

## ARTICLE

# Theoretical Study on Decomposition of CF<sub>3</sub>OH Catalyzed by Water Dimer and Ammonia

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The G3 and CBS-QB3 theoretical methods are employed to study the decomposition of CF<sub>3</sub>OH into FCFO and HF by water, water dimer, and ammonia. The decomposition of CF<sub>3</sub>OH into FCFO and HF is unlikely to occur in the atmosphere due to the high activated energy of 88.7 kJ/mol at the G3 level of theory. However, the computed results predict that the barrier for unimolecular decomposition of CF<sub>3</sub>OH is decreased to 25.1 kJ/mol from 188.7 kJ/mol with the aid of NH<sub>3</sub> at the G3 level of theory, which shows that the ammonia play a strong catalytic effect on the split of CF<sub>3</sub>OH. In addition, the calculated rate constants show that the decomposition of CF<sub>3</sub>OH by NH<sub>3</sub> is faster than those of H<sub>2</sub>O and the water dimer by 10<sup>9</sup> and 10<sup>5</sup> times respectively. The rate constants combined with the corresponding concentrations of these species demonstrate that the reaction CF<sub>3</sub>OH with NH<sub>3</sub> via TS4 is of great importance for the decomposition of CF<sub>3</sub>OH in the atmosphere.

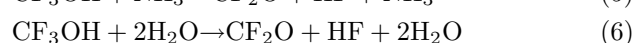
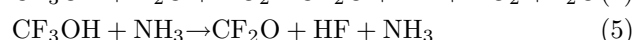
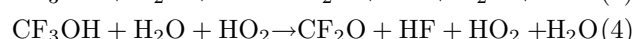
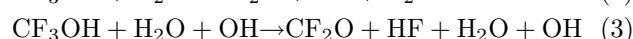
**Key words:** CF<sub>3</sub>OH, Ammonia, Quantum chemical calculation, Rate constant, Reaction mechanism

## I. INTRODUCTION

Trifluoromethanol (CF<sub>3</sub>OH) is the simplest perfluorinated primary alcohol produced as an intermediate in the atmospheric degradation of hydrofluorocarbons (HFCs) such as HFC-23, HFC-125, and HFC-143a that was about  $5.9 \times 10^{-9}$  [1–3] and hydrofluoroethers (HFEs) [4] and formed in the oxidation of fluorotelomer alcohols [4, 5] and fluorotelomer polymers [6]. In addition, the CF<sub>3</sub>O radical abstracts the hydrogen atom of the hydrocarbons [7–13] or water [14–15] and is responsible for the formation of the CF<sub>3</sub>OH.

The atmospheric mechanism of the CF<sub>3</sub>OH undergoes unimolecular decomposition to result in the formation of the carbonyl fluoride (CF<sub>2</sub>O) and hydrofluoric acid (HF) as proposed by Francisco [2, 16] and shown in reaction (1). The barrier for this reaction is calculated to be 188.7 kJ/mol by Francisco at the QCISD(T)/6-311G(2df,2p)+ZPE level [16] and 176.1 kJ/mol at the MP4/TZ2P+ZPE level by Schneider [1]. Dixon [17] and Francisco [18] recently reported the energy barrier to be 188.7 kJ/mol at

the CCSD(T)/CBS level and 192.0 kJ/mol at the CCSD(T)/6-311++G(2df,2p)//MP2/6-31G(d) level, respectively. The reaction is shown as follows:



However, there is an alternative mechanism of reaction (2) that the water molecule is used as a catalyst and responsible for the reduction of the activated barrier to 72.0 kJ/mol reported by Schneider [1] and 59.8 kJ/mol calculated by Donaldson [5] relative to the reactants. In addition, Francisco employs the quantum chemical methods to investigate another mechanism of the reaction (3) that the water molecule and HO are used as catalysts [18]. The calculated results demonstrate that the energy barrier is reduced to 46.0 kJ/mol. Additionally, computational prediction of Dixon *et al.* shows that the barrier is lowered to 36.4 kJ/mol utilizing the bimolecular HF and considers the reaction mechanism of 2CF<sub>3</sub>OH relevant to the conditions in solution [17]. In our previous work [19], we report that the activated barrier for the unimolecular decomposition of

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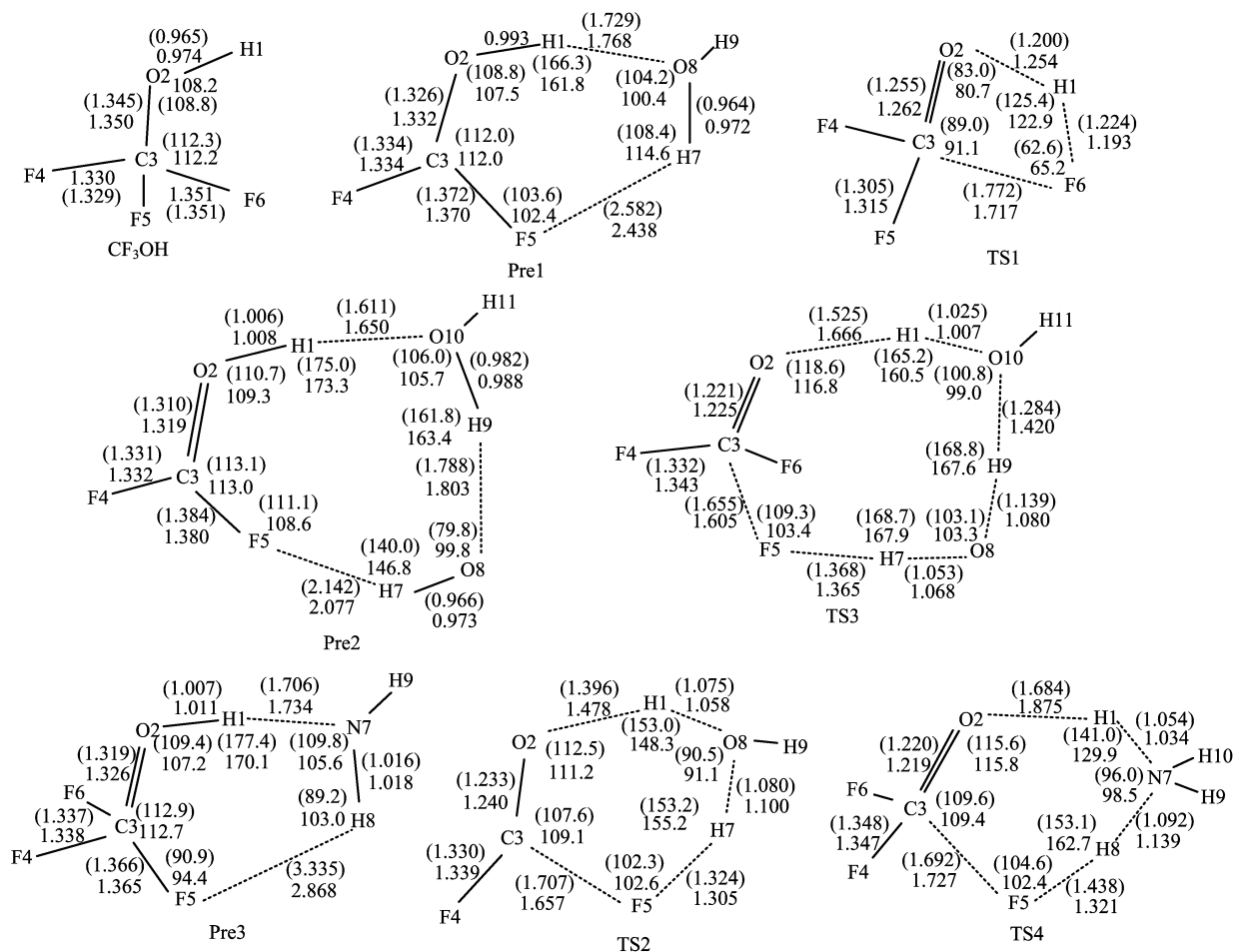


FIG. 1 The optimized geometries of the reactant and the complexes and transition states at the CBS-QB3 (in brackets) and G3 levels of theory. Bond distances in Å and angles in (°).

CF<sub>3</sub>OH is reduced from 191.2 kJ/mol to -0.4 kJ/mol for the cleavage with the HO<sub>2</sub> and H<sub>2</sub>O involved at the CCSD(T)//B3LYP/6-311G(d,p) level of theory (reaction (4)).

In this work, we apply the quantum chemical method to investigate the reaction mechanism of trifluoromethanol with NH<sub>3</sub> (reaction (5)) and a water dimer (reaction (6)). The catalytic role of the ammonia and the water dimer in split of CF<sub>3</sub>OH was evaluated.

## II. METHODS

The electronic structure calculations were performed with the Gaussian 03 [20] software. The geometries of reactants, pre-reactive complexes, transition states, intermediates and products were computed at the G3, CBS-QB3 levels of theory. The corresponding frequencies of optimized geometries were computed at the same level to prove the characters of the transition states and the stationary points. In addition, the single point energies of the stable points were refined at the G3 and CBS-QB3 levels of theory.

The rate constant was evaluated using the conventional transition state theory (CTST) [21–25] as

$$K(T) = \kappa \frac{k_B T}{h} \frac{Q_{TS}}{Q_R} \exp\left(-\frac{E_{TS} - E_R}{k_B T}\right) \quad (7)$$

where  $Q_{TS}$  and  $Q_R$  are the partition functions of the transition states and the reactants,  $k_B$  is the Boltzmann's constant,  $\kappa$  is the transmission coefficient, and  $E_{TS}$  and  $E_R$  stand for the energy of the transition state and the reactants with zero point energies involved. The tunneling factor was calculated in terms of the one-dimensional Eckart [26] correction carried out in the TheRate program [27].

## III. RESULTS AND DISCUSSION

### A. The unimolecular decomposition of CF<sub>3</sub>OH catalyzed by H<sub>2</sub>O

In order to compare the reaction mechanisms for the decomposition of the CF<sub>3</sub>OH, the split of the CF<sub>3</sub>OH into CF<sub>2</sub>O and HF is reproduced herein. From Fig.1,

TABLE I The reaction and activated energies  $\Delta E$ , enthalpies  $\Delta H$ , and free energies  $\Delta G$  for the unimolecular decomposition of  $\text{CF}_3\text{OH}$  and the reactions of  $\text{CF}_3\text{OH}$  with  $\text{H}_2\text{O}$ , water dimmer, and ammonia with zero-point correction included at 298 K (units in kJ/mol).

Compound	G3			CBS-QB3		
	$\Delta H$	$\Delta G$	$\Delta E$	$\Delta H$	$\Delta G$	$\Delta E$
$\text{CF}_3\text{OH}$	0.0	0.0	0.0	0.0	0.0	0.0
TS1	188.7	188.7	188.7	191.2	191.6	191.2
$\text{FCFO}+\text{HF}$	30.1	-13.8	27.6	31.4	-12.6	28.9
$\text{CF}_3\text{OH}+\text{H}_2\text{O}$	0.0	0.0	0.0	0.0	0.0	0.0
C2	-31.8	-5.4	-29.3	-30.5	2.9	-28.0
TS2	74.1	117.6	76.6	75.7	119.2	78.2
$\text{FCFO}+\text{C2A}$	-0.8	-18.0	-0.8	2.9	-11.3	2.9
$\text{CF}_3\text{OH}+2\text{H}_2\text{O}$	0.0	0.0	0.0	0.0	0.0	0.0
C3	-68.2	0.8	-63.2	-64.4	12.1	-59.4
TS3	20.1	100.4	25.1	19.7	105.9	24.3
$\text{FCFO}+\text{C3A}$	-30.5	-8.4	-28.0	-26.8	0.4	-24.3
$\text{CF}_3\text{OH}+\text{NH}_3$	0.0	0.0	0.0	0.0	0.0	0.0
C4	-48.5	-21.3	-46.0	-49.0	-17.2	-46.4
TS4	22.6	60.7	25.1	26.8	66.9	29.3
$\text{FCFO}+\text{C4A}$	-15.5	-28.5	-15.5	-13.8	-24.7	-13.8

it is worth noting that the geometrical parameters of the  $\text{CF}_3\text{OH}$  and the corresponding transition state are in good agreement with the MP2 calculated results [17]. In addition, the G3-optimized geometries of  $\text{CF}_3\text{OH}$  are reasonably consistent with the CBS-QBS optimized structures. From Table I the calculated barrier is 191.2 kJ/mol at the CBS-QB3 level of theory, which agrees with the value of 192.0 kJ/mol reported by Francisco [18] and the energy barrier is found to be 188.7 kJ/mol at the G3 level of theory, which is reasonably consistent with the value of 188.7 kJ/mol at the higher level reported by Dixon [17]. Thus, the energy barrier is so high that the reaction would not take place under the condition of atmosphere. Additionally, the reaction entropy and the free energy for HF elimination from monomer are 31.4 and -12.6 kJ/mol respectively at 298 K, agreeing well with results calculated by Dixon [17]. Therefore, the selected computational methods herein are reliable to describe the reaction system.

The HF elimination from  $\text{CF}_3\text{OH}$  by  $\text{H}_2\text{O}$  acting as a catalyst occur via a pre-reactive complex with a six-member ring structure involving double hydrogen bonds (C2) and proceeds through the six-member ring transition state (TS2) as depicted in Fig.1. The optimized post-complexes and products at the CBS-QB3 and G3 levels of theory are shown in Fig.2. From Fig.1, the structural parameters of the complex C2 at the G3 level are in agreement with those of the CBS-QB3 calculated results, which is reasonably consistent with the MP2 calculated results by Francisco [18]. The dihedral angle of the  $\text{H1O8H7F5}$  is  $-2.3^\circ$ , indicating that the four atoms approximately lay in the same plane. The bond length of  $\text{H1}\cdots\text{O8}$  is about 0.7 Å shorter than

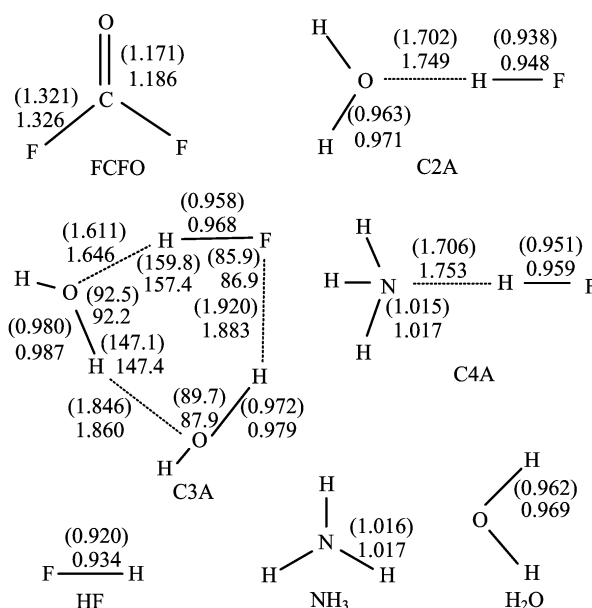


FIG. 2 The optimized post-complexes and products at the CBS-QB3 (in brackets) and G3 levels of theory. Bond distances in Å and angles in  $^\circ$ .

that of the  $\text{H7}\cdots\text{F5}$  in C2, reflecting that the bond strength of the  $\text{H1}\cdots\text{O8}$  is stronger than that of the  $\text{H7}\cdots\text{F5}$ . The binding energy is calculated to be -29.3 and -28.0 kJ/mol at the G3, CBS-QB3 levels of theory, which is agreeable with the value of -28.9 kJ/mol at the CCSD(T)/6-311++G(2df,2p)//MP2/6-31G(d) level by Francisco [18]. From Fig.1, The optimized geometries of the transition state (TS2) agree well with each other

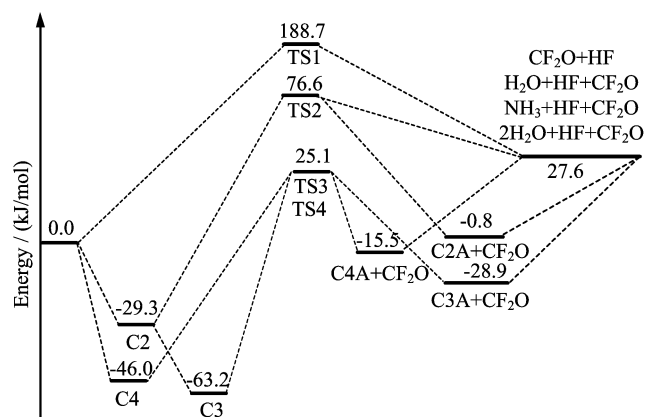


FIG. 3 The calculated potential energy profile at the G3 level of theory.

at the G3 and CBS-QB3 levels of theory. The energy barrier via TS2 is 76.6 and 78.2 kJ/mol at the G3, CBS-QB3 level of theory respectively, which is agreeable with the reported value of 82.0 kJ/mol at the CCSD(T)/6-311++G(2df,2p)//MP2/6-31G(d) level by Francisco [18], indicating that the single water molecule could play a catalytic role in decomposition of  $\text{CF}_3\text{OH}$ .

In addition, the intermediate product C2A is decomposed into water and HF due to the direct collision in the atmosphere as shown in Fig.3.

### B. The decomposition of $\text{CF}_3\text{OH}$ by water dimer

Herein, the water dimer is selected to estimate the role in the decomposition of  $\text{CF}_3\text{OH}$  because the water dimer may reduce the energy barrier and enhance the rate constant, which has been observed in the reactions of  $\text{H}_2\text{COO}$  [28],  $\text{CH}_2=\text{C}=\text{CN}$  [29],  $\text{SO}_3$  [30],  $\text{HCONH}_2$  [31],  $\text{N}_2\text{O}_5$  [32],  $\text{ClONO}_2$  [33],  $\text{CH}_2\text{O}$  [34], and peroxyacetyl nitrate [35]. The reaction occurs via the eight-member ring pre-reactive complex (C3) and proceeds by the eight-member ring transition state structure as displayed in Fig.1. The complex C3 with three hydrogen bonds is found to be  $-63.2$  and  $-59.4$  kJ/mol at the G3 and CBS-QB3 levels of theory, which is about two times stronger than the corresponding complex C2 as listed in Table I. From Fig.1, the H1O10 hydrogen-bonded interaction is stronger than those of H9O10 and H7F5 from the structural parameters because the H1O10 is shorter than those of the H9O10 and H7F5 respectively. The energy barrier by TS3 is reduced to be 25.1 kJ/mol from 188.7 kJ/mol relative to the reactants at the G3 level of theory. The formed post-complex C3A (Fig.2) with a binding energy of  $-55.6$  kJ/mol would not decompose into the water dimer and HF at the G3 level. The computed potential profile shows the reaction mechanism of decomposition of  $\text{CF}_3\text{OH}$  by the water dimer as provided in Fig.3.

### C. The decomposition of $\text{CF}_3\text{OH}$ by $\text{NH}_3$

The elimination of  $\text{CF}_3\text{OH}$  into HF and FCFO by ammonia proceeds via the pre-reaction complex (C4) and the corresponding transition state (TS4) is displayed in Fig.1. The C4 is a six-membered ring structure with one hydrogen bond between H1 and N7 and one weak interaction between F5 and H8. From the Fig.1, it is noted that the two methods used herein are not agreeable with each other, especially characterizing the interaction of F5 and H8. The F5H8 bond length is 2.868 Å at the G3 level of theory, whereas the bond distance is 3.335 Å. The interaction between  $\text{CF}_3\text{OH}$  and  $\text{NH}_3$  is predominated by the strength between H1 and N7 because the calculated geometries show that the H1N7 bond length is 0.034 Å shorter than that of H1O8 in complex C2. The calculated binding energy of C4 is  $-46.0$  and  $-46.4$  kJ/mol at the G3 and CBS-QB3 level respectively, which is about 13.0 kJ/mol lower than that of the C2.

The transition state is a six-member ring structure that the O2H1N7H8F5C3 six atoms are approximately in the same plane, which is similar to the structure of TS2. The energy barrier is 25.1 and 29.3 kJ/mol at the G3 and CBS-QB3 level of theory relevant to reactants respectively, which is about 163.0 kJ/mol lower than that of TS1 [1, 5, 18]. In addition, the barrier of TS4 is 23.0 kJ/mol lower than that of decomposition by the HF dimer reported by Dixon [17]. The post-reaction complex C4A is located as shown in Fig.1. The computed results show that the C4A has the binding energy of  $-43.1$  kJ/mol relative to the  $\text{NH}_3$  and HF as shown in Fig.2.

### D. Kinetics and the atmospheric implication

To clarify the importance of the reactions mentioned above in the atmosphere, the rate constants of TS2, TS3, and TS4 are reported herein with the temperature range of 220–320 K as listed in Table II. The rate constant of decomposition of  $\text{CF}_3\text{OH}$  by  $\text{H}_2\text{O}$  is  $3.35 \times 10^{-27}$  and  $4.11 \times 10^{-27}$   $\text{cm}^3/(\text{molecule s})$  at the G3 and CBS-QB3 levels of theory at 298 K, which agrees with each other. The rate constant of TS3 is  $2.68 \times 10^{-23}$   $\text{cm}^3/(\text{molecule s})$ , which is  $10^4$  greater than that of TS2, whereas the rate constant of TS4 with  $1.73 \times 10^{-18}$   $\text{cm}^3/(\text{molecule s})$  is  $10^9$  faster than that of TS2 at the G3 level of theory. If the decomposition of  $\text{CF}_3\text{OH}$  by  $\text{NH}_3$  plays an important role in atmosphere, the concentration of  $\text{NH}_3$  is  $10^{-9}$  and  $10^{-5}$  greater than those of the water and the water dimer respectively. Moreover, the typical values of these concentrations of  $\text{H}_2\text{O}$ , the water dimer [36, 37] and ammonia [37] are  $10^{17}$  and  $10^{14}$ , and  $10^{12}$   $\text{molecule}/\text{cm}^3$  respectively, which indicates that the concentration of  $\text{NH}_3$  is  $10^{-5}$  and  $10^{-2}$  greater than the corresponding the water and the water dimer. Therefore, the split

TABLE II The rate constant ( $K$ ,  $\text{cm}^3/(\text{molecule s})$ ) for individual reaction pathway at different temperature.

	Method	220 K	240 K	260 K	280 K	298 K	320 K
$K_{\text{TS2}}$	G3	$1.03 \times 10^{-31}$	$2.69 \times 10^{-30}$	$4.38 \times 10^{-29}$	$4.90 \times 10^{-28}$	$3.35 \times 10^{-27}$	$2.58 \times 10^{-26}$
	CBS-QB3	$1.31 \times 10^{-31}$	$3.36 \times 10^{-30}$	$5.42 \times 10^{-29}$	$6.02 \times 10^{-28}$	$4.11 \times 10^{-27}$	$3.14 \times 10^{-26}$
$K_{\text{TS3}}$	G3	$8.34 \times 10^{-26}$	$5.23 \times 10^{-25}$	$2.47 \times 10^{-24}$	$9.33 \times 10^{-24}$	$2.68 \times 10^{-23}$	$8.13 \times 10^{-23}$
	CBS-QB3	$7.51 \times 10^{-25}$	$3.28 \times 10^{-24}$	$1.14 \times 10^{-23}$	$3.32 \times 10^{-23}$	$7.75 \times 10^{-23}$	$1.89 \times 10^{-22}$
$K_{\text{TS4}}$	G3	$3.17 \times 10^{-20}$	$1.10 \times 10^{-19}$	$3.22 \times 10^{-19}$	$8.17 \times 10^{-19}$	$1.73 \times 10^{-18}$	$3.83 \times 10^{-18}$
	CBS-QB3	$1.09 \times 10^{-21}$	$5.02 \times 10^{-21}$	$1.85 \times 10^{-20}$	$5.72 \times 10^{-20}$	$1.41 \times 10^{-19}$	$3.68 \times 10^{-19}$

of  $\text{CF}_3\text{OH}$  by  $\text{NH}_3$  is the most preferable in the atmosphere.

Additionally, it is pointed out that the reaction of ammonia with  $\text{CF}_3\text{OH}$  is more kinetically favored than the corresponding reaction of  $\text{CF}_3\text{OH}$  with the  $\text{HO}_2 \cdots \text{H}_2\text{O}$  complex [19], whereas the barrier of TS4 is higher than the  $\text{CF}_3\text{OH} + \text{HO}_2 \cdots \text{H}_2\text{O}$  by about 25.1 kJ/mol. The lower energy barrier reported in Ref.[19] feasibly leads to the decomposition of  $\text{CF}_3\text{OH}$  via the excited OH overtone in the  $\text{CF}_3\text{OH}$  reaction with the  $\text{HO}_2 \cdots \text{H}_2\text{O}$  complex.

#### IV. CONCLUSION

The decomposition of  $\text{CF}_3\text{OH}$  by water, water dimer, and ammonia is investigated using the quantum chemical methods and the conventional transition state theory. The calculated results demonstrate that the barrier of decomposition of  $\text{CF}_3\text{OH}$  into HF by water dimer and ammonia is reduced to 25.1 and 29.3 kJ/mol from 188.7 kJ/mol at the G3 level. The rate constant of TS4 is  $1.73 \times 10^{-18} \text{ cm}^3/(\text{molecule s})$ , which is  $10^9$  and  $10^5$  times by those of TS2 and TS3 respectively. Thus, the decomposition of  $\text{CF}_3\text{OH}$  by  $\text{NH}_3$  is preferred in the atmosphere. In addition, the theoretical calculations predict that the ammonia plays a stronger catalytic role than the water molecule in the decomposition of  $\text{CF}_3\text{OH}$ . Therefore, the investigation might also provide a new insight on whether the ammonia is more reactive than the water molecule in the water-catalyzed the singlet dioxygen reaction [38]. It is noted that that reaction mechanism of  $\text{CF}_3\text{OH}$  with ammonia is similar to the reaction of  $\text{H}_2\text{O}_2$  with  $\text{O}_3$  [39].

#### V. ACKNOWLEDGMENTS

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