J. Phys. Chem. A **1998,** *102,* 3639−3642

Long-Lived, Multiply Charged Diatomic TiF^{n+} Ions ($n = 1-3$)

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Received: January 14, 1998; In Final Form: March 18, 1998

Cationic titanium monofluorides TiF^{n+} ($n = 1-3$) have been examined by mass spectrometric and theoretical methods, with particular attention being given to the question of the thermochemical stability of the multiply charged species. Diatomic TiF^{n+} cations can be generated by dissociative electron ionization of titanium(IV) fluoride. In addition, long-lived TiF^{2+} and TiF^{3+} are accessible by charge-stripping mass spectrometry of mass-selected mono- and dications, respectively. This method also allows the measurement of the corresponding vertical ionization energy (IE_v), which were determined as $IE_v(TiF^+) = 15.2 \pm 0.3$ eV and $IE_v(TiF^{2+}) = 28 \pm 3$ eV. These values are in agreement with those obtained from high-level ab initio calculations. Thus, TiF^{2+} is a thermochemically stable diatomic dication, while TiF^{3+} trication is metastable with respect to the $Ti^{2+} + F^+$ asymptote. No evidence for Coulomb explosion was observed, suggesting a very long lifetime for this triply charged diatomic. Theory further predicts the existence of ZrF^{3+} in the gas phase, which, however, is also metastable with respect to charge separation into $Zr^{2+} + F^+$.

Introduction

Thermochemically stable diatomic dications have attracted considerable attention by both experimentalists and theoreticians,[1] because their study provides insight into the principles of chemical bonding in the presence of multiple charges. In the gas phase, dications are referred to as "thermochemically stable" when their bound minimum lies lower in energy than the lowest atomic asymptote. These multiply charged ions are, of course, usually not stable in bimolecular collisions in which electron transfer often prevails owing to the low ionization energies (IEs) of most atoms and molecules. Conceptually, atomic data alone can be used to predict the existence of thermochemically stable polycations. Thus, if the lowest atomic asymptote of a polycation AB^{n+} corresponds to $A^{n+} + B$, that is, if $IE(A^{(n-1)+})$ is lower than IE(B), then there will exist a bound state of AB^{n+}, because the interaction between the positive ion A^{n+} and neutral B is always attractive.

In addition to the more elusive rare gas clusters,[2] thermochemically stable diatomic dications are expected to exist among the binary metal fluorides (Figure 1), because many metal cations M^+ have relatively low ionization energies (IEs) to the corresponding dications M^{2+}, while the ionization energy of the fluorine atom is high (17.4 eV).[3] Recent examples[4,5] for this type of dications are CaF^{2+}, MgF^{2+}, and SiF^{2+} with $IE(Ca^+) = 11.9$ eV, $IE(Mg^+) = 15.0$ eV, and $IE(Si^+) = 16.3$ eV, respectively.[6] In fact, owing to the potent binding properties of fluorine, thermochemically stable dications may even exist if $IE(M^+)$ exceeds IE(F) provided that the strength of the $M^{2+}-F$ bond is large enough, e.g., BeF^{2+}, AlF^{2+}, and PF^{2+} with $IE(Be^+) = 18.2$ eV, $IE(Al^+) = 18.8$ eV, and $IE(P^+) = 19.7$ eV, respectively.[6]

Diatomic trications[2,7] are more challenging because for these $IE(A^{2+})$ needs to be smaller than or close to IE(B). Thus, only for the experimentally less accessible rare gas compounds some thermochemically stable diatomic trication are guaranteed to exist.[2,8,9] Drawing upon the above results for the metal fluorides, we performed a combined experimental and theoretical study of diatomic TiF^{n+} and ZrF^{n+} cations ($n = 1-3$). These early transition metals have rather low ionization energies and form strong bonds with fluorine.[10]

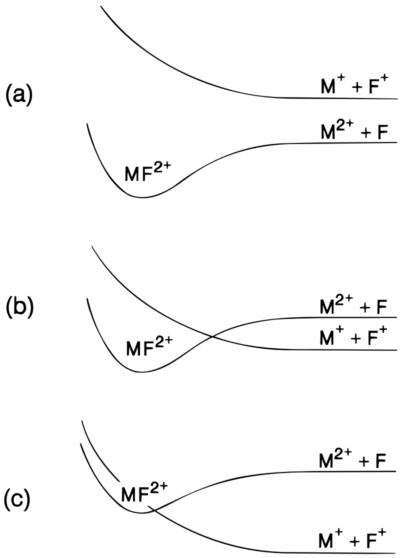

Figure 1. Schematic representation of potential-energy curves for binary metal fluoride dications MF^{2+}: (a) thermochemically stable dication with $IE(M^+) < IE(F)$, e.g., MgF^{2+} (ref 4b); (b) thermochemically stable dication with $IE(M^+) > IE(F)$, e.g., SiF^{2+} (ref 5b); (c) metastable dication with $IE(M^+) \gg IE(F)$, e.g., BF^{2+} (ref 6).

Experimental and Computational Procedures

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors), which has been described elsewhere.[11] TiF^{n+} cations ($n = 1-3$) were generated by electron ionization (electron energy 70 eV) of TiF_4 (Aldrich). After acceleration by a 8 kV voltage, the ions of

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S1089-5639(98)00782-8 CCC: $15.00

TABLE 1: Calculated Ionization Energies (IE in eV) of Titanium and Fluorine

property	theory[a,b]	experiment
IE(Ti^+)	13.12	13.58[c]
IE(Ti^{2+})	26.86	27.49[c]
IE(Ti^{3+})	42.63	43.27[c]
IE(F)	17.09	17.42[d]

[a] Calculated at the CCSD(T) level of theory; see computational details. [b] Relevant states: Ti^+ (^4F), Ti^{2+} (^3F), Ti^{3+} (^2D), Ti^{4+} (^1S), F (^2P), and F^+ (^3P), respectively. [c] Taken from: Martin, G. A.; Fuhr, J. R.; Wies, W. C. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 3. [d] Taken from ref 3.

interest were mass-selected using B(1)E(1) at a mass resolution of $m/\Delta m \approx 4000$. The charge-stripping experiments[1a−c,12] of monocations were performed by colliding the ions with oxygen (50−80% transmission, T); for charge stripping of dications, helium was used as collision gas. $Q_{\min}$ values were determined by energy scans with E(1) for B(1) mass-selected species at energy resolutions of $E/\Delta E \approx 6000$. As references for the calibration of the energy scale, we applied the commonly used toluene standard[1b] assuming $Q_{\min} = 15.7$ eV for the transition $C_7H_8^+ \rightarrow C_7H_8^{2+}$. The charge-exchange mass spectra of B(1)/E(1) mass-selected TiF^{3+} was scanned using B(2) using oxygen as a collision gas; note that E scans cannot be applied under these circumstances, because the incident energy of the trication amounts to 24 keV such that singly and doubly charged TiF^{n+} cannot be transmitted. Owing to hardware limitations of the A/D interface, the $Q_{\min}$ values were acquired as single scans with an *x*/*y*-recorder in order to achieve maximal energy resolution; indications for the presence of electronically excited precursor ions were not observed in the charge-stripping experiments.[1a,13] All other spectra were accumulated and online processed with the AMD/Intectra data system; 5−50 spectra were averaged to improve the signal-to-noise ratio.

Ab initio calculations were performed using the restricted open-shell coupled cluster method CCSD(T) as implemented in Molpro 96.[14] The ions involved are relatively well described by the single HF determinant at their equilibrium geometries, which justifies the use of a single-reference ansatz.[15] For each species, the minimum geometry was optimized stepwise to within 0.01 Å. The basis sets used for TiF^{n+} were atomic natural orbital (ANO) basis sets of (21s15p10d6f)/[6s,5p,4d,-2f] size for titanium[16] and of (14s9p4d)/[6s5p3d] size for fluorine.[17] For ZrF^{n+}, the correlation-consistent cc-pVDZ basis set of Dunning was used for fluorine,[18] and zirconium was described by a relativistic core potential for the inner 28 [Ar3d^{10}] electrons,[19] with the corresponding (8s7p6d)/[6s5p3d] basis set for the 4s4p4d5s valence electrons to which a single f primitive ($\alpha = 1.4$) was added. Pure spherical harmonic basis functions (5d, 7f) were used throughout, and only the valence electrons were correlated.

Results and Discussion

Let us begin with the theoretical description of the TiF^{n+} cations ($n = 1-3$). To evaluate the performance of the CCSD(T) approach, we first calculated some relevant atomic properties of titanium and fluorine (Table 1). As expected, the ionization energies are systematically somewhat underestimated owing to the moderately sized basis sets applied and the neglect of core correlation effects. Likewise the energies of the diatomic minima are expected to be slightly too high, but this shortcoming should not change the substance of our conclusions.

TABLE 2: Calculated Bond Lengths (r_{M-F} in Å) and Total Energies (hartree)[a] of TiF^{n+} and ZrF^{n+} Cations at the CCSD(T) Level of Theory

	r_{M-F}	CCSD(T)[b,c]
TiF^+ ($^3\Phi$)	1.81	−948.043 45
TiF^+ ($^3\Sigma^-$)	1.77	−948.0344 06
TiF^{2+} ($^2\Delta$)	1.66	−947.4879 07
TiF^{2+} ($^2\Delta$)	1.81[d]	−947.4742 45
TiF^{3+} ($^1\Sigma^+$)	1.65	−946.5003 01
ZrF^+ ($^3\Sigma^-$)	1.87	−145.9807 24
ZrF^{2+} ($^2\Delta$)	1.82	−145.4984 07
ZrF^{3+} ($^1\Sigma^+$)	1.78	−144.6659 05

[a] 1 hartree = 27.21 eV. [b] For the basis sets used, see computational details. [c] Selected total energies of the atoms: Ti^+ (^4F) −848.219 259, $F^\bullet$ (^2P) −99.618 651 and Zr^+ (^4F) −46.232 797, $F^\bullet$ (^2P) −99.527 502. [d] Energy of the dication at the equilibrium distance of the monocation; thus, $IE_v - IE_a$ amounts to 0.37 eV for TiF^+.

CCSD(T) predicts that the TiF^+ monocation has a $^3\Phi$ ground state (Table 2) with a $1\sigma^2 2\sigma^2 1\pi^4 1\delta^1 2\pi^1$ configuration in the molecular orbitals of the valence electrons.[20] Unlike the isoelectronic VO^+ cation,[21] but similar to $TiCl^+$ cation,[22] the $1\sigma^2 2\sigma^2 1\pi^4 1\delta^2$ configuration of TiF^+ ($^3\Sigma^+$) corresponds to a low-lying excited state ($\Delta E = 0.2$ eV) although the Ti−F bond of the $^3\Sigma^+$ state is somewhat shorter than in TiF^+ ($^3\Phi$). The different ground-state configurations in VO^+ and TiF^+ may be attributed to the smaller splitting of δ and π orbitals in the fluoride such that maximization of magnetic momentum favors the $^3\Phi$ ground state for TiF^+. The bond dissociation energy (D_e) of the TiF^+ ($^3\Phi$) monocation is calculated as $D_e(Ti^+{-}F) = 5.6$ eV.[23]

The vertical ionization energy (IE_v) of TiF^+ ($^3\Phi$) to TiF^{2+} ($^2\Delta$) with a $1\sigma^2 2\sigma^2 1\pi^4 1\delta^1$ configuration is calculated as 15.5 eV. In the ionization TiF^+ ($^3\Phi$) → TiF^{2+} ($^2\Delta$), one electron is removed from the antibonding 2π orbital, causing a decrease of the Ti−F bond length from 1.81 Å in TiF^+ ($^3\Phi$) to 1.65 Å in TiF^{2+} ($^2\Delta$). Hence, the adiabatic ionization energy (IE_a) of TiF^+ ($^3\Phi$) is 0.4 eV lower than IE_v and amounts to $IE_a(TiF^+) = 15.1$ eV. These computational results predict $D_e(Ti^{2+}{-}F) = 3.6$ eV. Further, TiF^{2+} ($^2\Delta$) is located 7.6 eV below the dissociation asymptote to Ti^+ (^4F) + F^+ (^3P), and hence TiF^{2+} ($^2\Delta$) constitutes a thermochemically stable dication.

For the TiF^{3+} trication, theory predicts a $^1\Sigma^+$ ground state with $IE_a(TiF^{2+}) = 26.9$ eV. Owing to the negligible difference (0.01 Å) in the Ti−F bond lengths in TiF^{2+} ($^2\Delta$) and TiF^{3+} ($^1\Sigma^+$), we assume $IE_v(TiF^{2+}) \approx IE_a(TiF^{2+})$. The bond dissociation energy $D_e(Ti^{3+}{-}F)$ is calculated as 3.6 eV, but nevertheless the Coulomb explosion into Ti^{2+} (^2D) + F^+ (^3P) cations is exothermic by 6.2 eV. Preliminary CASSCF calculations reveal, however, that charge separation is associated with a kinetic barrier of more than 2 eV at a Ti−F distance of ca. 2.9 Å. Thus, TiF^{3+} ($^1\Sigma^+$) trication is predicted to exist as a bound state residing in a decent potential well. Owing to the Coulomb barrier associated with charge separation, TiF^{3+} ($^1\Sigma^+$) is likely to have a lifetime long enough for its detection by mass spectrometric experiments operating in the microsecond time window.[1a−c,12]

As far as the ionization energies are concerned, these theoretical results are in good agreement with the experimental findings. In the charge-stripping spectrum of TiF^+, the TiF^{2+} signal is quite pronounced and only 10 times less abundant than that of the Ti^+ fragment. The $Q_{\min}$ value associated with the transition $TiF^+ \rightarrow TiF^{2+}$ is measured as 15.2 ± 0.3 eV. This result compares favorably with the calculated value, i.e., $IE_v(TiF^+) = 15.5$ eV, lending further confidence to the performance of the computational methods applied. Charge stripping of mass-selected TiF^{2+} ($m/z = 33.5$ for ^{48}Ti) with helium as collision gas gives rise to a small but distinct signal at $m/z =$

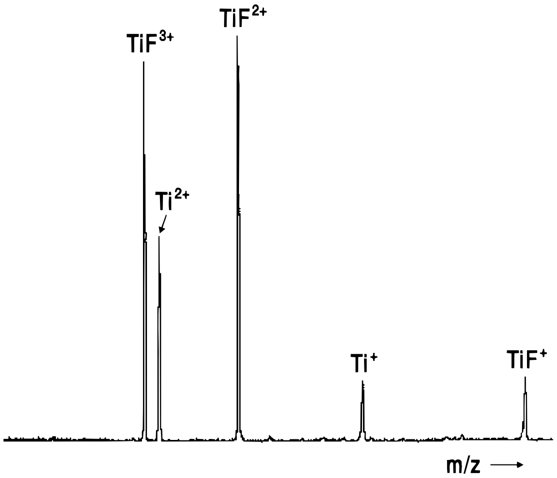

Figure 2. Charge-exchange spectrum (B(2) scan, oxygen, 60% transmission) of B(1)/E(1) mass-selected TiF^{3+} cations ($m/z = 22.3$) generated by electron ionization of TiF_4. In addition to Ti^{n+} ($n = 1, 2$; $m/z = 48$ and 24, respectively) fragments, the characteristic charge-exchange products TiF^{2+} and TiF^{+} are observed at $m/z = 33.5$ and 67, respectively.

22.3 corresponding to the formation of TiF^{3+}. Quantification of the energy demand for the process $TiF^{2+} \rightarrow TiF^{3+}$ is, however, much less straightforward as compared to charge stripping of monocations. In particular, we lack an appropriate reference to calibrate the energy scale of the experiment. For the time being, we rely on the toluene standard in conjunction with the additive method for calibration,[1b,4b,24] and derive a $Q_{\min}$ value of 28 ± 3 eV for the transition $TiF^{2+} \rightarrow TiF^{3+}$; the large error bar is mostly due to the lack of a reliable calibration reference for charge stripping of doubly charged ions.

It could be argued that the weak signal at $m/z = 22.3$ observed upon charge stripping of TiF^{2+} is due to some impurities and/or instrumental artifacts. To avert this objection, we searched for a more direct proof of the existence of metastable TiF^{3+} trication. To this end, the low abundant signal at $m/z = 22.3$, present in the electron ionization spectrum of titanium(IV) fluoride, was mass-selected and characterized experimentally. Collision of this ion with oxygen leads inter alia to signals at $m/z = 33.5$ and $m/z = 67$ (Figure 2), which can be attributed to the sequential occurrence of the charge-exchange reactions 1 and 2. These signals, detected at higher apparent masses than the incident precursor beam, can *only* be explained by the presence of a trication, and thus the charge-exchange spectrum provides unambiguous proof for the formation of TiF^{3+} upon ionization of TiF_4.

$$TiF^{3+} + O_2 \rightarrow TiF^{2+} + O_2^{\,+} \tag{1}$$

$$TiF^{2+} + O_2 \rightarrow TiF^{+} + O_2^{\,+} \tag{2}$$

As compared to previously characterized diatomic trications,[25] TiF^{3+} represents one of those long-lived, bound diatomic trications for which no lower lying states exist at the equilibrium distance. Nevertheless, TiF^{3+} ($^1\Sigma^+$) is metastable with respect to Coulomb explosion into separated atomic cations (Figure 3). The lack of a thermochemical stability of TiF^{3+} can obviously be attributed to the simple fact that IE(Ti^{2+}) is by about 10 eV larger than IE(F), and this difference cannot be compensated for by the covalent $Ti^{3+}{-}F$ bond.

Finally, we will briefly describe the ZrF^{n+} system (Table 2).[26] Here, IE(Zr^{+}) = 13.1 eV immediately implies that the ZrF^{2+} dication is thermochemically stable with respect to dissociation into Zr^{+} and F^{+}. Moreover, as IE(Zr^{2+}) = 23.0 eV is significantly lower than IE(Ti^{2+}) = 27.5 eV, ZrF^{3+} appears as a candidate for a thermochemically stable diatomic trication, provided that $D_e(Zr^{3+}{-}F)$ is large enough. Preliminary CCSD(T) calculations suggest, however, that this is not the case.[27] Thus, the calculated IE$_a$(ZrF^{2+}, $^2\Delta$) amounts to 22.7 eV with $D_e(Zr^{3+}{-}F)$ = 4.8 eV and an equilibrium distance of 1.78 Å in ZrF^{3+} ($^1\Sigma^+$). Accordingly, though prevented by a Coulomb barrier, the charge separation $ZrF^{3+} \rightarrow Zr^{2+} + F^{+}$ is still exothermic by 1.0 eV. Even though the theoretical description used here is by no means complete, the magnitude of this difference very much disfavors the perspective of ZrF^{3+} ($^1\Sigma^+$) being a thermodynamically stable diatomic trication. Unfortunately, we could not yet conduct an experimental study of the ZrF^{n+} system owing to the lack of precursors suitable for our experimental setup.[28]

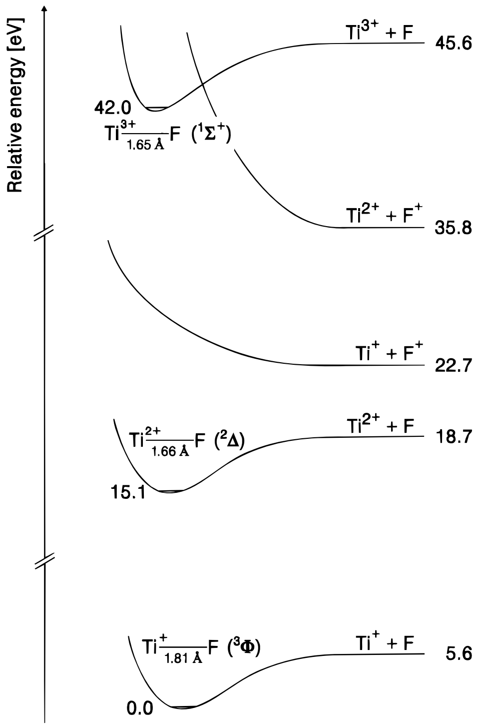

Figure 3. Summarized calculated thermochemistry (in eV) of TiF^{n+} diatomic cations ($n = 1-3$).

Conclusion

The diatomic transition-metal fluorides TiF^{n+} and ZrF^{n+} exhibit bound ground states for their mono-, di-, and tricationic forms. While TiF^{2+} and ZrF^{2+} represent thermochemically stable diatomic dications, the TiF^{3+} trication is only metastable with respect to charge separation to yield Ti^{2+} and F^{+} fragments. In comparison, the ZrF^{3+} trication is predicted to experience an even larger stabilization toward Coulomb explosion, but still it is not thermochemically stable by about 1 eV. Nevertheless, the diatomic trications TiF^{3+} and ZrF^{3+} represent the most stable structures at the corresponding equilibrium distances, while most of the few other diatomic trications experimentally studied so far[7,25] rest in bound potential-energy wells above the corresponding ground-state surfaces of the charge-separated atoms. Finally, the reasonable agreement between theory and experiment in conjunction with some experimental advantages suggests the use of the process $TiF^{2+} \rightarrow TiF^{3+}$ as a potential reference for a calibration of the energy scale in charge-stripping mass spectrometry for the generation of trications.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen Stiftung is gratefully acknowledged.

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(15) The calculations were performed in the C_{2v} Abelian point-group in which the $^3\Phi$ ground state of TiF$^+$ cannot be represented correctly by a single determinant. Instead, the ROHF wave function was used as a reference corresponding to a 1:1 mixture of $^3\Phi$ and $^3\Pi$ states. CASSCF and CASPT2 calculations were performed to estimate the difference between the 1:1 mixture and the $^3\Phi$ ground state. The latter was found to lie 9.5 mH lower than the mixture in the region of the minimum, and this value was used as a correction to the CCSD(T) results.

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(27) Calculated relative energies of the ZrF^{n+} system: ZrF$^+$ ($^3\Sigma^+$) = 0.0 eV, Zr$^+$ (^{4}F) + F (^{2}P) = 6.0 eV, ZrF^{2+} ($^2\Delta$) = 13.1 eV, Zr^{2+} (^{3}F) + F (^{2}P) = 18.1 eV, Zr$^+$ (^{4}F) + F$^+$ (^{3}P) = 22.7 eV, Zr^{2+} (^{3}F) + F$^+$ (^{3}P) = 34.8 eV, ZrF^{3+} ($^1\Sigma^+$) = 35.8 eV, Zr^{3+} (^{2}D) + F (^{2}P) = 40.6 eV.

(28) Attempts to generate ZrF^{n+} cations ($n \leq 3$) using ZrF$_4$ as well as zirconocen difluoride (Cp$_2$ZrF$_2$) as precursors gave only low yields of the ZrF$^+$ monocation and insufficient amounts of ZrF^{2+} dication. In the case of ZrF$_4$, the solid probe of our mass spectrometer could simply not reach the temperature required for evaporation.