

Ab Initio Quantum Mechanical Study for the Photolysis and Unimolecular Decomposition Reactions in the Atmosphere of CF₃OH

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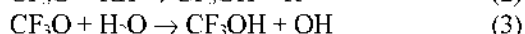
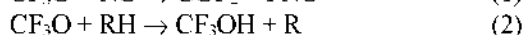
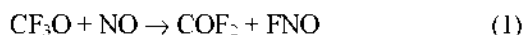
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The electronic transitions from the ground state to low-lying excited states of CF₃OH have been investigated using high level *ab initio* quantum mechanical techniques. Also the possible photodissociation procedures of CF₃OH have been considered. The highest level employed in this study is TZP CCSD(T) level of theory. The possible four low-lying excited states can result by the excitation of the lone pair electron (n) in oxygen to σ* molecular orbital in C-O or O-H bond. The vertical transition (n → σ*) energy is predicted to be 220.5 kcal/mol (130 nm) at TZ2P CISD level to theory. The bond dissociation energies of CF₃OH to CF₃O + H and CF₃+OH have been predicted to be 119.5 kcal/mol and 114.1 kcal/mol, respectively, at TZP CCSD level of theory. In addition, the transition state for the unimolecular decomposition of CF₃OH into CF₂O + HF has been examined. The activation energy and energy separation for this decomposition have been computed to be 43.6 kcal/mol and 5.0 kcal/mol including zero-point vibrational energy corrections at TZP CCSD(T) level of theory.

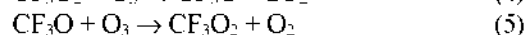
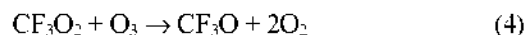
Introduction

It is well known that chlorofluorocarbons (CFCs) are responsible for the destruction of ozone layer.¹ Therefore, their usage has been restricted internationally. The primary candidates to replace CFCs are hydrofluorocarbons (HFCs) which have been known as environmentally acceptable alternatives.² However, the environmental impact of the atmospheric release of HFCs due to their large scale industrial use should be carefully considered.³ For this reason, there are a lot of experimental and theoretical investigations on the stabilities and reactivities of CF₃OH and CF₃O radicals.⁴ These species have been known to be formed from CF₃ radicals which are produced during the degradation by short-wavelength photolysis of various HFCs such as HFC-23,⁵ HFC-125,⁶⁻⁸ HFC-134a,^{9,10} and HFC-143a.¹¹ CF₃ radicals react rapidly with O₂ in the atmosphere to give CF₃O₂¹²⁻¹³ and ultimately to produce CF₃O¹⁴ radical. The fate of CF₃O radicals is the key to understand the environmental influence of HFCs and therefore, the atmospheric chemistry of CF₃O radicals has been the subject of intensive research. Since 1991, a lot of researches about the atmospheric degradation reactions of CF₃O radicals have been reported.¹⁵⁻²⁰ CF₃O radicals react with NO to produce COF₂ and FNO and also react with hydrocarbons or possibly H₂O to CF₃OH.



For reaction (3), the CF₃O-H bond strength should be larger than that of water which has the value of 119 kcal/mol.¹⁹ The CF₃O-H bond energy was first estimated by Batt and Walsh²¹ to be 109 kcal/mol using a combination of experimental data. In 1991 Francisco²² predicted this value to be 101 kcal/mol and more recently Schneider and Wallington²³ reported 119.4 ± 2 kcal/mol which can be comparable to the O-H bond strength in water. The possible

ozone (O₃) destruction mechanism of CF₃O and CF₃O₂ in the stratosphere has been proposed in 1993 by Biggs *et al.* as follows.²⁴



Many potentially catalytic ozone destruction cycles involving CF₃O_x radicals are also possible.²⁵ However several experimental studies show that the reaction (5) is not detected directly or very slow. The reactivity of CF₃O_x radicals with O₃ is also very low and there is a efficient chain termination reaction.²⁶⁻³⁰ In 1994, Solomon *et al.* concluded that the CF₃O_x based catalytic ozone destruction cycles has a negligible impact in the stratosphere.³

In 1995, Schneider and coworkers had performed *ab initio* molecular orbital calculations on the photolysis of CF₃OH to CF₃O + H and calculated the solar radiation flux as a function of altitude.³¹ And they concluded that the photolysis of CF₃OH in stratosphere is of no atmospheric importance. In the next year, they also reported the possible mechanism of unimolecular decomposition of CF₃OH to COF₂ and HF, which was predicted to be 42.05 kcal/mol for the activation energy.³² They proposed the water-mediated decomposition mechanism of CF₃OH which lowers this energy barrier to 17 kcal/mol. In 1994, Bock and coworkers reported a theoretical study on the reaction between CF₃O and CH₄, C₂H₆, and H₂O.³³ From their study, they concluded that the possibility of CF₃OH as a CF₃O radical reservoir in the atmosphere must be considered seriously and their conclusion was on a hot debate with Schneider and Wallington.^{34,35} The experimental ultraviolet (UV) spectrum was not yet directly observed because of the instability of CF₃OH. In the present paper, the ground and possible four low-lying excited states of CF₃OH have been examined using high level *ab initio* quantum mechanical techniques. Their geometrical parameters and relative energies will be reported and the UV spectrum of CF₃OH will be predicted. Also the CF₃-OH and to

CF₃-OH bond dissociation energies and the activation energy for the unimolecular decomposition of CF₃OH to CF₂O + HF have been investigated. The SCF harmonic vibrational frequencies will be used for the zero-point vibrational energy corrections.

Theoretical Approach

The four basis sets used in this study were of double zeta (DZ), DZ plus polarization (DZP), triple zeta (TZ) plus a set of polarization (TZP), and TZ plus double polarization (TZ2P) quality. The DZ basis set consists of the standard Huzinaga³⁶ and Dunning³⁷ (9s5p/4s2p) contracted gaussian functions for carbon (C), fluorine (F), and oxygen (O) and the (4s/2s) set for hydrogen (H). The DZP basis is DZ plus a single set of polarization *d* functions on C, F, and O, and a set of *p* function on hydrogen with orbital exponents $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{F}) = 1.0$, $\alpha_d(\text{O}) = 0.85$, and $\alpha_p(\text{H}) = 0.75$. The TZ basis consists of the Huzinaga³⁶ and Dunning³⁸ (10s6p/5s3p) set for C, F, and O, and the (5s/3s) set for H. The polarization functions in the TZP basis are the same as those in the DZP basis, and the TZ2P basis is of triple zeta (TZ) quality with two sets of polarization function with exponents $\alpha_d(\text{C}) = 1.5$, 0.375 , $\alpha_d(\text{F}) = 2.0$, 0.5 , $\alpha_d(\text{O}) = 1.7$, 0.425 and $\alpha_p(\text{H}) = 1.5$, 0.375 .

The structures for the ground and possible low-lying excited states of CF₃OH were fully optimized at the self-consistent field (SCF) level of theory using analytic techniques³⁹ with DZ, DZP, TZP, and TZ2P basis sets. The SCF equilibrium geometries were subsequently used to optimize structures at the single and double excited configuration (CISD) level with all four basis sets described above by employing analytic CISD gradient methods.⁴⁰ The CISD geometries of the ground state were finally used to obtain geometries optimized at the CCSD and CCSD(T) levels, which are the single and double excitation coupled cluster method and CCSD with the effects of connected triple excitation included perturbatively.⁴¹ For the CCSD and CCSD(T) optimized geometries, the DZ, DZP, and TZP basis sets were used because the TZ2P basis is too big for the CCSD and CCSD(T) calculations. In the CCSD and CCSD(T) wavefunctions with DZP and TZP basis sets, the five core-like occupied SCF molecular orbitals were frozen and the five highest virtual molecular orbitals were deleted from the correlation procedures.

For the CF₃O-H and CF₃-O-H bond dissociation energies and the unimolecular decomposition energy of CF₃OHI to CF₂O + HF, a "supermolecule" approach, composed of the two moieties separated by about 100 Å, was used to avoid the size-consistency problem associated with the truncated CI method like CISD. The possible low-lying excited states have open-shell singlet or triplet state, which is not available for the CCSD and CCSD(T) first derivative calculations. Harmonic vibrational frequencies and infrared (IR) for the ground and excited states of CF₃OH were evaluated using analytic second energy derivatives⁴² at the SCF level. All four basis sets were used for SCF frequencies. All computations described above were carried out with the PSI-2⁴³ suit

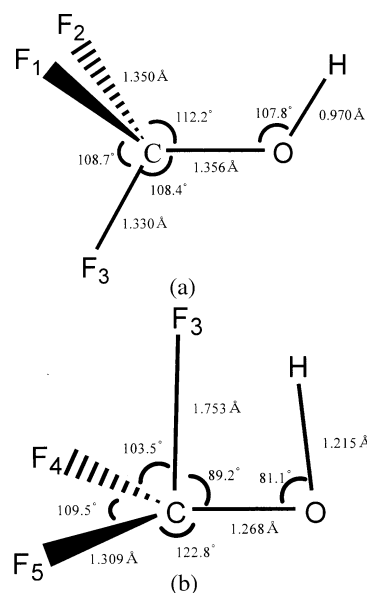


Figure 1. The optimized structures for (a) the ground state of CF₃OH and (b) the transition state for the unimolecular decomposition of CF₃OH to CF₂O + HF at the TZP CCSD(T) level of theory. All bond lengths are in angstroms (Å) and bond angles are in degrees (°).

of computer programs developed by Schaefer's group.

Results and Discussion

Structures. The optimized structure at the highest level of theory employed in this study for the ground state of CF₃OH appears in Figure 1(a). The geometrical parameters at all levels of theory are listed in Table 1. In general, bond distances decrease with increasing basis set size at SCF, CISD and CCSD levels, while bond angles are not varied significantly with the different basis set except DZ basis. Electron correlation, as expected, increases bond lengths in going from SCF to CISD and CCSD, but does not change bond angles importantly except C-O-H bond angle. The predicted C-F bond distances in CF₃ exhibit one "short" (1.330 Å) and two "long" (1.350 Å) bonds at the TZP CCSD(T) level of theory and this kind of pattern is common in Jahn-Teller distorted C_{3v} molecules. The C-O and O-H bond lengths have been predicted to be 1.356 Å and 0.972 Å, respectively, which are normal single bond lengths.

The transition state for the unimolecular decomposition of CF₃OH to CF₂O + HF has C_s symmetry and the optimized geometries at the TZP CCSD(T) level of theory are shown in Figure 1(b). The geometrical parameters at other levels of theory are listed in Table 2. The C-O bond distance is predicted to be 1.266 Å, which shows the double bond character, as expected, due to HF elimination process. The C-F and O-H bond lengths also have been elongated by about 0.426 and 0.244 Å, respectively, from CF₃OH structure and the C-O-H and F-C-O bond angles are reduced to 81.4° and 89.5° to form four-centered transition state. The torsional angle of C-F-F-O is predicted to be 14.4°.

The possible low-lying excited states of CF₃OHI can result

Table 1. Geometrical parameters for the ground state of CF_3OH at various levels of theory. All bond lengths are in angstroms (Å) and bond angles are in degrees (°)

	SCF				CISD				CCSD				CCSD (T)		
	DZ	DZP	TZP	TZ2P	DZ	DZP	TZP	TZ2P	DZ	DZP	TZP	TZ2P	DZ	DZP	TZP
R(C-O)	1.347	1.332	1.331	1.329	1.367	1.341	1.339	1.333	1.382	1.354	1.352	1.347	1.384	1.356	1.356
R(C-F ₃)	1.347	1.303	1.302	1.300	1.372	1.314	1.313	1.308	1.388	1.327	1.326	1.323	1.392	1.330	1.330
R(C-F ₁)	1.371	1.319	1.318	1.316	1.400	1.332	1.330	1.326	1.418	1.346	1.345	1.342	1.425	1.350	1.350
R(C-F ₂)	1.371	1.319	1.318	1.316	1.400	1.332	1.330	1.326	1.418	1.346	1.345	1.342	1.425	1.350	1.350
R(O-H)	0.956	0.949	0.948	0.943	0.973	0.958	0.958	0.949	0.984	0.969	0.969	0.960	0.985	0.970	0.972
∠(COH)	116.6	110.3	110.4	110.5	114.8	109.1	109.2	109.6	113.6	108.1	108.1	108.6	113.4	107.8	107.7
∠(F ₁ CF ₃)	108.3	108.6	108.6	108.6	108.3	108.6	108.6	108.6	108.3	108.7	108.7	108.6	108.3	108.7	108.7
∠(F ₂ CF ₃)	108.3	108.6	108.6	108.6	108.3	108.6	108.6	108.6	108.3	108.7	108.7	108.6	108.3	108.7	108.7
∠(F ₁ CF ₂)	106.0	106.7	106.7	106.8	105.8	106.6	106.6	106.7	105.7	106.6	106.6	106.6	105.6	106.5	106.5
∠(F ₁ CO)	109.4	108.9	108.9	108.8	109.1	108.7	108.7	108.6	108.9	108.5	108.5	108.5	108.9	108.4	108.5
∠(F ₂ CO)	112.4	112.0	112.0	112.0	112.6	112.1	112.1	112.1	112.7	112.2	112.2	112.2	112.8	112.2	112.2
∠(F ₂ CO)	112.4	112.0	112.0	112.0	112.6	112.1	112.1	112.1	112.7	112.2	112.2	112.2	112.8	112.2	112.2

Table 2. Geometrical parameters of the transition state for the unimolecular decomposition of CF_3OH to $CF_2O + HF$. All bond lengths are in angstroms (Å) and bond angles are in degrees (°)

	SCF				CISD				CCSD			CCSD (T)		
	DZ	DZP	TZP	TZ2P	DZ	DZP	TZP	TZ2P	DZ	DZP	TZP	DZ	DZP	TZP
C-O	1.264	1.244	1.240	1.237	1.282	1.253	1.248	1.242	1.296	1.264	1.261	1.299	1.268	1.266
C-F ₃	1.879	1.767	1.775	1.790	1.850	1.742	1.744	1.756	1.851	1.748	1.750	1.859	1.753	1.756
C-F ₁	1.313	1.269	1.267	1.263	1.348	1.287	1.285	1.277	1.370	1.303	1.301	1.377	1.309	1.308
O-H	1.176	1.173	1.169	1.158	1.214	1.198	1.198	1.182	1.233	1.213	1.214	1.234	1.215	1.216
H-F ₃	1.267	1.197	1.205	1.218	1.266	1.179	1.187	1.199	1.276	1.186	1.195	1.285	1.192	1.202
∠(COH)	91.9	83.6	84.0	84.7	89.6	81.7	82.0	83.0	88.9	81.2	81.5	88.9	81.1	81.4
∠(OCF ₃)	82.7	87.5	87.5	87.1	84.6	88.7	88.9	88.4	85.3	89.1	89.3	85.4	89.2	89.5
∠(OCF ₄)	122.9	122.2	122.2	122.2	122.9	122.1	122.0	122.1	122.8	122.1	122.0	122.8	122.1	122.0
∠(F ₃ CF ₄)	103.6	102.6	102.5	102.4	104.3	103.0	102.8	102.8	104.7	103.3	103.1	104.9	103.5	103.2
∠(F ₄ CF ₃)	110.6	110.9	111.0	111.1	109.5	110.1	110.3	110.5	108.9	109.7	109.9	108.7	109.5	109.8
∠(CF ₄ F ₃ O)	19.2	12.8	12.6	12.3	12.5	13.8	13.7	13.4	13.2	14.3	14.2	13.4	14.5	14.4

from the electronic transition of the lone-pair electron (n) of oxygen to the C-O or O-H anti-bonding molecular orbital (σ^*). The optimized geometries at the TZ2P CISD level of theory for the lowest singlet (S_1) and triplet (T_1) excited states of CF_3OH have been shown in Figure 2 and geometrical parameters at other levels of theory have been presented in Table 3. The $n \rightarrow \sigma_{C-O}^*$ electronic transition elongates the C-O bond distance to be 3.30 Å for S_1 and 3.212 Å for T_1 state. These excited states have the open-shell characters, which are not available for the calculations of the CCSD first or second derivatives in this study. The C-F bond lengths in CF_3 are predicted to be about same as 1.304-1.305 Å for both S_1 and T_1 states.

The $n \rightarrow \sigma_{O-H}^*$ electronic transition elongates the O-H bond distance and give the second low-lying excited singlet (S_2) and triplet (T_2) states, which have C_s symmetries. At the TZ2P CISD level of theory, the O-H bond lengths are predicted to be 3.698 Å for T_2 state and 3.945 Å for S_2 state as shown in Figure 3. Other predicted geometrical parameters at various levels of theory are listed in Table 4. With the large basis set like TZ2P, the electron correlation effect is very important for both T_2 and S_2 states. The potential wells

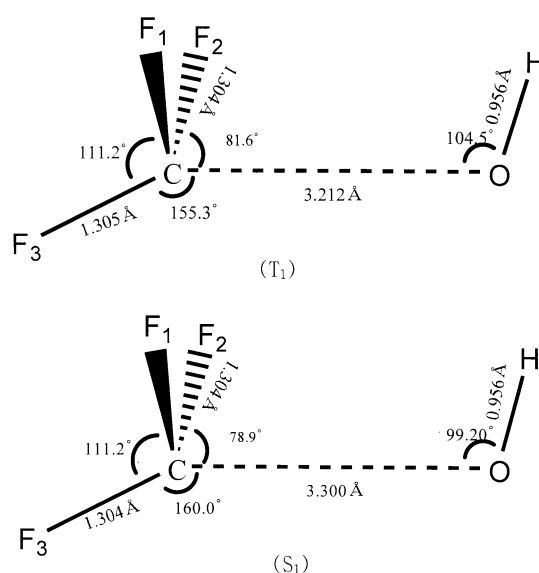
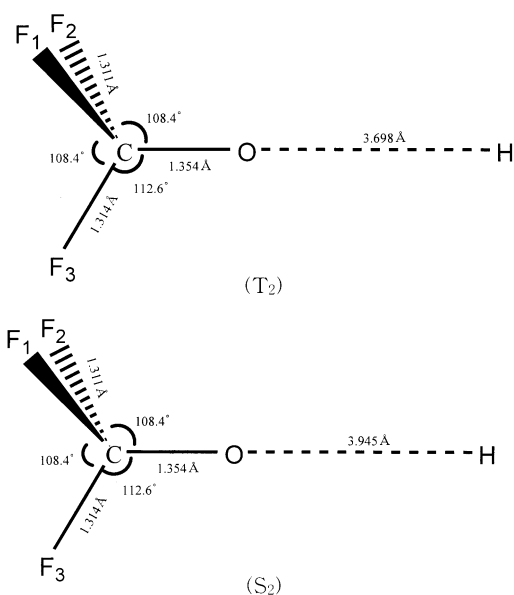
**Figure 2.** The optimized structures for the lowest excited triplet (T_1) and singlet (S_1) of CF_3OH at the TZ2P CISD level of theory. All bond lengths are in angstroms (Å) and bond angles are in degrees (°).

Table 3. Geometrical parameters for the lowest excited triplet (T_1) and singlet states (S_1) of CF_3OH . All bond lengths are in angstroms (\AA) and bond angles are in degrees ($^\circ$)

	T_1						S_1					
	SCF			CISD			SCF			CISD		
	DZ	DZP	TZ2P	DZ	DZP	TZ2P	DZ	DZP	TZ2P	DZ	DZP	TZ2P
R(C-O)	2.916	3.191	3.353	2.881	3.096	3.212	2.983	3.252	3.425	2.970	3.172	3.300
R(C-F ₃)	1.348	1.300	1.297	1.375	1.312	1.305	1.348	1.300	1.296	1.375	1.311	1.304
R(C-F ₁)	1.346	1.300	1.295	1.373	1.312	1.304	1.346	1.300	1.295	1.372	1.311	1.304
R(C-F ₂)	1.346	1.300	1.295	1.373	1.312	1.304	1.346	1.300	1.295	1.372	1.311	1.304
R(O-H)	0.969	0.957	0.950	0.988	0.967	0.956	0.969	0.957	0.950	0.988	0.967	0.956
$\angle(COH)$	126.6	105.8	111.8	125.6	99.6	104.5	124.9	102.8	108.7	125.2	95.0	99.2
$\angle(F_1CF_3)$	111.0	111.1	111.1	110.7	111.0	111.2	111.0	111.1	111.2	110.8	111.1	111.2
$\angle(F_2CF_3)$	111.0	111.1	111.1	110.7	111.0	111.2	111.0	111.1	111.2	110.8	111.1	111.2
$\angle(F_1CF_2)$	111.3	111.2	111.2	111.0	111.0	111.2	111.3	111.2	111.2	111.1	111.0	111.2
$\angle(F_1CO)$	149.5	155.0	152.0	148.1	155.3	155.3	152.5	158.0	115.2	152.5	159.8	160.0
$\angle(F_2CO)$	85.0	81.8	83.4	86.2	81.8	81.6	83.2	80.2	81.6	83.6	79.24	78.9
$\angle(F_3CO)$	85.0	81.8	83.4	86.2	81.8	81.6	83.2	80.2	81.6	83.6	79.24	78.9

**Figure 3.** The optimized structures for the second excited triplet (T_2) and singlet states (S_2) of CF_3OH at the TZ2P CISD level of theory. All bond lengths are in angstroms (\AA) and bond angles are in degrees ($^\circ$).

for these two states are less than 1 kcal/mol, which means that these barriers may disappear at the higher level of theory such as CCSD or CCSD(T). However the calculations for these levels are not possible in this study because they have open-shell singlet and triplet spins.

Energetics. The bond dissociation energies to $CF_3 + OH$ and $CF_3O + H$ have been predicted at various levels of theory and listed in Table 5. To avoid the size consistency problem for the truncated correlation interaction (CI) method like CISD, a super-molecule approach composed of the two molecules separated about 100 \AA has been applied to obtain the dissociation energies to $CF_3 + OH$ and $CF_3O + H$. Generally the electron correlation effects increase the dissociation energies in going from SCF to CISD and CCSD. At the

highest level of theory employed in this study, TZP CCSD(T), the CF_3-OH and CF_3-OH dissociation energies are predicted to be 114.1 kcal/mol and 119.5 kcal/mol.

In 1982, the CF_3OH bond strength has been predicted to be 109 kcal/mol by Batt and Walsh,²¹ and Francisco²² reported this value to be 101 kcal/mol. More recently, Schneider and Wallington²³ predicted 119.4 kcal/mol, which is slightly larger than that of water. They also reported the CF_3-OH bond strength of 116.2 kcal/mol. In comparison with our predictions of 119.5 kcal/mol for CF_3O-H and 114.1 kcal/mol for CF_3-OH , their prediction for CF_3-OH is in good agreement with our prediction, while that for CF_3-OH is slightly over-estimated (about 2 kcal/mol). In general the O-H bond strength in most alcohols is approximately 15 kcal/mol lower than that of water, however, our and Schneider and Wallington's predictions show the CF_3-OH bond strength is comparable with that in water. The CF_3-OH bond strength is also larger than that of CH_3-OH , which is experimentally estimated to be 92.47 kcal/mol.⁴⁴ The reason for this kind of extra strengths in fluorinated alcohol can be explained using hyper-conjugation between vacant anti- σ orbitals on CF_3 and the lone pair electrons on the OH group.⁴⁵

In Table 6, the absolute and the relative energies for the possible low-lying excited states (T_1 , T_2 , S_1 , and S_2 states) of CF_3OH have been listed and the vertical electronic transition energies from the ground state ($^1A'$) to the lowest triplet ($^3A''$) and singlet ($^1A''$) states at the fixed geometry of the ground state also have been presented. For the T_1 and S_1 states, the potential energy surfaces possess the well with a depth of about 3.9 kcal/mol, while the T_2 and S_2 states have well of only 0.5 kcal/mol depth, which means there are no actual potential wells. The vertical electronic transition ($n \rightarrow \sigma^*$) energies from the non-bonding electron of oxygen to the anti-bonding orbital of CH_3O-H have been predicted to be 210.7 kcal/mol for a high-spin state and 220.5 kcal/mol for an open-shell singlet state at the TZ2P CISD level of theory. Because the electronic transition from a singlet to a triplet state is restricted by a spin selection rule, the ultra-violet

Table 4. Geometrical parameters for the second excited triplet (T_2) and singlet states (S_2) of CF₃OII. All bond lengths are in angstroms (Å) and bond angles are in degrees (°)

	T_2						S_2					
	SCF			CISD			SCF			CISD		
	DZ	DZP	TZ2P	DZ	DZP	TZ2P	DZ	DZP	TZ2P	DZ	DZP	TZ2P
R(C-O)	1.392	1.358	1.352	1.411	1.364	1.354	1.392	1.358	1.352	1.411	1.364	1.354
R(C-F ₃)	1.357	1.308	1.305	1.385	1.320	1.314	1.357	1.308	1.305	1.385	1.320	1.314
R(C-F ₁)	1.354	1.305	1.302	1.383	1.318	1.311	1.354	1.305	1.302	1.383	1.318	1.311
R(C-F ₂)	1.354	1.305	1.302	1.383	1.318	1.311	1.354	1.305	1.302	1.383	1.318	1.311
R(O-H)	3.548	3.561	4.906	3.469	3.407	3.698	3.664	3.677	5.036	3.612	3.610	3.945
$\angle(F_3OH)$	147.4	147.7	148.0	147.6	147.9	146.5	147.6	147.8	148.7	147.8	147.8	145.8
$\angle(F_1CF_3)$	108.2	108.5	108.5	108.0	108.4	108.4	108.2	108.5	108.5	108.0	108.4	108.4
$\angle(F_2CF_3)$	108.2	108.5	108.5	108.0	108.4	108.4	108.2	108.5	108.5	108.0	108.4	108.4
$\angle(F_1CF_2)$	110.0	110.5	110.5	110.1	110.6	110.6	110.0	110.5	110.5	110.1	110.6	110.6
$\angle(F_3CO)$	112.5	112.3	112.3	112.9	112.6	112.6	112.5	112.3	112.3	112.9	112.6	112.6
$\angle(F_1CO)$	109.0	108.6	108.6	108.9	108.4	108.4	109.0	108.6	108.6	108.9	108.4	108.4
$\angle(F_2CO)$	109.0	108.6	108.6	108.9	108.4	108.4	109.0	108.6	108.6	108.9	108.4	108.4

Table 5. Energies of CF₃O+H, CF₃+OH and bond dissociation energies (D_0) of CF₃OH at various levels of theory

Method	Basis set	CF ₃ OH (hartree)	CF ₃ O+H (hartree)	CF ₃ +OH (hartree)	D_0 (CF ₃ O-H) (kcal/mol)	D_0 (CF ₃ -OH) (kcal/mol)
DZ	SCF	-411.591400	-411.450286	-411.476766	88.6	71.9
DZP	SCF	-411.768154	-411.618350	-411.626871	94.0	88.7
TZP	SCF	-411.815944	-411.668030	-411.675670	92.9	88.0
TZ2P	SCF	-411.822348	-411.672541	-411.682394	94.0	87.8
DZ	CISD	-412.131100	-411.964825	-411.986713	104.3	90.6
DZP	CISD	-412.544549	-412.362592	-412.369831	114.1	109.6
TZP	CISD	-412.678509	-412.499108	-412.505614	112.6	108.5
TZ2P	CISD	-412.776935	-412.593698	-412.602493	115.0	109.5
DZ	CCSD	-412.210715	-412.038225	-412.060602	108.2	94.2
DZP	CCSD	-412.596385	-412.405428	-412.415939	119.8	113.2
TZP	CCSD	-412.733426	-412.544460	-412.554939	118.6	112.0
DZ	CCSD(T)	-412.157243	-411.984678	-412.005528	108.3	95.2
DZP	CCSD(T)	-412.615876	-412.424104	-412.432699	120.3	114.9
TZP	CCSD(T)	-412.759541	-412.569069	-412.577633	119.5	114.1

Table 6. Absolute (in hartree) and relative energies (in kcal/mol) for the adiabatic and the vertical transitions from the ground state of CF₃OH to the excited states

		$T_1(^3A'')$	$T_2(^3A'')$	vertical transition energy (T)	$S_1(^1A')$	$S_2(^1A')$	vertical transition energy (S)
DZ	SCF	-411.486833 (65.62)	-411.45219974 (87.35)	-411.250830 (213.71)	-411.486493 (65.83)	-411.452184 (87.36)	-411.226134 (229.21)
DZP	SCF	-411.633551 (84.46)	-411.619387 (93.35)	-411.420957 (217.87)	-411.633417 (84.55)	-411.619373 (93.36)	-411.399360 (231.42)
TZ2P	SCF	-411.688222 (84.17)	-411.673407 (93.46)	-411.508198 (197.13)	-411.688137 (84.22)	-411.673407 (93.46)	-411.493681 (206.24)
DZ	CISD	-411.996558 (84.43)	-411.966489 (103.29)	-411.780568 (219.96)	-411.996057 (84.74)	-411.966466 (103.31)	-411.753624 (236.87)
DZP	CISD	-412.376851 (105.23)	-412.363517 (113.60)	-412.181567 (227.77)	-412.376642 (105.36)	-412.363488 (113.62)	-412.158565 (242.21)
TZ2P	CISD	-412.608750 (105.53)	-412.594490 (114.49)	-412.441156 (210.70)	-412.608623 (105.61)	-412.594478 (114.49)	-412.425589 (220.47)

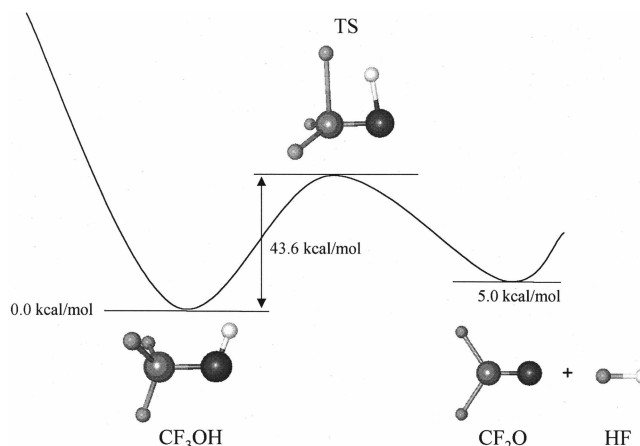
Table 7. The activation energy (E_a) for the unimolecular decomposition of CF_3OH to $\text{CF}_2\text{O} + \text{HF}$ and energy separation (ΔE) between them

		CF_3OH	TS state	$\text{CF}_2\text{O} + \text{HF}$	E_a	ΔE
		(Hartree)	(Hartree)	(Hartree)	(kcal/mol)	(kcal/mol)
DZ	SCF	-411.591400	-411.486754	-411.571388	65.7	12.6
DZP	SCF	-411.768154	-411.668432	-411.746417	62.6(58.6)	13.6(9.8)
TZP	SCF	-411.815944	-411.717514	-411.796546	61.8(57.7)	12.2(8.4)
TZ2P	SCF	-411.822348	-411.725211	-411.80714	61.0(57.0)	9.5(5.7)
DZ	CISD	-412.131100	-412.039644	-412.119115	57.4	7.5
DZP	CISD	-412.544549	-412.455056	-412.521723	56.2(52.2)	14.3(10.5)
TZP	CISD	-412.678509	-412.590452	-412.658655	55.3(51.2)	12.5(8.7)
TZ2P	CISD	-412.776935	-412.688371	-412.760258	55.6(51.6)	10.5(6.7)
DZ	CCSD	-412.210715	-412.126054	-412.204492	53.1	3.9
DZP	CCSD	-412.596385	-412.514009	-412.577870	51.7(47.7)	11.6(7.8)
TZP	CCSD	-412.733426	-412.652363	-412.717949	50.9(46.8)	9.7(5.9)
DZ	CCSD(T)	-412.224902	-412.145163	-412.220539	50.0	2.7
DZP	CCSD(T)	-412.615876	-412.538065	-412.598529	48.8(44.8)	10.9(7.1)
TZP	CCSD(T)	-412.759541	-412.683590	-412.745631	47.7(43.6)	8.8(5.0)

The values in parentheses are including the zero-point vibrational energy corrections.

(UV) spectrum of CF_3OH can be estimated to have a maximum around 130 nm (9.56 eV) caused by a singlet ($^1A'$)-to-singlet ($^1A''$) transition. This result is in reasonably good agreement with a previous prediction of 137 nm by Schneider and coworkers.³⁰ Even though the $\text{CF}_3\text{-OH}$ bond dissociation energy is lower than that of $\text{CF}_3\text{O-H}$, the photolysis of CF_3OH will give the fragments of CF_2O and H because the vertical electronic transition occurs to the $\text{CF}_3\text{O-H}$ anti-bonding orbital as verified by the molecular orbital analysis.

Another possible loss mechanism of CF_3OH is unimolecular decomposition to CF_2O and HF. The relative energies and the energy barriers for this process are shown in Table 7 and Figure 4. The energy separation between CF_3OH and $\text{CF}_2\text{O} + \text{HF}$ is predicted to be 47.7 kcal/mol and is lowered to be 43.6 kcal/mol by inclusion of zero-point vibrational energy (ZPVE) at the TZP CCSD(T) level of theory. The SCF vibrational frequencies shown in Table 8 were used for

**Figure 4.** The potential energy surfaces for the unimolecular decomposition of CF_3OH to $\text{CF}_2\text{O} + \text{HF}$ at the TZP CCSD(T) level of theory.**Table 8.** Harmonic vibrational frequencies (in cm^{-1}) and zero-point vibrational energies (in kcal/mol) of CF_3OH , CF_2O , HF and the transition state, $[\text{CF}_3\text{OH}]^\ddagger$ at DZP, TZP and TZ2P SCF level of theory

	CF_3OH			TS $[\text{CF}_3\text{OH}]^\ddagger$			CF_2O			HF		
	DZP	TZP	TZ2P	DZP	TZP	TZ2P	DZP	TZP	TZ2P	DZP	TZP	TZ2P
ω_1	4160	4129	4145	2242	2246	2260	2180	2158	2138	4493	4467	4478
ω_2	1562	1557	1554	1797	1785	1759	1456	1446	1422	-	-	-
ω_3	1473	1459	1441	1565	1563	1540	1099	1096	1084	-	-	-
ω_4	1364	1358	1333	1104	1102	1093	881	879	890	-	-	-
ω_5	1246	1246	1238	1054	1047	1039	684	689	691	-	-	-
ω_6	998	997	989	932	930	932	640	640	642	-	-	-
ω_7	698	697	696	738	727	716	-	-	-	-	-	-
ω_8	685	685	682	619	623	625	-	-	-	-	-	-
ω_9	659	659	658	599	595	592	-	-	-	-	-	-
ω_{10}	493	495	491	358	348	343	-	-	-	-	-	-
ω_{11}	481	482	482	278	278	269	-	-	-	-	-	-
ω_{12}	251	266	246	2028i	2000i	2004i	-	-	-	-	-	-
ZPVE	20.1	20.1	20.0	16.1	16.1	16.0	9.9	9.9	9.8	6.4	6.4	6.4

the ZPVE corrections. The activation energy for the unimolecular decomposition of CF₃OH to CF₂O + HF is predicted to be 5.0 kcal/mol including ZPVE. The transition state is confirmed by the vibrational frequencies shown in Table 8, which reveals a single imaginary mode of absolute value 2004 cm⁻¹. This reaction coordinate is composed of C-F and O-H stretching and F-C-O and C-O-H bending motions. Our results for the potential energy barrier and the energy separation can be favorably compared with the previous theoretical predictions of 45.1 ± 2 kcal/mol and 7.8 ± 2 kcal/mol by Francisco.⁴⁶

Conclusions

The ground and possible four low-lying excited states of CF₃OH have been examined using high level *ab initio* quantum mechanical method. The CF₃-OH and CF₃O-H bond dissociation energies are predicted to be 114.1 kcal/mol and 119.5 kcal/mol, respectively, which are in reasonably good agreement with previous theoretical results.²³ The vertical electronic transition ($n \rightarrow \sigma^*$) energy of CF₃OH has been predicted to be 220.5 kcal/mol (130 nm). This electronic transition occurs from the ground state to the CF₃O-H antibonding orbital, which implies that the photolysis of CF₃OH will produce CF₃O and H fragments, even though the CF₃-OH bond strength is lower than that of CF₃O-H. The activation energy for the unimolecular decomposition of CF₃OH to CF₂O + HF has been predicted to be 43.6 kcal/mol including zero-point vibrational energy correction and the energy separation between them is computed to be 5.0 kcal/mol at the TZP CCSD(T) level of theory. The real vibrational frequencies for all modes confirm the existence of potential minima for CF₃OH, CF₃O, HF and a single imaginary frequency makes sure of a transition state. The imaginary mode for the transition state has an absolute frequency of 2004 cm⁻¹, which is composed of C-F and O-H stretching and F-C-O and C-O-H bending motions.

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