



# Ion-Molecule Reaction of $Ti^+$ Ion with Trifluoroacetone in the Gas Phase

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**Abstract:** Gas-phase ion-molecule reactions of  $Ti^+$  with 1,1,1-trifluoroacetone were studied by laser ablation/molecular-beam method and density function theory calculations. In the reaction of the  $Ti^+$  ions with acetone,  $Ti^+$  ion insertion into the C=O bond is the preferred decomposition pathway and produce  $TiO^+$  predominantly. Substitution of  $CH_3$  in acetone molecule with electronegative  $CF_3$  group greatly alters the reaction pathway, which is confirmed from  $TiF_2^+$  and  $TiO^+$  observations by mass spectrometry. This is interpreted as the dominant reaction channels via  $Ti^+$  insertions into C-F and C=O bonds of trifluoroacetone molecule. In addition, geometries and energies of the intermediates and transition states involved in two pathways are located by DFT calculations. On the basis of these results, two pathways are considered as competitive and the most favorable pathway proceeds via  $Ti^+$  induced C-F bond activation processes.

**Keywords:** Ion-molecule Reaction, Titanium, 1,1,1-Trifluoroacetone, Mass Spectrometry

## 1. Introduction

The reactions of various metal cations with acetone (ACT) as a model system of ketones have been extensively studied and each reaction pathway appears to vary depending on the involved metal ion. The reaction of late transition metal ions ( $Fe^+$  and  $Co^+$ ) with ACT, studied by ion cyclotron resonance (ICR) and kinetic energy release distribution (KERD) experiments [1-2], mainly gave  $MCO^+$  (where M stands for a transition metal) and  $CH_3-CH_3$  as products. It was proposed that this decarbonylation proceeded through the oxidative insertion of metal ion into the C-C bond of acetone followed by the methyl group migration and reductive dissociation. Subsequently, the real time observation of a bimolecular

reaction,  $Co^+$  ( $^3F_4$ ) with ACT, focused on  $CoCO^+$  ( $+C_2H_6$ ) and  $CoC_2H_6^+$  ( $+CO$ ) formations and the rate-limiting transition state which was involved insertion of  $Co^+$  ion onto a C-C bond of ACT molecule [3]. On the other hand, early transition metal ions ( $Sc^+$  and  $Ti^+$ ) and lanthanoid series metal ions ( $Gd^+$  and  $Pr^+$ ) with ACT only exhibited an oxidation pathway producing  $MO^+$  and  $C_3H_6$  in ion beam studies [4-5]. The substitution of the methyl group in ACT with the highly electronegative  $CF_3$  group is possessing two functional groups, namely trifluoromethyl ( $CF_3$ ) and carbonyl (C=O) groups. The reaction of  $Cr^+$  metal ions with F substitute carbonyl compounds (monofluoroacetone, 1,1,1-trifluoroacetone, hexafluoroacetone pentafluorobenzaldehyde, and 2,3,4,5,6-pentafluoroacetophenone) have been

investigated [6-7]. The most noteworthy findings in these studies were effective association complex formation and C–F bond hydrolysis. With 1,1,1-trifluoroacetone, the first association (95%) and second association (80%) dominated the reactivity along with primary  $\text{CrF}^+$  formation. The low quantities of  $\text{CrF}^+$  detection indicated that the insertion of  $\text{Cr}^+$  onto C–F bond only minor. Recently, theoretical studies for the reactions of  $\text{Ni}^+$  and  $\text{Ti}^+$  with ACT have been investigated using density function theory (DFT) calculations [8-9]. These theoretical studies not only rationalized experimental findings for these reactions, but also provided a comprehensive understanding to the reaction mechanism. With respect to the generation of  $\text{CrF}^+$  in the reaction of  $\text{Cr}^+$  with 1,1,1-trifluoroacetone, the reaction of  $\text{Ti}^+$  with 1,1,1-trifluoroacetone has been investigated, since,  $\text{Ti}^+$  ion can activated both C=O and C–F bonds in gas phase. Although few studies of the reaction of  $\text{Cr}^+$  ions with fluorosubstituted ACT are available in literature, no study have been examined the reactions of  $\text{Ti}^+$  ions with a fluorine substituted ACT possessing more than one functional group.

In the present work, the reaction of  $\text{Ti}^+$  with 1,1,1-trifluoroacetone (TFA) is experimentally and theoretically investigated. Since TFA has highly electronegative F atoms and C=O, it provides a good model molecules for elucidating substituent effects on the reaction pathway of  $\text{Ti}^+$  with acetone. A combination of laser ablation and supersonic gas expansion was used to examine the gas phase reaction of the proposed system. This approach not only gives an insight to the reaction between  $\text{Ti}^+$  and TFA but also provides activities of  $\text{Ti}^+$  within TFA clusters. In addition, DFT calculations were performed to rationalize the detailed reaction pathways of reaction of  $\text{Ti}^+$  with TFA.

## 2. Experimental and Calculation Details

### 2.1. Experiments

The experimental details for the experiments carried out in this work are the same as those described previously [10-12], and therefore only brief description is given here.  $\text{Ti}^+$  ions were generated by focusing the third harmonic (355 nm) of a Nd:YAG laser with a ~1 mm diameter spot on a rotating pure titanium disk. A pulse valve was employed to produce TFA clusters by supersonic expansion of the sample vapor seeded in argon with a stagnation pressure of 1–3 atm. The laser-generated species, including  $\text{Ti}^+$ , traversed the supersonic jet stream perpendicularly, forming a series of  $\text{Ti}^+(\text{TFA})_n$  species. The nascent clusters then skimmed by a conical skimmer (1 mm diameter) and traveled to the extraction region of the reflectron time-of-flight mass spectrometer (RTOFMS). Finally the ions were detected with a Chevron microchannel plate (MCP) detector. The mass spectra of the cluster ions were processed using a 500 MHz digital oscilloscope. Spectral grade of TFA (99.5%) (Aldrich Chemical) were used after several freeze-thaw cycles to remove high vapor pressure impurities. For further precaution, since a layer of TiO could form on the metal

surface, the mass spectrum was acquired after 20 min of laser shining on the metal target.

### 2.2. Computations

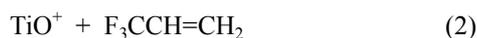
The quartet and doublet potential energy surface (PES) for the ion-molecule reaction of  $\text{Ti}^+$  with  $\text{CF}_3\text{COCH}_3$  were calculated, because these two states are quite close in energy and may interconvert during the reaction process. The three parameter hybrid B3LYP function [13-14] was used for the DFT calculations. The molecular geometries of reactants, products, intermediates, and transition states in both electronic states were fully optimized at B3LYP/6-311++G(d,p) levels of theory. Vibrational frequency calculations were carried out at the same level of theory to estimate all stationary points as either minima or transition states and to calculate the zero point energy (ZPE) for all reported energies. All transition states presented in this work were identified by a single imaginary frequency and were confirmed using the intrinsic reaction coordinate (IRC) method [15-16]. We also used the natural population analysis (NPA) for characterizing atomic charges and electronic structures [14, 17-18]. All DFT calculations were performed using the Gaussian 03 package [19].

## 3. Results and Discussion

### 3.1. Reactions of $\text{Ti}^+$ with TFA Clusters

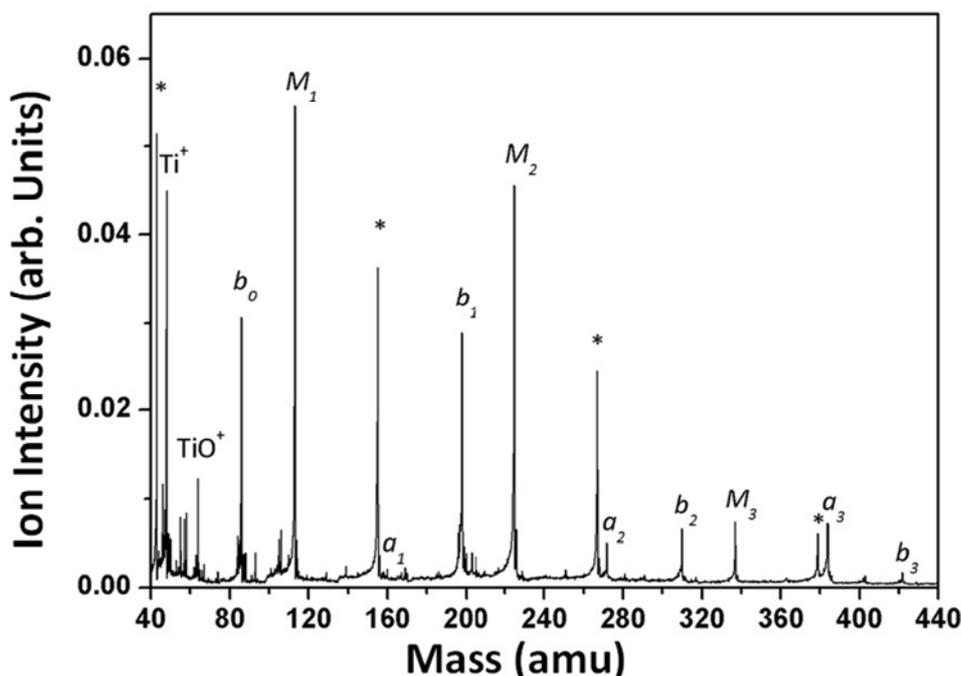
TFA is a particularly interesting molecule because it possesses two functional groups, namely trifluoromethyl ( $\text{CF}_3$ ) and carbonyl (C=O) groups. The substitution of the methyl group in ACT with the highly electronegative  $\text{CF}_3$  group is expected to alter the reaction pathways, offering an opportunity to further investigate the chemical reactivity of  $\text{Ti}^+$  in the metal ion insertion reactions for ACT. As expected, the reaction between  $\text{Ti}^+$  and TFA shows different major sequences of heterocluster ions. A typical mass spectrum of the products of the reaction between  $\text{Ti}^+$  and TFA cluster is shown in Figure 1.

The spectrum contains pentads of peaks corresponding to the Ti isotopes ( $^{46}\text{Ti}$ , 8.0%;  $^{47}\text{Ti}$ , 7.3%;  $^{48}\text{Ti}$ , 73.8%;  $^{49}\text{Ti}$ , 5.5%;  $^{50}\text{Ti}$ , 5.4%), with the relative intensities of these isotopomers reflecting their natural abundance. The characteristic abundance of the Ti isotopomers enables its complex with ACT clusters to be readily identified. Unless otherwise noted, the results presented below refer to complexes involving the most abundant isotope.  $\text{H}^+(\text{TFA})_n$  cluster ions (denoted  $M_n$ ) can be attributed to the intracuster protonation of the parent  $(\text{TFA})_n^+$  ions formed in the region where laser ablated plume and supersonic TFA cluster beam intersect. In addition,  $(\text{CH}_3\text{CO})^+(\text{TFA})_n$  ions (denoted as \*) is due to the fragments formed by the loss of  $\text{CF}_3$  from the  $(\text{TFA})_n^+$  ions. In the low mass region, the reaction products consist of  $\text{TiO}^+$  ( $m/e = 64$ ) and  $\text{TiF}_2^+$  ( $m/e = 86$ ) produced by ion-molecule reactions of  $\text{Ti}^+$  and TFA. These fragmentation ions are attributed to the following reactions.



Unlike the  $\text{Ti}^+ + \text{ACT}$  reaction, in which only  $\text{TiO}^+$  ions are generated by insertion of  $\text{Ti}^+$  ions into the  $\text{C}=\text{O}$  bond of ACT molecules followed by elimination of propene ( $\text{CH}_2=\text{CHCH}_3$ ) via hydrogen migrated  $[\text{O}-\text{Ti}^+-\text{C}(\text{H})\text{CH}_2(\text{CH}_3)]$  transition state [9, 20], both  $\text{TiF}_2^+$  and  $\text{TiO}^+$  ions are observed in the reaction of  $\text{Ti}^+$  and TFA. This finding implies that rupturing of  $\text{Ti}^+-\text{C}$  bond of  $[\text{O}-\text{Ti}^+-\text{C}(\text{F})\text{CF}_2(\text{CH}_3)]$  intermediate in the reaction of  $\text{Ti}^+ + \text{TFA}$  is less favorable than other product pathways, possibly due to the different geometry of  $[\text{Ti}^+\cdots\text{CF}_3\text{COCH}_3]$  association complex compared to that of

$[\text{Ti}^+\cdots\text{CH}_3\text{COCH}_3]$  association complex. Recently Yang *et al* [21] reported that the  $\text{Mg}^+-2,2,2$ -trifluoroethanol (TFE) complex shows five-membered ring structure, in which  $\text{Mg}^+$  is attached to both O atom and one of three F atoms in TFE. In addition, similar examples can be found in the reactions of  $\text{Fe}^+ + \text{ClCH}_2\text{CH}_2\text{Br}$  and  $\text{Co}^+ + \text{ClCH}_2\text{CH}_2\text{OH}$ , in which metal ions interact with both functional groups in a five-membered ring configuration, leading to the formation of  $\text{FeClBr}$  and  $\text{CoClOH}$  by elimination of ethylene [22]. Similarly, the observation of dominant signal of  $\text{TiF}_2^+$  ion in the reaction of  $\text{Ti}^+$  with TFA strongly suggests that the reaction undergoes via a five-membered ring structure of  $\text{Ti}^+(\text{TFA})$  association complex. Details on structure and energetics during the reaction of  $\text{Ti}^+$  and TFA are discussed latter.



**Figure 1.** Mass spectrum of the cluster ions produced by reactions of  $\text{Ti}^+$  with 1,1,1-trifluoroacetone (TFA) clusters.  $a_n$ :  $\text{Ti}^+(\text{TFA})_n$ ;  $b_n$ :  $\text{TiF}_2^+(\text{TFA})_n$ ;  $M_n$ :  $\text{H}^+(\text{TFA})_n$ ; \* corresponds fragmented  $\text{CH}_3\text{CO}^+(\text{TFA})_n$  clusters.

The mass spectrum shows a major sequence of heterocluster ions with a formula of  $\text{TiF}_2^+(\text{TFA})_n$  (denoted  $b_n$ ). Contrary to the reactions between  $\text{Ti}^+$  and ACT clusters in which oxidation pathway is only possible reaction channel, the predominant reaction pathway can be speculated as an association of  $\text{Ti}^+$  ion into the  $(\text{TFA})_n$  clusters followed by successive F atom abstractions on a single TFA molecule within the parent  $\text{Ti}^+(\text{TFA})_n$  ( $a_n$  series) clusters. It might be argued that successive F atom abstractions can occur on several TFA molecules. Total absence of peaks with the formula of  $\text{TiF}^+(\text{TFA})_n$ , however, suggests that  $\text{TiF}_2^+$  formation process occurs only on single TFA molecule within  $\text{Ti}^+(\text{TFA})_n$  clusters. This formation is also analogous to the effective formation of  $\text{TiF}_2^+$  (72%) in the reaction of  $\text{Ti}^+$  with hexafluorobenzene, where six F atoms are available to migrate [23]. These findings thus indicate that as far as the

intracluster reaction of  $\text{Ti}^+$  with ACT clusters is concerned, the dominant reaction pathway is altered by replacing the H atoms on the  $\text{CH}_3$  group of acetone with F atoms. In addition, both  $\text{TiF}_2^+$  and  $\text{TiO}^+$  ions are generated in the ion-molecule reaction between  $\text{Ti}^+$  and TFA as shown in low mass region of spectrum, but even in this case,  $\text{TiF}_2^+$  formation channel is more efficient than  $\text{TiO}^+$  formation pathway.

### 3.2. Energetics and Reaction Mechanism of Reaction Between $\text{Ti}^+$ and TFA

As discussed, the ion-molecule reactions of  $\text{Ti}^+$  with TFA produced major products of  $\text{TiF}_2^+$  and  $\text{TiO}^+$ , which were attributed to the successive abstraction of F atoms and the insertion of  $\text{Ti}^+$  into  $\text{C}=\text{O}$  bond of TFA, respectively.

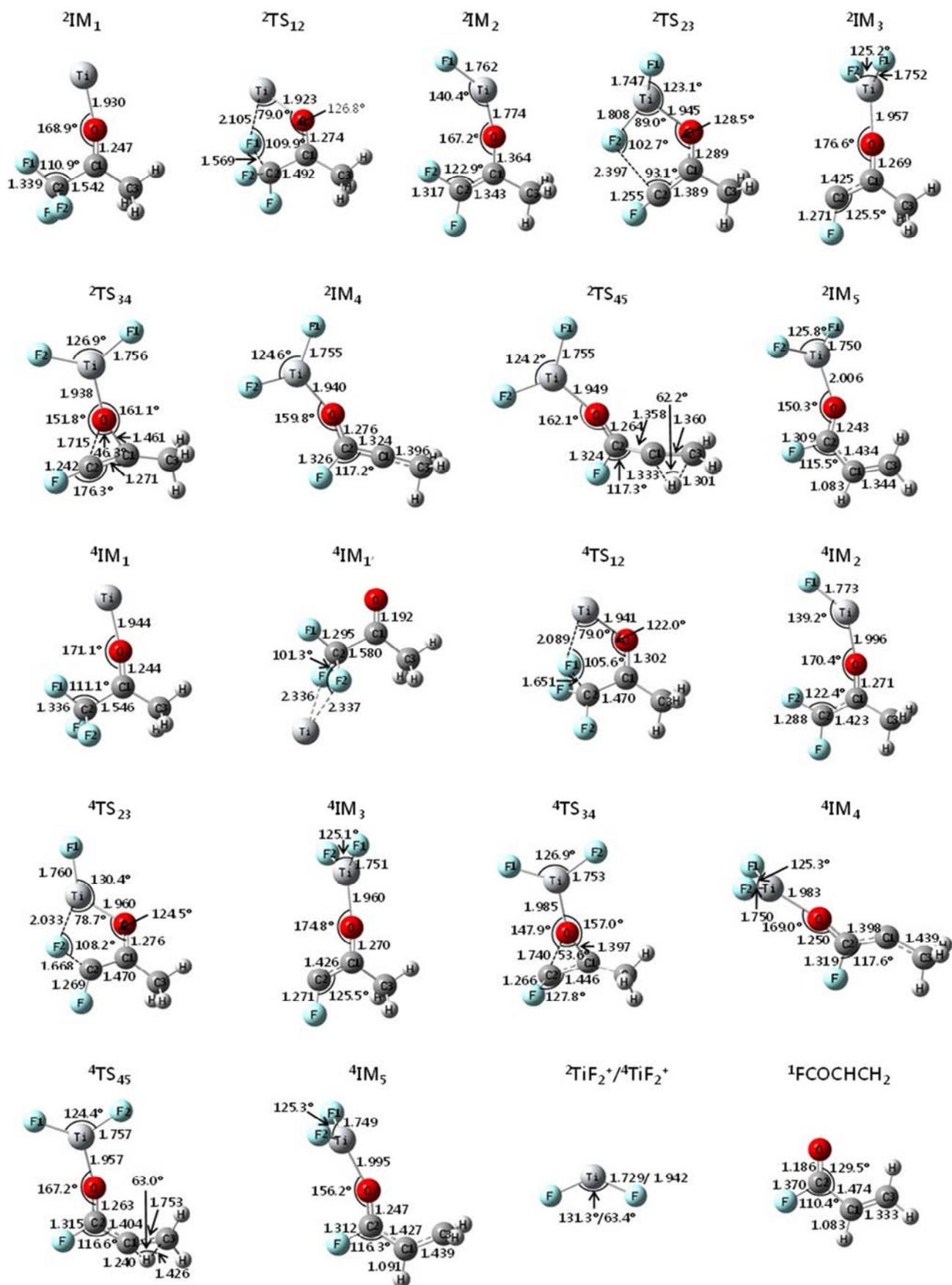
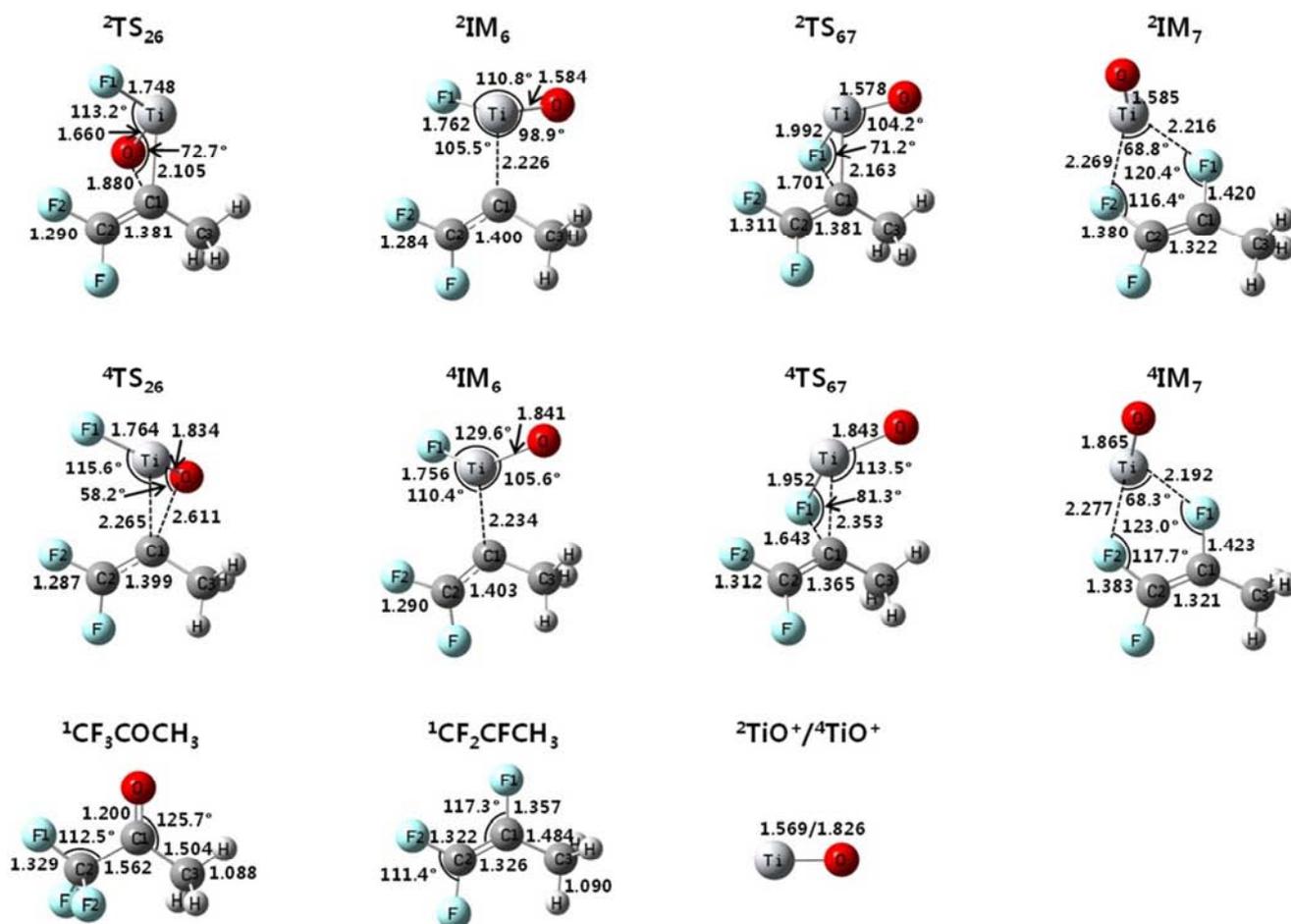


Figure 2. Optimized geometries and selected structural parameters (bond lengths in Å and angles in degrees) at the B3LYP/6-311++G(d,p) levels of theory for the reactants, products, intermediates and saddle points involved in the F atoms abstraction of TFA with  $Ti^+$  on the doublet and quartet states.



**Figure 3.** Optimized geometries and selected structural parameters (bond lengths in Å and angles in degrees) at the B3LYP/6-311++G(d,p) levels of theory for the reactants, products, intermediates and saddle points involved in the oxidation pathway of TFA with  $\text{Ti}^+$  on the doublet and quartet states.

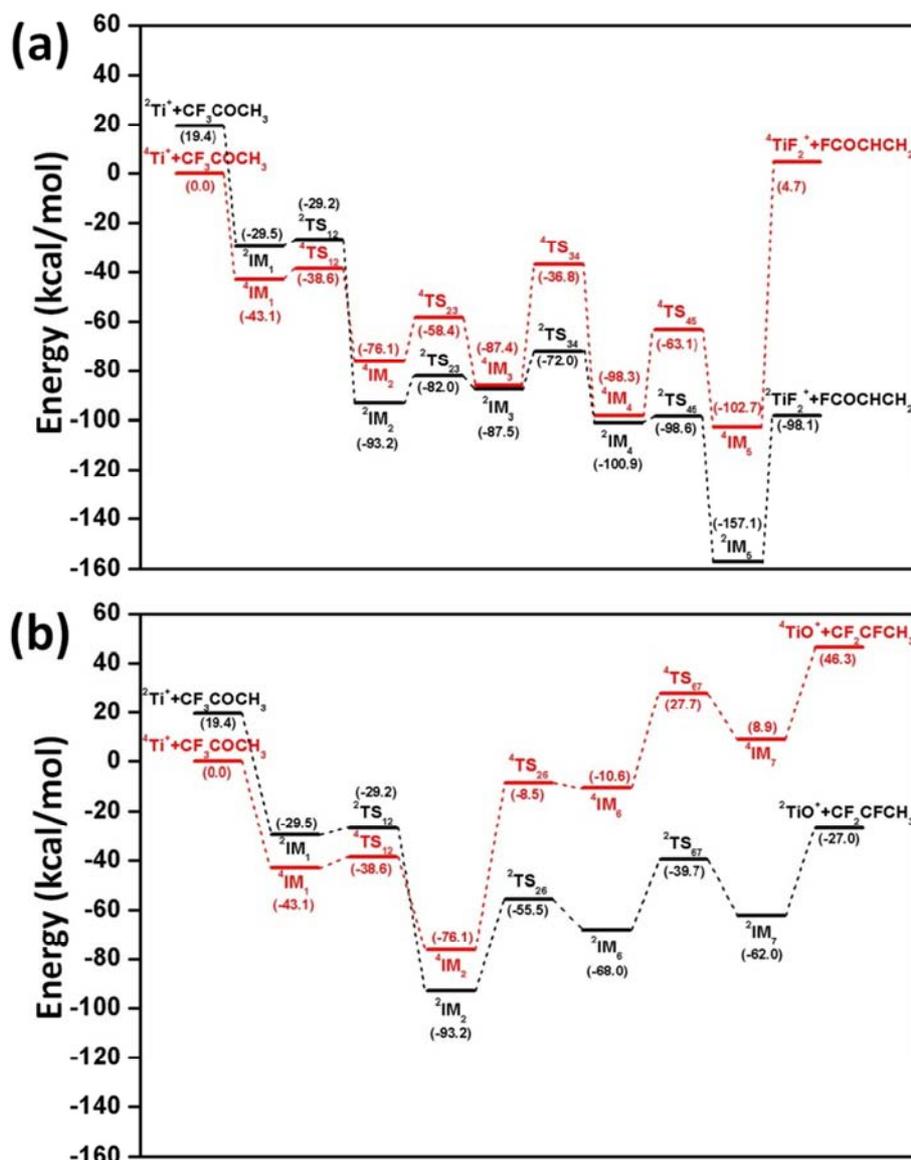
To interpret the experimental findings and gain further insight into the reaction mechanism, the electronic structure calculations were performed to propose two possible reaction pathways for the reaction between  $\text{Ti}^+$  and TFA: one is  $\text{TiF}_2^+$  formation from five-membered ring structure and the other is  $\text{TiO}^+$  formation channel in which  $\text{Ti}^+$  ion inserts into C=O bond of TFA followed by intramolecular F atom transfer process (oxidation process). The optimized geometries of the stationary points in both doublet and quartet states for these two above mention channels,  $\text{TiF}_2^+$  and  $\text{TiO}^+$  formation, are depicted in Figures 2 and 3, respectively.

Figures 4(a) and 4(b) show the relevant PES along with the pathway of  $\text{TiF}_2^+$  and  $\text{TiO}^+$  formation, respectively.  ${}^4\text{Ti}^+$  (the superscript denotes the spin multiplicity) with TFA was used for the reference energy on all reaction PESs since the ground state  $\text{Ti}^+({}^4\text{F})$  was computed to lie 19.4 kcal·mol<sup>-1</sup> below the excited state  $\text{Ti}^+({}^2\text{F})$ . We used notations of  $\text{IM}_n$  and  $\text{TS}_{nm}$  for the intermediate  $n$  and the transition state between the  $\text{IM}_n$  and the  $\text{IM}_m$ , respectively. To validate the theoretical results, the bond dissociation energies of  $\text{Ti}^+(\text{H}_2\text{O})$  and  $\text{Ti}^+(\text{NH}_3)$  at the B3LYP/6-311++G(d,p) levels were also first calculated, which were computed to be 37.2 and 46.8 kcal·mol<sup>-1</sup>, respectively. These values are agreeing well with

experimental values, confirming the validity of the calculation results.

As discussed in the experimental results, the geometry of initial association complex in the reaction of  $\text{Ti}^+$  with TFA is expected to be different with that in the reaction of  $\text{Ti}^+$  and ACT. To classify the geometry of association complex, two plausible structures ( ${}^4\text{IM}_1$  and  ${}^4\text{IM}_1'$ ) of association complex in quintet states were calculated.  ${}^4\text{IM}_1$  corresponds to the case in which  $\text{Ti}^+$  interacts with the O atom of TFA. Ongoing from the free TFA to  ${}^4\text{IM}_1$ , the C(1)=O bond is lengthened by 0.044 Å. It is likely that this bond weakening ultimately leads to the rupture of this bond.

On the other hand,  ${}^4\text{IM}_1'$  represents the case in which the  $\text{Ti}^+$  approaches to two F atoms of the  $\text{CF}_3$  group, leading to the formation of  $\text{TiF}_2^+$  via C-F activation. Note that  ${}^4\text{IM}_1'$  is more stable than  ${}^4\text{IM}_1$ , by 26.1 kcal·mol<sup>-1</sup>, suggesting that  ${}^4\text{IM}_1'$  is the more favorable structure of the association complex in the reaction of  $\text{Ti}^+$  with TFA. In addition, NPA analysis on the free TFA implies that the atomic charge of O (-0.487) is more negative than that of the adjacent F(1) atom (-0.332). The linkage of  $\text{Ti}^+$  to O and F(1) atoms in the  ${}^4\text{IM}_1$  is consistent with our observations that the reaction of  $\text{Ti}^+$  with TFA leads to the facile production of  $\text{TiF}_2^+$  and  $\text{TiO}^+$ .



**Figure 4.** Potential energy diagrams along the reaction pathway, (A) F atoms abstraction and (B) oxidation reactions of TFA with  $\text{Ti}^+$  on the doublet and quartet potential energy surfaces. All the relative energies are reported with ZPE corrections with the scaling factor of 0.961.

Initially a  $\text{Ti}^+$  ion attacks the electron-rich oxygen of the TFA and forms stable association complexes  ${}^2\text{IM}_1$  and  ${}^4\text{IM}_1$ . These complexes are calculated to be more stable by  $43.1 \text{ kcal}\cdot\text{mol}^{-1}$  ( ${}^4\text{IM}_1$ ) and  $29.5 \text{ kcal}\cdot\text{mol}^{-1}$  ( ${}^2\text{IM}_1$ ), respectively, than the isolated reactants ( ${}^4\text{Ti}^+ + \text{CF}_3\text{COCH}_3$ ). The  $\text{C}_s$  symmetric complex  ${}^4\text{IM}_1$  has a nearly linear binding of  $\text{Ti}^+-\text{O}-\text{C}(1)$  ( $171.1^\circ$ ), remarkably different from the bent geometry of the  $\text{Ni}^+-\text{CH}_3\text{COCH}_3$  complex ( $\text{Ni}^+-\text{O}-\text{C} = 138.8^\circ$ ), which produces  $\text{Ni}^+\text{CO} + \text{C}_2\text{H}_6$  fragments. Upon binding with  ${}^4\text{Ti}^+$ , the largest change in TFA is the stretching of  $\text{O}-\text{C}(1)$  bond distance (3.7%) due to the oxygen polarizing charge toward  $\text{Ti}^+$ . Once the association complexes formed, the next step can carry the association complex  $\text{IM}_1$  to the fluoride-containing species  $\text{IM}_2$  via transition state  $\text{TS}_{12}$ . As shown in Figure 2, this process is strictly analogous to the migration of the hydrogen atom for  $\text{HMg}^+-\text{OCHCH}_2$  from  $\text{Mg}^+-\text{OCHCH}_3$ , in which the transition state ( ${}^4\text{TS}_{12}$ ) has a five-membered structure. The five-membered ring structure

is also similar to the intermediates in cases of  $\text{Mg}^+ + o\text{-C}_6\text{H}_4\text{F}_2$ ,  $\text{Mg}^+ + \text{CF}_3\text{CH}_2\text{OH}$ ,  $\text{Fe}^+ + \text{BrCH}_2\text{CH}_2\text{Cl}$ , and  $\text{Co}^+ + \text{ClCH}_2\text{CH}_2\text{OH}$  reactions [21-22, 24].

Similar to recent calculations of  $\text{Ti}^+ + \text{ACT}$  reaction [9, 20], we focus on the intersystem crossing (ISC) point between  ${}^4\text{TS}_{12}$  and  ${}^2\text{IM}_2$ , because this ISC point is directly related to the most favorable reaction pathway of the direct metal-ion insertion. The ISC has also been reported in the reactions of  $\text{Ti}^+$  with small organic molecules such as  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CN}$  [25-27]. Figure 4(a) and 4(b) show that there is an ISC between  ${}^4\text{TS}_{12}$  and  ${}^2\text{IM}_2$ . In addition, it is unlikely that the reaction proceeds on the quartet PES, because the fourth coming barriers height between  ${}^4\text{IM}_3$  and  ${}^4\text{TS}_{34}$  ( $50.6 \text{ kcal}\cdot\text{mol}^{-1}$ ) &  ${}^4\text{IM}_2$  and  ${}^4\text{TS}_{26}$  ( $67.6 \text{ kcal}\cdot\text{mol}^{-1}$ ) are too high. Therefore, the reaction of  ${}^4\text{Ti}^+$  with TFA predominantly occurs on the doublet PES after  ${}^2\text{IM}_2$  formation.

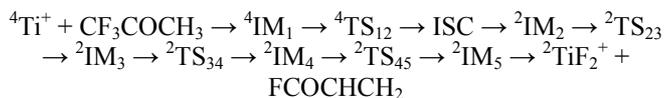
After  ${}^2\text{IM}_2$ , there are two alternative pathways along the

reaction coordinate. The energy sketch of the  $\text{TiF}_2^+$  formation channel is shown in Figure 4(a). Along this pathway, a  $\text{C}(1)\text{-O-Ti}^+$  scissor vibration in  ${}^2\text{IM}_2$  can transfer the second F atom to the metal center to form complex  ${}^2\text{IM}_3$  through  ${}^2\text{TS}_{23}$ . Similar to the  ${}^4\text{IM}_2$  and  ${}^2\text{IM}_2$ , the five-membered doublet transition state  ${}^2\text{TS}_{23}$  ( $E_{\text{rel}} = -82.0 \text{ kcal}\cdot\text{mol}^{-1}$ ) is more stable than  ${}^4\text{TS}_{23}$ . It is interesting to note that both  ${}^4\text{IM}_3$  and  ${}^2\text{IM}_3$  indeed have an almost identical stability ( ${}^2\text{IM}_3$  is  $0.1 \text{ kcal}\cdot\text{mol}^{-1}$  stable than  ${}^4\text{IM}_3$ ) as well as same structure whose  $\text{Ti}^+\text{-O}$  bond is largely weakened ( $R_{\text{TiO}} = 1.957 - 1.960 \text{ \AA}$ ): thus  $\text{TiF}_2^+$  is effectively dissociated from association complex. The forward intermediate from  ${}^2\text{IM}_3$  is  ${}^2\text{IM}_4$ , which involves a three-membered ring  ${}^2\text{TS}_{34}$  with a barrier of  $15.5 \text{ kcal}\cdot\text{mol}^{-1}$ . An interaction takes place between O and both C(1) and C(2) in the  $\text{TS}_{34}$ . The energy of  ${}^2\text{IM}_4$  is  $13.4 \text{ kcal}\cdot\text{mol}^{-1}$  lower than that of  ${}^2\text{IM}_3$ . The H atom then migrates into C(1) from C(3) atoms, forming electrostatic complex,  $\text{IM}_5$  between  $\text{TiF}_2^+$  and  $\text{FCOCHCH}_2$ , the direct precursor of products in the  $\text{TiF}_2^+$  formation pathway ( $\text{TiF}_2^+ + \text{FCOCHCH}_2$ ). Energetically  ${}^2\text{IM}_5$  is located at  $E_{\text{rel}} = -157.1 \text{ kcal}\cdot\text{mol}^{-1}$ , which represents the deepest barrier along the doublet surface of the F atoms abstraction pathway due to the strong stabilization of both the constituent entities ( ${}^2\text{TiF}_2^+$  and  $\text{FCOCHCH}_2$ ). Fragmentation of the  $(\text{FCOCHCH}_2)\text{-TiF}_2^+$  bond of  ${}^2\text{IM}_5$  gives rise to the products in F atoms abstraction pathway and the overall reaction energy of the  ${}^4\text{Ti}^+ + \text{CF}_3\text{COCH}_3 \rightarrow {}^2\text{TiF}_2^+ + \text{FCOCHCH}_2$  is calculated to be  $-98.1 \text{ kcal}\cdot\text{mol}^{-1}$ .

Another reaction pathway is the oxidation pathway to account for the final products of  $\text{TiO}^+ + \text{CF}_2\text{CFCH}_3$ . The PES for the oxidation process is shown in Figure 4(b). This pathway also starts  ${}^4\text{IM}_1$ , passes through ISC, and subsequently  ${}^2\text{IM}_2$  is formed as in the pathway of F atoms abstraction. After  $\text{IM}_2$ , intermediate  $\text{IM}_6$  is formed as a result of the insertion of  $\text{Ti}^+$  into the  $\text{C}(1)=\text{O}$  bond of TFA via  ${}^2\text{TS}_{26}$  and  ${}^4\text{TS}_{26}$  with a barrier of  $37.7$  and  $67.6 \text{ kcal}\cdot\text{mol}^{-1}$ , respectively.  $\text{TS}_{26}$  is characterized by a three-membered ring of  $\text{Ti-O-C}(1)$  and  $\text{Ti}^+$  directly coordinated with the C(1) atom. The  $\text{C}(1)\text{-O}$  bond is weakened and substantially elongated in both  ${}^2\text{TS}_{26}$  and  ${}^4\text{TS}_{26}$  compared with  ${}^2\text{IM}_2$ . The barrier height between the  ${}^2\text{IM}_2$  and  ${}^2\text{TS}_{26}$  is the largest ( $37.7 \text{ kcal}\cdot\text{mol}^{-1}$ ) on the double PES of this pathway which implies that the  $\text{Ti}^+$  insertion onto the  $\text{C}=\text{O}$  bond is the rate-determining step of the oxidation pathway. The intra-rotation of  $\text{Ti}^+\text{-F}$  bond produces an electrostatic complex,  $\text{IM}_7$  between  $\text{CF}_2\text{CFCH}_3$  and  $\text{TiO}^+$ , the direct precursor of the oxidation products. The  ${}^2\text{IM}_6$  proceeds via the  ${}^2\text{TS}_{67}$  structure to the  ${}^2\text{IM}_7$ , which is well characterized by the five-membered ring structure. The dissociation of the  $(\text{CF}_2\text{CHCH}_3)\text{-TiO}^+$  bond of  $\text{IM}_7$  gives rise to  $\text{TiO}^+ + \text{CF}_2\text{CFCH}_3$  and the overall oxidation is computed to be exothermic by  $27.0 \text{ kcal}\cdot\text{mol}^{-1}$  for  $\text{TiO}^+({}^2\Delta) + \text{CF}_2\text{CFCH}_3$ . In analogous to the reaction of  $\text{Ti}^+$  with ACT, the alternative pathway in the formation  $\text{TiO}^+$  via H atom migration was also studied. However, the electron rich F atom doesn't allow direct insertion of  $\text{Ti}^+$  ion onto the  $\text{C}=\text{O}$  bond in the relatively

stable association complex,  ${}^4\text{IM}_1$ . The H atom migration channel (1b), hence, should be eliminated from the production of  $\text{TiO}^+$  in present study.

Among the reaction pathway of  $\text{Ti}^+ + \text{TFA}$ , the more favorable reaction pathway can be estimated from the PESs in Figure 4. Although reaction mechanism of  $\text{TiF}_2^+$  formation pathway is rather complex than that of the oxidation pathway, a comparison between the values of the relative energies of the highest TSs for both reaction channels shows that  ${}^2\text{TS}_{26}$  for the oxidation pathway has a larger value ( $37.7 \text{ kcal}\cdot\text{mol}^{-1}$ ) than  ${}^2\text{TS}_{34}$  ( $15.5 \text{ kcal}\cdot\text{mol}^{-1}$ ) in F atoms abstraction. On the basis of above results, the F atoms abstraction pathway is likely to be the more favorable pathway for the reaction of  $\text{Ti}^+$  with TFA. The reaction pathway can be summarized as follows:



During this reaction pathway,  $\text{Ti}^+$  efficiently abstracts F atoms in TFA via C-F bond activation. However, relatively small difference of activation energy between two highest energy stationary points for both reaction pathways indicates that two reaction mechanisms should be considered as competitive reaction pathways in our experimental conditions. These calculation findings suggest that the  $\text{TiF}_2^+$  ions are primary reaction products and the oxidation pathway is a less efficient route, which are well in agreement with our experimental observations.

In addition, it is mentionable that the reaction of  $\text{Ti}^+$  and TFA with 1:1 ratio for primary reaction products is considered in our calculation. So, the reactions of  $\text{Ti}^+$  ion with TFA only lead to ion-molecule products. On the other hand, the reaction of  $\text{Ti}^+$  with TFA is carried out inside the clusters, where orbital overlapping or Van der waal attraction is the driving force for cluster formation. So, all the ligated TFAs in association cluster  $\text{Ti}^+(\text{THA})_n$  ions are not equivalent.  $\text{Ti}^+$  ion, thus, only can reacts with TFA ligand, which is the closest to it, and produces various types of product ions followed by stabilization with surrounding ligands. Considering the reaction environment, the calculation results on the resulting species  $\text{TiF}_2^+$  and  $\text{TiO}^+$  ions, which are also observed in the mass spectrum, should be same even upon clustering. Moreover, although recently few studies have done on the electronic structure calculation on the growth of cluster formation [28-29], however, there is no any computational result yet about the ion-molecule reaction which occurred inside the cluster itself.

## 4. Conclusions

In the present study ion-molecule reactions of  $\text{Ti}^+$  with TFA in the gas phase was investigated using a combination of laser ablation and supersonic beam expansion and DFT calculation methods. The primary reactions produce a major sequence of  $\text{TiF}_2^+(\text{TFA})_n$  ions which is attributed to the successive F atom abstraction within the parent  $\text{Ti}^+(\text{TFA})_n$

clusters. Substitution of the CH<sub>3</sub> group in ACT with the more electronegative CF<sub>3</sub> group alters the reaction pathway such that TiF<sub>2</sub><sup>+</sup> and TiO<sup>+</sup> ions are generated in the ion-molecule reactions due to the distinct geometry of the association complex. In addition, detailed reaction mechanisms for two plausible reaction pathways were unraveled by DFT calculations. The molecule structures of intermediate and transition states involved in these pathways are fully optimized and the resulting reaction coordinates describe how Ti<sup>+</sup> activates TFA and yields TiF<sub>2</sub><sup>+</sup> and TiO<sup>+</sup> ions as competitive reaction pathways. These experimental and theoretical results improve our understanding for the reactions of transition metal ion with ketone possessing more than one functional group.

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