# Ab Initio and RRKM Calculations for the Reaction Channels of $O(^{1}D) + CH_{3}CHF_{2}$

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**ABSTRACT:** Ab initio and Rice–Ramsperger–Kassel–Marcus theories are carried out to study the potential energy surface and the energy-dependent rate constants and branching ratios of the products for  $O(^{1}D) + CH_{3}CHF_{2}$  reaction. Optimized geometries and vibrational frequencies have been obtained by MP2/6-311G(d,p) method. The main products of the title reaction are CH<sub>3</sub>CFO + HF, CH<sub>2</sub>CFOH + HF, and CH<sub>3</sub> + CF<sub>2</sub>OH at lower collision energy; and CH<sub>3</sub> + CF<sub>2</sub>OH, CH<sub>3</sub>CF<sub>2</sub> + OH are the main products at higher collision energy. CHF<sub>2</sub> + CH<sub>2</sub>OH are the main products in the whole range of collision energy. © 2011 Wiley Periodicals, Inc. Int J Quantum Chem 112: 1353–1362, 2012

**Key words:** energy-dependent rate constant; RRKM; O(<sup>1</sup>D) + CH<sub>3</sub>CHF<sub>2</sub>; branching ratio

#### **1. Introduction**

C oncerns about the detrimental effects of chlorinated hydrocarbons on the Earth's ozone layer have focused attention on the environmental acceptability of nonchlorinated substitutes for many industrial chemicals. Hydrofluorocarbon

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(HFC) compounds are used as substitutes for the ozone-destroying chlorofluorocarbon (CFC) compounds [1–7]. HFCs do not lead to ozone destruction, because they do not contain C1 or Br atoms that participate in the catalytic ozone destruction cycles. However, such fluorinated hydrocarbons can be strong absorbers of infrared radiation, thus, raising concern about their possible roles as greenhouse gases [8]. Therefore, the reaction rate coefficient of HFC with  $O(^{1}D)$  atom plays the important role of controlling the atmospheric lifetime of the HFCs [9] and the significance to atmospheric and combustion chemistry. It is essential to study the mechanism of HFCs with  $O(^{1}D)$  and to forecast the products of the reactions.

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There are several groups who have studied the reaction of HFC with O atom. Kono et al. [1] have studied the reaction process of O(<sup>1</sup>D) with CH<sub>3</sub>CHF<sub>2</sub> (HFC-152a) by laser-induced fluorescence techniques and obtained the branching ratio of OH in the reaction of  $O(^{1}D) + CH_{3}CHF_{2}$  to be about 15%. Rate coefficient of  $O(^{1}D) + CH_{3}CHF_{2}$ was determined from the decay curve of  $O(^{1}D)$ signal to be (20.2  $\pm$  1.5)  $\times$  10<sup>-11</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> [1]. Zhang et al. [9] and Liu et al. [10] have studied the kinetics and mechanism of  $O(^{3}P)$  + CH<sub>3</sub>CHF<sub>2</sub> using ab initio direct dynamics methods. Based on their calculations, the  $O(^{3}P)$  + reveals H-abstraction  $CH_3CHF_2$ reaction mechanism.

To date, no direct theoretical study of the  $O(^{1}D) + CH_{3}CHF_{2}$  reaction have been reported. In this article, ab initio calculations based on QCISD(T)/6-311++G(d,p)//MP2/6-311G(d,p) method have been performed to explore the ground state potential energy surface of the  $O(^{1}D) + CH_{3}CHF_{2}$  reaction. The Rice–Ramsperger–Kassel–Marcus (RRKM) theory has been used to study the branching ratios of the products, and the results have been compared with earlier researches.

## 2. Quantum Mechanical Calculations and Results

Geometries of the reactants, products, intermediates, and transition states have been optimized at the second-order Moller-Plesset perturbation MP2/6-311G(d,p) [11, 12] level of theory. Vibrational frequencies, also calculated at the MP2/6-311G(d,p) level, have been used to characterize stationary points, zero-point energy (ZPE) corrections, and rate constant calculations. The numbers of imaginary frequencies for intermediates and transition states are 0 and 1, respectively. All the tight transition states are verified by the intrinsic reaction coordinate calculations. The energies of the stationary points are refined at QCISD(T)/6-311++G(d,p) [13, 14] level. All the calculations have been carried out using the Gaussian 03 [15] suit of programs.

The optimized geometries of various stationary points are presented in Figure 1 along with the available experimental data [16–18]. The calculated geometries of  $H_2$ , OH, and  $H_2O$  are in good agreement with the corresponding experimental values. Vibrational frequencies (scaled by a factor of 0.9496 [19]) and moments of inertia are listed in Table I. Table II contains energies and molecular parameters for variational transition states obtained using the microcanonial variational transition state theory (MVTST) approach. The potential energy profile is depicted in Figure 2. Note that the energy of the reactants is set to zero as a reference. Unless stated, the energy differences below are all at the QCISD(T) level with ZPE corrections at the MP2/6-311G(d,p) level of theory.

As shown in Figure 2, a typical insertion-elimination mechanism for  $O(^{1}D) + CH_{3}CHF_{2}$  reaction is revealed.  $O(^{1}D) + CH_{3}CHF_{2}$  reaction produces three intermediates, CH<sub>3</sub>CHFOF, IM1, and IM2. The  $O(^{1}D) + CH_{3}CHF_{2}$  reaction is largely exothermic and occurs without an entrance barrier except the formation of CH<sub>3</sub>CHFOF. The formation of  $CH_3CHFOF$  is the O(<sup>1</sup>D) atom inserting into one of the C-F bonds of CH<sub>3</sub>CHF<sub>2</sub> via transition state TS0. The barrier of the process is 20.8 kcal/mol. IM1 and IM2 form via O(<sup>1</sup>D) directly inserting into one of the C-H bonds of CH<sub>3</sub>CHF<sub>2</sub>. The C-O and O-F bonds in CH<sub>3</sub>CHFOF are 1.389 and 1.437 Å, respectively. The newly formed C-O bonds in IM1 and IM2 are 1.360 and 1.414 Å, respectively. The distance of H-O bonds in IM1 and IM2 are 0.964 and 0.958 Å, respectively. The energies of CH<sub>3</sub>CHFOF, IM1, and IM2 are 59.0, 155.4, and 134.8 kcal/mol, respectively, lower than  $O(^{1}D) + CH_{3}CHF_{2}$ . So,  $CH_{3}CHFOF$ , IM1, and IM2 should be highly chemical activated complexes and can undergo various possible production channels. Two production channels of CH<sub>3</sub>CHFOF, eight production channels of IM1, and ten production channels of IM2 have been found and will be discussed below.

#### 2.1. PRODUCTION PATHWAYS OF CH<sub>3</sub>CHFOF

$$H_3CHFOF \rightarrow [TS1] \rightarrow CH_3CFO + HF$$
 (1)

$$CH_3CHFOF \rightarrow [TS2] \rightarrow IM1$$
 (2)

Channel (1) is HF-elimination process leading to  $CH_3CFO + HF$  through the transition state TS1, located 30.9 kcal/mol higher with an imaginary frequency of 2216.7i cm<sup>-1</sup>. TS1 is a four-membered ring structure. The breaking  $C_2$ -H<sub>5</sub> and  $F_4$ -O<sub>6</sub> bonds are elongated to 1.231 and 1.845 Å, respectively. The forming H<sub>5</sub>-F<sub>4</sub> bond is 1.553 Å. Channel (2) involves the isomerization to IM1 via tight transition state TS2, located 35.8 kcal/mol

C

higher. TS2 is a four-membered ring structure. The breaking  $C_2$ —H<sub>5</sub> and  $F_4$ —O<sub>6</sub> bonds are elongated to 1.391 and 1.742 Å, respectively. The forming  $C_2$ —F<sub>4</sub> and O<sub>6</sub>—H<sub>5</sub> bonds are 2.521 and 1.136 Å, respectively.

TS8

#### 1.437 0.958 $_{1.092}$ $H_{8}$ 0.964 $O_3^-$ O3-H5 H<sub>8</sub>//// $O_3 - H_5$ $H_8 / \frac{1.090}{100}$ $F_8 / \frac{1.358}{11}$ 1.091 1.389 H. 1.091 1.414 1.360, 4 1.503 $C_{1_{1.501}}$ H<sub>2</sub> H H $C_{1}_{1.509}$ 1.365 1 374 $H_0$ <sup>1</sup>1.511 $F_7$ 1.091 /1.091 1.369 H<sup>1.091</sup> 1.089 1364 . F<sub>6</sub> $F_4$ $H_6$ 1.365 $H_4$ $H_6$ $H_4$ $F_6$ A(7,2,1)=109.9 D(9,1,2,7)=175.4 A(6,2,1)=110.5 D(9,1,2,7)=177.7 A(9,1,2)=109.2 D(8,1,2,6)=-177.7 A(6.2,1)=108.0 D(9.1.2,7)=-172.2 $\begin{array}{l} A(9,1,2) = 110.6 \quad D(8,1,2,6) = -175.8 \\ A(3,2,1) = 105.3 \quad D(9,1,2,3) = -65.6 \end{array}$ A(2,3,5)=107.1 D(8,1,2,6)=-168.7 D(5,1,2,8)=-180.0 A(3,2,1)=110.9 D(9,1,2,3)=-60.1A(2,3,5)=106.7 D(1,2,3,5)=-180.0A(3,2,1)=106.7 D(9,1,2,3)=-50.9 A(8,1,2)=110.2 D(1,2,3,5)=-166.6 D(3,1,2,7)=180.0D(4,1,2,6)=-180.0A(2,3,5)=105.6 D(1,2,3,5)=168.0 A(4,1,2)=108.4 D(4,1,2,3)=174.1 A(4,1,2)=108.9 D(4,1,2,3)=180.0 A(4,1,2)=108.8 D(4,1,2,3)=-171.7 IM2(CHF<sub>2</sub>CH<sub>2</sub>OH) CH<sub>3</sub>CHFOF IM1(CH<sub>3</sub>CF<sub>2</sub>OH) CH<sub>3</sub>CHF<sub>2</sub> 1.329 F<sub>3</sub> 1.373 F<sub>3</sub> 1.326 $F_3$ 1.489 $C_2$ 1.273H7 // "<sup>H</sup>3 H- ${\rm H}_7$ $\frac{1.489}{C_2}$ H-1.529 C 1.231 H<sub>5</sub> H<sub>8</sub> H. H 1.4821.273 Н 1.553 1.792 2.521 1.779 > H5 $F_4$ 1.268 $-F_4$ H' 06 H<sub>0</sub> . O<sub>6</sub>-06 2.035 F<sub>6</sub> 1.136 <sup>1.214</sup> H<sub>5</sub> · 1.180 1.845 F<sub>4</sub> 1.742 05-1.514 A(1,2,3)=110.8 D(1,2,3,6)=-140.9 A(1,2,3)=113.7 D(1,2,3,6)=-147.1 A(1,2,3)=112.7 D(1,2,3,6)=-154.6 A(1,2,6)=119.2 D(2,6,4,5)=-9.4 A(6,2,5)=92.7 D(5,2,1,7)=-62.9 A(1,2,3)=117.1 D(1,2,3,6)=-108.2 A(1,2,6)=120.9 D(2,5,6,4)=89.4 A(1,2,6)=124.2 D(2,6,5,4)=3.0 A(6,2,4)=88.3 D(4,2,1,7)=-65.3 D(5,2,1,7)=-62.9A(1,2,6)=108.9 D(2,6,5,4)=-25.5 A(6,2,5)=49.4 D(5,2,1,7)=-108.9 D(3,2,1,8)=-68.4 A(6,2,4)=116.8 D(4,2,1,7)=158.8A(2,5,4)=109.4 D(3,2,1,8)=-65.8 A(2,5,6)=62.1 A(2,4,5)=61.4 D(3,2,1,8)=-166.9 A(5,4,6)=63.6 D(9,1,2,3)=174.8 A(2,6,5)=75.5 D(3,2,1,8)=-48.0 A(2,4,6)=29.5 D(9,1,2,3)=174.2 A(4,5,6)=128.6 D(9,1,2,3)=74.8 A(4,2,5)=91.2 D(9,1,2,3)=-168.7 TS1 TS<sub>2</sub> TS3 TS0 H<sub>5</sub>0.963 , 1.3291 .C.' <sup>Н</sup>7/, H<sub>8</sub>/// 1.357 O<sub>3</sub> $\mathcal{L}_{C_1}$ 1.311 F<sub>2</sub> H. 1.301 1.417 H $^{1.224}$ $-C_{1.520}^{1.520}C_{6}$ H <sup>1.361</sup> F<sub>6</sub> ▼O<sub>3'</sub>///H<sub>5</sub> H<sub>8</sub> 0.868 H<sub>9</sub><sup>1.231</sup> 1.980 1.302 0.967 1.291 1.382 1.507 1.768 $H_6$ 1.897 H<sub>6</sub> $H_9$ $H_5$ $H_5$ 0.969 $F_4$ . H. H9~ $F_4$ $F_{4_{1.249}}$ A(2,3,5)=104.8 D(7,1,2,3)=84.7 A(1,2,7)=120.5 D(1,2,3,5)=160.6 A(1,2,4)=87.6 D(1,2,3,7)=-165.8 A(1,2,4)=109.3 D(9,1,2,4)=-41.8A(1,2,3)=109.5 D(6,2,1,7)=-35.6A(1,2,3)=116.0 D(1,2,9,4)=2.2 A(1,2,3)=95.6 D(1,2,3,9)=2.2 A(2,3,9)=68.3 D(5,3,2,4)=-15.2 A(1,9,3)=123.9 D(6,2,1,7)=143.1 D(1,2,3,7) = -165.8A(2,1,4)=90.8 D(5,3,2,1)=-122.0 A(1,2,9)=74.8 D(6,2,1,7)=149.1 A(2,4,6)=58.8 D(1,2,4,6)=0.1 A(8,1,9)=41.4 D(1,2,3,4)=120.7 A(4.6.1)=135.0 $\begin{array}{l} A(5,3,2) = 106.7 \quad D(8,1,2,3) = -156.2 \\ A(7,1,2) = 120.1 \quad D(6,2,3,5) = 98.1 \end{array}$ D(8, 1, 2, 3) = 149.3A(1,8,9)=69.7 D(1,2,3,5)=39.1 A(1,2,4)=120.7 D(8,1,2,4)=-143.9 A(2,3,5)=108.4 D(9,1,2,4)=109.4 A(9,3,5)=111.1 D(6,2,3,5)=-128.6 TS6 TS7 TS4 TS5 $H_9$ 1.314 O3 1.437 <sup>1.342</sup>.O₃♥H<sub>7</sub> H<sub>8</sub>///, 360 1.418 H<sub>6</sub> H<sub>5</sub> 0.971 1.527 1 512 H<sub>5</sub>0.966 .172 H<sub>9</sub> $\frac{1.368}{1.433}$ (2.1.363)<sup>г</sup>л<sub>Н7</sub> **'**O<sub>3</sub> 1350 1367 $\mathbf{F}_{4}$ 1.256 1.396 1368 C 21.363 1357 1.745 2 074 1.754 $H_6$ 1.638 $H_6$ H<sub>5 0.833</sub> E. $H_{5} O_{3 1.105}$ . 1297 A(7,2,5)=95.6 D(4,1,2,3)=-54.7 $H_4$ A(5,2,3)=109.9 D(2,3,6,5)=-0.6 A(6,2,5)=27.9 D(4,1,2,3)=-163.5 A(2,3,6)=54.2 D(8,1,2,7)=40.0 A(1,2,3)=118.2 D(1,2,3,6)=108.5 A(2,3,5)=104.3 D(7,1,2,3)=-169.4 A(2,1,3)=95.7 D(1,2,9,3)=0.8 A(1,2,4)=107.7 D(9,1,2,4)=100.5 A(1,2,3)=111.7 D(6,2,1,7)=71.6 A(2,9,3)=118.5 D(5,3,1,2)=-101.9 A(4,1,2)=110.1 D(4,1,2,7)=159.7 A(935)=1065 D(6217)=1375A(8,1,9)=30.1 A(1,8,9)=32.5 D(1,2,3,4)=122.4 D(1,2,3,5)=50.6 A(1,2,4)=115.3 D(8,1,2,4)=-143.0A(4,1,2)=110.1 D(1,2,6,5)=-50.3 **TS11** A(1,2,6)=115.9 D(6,2,9,3)=-110.4

**FIGURE 1.** The optimized MP2/6-311G(d,p) geometrical parameters for the stationary points on the potential energy surface. The distances are in Å, the angles are in degrees. The values in the parentheses are the experimental values [16–18].

TS9

**TS10** 

#### 2.2. DECOMPOSITION CHANNELS OF IM1

$$IM1 \rightarrow [TS3] \rightarrow CH_3CFO + HF$$
 (3)

$$IM1 \rightarrow [TS4] \rightarrow CH_2CFOH + HF$$
 (4)

 $IM1 \rightarrow [TS5] \rightarrow CH_2CF_2 + H_2O \tag{5}$ 



FIGURE 1. Continued.

Species	$I_A, I_B, I_C^a$	Vibrational frequencies <sup>b</sup>			
CH <sub>3</sub> CHFOF		146.6, 204.4, 277.8, 355.3, 515.8, 559.0, 837.4, 876.0, 916.2, 1078.6, 1115.5,			
TS0		721.0i, 109.8, 237.3, 306.5, 327.2, 443.2, 513.6, 819.6, 866.7, 972.9, 1106.3, 1179.3, 1278.5, 1351.3, 1396.4, 1413.3, 1445.8, 2922.1, 3035.3, 3039.8, 3094.1			
TS1		2216.7i, 153.5, 218.2, 316.8, 382.6, 511.1, 529.8, 591.6, 826.8, 980.7, 1041.9, 1053.4, 1112.8, 1313.2, 1358.5, 1421.2, 1436.2, 1776.8, 2949.9, 3047.1, 3067.2			
TS2		1315.1i, 148.3, 160.1, 188.6, 398.3, 506.8, 545.5, 594.7, 753.8, 819.1, 981.1, 997.3, 1221.4, 1334.9, 1350.3, 1414.4, 1420.0, 2274.2, 2929.7, 3022.8, 3061.4			
IM1	15.4, 16.3, 16.4	217.0, 291.0, 360.2, 368.2, 525.1, 542.7, 557.2, 798.5, 913.3, 956.7, 1087.0, 1159.1, 1245.7, 1332.3, 1425.8, 1426.8, 1435.0, 2959.1, 3059.2, 3059.4, 3672.4			
TS3	14.8, 17.5, 19.1	1679.0i, 200.4, 220.5, 328.7, 401.9, 539.3, 650.2, 688.1, 853.8, 870.6, 994.5, 1061.9, 1248.5, 1359.3, 1411.7, 1424.3, 1544.9, 2000.6, 2949.9, 3042.9, 3079.9			
TS4	15.5, 18.6, 19.1	1675.4i, 245.0, 281.7, 385.3, 428.8, 448.6, 531.8, 558.6, 728.5, 860.0, 910.9, 988.2, 1154.3, 1305.3, 1373.4, 1401.8, 1559.3, 1750.4, 3041.7, 3145.3, 3636.4			
TS5	15.8, 17.4, 17.6	1770.3i, 249.7, 312.7, 328.4, 422.4, 466.7, 491.3, 634.5, 660, 797.2, 817.4, 900.5, 955.5, 1283.8, 1334.9, 1399.1, 1467.6, 1750.5, 3040, 3139.9, 3601.7			
TS6	15.6, 16.1, 16.6	1452.8i, 218.8, 347.1, 364.7, 456.6, 521.2, 525.0, 575.6, 751.5, 803.8, 847.6, 1018.2, 1109.0, 1227.1, 1234.9, 1338.9, 1410.4, 2170.7, 2919.8, 3021.5, 3685.9			
IM2	9.3, 22.6, 29.3	115.4, 140.9, 245.9, 424.6, 463, 562.5, 884.4, 1046.6, 1073.4, 1097.3, 1123.3, 1211.2, 1230.6, 1324.3, 1378.8, 1441.7, 1457.4, 2914.1, 2970, 3008.7, 3732.2			
TS7	12.7, 21.0, 28.2	1919i, 153.6, 225.2, 247.6, 278.6, 509, 616.7, 667, 809.8, 946.1, 1022.5, 1126.4, 1209.8, 1243.8, 1255.3, 1363.9, 1511.1, 1652.3, 3012.9, 3109.7, 3725.3			
TS8	14.4, 20.6, 33.2	1085.5i, 142.1, 162.1, 259.1, 347.2, 496.9, 554.2, 642.7, 919.8, 1040.7, 1096.2, 1167.7, 1178.8, 1233.6, 1348.8, 1385.3, 1409.5, 1976.4, 2881.2, 2949.1, 3618.1			
TS9	10.8, 24.4, 30.0	1572i, 117.1, 260.9, 367.9, 438, 450.7, 618.1, 647.7, 751.8, 843.6, 895.7, 1028.6, 1103.9, 1144.3, 1302.5, 1410.4, 1423.8, 1791.9, 3007.2, 3119.0, 3556.0			
TS10	9.5, 22.0, 28.5	971.9i, 147.1, 242.6, 406.6, 460.7, 549.2, 606.1, 689.7, 707.1, 922.4, 963.4, 1072.1, 1116.0, 1184.3, 1288.4, 1321.9, 1341.2, 1398.4, 2926.5, 2975.7, 3676.4			
TS11	9.4, 22.3, 29.0	2078.2i, 131.8, 231.7, 394.2, 451.3, 549.1, 754.4, 898.3, 937.7, 968.5, 1090.9, 1138.9, 1218.5, 1285.1, 1314.3, 1356.4, 1415.2, 1939.3, 2268.6, 2844.9, 2996.0			

TABLE I	
Scaled vibrational frequencies ( $cm^{-1}$ ), moments of MP2/6–311G(d,p) level of theory.	of inertia (10 <sup>-46</sup> kg m <sup>2</sup> ) of molecular species at

<sup>a</sup> Moments of inertia.

<sup>b</sup> Scaled by a factor of 0.9496 [19].

$$IM1 \rightarrow [TS6] \rightarrow CHCF_2OH + H_2 \tag{6}$$

$$IM1 \rightarrow CH_3CF_2 + OH$$
 (7)

$$IM1 \rightarrow CH_2CF_2OH + H$$
 (8)

$$IM1 \rightarrow CH_3CF_2O + H$$
 (9)

$$IM1 \to CH_3 + CF_2OH \tag{10}$$

Channel (3) is the energetically most favorable reaction path, via a four-membered ring transition state TS3. The breaking  $C_2$ — $F_4$  and  $O_6$ — $H_5$  bonds are 1.779 and 1.180 Å, respectively. The forming  $H_5$ — $F_4$  bond is 1.214 Å. The barrier height is 41.4 kcal/ mol. The overall reaction of  $O(^1D) + CH_3CHF_2 \rightarrow CH_3CFO + HF$  is highly exothermic by 155.8 kcal/ mol. Channel (4) of IM1 produces  $CH_2CFOH + HF$ 

via transition state TS4, located about 63.6 kcal/ mol higher. TS4 is a four-membered ring structure. The breaking  $C_1$ —H<sub>6</sub> and  $C_2$ —F<sub>4</sub> bonds are elongated to 1.291 and 1.980 Å, respectively. The forming H<sub>6</sub>—F<sub>4</sub> bond is 1.289 Å. Channel (5) is the formation of CH<sub>2</sub>CF<sub>2</sub> + H<sub>2</sub>O via transition state TS5 over a barrier of 83.3 kcal/mol. TS5 is a fourmembered ring transition state. The breaking  $C_2$ —O<sub>3</sub> and  $C_1$ —H<sub>9</sub> bonds are 1.768 and 1.507 Å, respectively. The forming H<sub>9</sub>—O<sub>3</sub> bond is 1.172 Å. Channel (6) is the formation of CHCF<sub>2</sub>OH + H<sub>2</sub> via TS6 over a barrier of 113.9 kcal/mol. TS6 is a threemembered ring transition state. The breaking  $C_1$ —H<sub>8</sub> and  $C_1$ —H<sub>9</sub> bonds are 1.224 and 1.231 Å, respectively. The forming H<sub>9</sub>—H<sub>8</sub> bond is 0.868 Å.

#### TABLE II

Energies and molecular parameters for variational transition states obtained using the MVTST approach.

Species		I <sub>A</sub> , I <sub>B</sub> , I <sub>C</sub> <sup>a</sup>		Vibrational frequencies <sup>b</sup>
CH <sub>3</sub> CF <sub>2</sub> —OH <sup>c</sup>	2.8 <sup>e</sup>	16.5, 29.5, 30.5	96.4 <sup>f</sup>	233.3i, 34.0, 136.2, 155.8, 224.1, 368.8, 476.0, 546.5, 643.2, 845.4, 954.3, 1066.8, 1226.3, 1260.8, 1372.5, 1409.3,
CH <sub>3</sub> CF <sub>2</sub> O—H <sup>c</sup>	2.3 <sup>e</sup>	15.2, 16.9, 17.1	102.8 <sup>f</sup>	1419.1, 2907.1, 3018.0, 3060.0, 3551.8 965.8i, 206.9, 331.9, 354.8, 436.3, 483.9, 529.9, 546.6, 585.5, 799.8, 897.0, 921.9, 1107.6, 1154.8, 1226.7, 1339.0, 1415.4, 1428.1, 2054.6, 2054.0, 2068.4
CH <sub>2</sub> CF <sub>2</sub> OH—H <sup>c</sup>	2.6 <sup>e</sup>	15.7, 17.2, 17.4	95.2 <sup>f</sup>	1420.1, 2954.0, 3054.9, 3060.4 828.7i, 275.7, 340.8, 371.2, 375.2, 485.2, 516.9, 544.1, 580.2, 585.0, 790.7, 824.4, 925.5, 1007.4, 1109.4, 1248.4, 1353.0, 1420.0, 2024.0, 2150.1, 2671.4
CH <sub>3</sub> —CF <sub>2</sub> OH <sup>c</sup>	2.4 <sup>e</sup>	15.5, 23.9, 24.1	67.1 <sup>f</sup>	290.6i, 53.5, 136.3, 210.1, 213.7, 505.6, 519.5, 604.9, 648.3, 654.5, 908.4, 949.8, 1161.7, 1234.1, 1276.0, 1379.0, 1380.4, 2068.0, 2126.0, 2120.0, 2582.2
CHF <sub>2</sub> —CH <sub>2</sub> OH <sup>d</sup>	3.0 <sup>e</sup>	10.4, 49.3, 55.5	81.3 <sup>9</sup>	200.2i, 37.7, 107.4, 147.6, 263.7, 352.4, 534.5, 551.7, 880.7, 960.0, 1043.1, 1114.9, 1160.1, 1165.9, 1323.1, 1327.0, 1440.5, 2973.5, 3009.0, 3104.9, 3692.6
CHF <sub>2</sub> CHOH—H <sup>d</sup>	2.6 <sup>e</sup>	10.2, 23.2, 29.4	86.6 <sup>g</sup>	708.6i, 154.1, 257.9, 395.5, 426.4, 458.7, 518.8, 558.1, 625.3, 783.1, 949.6, 1090.2, 1122.2, 1189.2, 1217.0, 1312.1, 1358.3, 1442.4, 2938.8, 3043.3, 3680.8
CHF <sub>2</sub> CH <sub>2</sub> O—H <sup>d</sup>	2.2 <sup>e</sup>	9.5, 23.3, 30.2	98.1 <sup>g</sup>	1047.6i, 124.9, 260.1, 414.4, 455.2, 491.1, 561.1, 593.6, 884.6, 1015.0, 1074.6, 1094.7, 1117.3, 1193.3, 1278.6, 1358.4, 1374.3, 1459.0, 2889.7, 2947.2, 3009.9
CHF <sub>2</sub> CH <sub>2</sub> —OH <sup>d</sup>	2.8 <sup>e</sup>	9.6, 32.4, 38.8	82.5 <sup>9</sup>	300.7i, 116.7, 134.8, 304.8, 374.3, 396.7, 469.7, 537.5, 689.8, 782.0, 862.1, 1015.9, 1100.8, 1125.7, 1334.0, 1354.8, 1420.7, 3020.8, 3031.2, 3149.5, 3488.7
CF <sub>2</sub> CH <sub>2</sub> OH—H <sup>d</sup>	2.7 <sup>e</sup>	10.2, 23.8, 29.6	93.1 <sup>g</sup>	744.6i, 123.6, 164.1, 248.8, 412.6, 428.1, 466.4, 489.2, 574.0, 854.2, 978.9, 1079.7, 1179.2, 1192.9, 1233.3, 1278.1, 1416.5, 1440.8, 2864.8, 2954.1, 3724.8

<sup>a</sup> Moments of inertia.

- <sup>b</sup> Scaled by a factor of 0.9496 [19].
- <sup>c</sup>CH<sub>3</sub>CF<sub>2</sub>OH is IM1. <sup>d</sup>CHF<sub>2</sub>CH<sub>2</sub>OH is IM2.
- <sup>e</sup>Bond length.
- <sup>f</sup>The energy is relative to IM1.
- <sup>g</sup> The energy is relative to IM2.

The last four channels are all single bond fission processes without well-defined transition states. The O–H, C–H, C–C, and C–O bond fissions of IM1 produce  $CH_3CF_2O + H$ ,  $CH_2CF_2OH + H$ ,  $CH_3$ +  $CF_2OH$ , and  $CH_3CF_2$  + OH, respectively. These channels are endothermic relative to IM1 by 109.0, 101.0, 96.5, and 105.1 kcal/mol, respectively.

#### **2.3. DECOMPOSITION CHANNELS OF IM2**

- $IM2 \rightarrow [TS7] \rightarrow CHFCHOH + HF$ (11)
- $IM2 \rightarrow [TS8] \rightarrow CFCH_2OH + HF$ (12)
- $IM2 \rightarrow [TS9] \rightarrow CH_2CF_2 + H_2O$ (13)
- $IM2 \rightarrow [TS10] \rightarrow CHF_2COH + H_2$ (14)



**FIGURE 2.** Potential energy profile of  $O(^{1}D) + CH_{3}CHF_{2}$  at QCISD(T)/6-311++G(d,p)//MP2/6-311G(d,p) level of theory.

$$IM2 \rightarrow [TS11] \rightarrow CHF_2CHO + H_2$$
 (15)

$$IM2 \rightarrow CHF_2CH_2 + OH$$
 (16)

$$IM2 \rightarrow CHF_2 + CH_2OH$$
(17)  
$$IM2 \rightarrow CF_2CH_2OH + H$$
(18)

$$IM2 \rightarrow CF_2CH_2OH + H \tag{10}$$

$$IIVI2 \rightarrow CI IF_2 CI IOI I + II$$
(19)

$$IM2 \rightarrow CHF_2CH_2O + H \tag{20}$$

The energetically most favorable reaction path is channel (11) via a four-membered ring transition state TS7. The breaking  $C_1$ — $F_4$  and  $O_2$ — $H_9$  bonds are 1.897 and 1.333 Å, respectively. The forming  $H_9$ — $F_4$  bond is 1.249 Å. The barrier height is 69.0 kcal/mol. Channel (12) is also a HF-elimination process, which produces CFCH<sub>2</sub>OH + HF via transition state TS8, locating about 70.1 kcal/mol higher. TS8 is a three-membered ring structure. The breaking  $C_1$ — $H_9$  and  $C_1$ — $F_8$  bonds are elongated to 1.256 and 2.074 Å, respectively. The forming  $H_9$ — $F_8$  bond is 1.172 Å. Channel (13) of

IM2 is the formation of  $CH_2CF_2 + H_2O$  via transition state TS9 over a barrier of 81.0 kcal/mol. TS9 is a four-membered ring transition state. The breaking  $C_1$ — $O_3$  and  $C_2$ — $H_9$  bonds are 1.754 and 1.638 Å, respectively. The forming  $H_9$ — $O_3$  bond is 1.105 Å. IM2 can also decompose to  $CHF_2COH +$  $H_2$  and  $CHF_2CHO + H_2$  via transition states TS10 and TS11, respectively. The barrier heights are 87.7 and 93.1 kcal/mol, respectively.

The last five channels are all single bond fission processes without well-defined transition states. The O–H, C–H, C–C, and C–O bond fissions of IM2 produce  $CHF_2CH_2O+H$ ,  $CHF_2CHOH + H$ ,  $CF_2CH_2OH + H$ ,  $CHF_2 +$  $CH_2OH$ , and  $CHF_2CH_2 + OH$ , respectively. These channels are endothermic relative to IM2 by 100.3, 91.8, 98.5, 87.5, and 88.0 kcal/mol, respectively.

#### **3. Energy-Dependent Rate Constants**

The energy-dependent rate constants for individual unimolecular reaction steps are computed using RRKM theory [20]. For a unimolecular reaction

$$\mathbf{R}^* \to \mathbf{R}^{\neq} \to \mathbf{P},\tag{21}$$

where R\* is energized reactant,  $R^{\neq}$  is the activated complex or transition state on the potential energy surface, and P represents product, the microcanonical rate constant, k(E), can be expressed as

$$k(E) = \left(\mathbf{I}^{\neq} / \mathbf{I}\right)^{1/2} \frac{\sigma}{h} \frac{W^{\neq} (E - E^{\neq})}{\rho(E)}, \qquad (22)$$

according to RRKM theory. Here,  $\sigma$  is the reaction path degeneracy, h is Plank's constant,  $W^{\neq}(E - E^{\neq})$  denotes the total number of states of the transition state with activation energy  $E^{\neq}$ , and  $\rho(E)$ represents the density of states of the energized reaction molecule.  $I^{\neq}$  and I are the overall moments of inertia for transition states and the reactant, respectively. The direct count method [21] is used to calculate the  $W^{\neq}(E - E^{\neq})$  and  $\rho(E)$ values in this work. The total available internal energy E is taken as the energy of chemical activation (the energy released in the  $O(^{1}D) + CH_{3}CHF_{2} \rightarrow IM1$  (IM2) reaction) plus a collision energy,  $E_{col}$ . For the reaction without an energy barrier, for instance, the breaking of the C—O (or C—H, O—H) bond in IM1, the rate constant is determined by the criterion according to the MVTST [22, 23]:

$$\frac{\partial W^{\neq} (E - E^{\neq})}{\partial R_{\rm C}} = 0 \tag{23}$$

For the C–O bond cleavage case,  $R_{\rm C}$  is the distance between C and O atoms. The number of states  $W^{\neq}(E - E^{\neq})$  along this coordinate was calculated, and the R<sub>C</sub> point that satisfies the criterion of Eq. (3) is considered to be the variational TS point for this bond-breaking barrierless reaction. The potential energy surface was scanned at MP2/6-311G(d,p) level along the bond distance, which was taken as the length of the breaking C–O bond. To do that we carried out the partial geometry optimization for a series of fixed values of this bond distance, while all other geometric parameters were optimized. The energies of the partially optimized structures are then refined at QCISD(T)/6-311++G(d,p) level. The calculated energies at the QCISD(T)/6-311++G(d,p) level plus zero point energy at the MP2/6-311G(d,p) level are considered to be the energy of this species at this structure. With this computational procedure, the  $W^{\neq}(E - E^{\neq})$  value at every C - Obond distance increasing by 0.1 Å was calculated until a minimal  $W^{\neq}(E - E^{\neq})$  was found.

From Figure 1, the formation of CH<sub>3</sub>CHFOF should overpass transition state TS0 over a barrier of 20.8 kcal/mol, whereas the formations of IM1 and IM2 are barrierless processes. In addition,



**FIGURE 3.** The product branching ratios of IM1 versus collision energy.



**FIGURE 4.** The product branching ratio of IM2 versus collision energy.

 $CH_3CHFOF$  can isomerize to IM1 via TS1, which in part contributes to the formation of IM1. Here, we only calculate the rate constants and branching ratios for IM1 and IM2.

The energy-dependent rate constants and the branching ratios for the production channels in the range of collision energies from 0 to 350 kcal/ mol for IM1 and IM2 have been calculated. Then, we get the graphs of the branching ratios for products of IM1 and IM2 as a function of collision energies, which are depicted in Figures 3 and 4.

## **3.1. THE PRODUCT BRANCHING RATIOS OF IM1**

From Figure 3, the branching ratio of HF is the highest (50.41%) followed by CH<sub>3</sub> (49.17%) with the branching ratio of about 1.03/1 at the collision energy of 0. Therefore, at the collision energy of 0, the major products are CH<sub>3</sub>CFO + HF,  $CH_2CFOH + HF$ , and  $CH_3 + CF_2OH$ . The branching ratios of H<sub>2</sub>, H, and H<sub>2</sub>O increase with the collision energy except that of HF, which decreases with the collision energy. According to Figure 3, when the collision energy changes from 0 to 350 kcal/mol, the branching ratios of  $H_2$ ,  $H_1$ , and  $H_2O$  change from 0, 0.02, and 0.08% to 0.13, 2.64, and 1.05%, respectively, but these channels remain negligible ones, and the branching ratio of HF decreases from 50.41 to 4.06%. The branching ratio of CH<sub>3</sub> increases from 49.17 to 74.73% when  $E_{\rm col}$  increases from 0 to 90 kcal/mol, and the branching ratio decreases to 54.69% when  $E_{col}$ rises to 350 kcal/mol. The branching ratio of OH increase from 0.33 to 37.43% when  $E_{\rm col}$  increases from 0 to 350 kcal/mol. It is obvious in Figure 3 that OH and CH<sub>3</sub> become to compete as the increment of the collision energy. At the collision energy of 350 kcal/mol, the branching ratios of OH and CH<sub>3</sub> are 37.43 and 54.69%, respectively, with the branching ratio of 0.68/1 between them. The branching ratios of OH and HF are equal to be 12.20% at the collision energy of 115.2 kcal/ mol. Above 115.2 kcal/mol, the branching ratio of OH overpasses that of HF. To make a summary of this part, the main decomposition products of IM1 are CH<sub>3</sub>CFO + HF, CH<sub>2</sub>CFOH + HF, and CH<sub>3</sub>+ CF<sub>2</sub>OH at collision energy smaller than 115.2 kcal/mol; CH<sub>3</sub>+ CF<sub>2</sub>OH and CH<sub>3</sub>CF<sub>2</sub> + OH are the main products at higher collision energy bigger than 115.2 kcal/mol.

## **3.2. THE PRODUCT BRANCHING RATIOS OF IM2**

From Figure 4, the branching ratio of CH<sub>2</sub>OH is the highest (48.79%) followed by HF (45.13%) with the branching ratio of about 1.08/1 at the collision energy of 0. Therefore, at the collision energy of 0, the major products of IM2 are CHF<sub>2</sub> + CH<sub>2</sub>OH, CHFCHOH + HF, and CFCH<sub>2</sub>OH + HF. The branching ratios of OH, H<sub>2</sub>O, H<sub>2</sub>, and H increase with the collision energy except that of HF, which decreases with the collision energy. The branching ratio of HF decreases from 45.13 to 7.20% when  $E_{col}$  increases from 0 to 350 kcal/mol. According to Figure 4, when the collision energy increases from 0 to 350 kcal/mol, the branching ratios of OH, H<sub>2</sub>O, H<sub>2</sub>, and H increase from 4.18, 1.24, 0.14, and 0.52% to 8.78, 1.95, 1.18, and 9.38%, respectively, but these channels remain negligible ones. The branching ratio of CH<sub>2</sub>OH increases from 48.79 to 72.30% when  $E_{\rm col}$  increases from 0 to 180 kcal/mol and then decrease to 71.52% when collision energy changes from 180 to 350 kcal/mol. The main decomposition products of IM2 are  $CHF_2 + CH_2OH$ , CHFCHOH + HF, and  $CFCH_2OH + HF$  at lower collision energy and  $CHF_2 + CH_2OH$  are the main products of IM2 at higher collision energy.  $CHF_2 + CH_2OH$  are the main products in the whole range of collision energy, which implies that C-C bond fission process is the most feasible pathway for the decomposition of IM2.

The formation of IM1 releases much more energy than IM2, so IM1 is more stable with respect to IM2. It is concluded that the main decomposition products of IM1 are the main products of the title reaction. Kono et al. [1] have

obtained the branching ratio of OH in the reaction of  $O(^{1}D)$  with  $CH_{3}$ — $CHF_{2}$  to be about 15% by laser-induced fluorescence techniques. Our branching ratio of OH cannot compare with their result simply, because we cannot know the collision energy of the experiment. However, the result of CHF<sub>2</sub> + CH<sub>2</sub>OH being the main products in the whole range of collision energy is consistent with the conclusion of Kono et al. [1]: C-C bond fission process is the most feasible as the pathway in the reaction of HFCs +  $O(^{1}D)$ . Kono et al. did not perform the estimation of the reaction branching using RRKM theory, we believe that our theoretical calculations can help explain the experimental results and can forecast the branching ratios of the products in a wide range of collision energy.

#### 4. Summary

The reaction of  $O(^{1}D) + CH_{3}CHF_{2}$  has been studied by QCISD(T)/6-311++G(d,p)//MP2/ 6-311G(d,p) method. The calculations reveal an insertion-elimination reaction mechanism for the title reaction. The title reaction produces three intermediates. RRKM theory has been used to calthe energy-dependent rate constants culate through the intermediates. According to the calculated results, the main products of the title reaction are CH<sub>3</sub>CFO + HF, CH<sub>2</sub>CFOH + HF, and CH<sub>3</sub>+ CF<sub>2</sub>OH at lower collision energy; and  $CH_3 + CF_2OH$ ,  $CH_3CF_2 + OH$  are the main products at higher collision energy.  $CHF_2 + CH_2OH$ are the main products in the whole range of collision energy.

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