$) have all real vibrational frequencies. $\text{HCOO}^-(\text{H}_2\text{O})_n$ ($n = 3, 4$) have imaginary vibrational frequencies. Therefore, the conformations of $\text{HCOO}^-(\text{H}_2\text{O})_n$ ($n = 3, 4$) are not local minima. Probably, the conformations of $\text{HCOO}^-(\text{H}_2\text{O})_n$ ($n = 5, 6$) in Fig. 1 are not local minima. However, it is predicted that the structure of HCOO^- in those conformations is almost equal to that in several local minima.

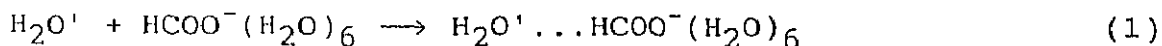
3. Effect of Water Molecules around O' of $\text{HCOO}^-(\text{H}_2\text{O}')_6$.

The geometry and charges on atoms of HCOO^- in $\text{HCOO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$ ($m = 1, 2$) are equal to the geometry and charge in

$\text{HCOO}^-(\text{H}_2\text{O})_6$. It is predicted that water molecules around O' of $\text{HCOO}^-(\text{H}_2\text{O})_6$ do not affect the structure of HCOO^- .

4. Effect of Water Molecules around H' of $\text{H}'\text{COO}^-(\text{H}_2\text{O})_6$.

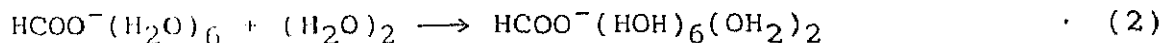
The structural changes in HCOO^- by



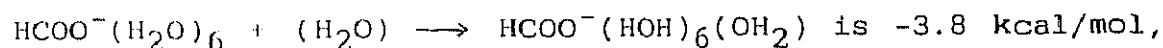
are as follows: $\Delta \overset{\circ}{\text{C}}\text{-H} = +0.005 \text{ \AA}$; $\Delta \overset{\circ}{\text{C}}\text{-O} = 0.005 \text{ \AA}$; $\Delta \text{HCO} = 0.5^\circ$. The changes in charges on H, C, and O in HCOO^- are 0.05, -0.02, and -0.02 e, respectively. It is predicted that the structural changes by reaction 1 are due to the destabilization of the resonance structure, $\text{H}^-\dots\text{CO}_2$, by electrostatic interaction between water molecule and the H' of $\text{H}'\text{COO}^-(\text{H}_2\text{O})_6$. The stabilization energy by reaction 1 is only -0.3 kcal/mol, which is much smaller than the dimerization energy of H_2O (-8.7 kcal/mol in the 3-21+G basis set). Thus, in aqueous solution, it is predicted that the water molecules around the H' of $\text{H}'\text{COO}^-(\text{H}_2\text{O})_6$ are attracted to another water molecules. Consequently, it is predicted that the effect of water molecules around the H of HCOO^- in aqueous solution is very small.

5. Effect of Water Molecules around H' of $\text{HCOO}^-(\text{HOH}')_6$.

The structural changes in HCOO^- by



are as follows: $\Delta \overset{\circ}{\text{C}}\text{-H} = 0.002 \text{ \AA}$; $\Delta \overset{\circ}{\text{C}}\text{-O} = 0.000 \text{ \AA}$; $\Delta \text{HCO} = -0.3^\circ$. The changes in charges on H, C, and O in HCOO^- are -0.01, -0.01, and 0.00 e, respectively. The structural changes by reaction 2 are nearly the reverse of the change by reaction 1 except for the charge on C. Because the stabilization energy by



it is predicted that the water molecules around H' of HCOO^- (HOH')₆ are attracted to other water molecules in aqueous solution. Consequently, in aqueous solution, it is predicted that the effect of water molecules around the H' of HCOO^- (HOH')₆ is small.

6. Structure of HCOO^- in Aqueous Solution.

The previous estimations show that the effect of water molecules in the first solvent shell on the structure of HCOO^- is significant. The effect of water molecules around the O' of HCOO^- ($\text{H}_2\text{O}'$)₆, the effect of water molecules around the H' of $\text{H}'\text{COO}^-$ (H_2O)₆, and the effect of water molecules around H' of HCOO^- (HOH')₆ are small. Thus, structure of HCOO^- in aqueous solution is nearly the same as the structure of HCOO^- in $\text{HCOO}^-(\text{H}_2\text{O})_6$. On the basis of these suggestions, Table 2 shows the structure of HCOO^- in aqueous solution: (1) the C-H bond length of HCOO^- in aqueous solution is smaller than the C-H bond length of HCOO^- in the gas phase by 0.017 \AA ; (2) the charge on the H of HCOO^- in aqueous solution is more positive than the charge on the H of HCOO^- in the gas phase by $0.087 e$; (3) the charge on the C of HCOO^- in aqueous solution is more positive than the charge on the C of HCOO^- in the gas phase by $0.087 e$.

CH_3COO^-

1. The reliability of the 6-31++G(d) basis set.

The proton affinity difference evaluated by the 6-31++G(d) basis set ($\Delta E = -45.7 \text{ kcal/mol}$) agrees with the proton affinity difference determined using an experimental enthalpy ($\Delta H = -42.3$

kcal/mol) [19]. The optimized C-C bond length of CH_3COO^- with the 6-31++G(d) basis set is shorter than the optimized C-C bond length of CH_3COO^- with MP3/6-31++G(d) by 0.004 \AA . The optimized C-H bond length of CH_3COO^- with the 6-31++G(d) basis set is shorter than the optimized C-H bond length of CH_3COO^- with MP3/6-31++G(d) by $0.007 - 0.011 \text{ \AA}$. The optimized C-O bond length of CH_3COO^- with the 6-31++G(d) basis set is shorter than the optimized C-O bond length of CH_3COO^- with MP3/6-31++G(d) by $0.021 - 0.022 \text{ \AA}$.

Table 4 shows $-\Delta H^{298\text{K}}_{n-1,n}$ in the 6-31++G(d) basis set is near the experimental $-\Delta H^0_{n-1,n}$. In the 6-31++G(d) basis set, $-\Delta H^{298\text{K}}_{1,2}$ are higher than $-\Delta H^{298\text{K}}_{0,1}$ resulting from the hydrogen bonding between two water molecules in $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_2$. Why is experimental $-\Delta H^{298\text{K}}_{1,2}$ lower than $-\Delta H^{298\text{K}}_{0,1}$?

(1) According to Meot-Ner [20], it is possible that several different structures are present in the equilibrium cluster population.

(2) If I use more accurate calculations, $-\Delta H^{298\text{K}}_{0,1}$ may be higher than $-\Delta H^{298\text{K}}_{1,2}$ in the calculation.

I concluded that the 6-31++G(d) results were reasonable. With the corrections for the C-C ($+0.004 \text{ \AA}$), C-H ($+0.007 - +0.011 \text{ \AA}$) and C-O ($0.021 - 0.022 \text{ \AA}$) bond lengths optimized with the 6-31++G(d) basis set, I can obtain acceptable bond lengths for C-C, C-H and C-O in this study.

2. Effect of water molecules in the first solvent shell.

Table 5 and 6 show the changes in structural parameters and charges on atoms in $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ with each n increment. When n

becomes larger; (1) the C-C bond length becomes smaller; and (2) the charge on the CH₃ of CH₃COO⁻(H₂O)_n becomes less negative.

Table 7 shows the changes in the energy level of HOMO and next HOMO with each n increment. When n becomes larger, the energy level of the HOMO and next HOMO become lower.

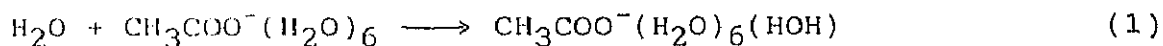
CH₃COO⁻(H₂O)_n (n = 0 — 6) have all real vibrational frequencies. In n = 1—6, all water molecules exist in first solvent shell. For the similar reason for HCOO⁻, the C-C bond length becomes shorter with the n increment. CH₃COO⁻(H₂O)₇ does not exist because the seventh water molecule invariably migrated to the second solvent shell during the optimization, leading to a structure best represented as CH₃COO⁻(H₂O)₆(H₂O). Thus, the maximum number of water molecules in the first solvent shell is six.

It is predicted that conformation A, B and C of CH₃COO⁻(H₂O)₆ in Fig. 2 are most stable due to the hydrogen bonding between water molecules. Thus, I attempted to optimize conformation A, B and C of CH₃COO⁻(H₂O)₆. However, all conformations converged the same optimized structure (conformation B). Later, I use conformation B.

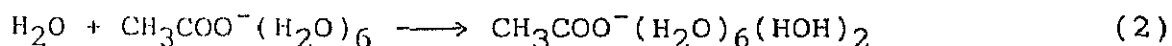
For n = 1 — 5, several conformations may exist. However, it is predicted that the structure of CH₃COO⁻ in one conformer is almost equal to that in other conformer. Therefore, conformation search for n = 1 — 5 are not carried out.

3. Effect of water molecules around O' of CH₃COO⁻(H₂O')₆.

The energy changes for



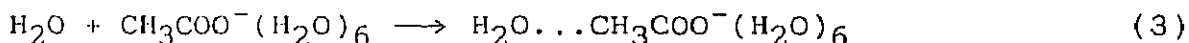
is -8.4 kcal/mol, which is larger than dimerization energy of H₂O (-5.4 kcal/mol in the 6-31++G(d) basis set). The structural changes in CH₃COO⁻ by



are nothing. The changes in the charges on C₁, C₂, H₃, O₄, O₅, H₆ and H₇ are -0.01, 0.00, -0.01, +0.01, -0.01, 0.00 and +0.02 e, respectively. The changes in the energy level of HOMO and next HOMO for this reaction are -0.017 and -0.018 a.u., respectively. Thus, It is predicted that water molecules around O' of CH₃COO⁻(H₂O')₆ do not affect the structure of CH₃COO⁻ in aqueous solution.

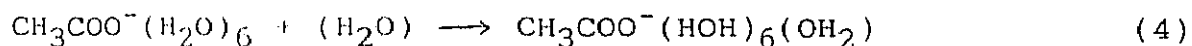
4. Effect of water molecules around CH₃ of CH₃COO⁻(H₂O)₆.

The structural changes in CH₃COO⁻ by



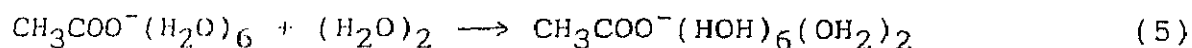
are as follows: $\Delta \text{C}-\text{C} = +0.004 \overset{\circ}{\text{A}}$; $\Delta \text{H}_3-\text{C}_2 = +0.003 \overset{\circ}{\text{A}}$. The energy change by reaction (3) is positive. Thus, in aqueous solution, it is predicted that the water molecules around the CH₃ of CH₃COO⁻(H₂O)₆ are attracted to other water molecules. Consequently, it is predicted that the effect of water molecules around the CH₃ of CH₃COO⁻ on the structure of CH₃COO⁻ in aqueous solution is very small.

5. Effect of water molecules around H' of CH₃COO⁻(HOH')₆.



The energy change by this reaction is -7.6 kcal/mol.

The structural changes in CH₃COO⁻ by



are as follows: $\Delta \text{C}-\text{C} = 0.001 \overset{\circ}{\text{A}}$. The changes in charges on the

C_1, C_2, H_3, O_4, O_5 and H_6 are nothing, respectively. The changes in the energy level of HOMO and next HOMO for this reaction are -0.002 and -0.003 a.u., respectively.

The structural changes by reaction (5) is small. Consequently, in aqueous solution, it is predicted that the effect of water molecules around H' of $CH_3COO^-(HOH')_6$ on the structure is small.

6. Structure of CH_3COO^- in aqueous solution.

The previous estimations show that the effect of water molecules in the first solvent shell on the structure of CH_3COO^- is significant. The effect of water molecules around the O' of $CH_3COO^-(H_2O')_6$, the effect of water molecules around the CH_3 of $CH_3COO^-(H_2O)_6$ and the effect of water molecules around H' of $CH_3COO^-(HOH')_6$ are small. Thus, structure of CH_3COO^- in aqueous solution is nearly the same as the structure of CH_3COO^- in $CH_3COO^-(H_2O)_6$. Based on these suggestions, in aqueous solution: $C_2-C_1 = 1.529$; $H_3-C_2 = 1.091$; $O_4-C_1 = 1.262$; $O_5-C_1 = 1.266$; $H_6-C_2 = 1.092$; $H_7-C_2 = 1.097 \overset{\circ}{\text{Å}}$; $H_3C_2C_1 = 111.8$; $O_4C_1C_2 = 117.9$; $O_5C_1C_2 = 116.3$; $H_6C_2C_1 = 109.6$; $H_7C_2C_1 = 109.1 \overset{\circ}{\text{Å}}$. The CH_3COO^- in aqueous solution has C_{2v} symmetry. (1) The C-C bond length of CH_3COO^- in aqueous solution is smaller than the C-C bond length of CH_3COO^- in the gas phase by $0.022 \overset{\circ}{\text{Å}}$; and (2) The charge on the CH_3 of CH_3COO^- in aqueous solution is less negative than the charge on the CH_3 of CH_3COO^- in the gas phase by 0.06 e.

$FCOO^-$

1. Effect of Water Molecules in the First Solvent Shell.

Table 8 and 9 show the changes in structural parameters and charges on atoms in $\text{FCOO}^-(\text{H}_2\text{O})_n$ with each n increment. The C-F bond length of FCOO^- is much longer than that of FCOOH . When n becomes larger, (1) the C-F bond length becomes smaller because of the similar reason for HCOO^- , and (2) the charge on the F of $\text{FCOO}^-(\text{H}_2\text{O})_n$ becomes less negative.

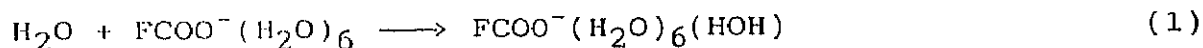
$\text{FCOO}^-(\text{H}_2\text{O})_n$ ($n = 0 - 6$) have all real vibrational frequencies. In $n = 1-6$, all water molecules exist in first solvent shell. $\text{FCOO}^-(\text{H}_2\text{O})_7$ does not exist because the seventh water molecule invariably migrated to the second solvent shell during the optimization, leading to a structure best represented as $\text{FCOO}^-(\text{H}_2\text{O})_6(\text{H}_2\text{O})$. Thus, the maximum number of water molecules in the first solvent shell is six.

For the similar reason for $\text{HCOO}^-(\text{H}_2\text{O})_6$, I attempted to optimize three different conformations, A, B and C, of $\text{FCOO}^-(\text{H}_2\text{O})_6$ using B3LYP/6-311++G(2d,p). The conformation B can be optimized. However, the conformations A and C can not be optimized. Using the 6-31++G(d) basis set, all optimizations for the three conformations converged to the same optimized structure (conformation B). The hydrogen bond interactions between water molecules stabilize the conformation B.

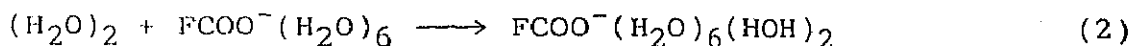
For $n = 1 - 5$, several conformations may exist. However, for the similar reason for $\text{HCOO}^-(\text{H}_2\text{O})_n$, conformational searches for $n = 1 - 5$ were not carried out.

2. Effect of Water Molecules around O' of $\text{FCOO}^-(\text{H}_2\text{O}')_6$.

The energy change for



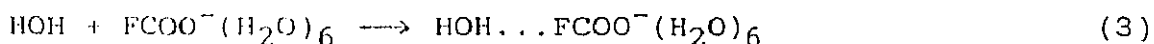
is -8.1 kcal/mol, which is larger than dimerization energy of H₂O (-5.4 kcal/mol with the 6-31++G(d) basis set). The structural changes in FCOO⁻ by



are negligible. The changes in the charges on C₁, F₂, O₃ and O₄ are 0.02, -0.01, -0.01, and -0.01 e, respectively. Thus, it is predicted that water molecules around O' of FCOO⁻(H₂O')₆ were little impact on the structure of FCOO⁻ in aqueous solution.

3. Effect of Water Molecules around F of FCOO⁻(H₂O)₆.

The structural changes in FCOO⁻ by



are as follows: $\Delta C-F = +0.011 \text{ \AA}$. The changes in the charges on C₁, F₂, O₃ and O₄ are 0.00, -0.02, +0.01, and +0.01 e, respectively. The energy change associated with reaction (3) is -4.4 kcal/mol.

It is predicted that the structural changes associated with reaction (3) are due to the stabilization of the resonance structure, F⁻...CO₂, by electrostatic interaction between the water molecule and the F in FCOO⁻(H₂O)₆. For HCOO⁻ in aqueous solution, it is predicted that the water molecules around the H of HCOO⁻ are attracted to other water molecules. In the case of FCOO⁻ in aqueous solution, because the energy change by reaction (3) is -4.4 kcal/mol, which is almost equal to the dimerization energy of H₂O (-5.4 kcal/mol in the 6-31++G(d) basis set), it is predicted that such an attraction does not occur.

4. Effect of Water Molecules around H' of FCOO⁻(HOH')₆.

I tried to estimate this effect using the 6-31++G(d) basis

set, but were unsuccessful. In HCOO^- , this effect was very small. Thus, it is predicted that the effect of water molecules around the H' of $\text{FCOO}^-(\text{HOH}')_6$ on the structure of FCOO^- in aqueous solution is very small.

5. Bulk effect.

SCFR calculation shows that the bulk effect on the C-F bond length of $\text{HOH}\dots\text{FCOO}^-(\text{H}_2\text{O})_6$ is -0.002 \AA . The changes in the charges on C_1 , F_2 , O_3 and O_4 are 0.00, +0.01, -0.01 and -0.01 e, respectively. Therefore, it is predicted that the bulk effect is very small.

6. Structure of FCOO^- in aqueous solution.

From the previous estimations, the following effects of water molecules on the structure of FCOO^- in aqueous solution are predicted: (A) The effect of the first solvent shell is significant. (B) The effect of water molecules around the O' of $\text{FCOO}^-(\text{H}_2\text{O}')_6$ is negligible. (C) The effect of water molecules around the F of $\text{FCOO}^-(\text{H}_2\text{O})_6$ is significant. (D) The effect of water molecules around the H' of $\text{FCOO}^-(\text{HOH}')_6$ is negligible. (E) The bulk effect is very small. Considering these effects, the structure of FCOO^- in aqueous solution is predicted: The C-F bond length = 1.422 \AA ; the C-O bond length = 1.231 \AA ; the FCO bond angle = 113.3° . The C-F bond length of FCOO^- in aqueous solution is predicted to be smaller than that in the gas phase by 0.09 \AA .

Appendix

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

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Table 1

Stabilization Energy ($-\Delta E_{n-1,n}$) for $\text{HCOO}^-(\text{H}_2\text{O})_n$ Cluster (in kcal/mol)

n	$-\Delta E_{n-1,n}$		$-\Delta H_{n-1,n}^0$	
	3-21+G	6-31++G(d)	HCOO^- ^a	CH_3COO^- ^b
1	21.0 (18.5) ^c [20.9] ^d	15.5	16.0	15.8
2	19.2 (16.6) ^c	14.2		12.8
3	15.1	10.8		11.8

^aM.Meot-Ner and L.W.Sieck, *J.Am.Chem.Soc.* 108(1986)7525.

^bM.Meot-Ner, *J.Am.Chem.Soc.* 110(1988)3858.

^cZero-point vibration energy was included.

^dMP2/6-31G(d,p) result in G.Alagona, C.Ghio and P.Kollman, *J.Am.Chem.Soc.* 105(1983)5226.

Table 2

The 3-21+G Optimized Structure of $\text{HCOO}^-(\text{H}_2\text{O})_n$ Cluster^a

n	HCOO^-						H_2O	
	C-H	C-O	HCO	q_{H}	q_{C}	q_{O}	O...H	q_{O}
0	1.103	1.266	115.2	0.044	0.742	-0.893		
1	1.098	1.264	115.6	0.063	0.769	-0.898	1.658	-1.084
2	1.094	1.263	115.9	0.080	0.796	-0.906	1.684	-1.078
3	1.091	1.265	116.4	0.099	0.801	-0.894	1.719	-1.076
4	1.089	1.266	116.4	0.114	0.809	-0.892	1.757	-1.068
5	1.087	1.269	116.6	0.124	0.818	-0.900	1.812	-1.053
6	1.086	1.270	116.7	0.131	0.829	-0.912	1.858	-1.048
HCOOH	1.073	1.282	117.9	0.179	0.762	-0.739		
$\text{HCOO}^-_{\text{aq}}$ ^b	1.112	1.260	116.6	0.129	0.826	-0.913		

^aMean values. Bond distances in Å; angles in degrees. q_{X} : charge on the X.

^bThe C-H and C-O bond distances were corrected from $\text{HCOO}^-(\text{H}_2\text{O})_6$ by +0.026 and -0.010 Å, respectively.

Table 3

The 6-31++G(d) Optimized Structure of $\text{HCOO}^-(\text{H}_2\text{O})_n$ Cluster^a

n	HCOO^-						H_2O	
	C-H	C-O	HCO	q_{H}	q_{C}	q_{O}	O...H	q_{O}
0	1.117	1.235	114.7	-0.044	0.812	-0.904		
1	1.112	1.235	115.2	0.016	0.824	-0.906	1.812	-1.033
2	1.107	1.235	115.5	0.032	0.838	-0.912	1.840	-1.028
3	1.104	1.236	115.8	0.045	0.841	-0.913	1.891	-1.020
4	1.101	1.237	115.7	0.056	0.846	-0.915	1.926	-1.018
HCOOH	1.083	1.253	117.6	0.138	0.817	-0.735		

^aSee Table 2.

Table 4

Enthalpy change ($-\Delta H^{298K}_{n-1,n}$) for $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ cluster (in kcal/mol)

n	6-31++G(d)	Experiment ^a
1	13.7	15.8
2	15.6	12.8
3	11.0	11.8
4	11.2	
5	8.5	
6	6.7	

^aRef. [10].

Table 5

The 6-31++G(d) optimized structure of $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ cluster^a

A. Bond lengths (Å)

n	C_2C_1	H_3C_2	O_4C_1	O_5C_1	H_6C_2	H_7C_2	H_8O_5
0	1.547	1.086	1.238	1.238	1.090	1.086	
	(1.551)	(1.095)	(1.259)	(1.260)	(1.097)	(1.097)	
1	1.540	1.085	1.230	1.248	1.087	1.087	
2	1.534	1.084	1.236	1.245	1.087	1.087	
3	1.529	1.083	1.230	1.252	1.086	1.086	
4	1.526	1.083	1.240	1.245	1.086	1.086	
5	1.524	1.082	1.231	1.255	1.086	1.086	
6	1.525	1.082	1.241	1.244	1.085	1.086	
CH_3COOH	1.501	1.080	1.189	1.332	1.084	1.084	0.953

B. Bond angles (degrees)

n	$\text{H}_3\text{C}_2\text{C}_1$	$\text{O}_4\text{C}_1\text{C}_2$	$\text{O}_5\text{C}_1\text{C}_2$	$\text{H}_6\text{C}_2\text{C}_1$	$\text{H}_7\text{C}_2\text{C}_1$
0	111.2	115.6	115.6	108.5	111.2
	(111.2)	(116.4)	(115.0)	(109.4)	(109.4)
1	111.6	117.3	114.6	109.6	109.6
2	111.5	117.3	115.3	109.4	109.6
3	111.3	118.0	115.4	109.5	109.5
4	111.3	117.8	116.3	109.2	109.7
5	111.3	118.3	115.9	109.3	109.6

6	111.8	117.9	116.3	109.6	109.1
CH ₃ COOH	109.6	125.7	112.0	109.6	109.6

^aParentheses are MP3/6-31++G(d) results.

Table 6

The charges on atoms of $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ cluster by the 6-31++G(d) basis set

n	C ₁	C ₂	H ₃	O ₄	O ₅	H ₆	H ₇	CH ₃
0	0.94	-0.70	0.19	-0.90	-0.90	0.19	0.19	-0.13
1	0.95	-0.69	0.19	-0.88	-0.92	0.19	0.19	-0.12
2	0.96	-0.69	0.20	-0.89	-0.92	0.20	0.20	-0.09
3	0.97	-0.69	0.20	-0.87	-0.95	0.20	0.20	-0.09
4	0.98	-0.70	0.20	-0.91	-0.92	0.21	0.21	-0.08
5	0.99	-0.69	0.21	-0.88	-0.97	0.21	0.21	-0.06
6	0.99	-0.70	0.21	-0.93	-0.94	0.21	0.21	-0.07
CH ₃ COOH	0.96	-0.70	0.24	-0.70	-0.79	0.24	0.23	-0.01

Table 7

The energy level of HOMO and next HOMO for $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$ cluster (a.u.)

n	HOMO	next HOMO
0	-0.187	-0.190
1	-0.200	-0.207
2	-0.238	-0.241
3	-0.259	-0.260
4	-0.277	-0.278
5	-0.291	-0.293
6	-0.305	-0.305
CH_3COOH	-0.458	-0.489

Table 8

The B3LYP/6-311++G(2d,p) optimized structure of $\text{FCOO}^-(\text{H}_2\text{O})_n$ cluster^a

n	F_2C_1	O_3C_1	O_4C_1	$\text{O}_3\text{C}_1\text{F}_2$	$\text{O}_4\text{C}_1\text{F}_2$	H_5O_3	$\text{H}_5\text{O}_3\text{C}_1$
0	1.511	1.220	1.220	111.1	111.1		
1	1.469	1.216	1.233	112.9	111.5		
2	1.441	1.227	1.227	113.0	113.0		
3	1.423	1.220	1.241	114.1	112.1		
4	1.410	1.230	1.235	113.9	113.1		
5	1.432	1.224	1.232	113.2	112.6		
6	1.413	1.231	1.231	113.3	113.3		
FCOOH	1.333	1.330	1.185	107.8	123.6	0.969	107.4

^aBond lengths in Å; bond angles and torsional angles in degrees.

Table 9

The charges on atoms of $\text{FCOO}^-(\text{H}_2\text{O})_n$ clusters from B3LYP/6-311++G(2d,p)

n	C ₁	F ₂	O ₃	O ₄
0	1.05	-0.54	-0.75	-0.75
1	1.06	-0.50	-0.73	-0.79
2	1.08	-0.47	-0.77	-0.77
3	1.09	-0.46	-0.74	-0.81
4	1.09	-0.44	-0.78	-0.79
5	1.09	-0.46	-0.75	-0.81
6	1.10	-0.44	-0.81	-0.81
FCOOH	1.10	-0.34	-0.68	-0.58

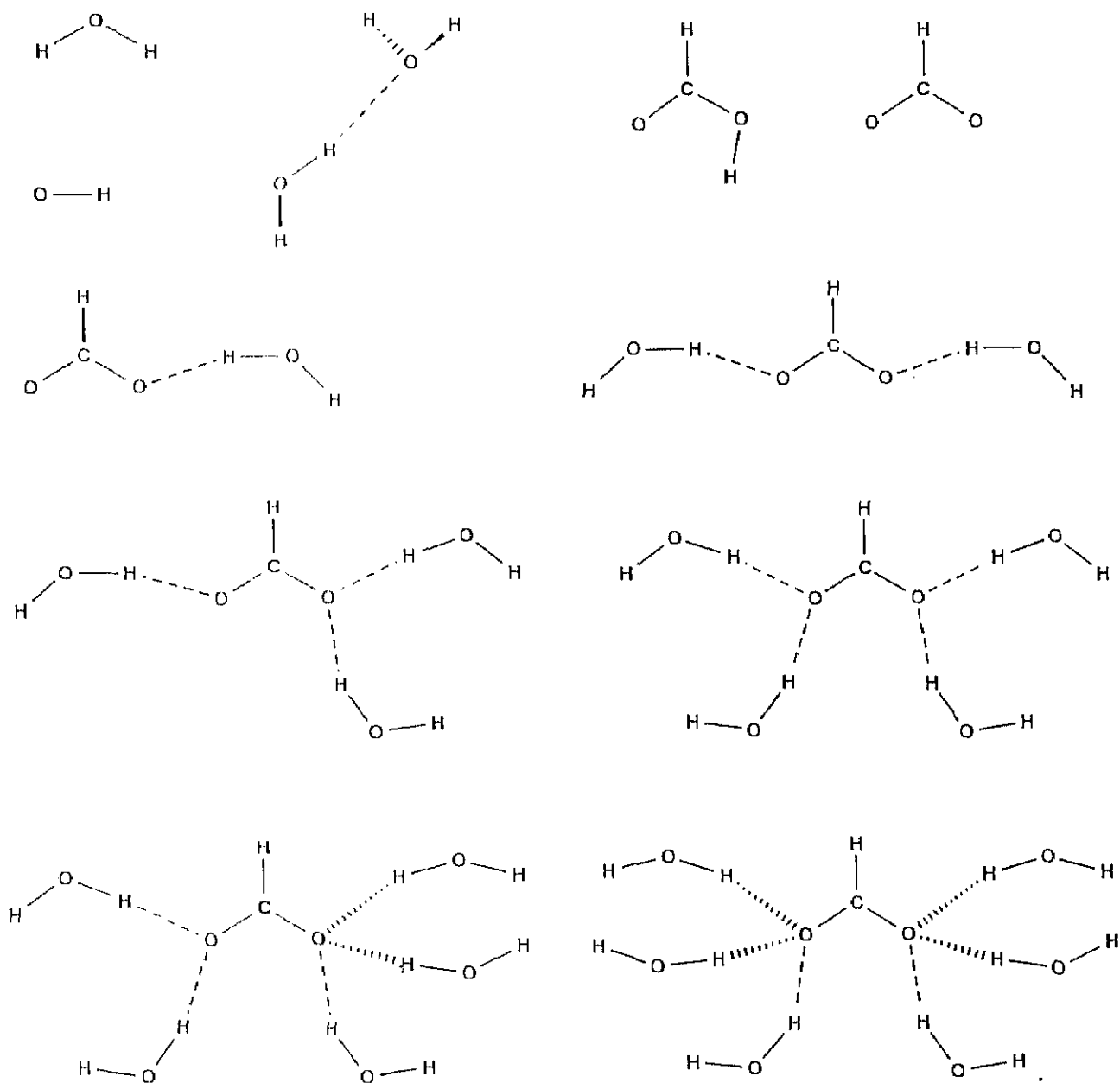


Fig. 1. The structures of $\text{HCOO}^-(\text{H}_2\text{O})_n$, $\text{H}_2\text{O}\dots\text{HCOO}^-(\text{H}_2\text{O})_6$, $\text{HCOO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$, $\text{HCOO}^-(\text{H}_2\text{O})_6(\text{OH}_2)_m$ clusters and HCOOH .

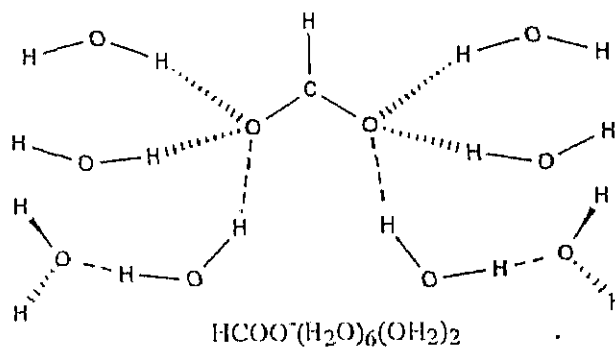
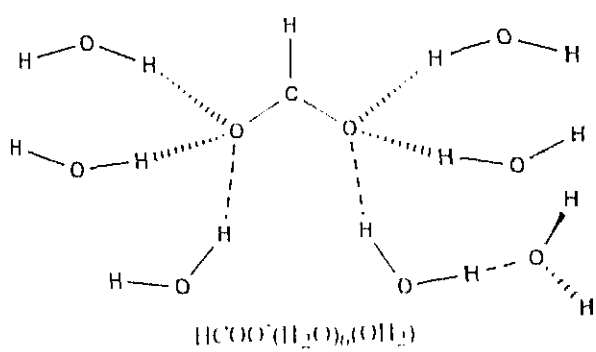
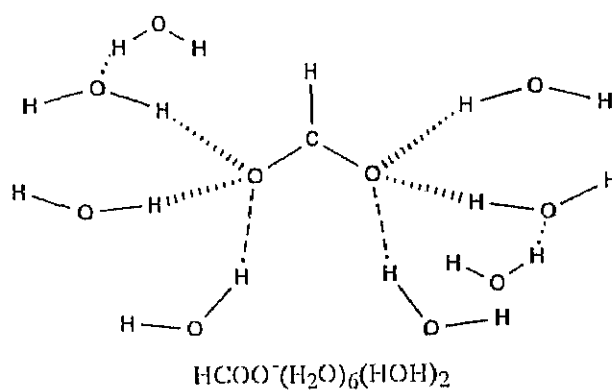
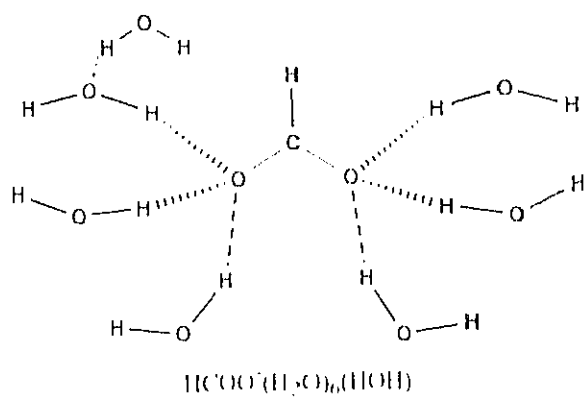
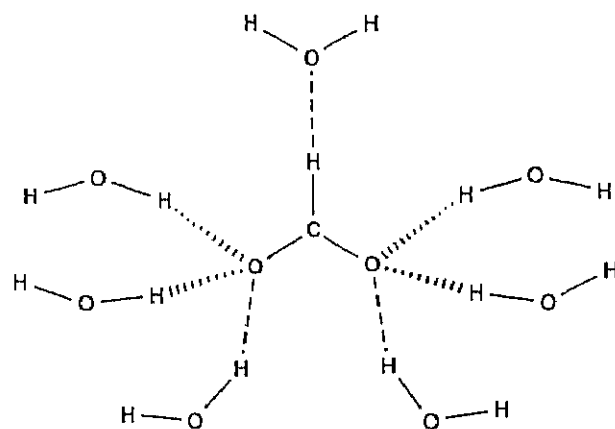


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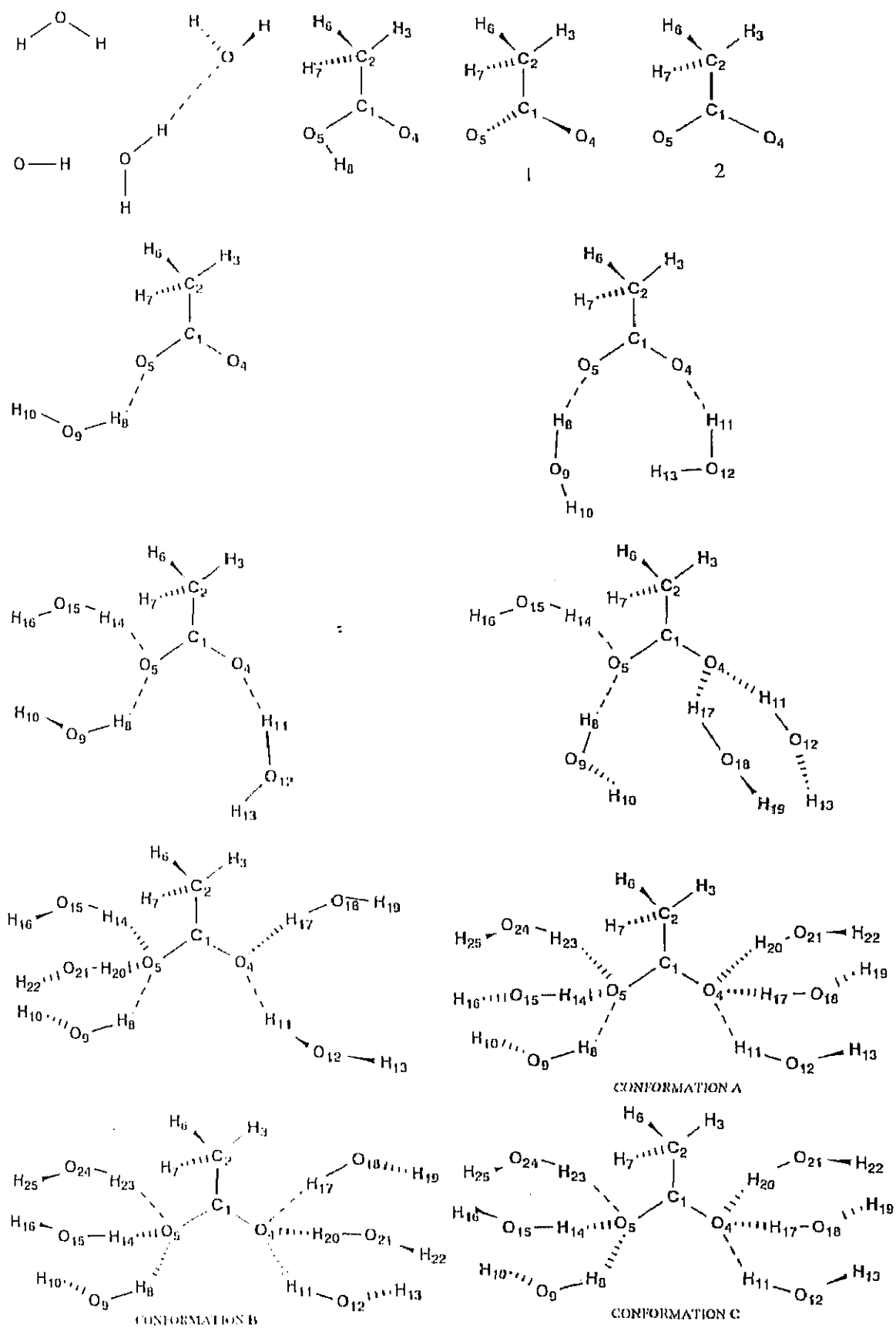


Fig. 2. The structures of $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_n$, $\text{H}_2\text{O}\dots\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_6$, $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$, $\text{CH}_3\text{COO}^-(\text{H}_2\text{O})_6(\text{OH}_2)_m$ clusters and CH_3COOH .

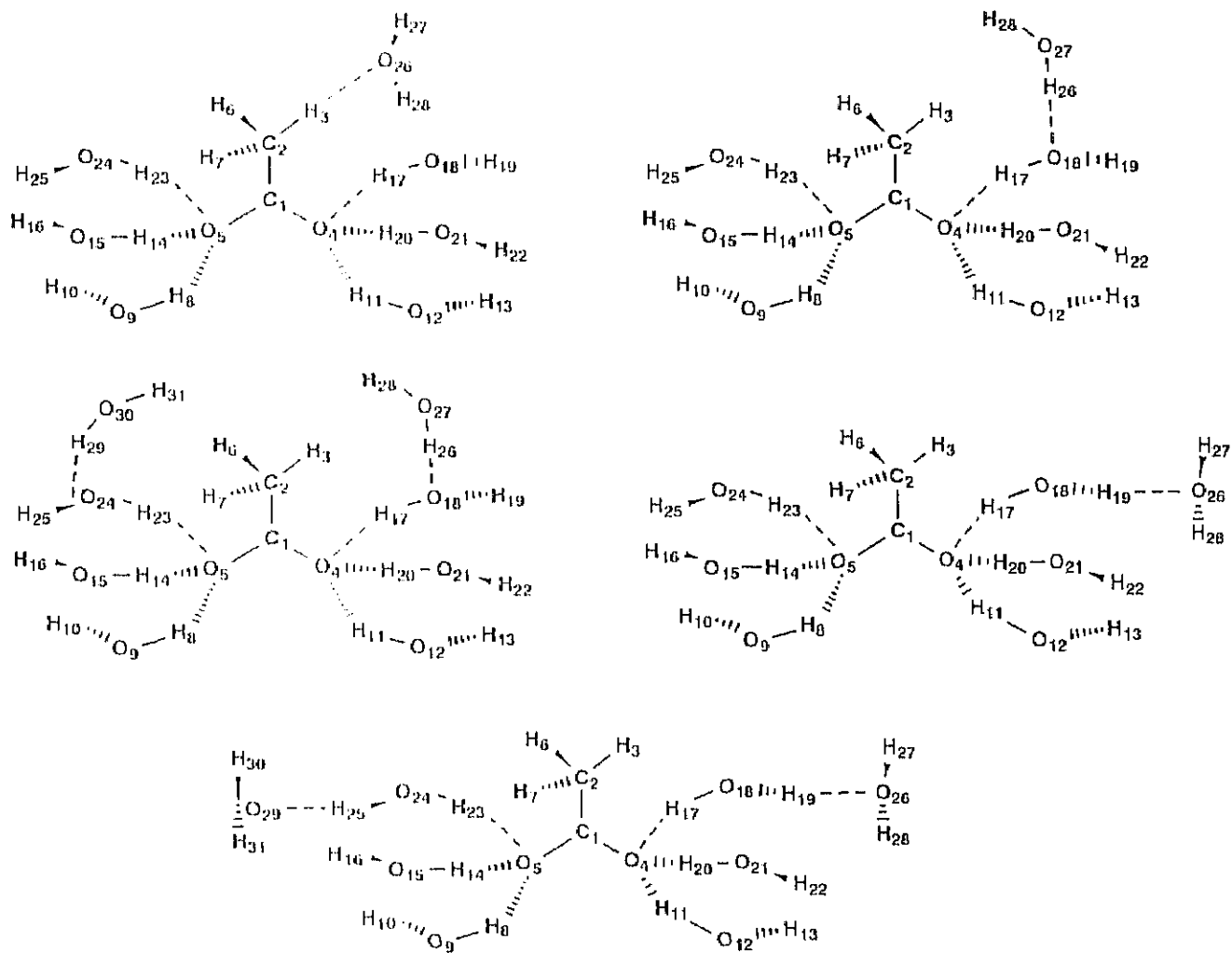


Fig. 2. Continued.

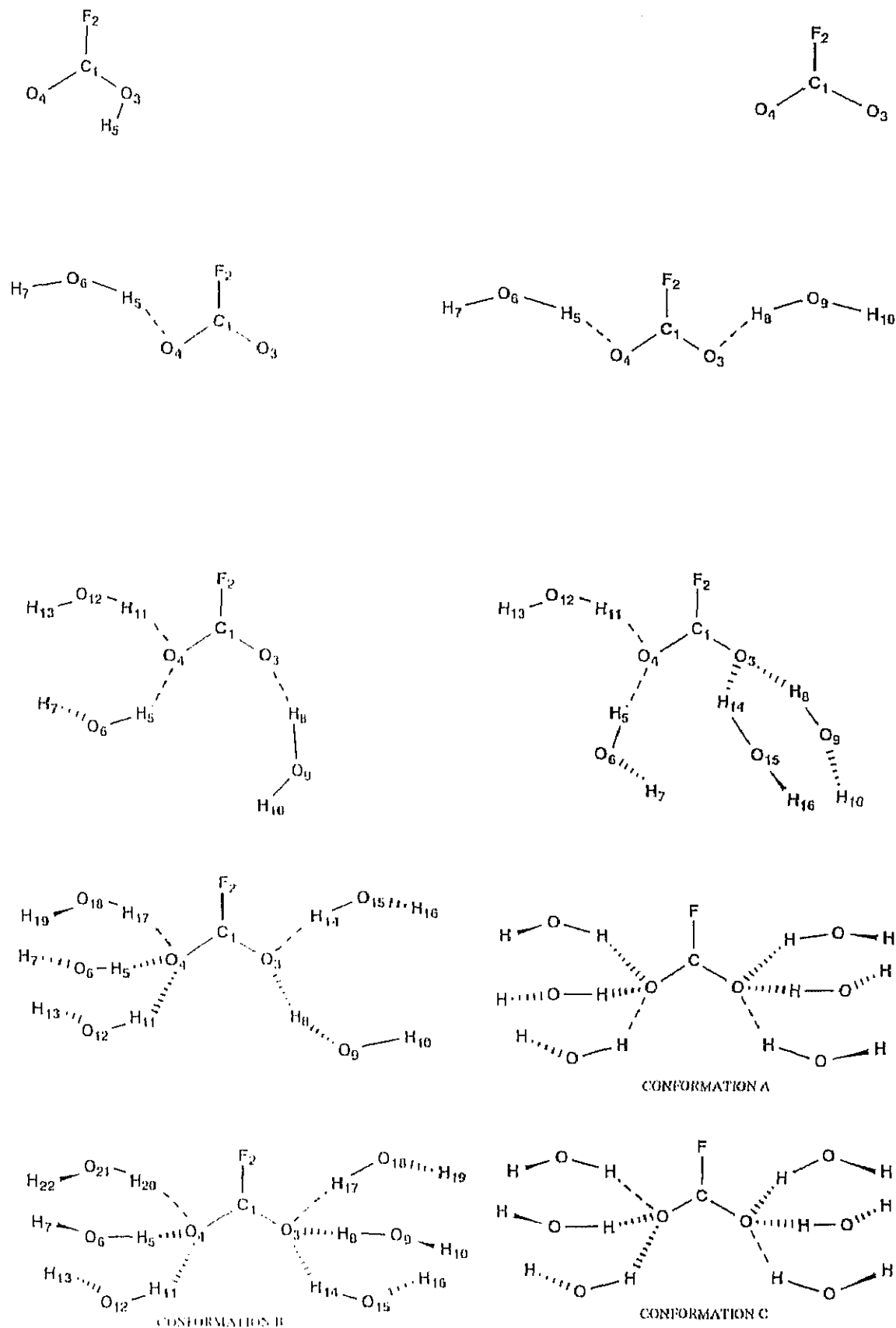
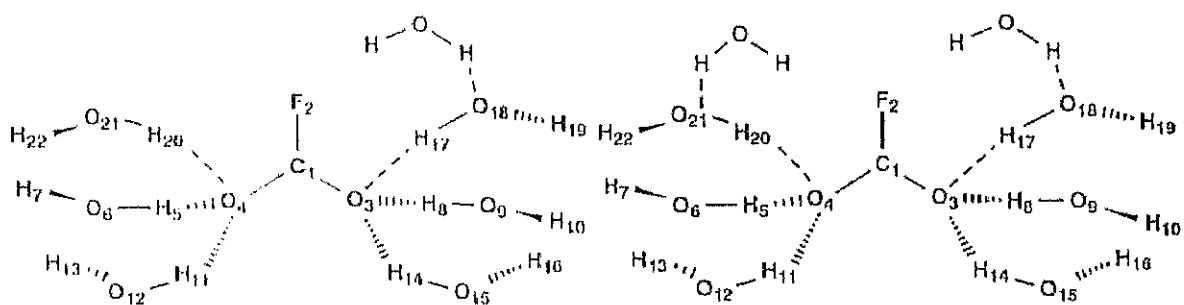
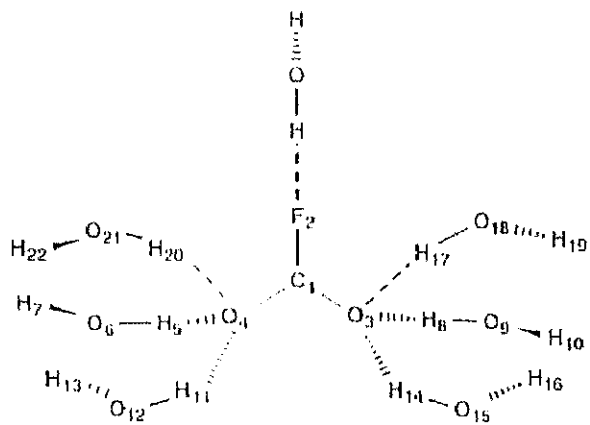


Fig. 3. The structures of $\text{FCOO}^-(\text{H}_2\text{O})_n$, $\text{H}_2\text{O}\dots\text{FCOO}^-(\text{H}_2\text{O})_6$ and $\text{FCOO}^-(\text{H}_2\text{O})_6(\text{HOH})_m$ clusters and FCOOH .



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Fig. 3. Continued.