

FTICR/MS studies of gas-phase actinide ion reactions: fundamental chemical and physical properties of atomic and molecular actinide ions and neutrals

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Abstract. Fundamental aspects of the chemical and physical properties of atomic and molecular actinide ions and neutrals are being examined by Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS). To date, gas-phase reactivity studies of bare and ligated An^+ and An^{2+} ions, where $An = Th, Pa, U, Np, Pu, Am,$ and Cm , with oxidants and with hydrocarbons have been performed. Among the information that has been deduced from these studies are thermodynamic properties of neutral and ionic actinide oxide molecules and the role of the $5f$ electrons in actinide chemistry. Parallel theoretical studies of selected actinide molecular ions have also been carried out to substantiate the interpretation of the experimental observations.

PACS. 82.30.Fi Ion-molecule, ion-ion, and charge-transfer reactions – 82.60.-s Chemical thermodynamics – 82.80.Nj Fourier transform mass spectrometry

1 Introduction — Gas-phase actinide ion chemistry in the FTICR mass spectrometer

Systematic studies of gas-phase reactions of bare and ligated monopositive and dipositive actinide cations with various neutral reagents, based on the use of Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS), are contributing to fundamental aspects of actinide science. In this type of study, the physical and chemical properties of ionic species are examined in the absence of perturbing factors that occur in condensed phases, solution or solid, where the dense environments formed by the solvent or lattice have important contributions. In a simplified classical view of a gas-phase ion/molecule reaction, a long-range attractive force is established between an ion and a neutral molecule, due to an ion-induced dipole interaction and, depending on the specific case, ion-permanent dipole and/or ion-quadrupole interactions. This attractive force induces an initial well in the potential energy surface which may confer to the nascent ion-neutral complex enough energy to overcome barriers and proceed to reaction products. Due to the low

pressure environment of FTICR/MS, ion/molecule reactions are mainly sequential bimolecular processes and, owing to the large excess of neutral molecules relative to ions, the reactions follow pseudo-first-order kinetics. The rate constants, k , that can be obtained are normally compared with theoretical collisional rate constants, k_{COL} , which depend on the particular ion/neutral pair. The ratio of the two constants, k/k_{COL} , defines the reaction efficiency, that represents the fraction of ion/neutral collisions that are effective in the formation of products; these efficiencies are useful measures of the relative reactivities of the ions. At this fundamental bimolecular interaction level, the reactivity correlates directly with the electronic structures of the reactants and with the energetics of the reaction processes.

FTICR/MS is an ion trapping technique that is specially suited to the study of ion/molecule reactions, due to the ability to perform complex sequences of ion manipulation [1]. Briefly, crossed magnetic and electrical fields are used to confine in the ICR trap ions generated by any ionization technique, such as for instance laser desorption/ionization (LDI) in the case of metal ions. There, the ions can be selected, collided with neutral species, the temporal evolution of reactions can be monitored, and the produced ionic species can be identified. The technique

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permits the measurement of reaction kinetics, the analysis of reaction sequences by isolating intermediate reaction products and examining their subsequent reactions, and the study of collision-induced dissociations (CID), in which the structures of complex ions are probed by translationally exciting the ions, allowing them to collide with an inert gas, and observing the fragment ions formed thereafter. Another feature of FTICR/MS is the capacity to provide quantitative information on ion and neutral thermodynamics. If the reactant ions are properly thermalized, the reactions that are observed are either exothermic or thermoneutral, although in some cases kinetic barriers may preclude the observation of even substantially exothermic reactions. With a careful selection of the ion/neutral reactions, and if the thermodynamic properties of some of the reaction partners are known, estimates can be obtained for unknown energies of bonds being formed and/or broken, or for unknown ionization energies. In particular cases, the reaction efficiencies, k/k_{COL} , can also be of use in such estimates. Experimental techniques and methodologies available for studying the thermochemistry of ions in the gas phase, including those based on FTICR/MS, have been recently reviewed [2].

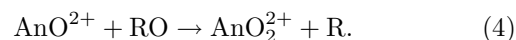
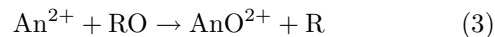
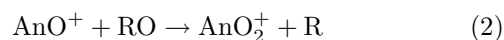
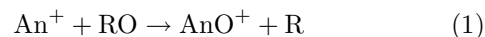
Gas-phase actinide ion chemistry studies have been carried out over the course of the past two decades and have been comprehensively reviewed through mid-2005 [3, 4]. Initial studies unsurprisingly focused on naturally occurring Th and U and were later extended to several of the more radioactive members of the actinide series, namely Pa, and Np through Es, by means of a special mass spectrometric technique designated laser ablation with prompt reaction and detection (LAPRD) [3]. In 2001, we initiated the study of the gas-phase ion chemistry of some of the more radioactive actinides using FTICR/MS and thus far have examined or re-examined different aspects of the chemistry of Th, Pa, U, Np, Pu, Am, and Cm [5–12]. In our experimental set-up, a Finnigan FT/MS 2001-DT FTICR mass spectrometer equipped with a 3 T magnet, we produce singly or doubly charged actinide cations by LDI of dilute ($\sim 2\text{--}5$ wt.%) An/Pt alloys, in which An = natural Th-232, Pa-231, depleted U, Np-237, Pu-242, Am-243, or Cm-248. No negative ions of the electropositive actinide metals are detected under these experimental conditions. The An cations enter the ICR ion trap directly, eliminating losses associated with ion transfer optics, and resulting in efficient sample utilization. The LDI targets contain milligram quantities of the actinide but only a very small fraction of the sample is consumed in the course of multiple experiments. In our experiments, the An metal cations, after being produced by LDI and prior to reactions, are cooled to room temperature (ca. 300 K) by collisions with argon, typically present in a tenfold excess over the reagents; thermalization is confirmed by the reproducibility of product distributions and reaction kinetics, as well as by linearity of the pseudo-first-order reactant ion decay plots.

We have performed reactivity studies with oxidants and with hydrocarbons, which have allowed us to determine thermodynamic properties of neutral and ionic ac-

tinide oxides and to probe the role of the $5f$ electrons in actinide chemistry. The electronic structure and energetics of the actinides are affected by relativistic effects which determine their unique chemical behavior. Ab initio theoretical studies of selected actinide molecular ions, using spin-orbit configuration interaction calculations with single and double electron excitations (SOCISD) and relativistic effective core potentials (RECPs) [13], have also been carried out to complement and understand some of the experimental observations. In the following sections we summarize some key results obtained and present some ideas on the application of these types of studies to the later actinides and the transactinides.

2 Reactions of actinide ions with oxidants — Measuring actinide oxide thermodynamics and more

Oxidation reactions as a means to study actinide oxide thermodynamics have been an initial focus of our work. We have examined the reactions represented by equations (1) to (4) with oxidizing reagents (RO) having a large range of oxygen-atom dissociation energies, $D[\text{R-O}]$, listed here in decreasing order of thermodynamic oxidizing ability (i.e., increasing order of $D[\text{R-O}]$): $\text{N}_2\text{O} > \text{C}_2\text{H}_4\text{O}$ (ethylene oxide) $> \text{H}_2\text{O} > \text{O}_2 > \text{CO}_2 > \text{NO} > \text{H}_2\text{O}$.



These oxidation studies allowed us to prepare for the first time the “bare” actinyl ions NpO_2^{2+} and PuO_2^{2+} [7]. Intriguing examples of the outcomes of reactions (3) and (4) were the formation of CmO^{2+} , formally a Cm(IV) species, in the reaction of Cm^{2+} with N_2O [10], and of PaO_2^{2+} , formally a Pa(VI) species of the actinyl type, in the reaction of PaO^{2+} with N_2O [9]. Electronic structure calculations [9] have revealed that the actual oxidation state in PaO_2^{2+} is intermediate between Pa(V) and Pa(VI). The syntheses of the dipositive curium monoxide ion and of the protactinyl ion illustrate the existence of novel gas-phase species that are unknown in condensed phase chemistry.

From the occurrence and the efficiencies of reactions (1) to (4), we were able to estimate unknown bond dissociation energies, $D[\text{An}^+-\text{O}]$, $D[\text{An}^{2+}-\text{O}]$, $D[\text{OAn}^+-\text{O}]$, and $D[\text{OAn}^{2+}-\text{O}]$, and verify or correct literature values for these quantities for An = Th [5, 7], Pa [9], U [5, 7], Np [5, 7], Pu [5, 7], Am [6, 7], and Cm [10]. In Table 1, we summarize the bond dissociation energies estimated from our experiments. A particularly notable result of these studies was the conclusion that the literature values for $D[\text{OPu}^+-\text{O}]$ of 250–260 kJ/mol [14, 15] were too low by at least ca. 250 kJ/mol [5].

Some of the singly and doubly charged actinide monoxide and dioxide cations produced via these oxidation reactions were the object of further studies, aimed at the

Table 1. Bond dissociation energies (D) of ionic actinide oxides (kJ/mol)^a.

An	D[An ⁺ -O]	D[OAn ⁺ -O]	D[An ²⁺ -O]	D[OAn ²⁺ -O]
Th	≥751 ^b	≥354 ^b	≥751 ^c	–
Pa	800 ± 50 ^d	800 ± 50 ^d	≥751 ^d	≥167 ^d
U	≥751 ^b	≥632 ^b	690 ± 60 ^c	560 ± 30 ^c
Np	≥751 ^b	580 ± 70 ^b	530 ± 30 ^c	520 ± 20 ^c
Pu	≥632 ^b	520 ± 20 ^b	460 ± 50 ^c	410 ± 100 ^c
Am	560 ± 30 ^e	390 ± 40 ^e	400 ± 50 ^c	260 ± 100 ^c
Cm	≥632 ^f	–	≥167 ^f	–

^aAs estimated from our experiments; for literature values see [14,34]; an assessment of the available data is under way [10]; ^bfrom [5]; ^cfrom [7]; ^dfrom [9]; ^efrom [6]; ^ffrom [10].

Table 2. First and second ionization energies (IE) of actinide oxides (eV)^a.

An	IE[AnO]	IE[AnO ₂]	IE[AnO ⁺]	IE[AnO ₂ ⁺]
Th	–	–	≤12.8 ^b	–
Pa	5.9 ± 0.5 ^c	5.9 ± 0.5 ^c	≤13.1 ^c	16.6 ± 0.4 ^c
U	–	–	12.7 ± 0.8 ^b	14.6 ± 0.4 ^b
Np	6.1 ± 0.2 ^d	6.33 ± 0.18 ^d	13.8 ± 0.6 ^b	15.1 ± 0.4 ^b
Pu	6.1 ± 0.2 ^d	7.03 ± 0.12 ^e	13.7 ± 0.8 ^b	15.1 ± 0.4 ^b
Am	6.2 ± 0.2 ^d	7.23 ± 0.15 ^f	13.7 ± 0.6 ^b	15.7 ± 0.9 ^b
Cm	6.4 ± 0.2 ^g	–	≥13.9 ^g	–

^aAs determined from our experiments; for literature values see [14,15,17–20]; an assessment of the available data is under way [10]; ^bfrom [7]; ^cfrom [9]; ^dfrom [8]; ^efrom [5]; ^ffrom [6]; ^gfrom [10].

determination of the ionization energies of the corresponding neutral and monpositive monoxides and dioxides, IE[AnO], IE[AnO₂], IE[AnO⁺], and IE[AnO₂⁺]. In Table 2, we summarize the IE values obtained in our experiments.

From the study of reactions of AnO⁺ with dienes, using a model developed by Cornehl et al. for the lanthanide monoxides [16] and a recent accurate spectroscopic determination of IE[UO] by Han et al. [17,18] as an “anchor” value, we were able to determine new values for the ionization energies IE[NpO] [6,8] and IE[PuO] [6,8], and obtain for the first time values for IE[AmO] [6,8] and IE[CmO] [10].

With the study of reactions of AnO₂⁺ ions with neutral organic compounds having well-known ionization energies, we established the occurrence or non-occurrence of electron transfer from the neutrals to the AnO₂⁺ ions to establish lower and upper limits for the ion electron affinities, which are equivalent to the ionization energies of the corresponding neutrals, IE[AnO₂]. With these “bracketing” experiments, we were able to determine IE[AmO₂] for the first time [6], determine a new value for IE[NpO₂] [8] which is more than 1 eV higher than the literature value [14], and determine a new value for IE[PuO₂] [5] which is lower by ca. 2.5–3 eV than the literature values [14,15] but is fully consistent with our derived plutonium oxide bond energies (see above). One of the literature values for IE[PuO₂] [15] was recently redetermined [19] but this latter work has been the object of some controversy [20].

We also studied electron-transfer reactions of AnO₂²⁺ ions (An = Pa [9], U [7], Np [7], Pu [7]) with neutrals to obtain estimates of the second ionization energies of AnO₂ species, IE[AnO₂⁺]. We developed an adaptation of the “bracketing” technique used for singly charged ions, since the method is not as straightforward for doubly charged ions due to the fact that two positively charged species are formed in the reactions and energy barriers arise due to the repulsive Coulombic interactions between the products [21]. It was also possible to estimate the second ionization energy of AmO₂ from a comparative analysis of known aqueous phase thermodynamic properties of actinide species in conjunction with our estimated second ionization energies of UO₂, NpO₂, and PuO₂ [7]. Complementary theoretical studies that we have performed for PaO₂⁺ and PaO₂²⁺, besides providing insights into the nature of the latter intriguing protactinyl species (see above), have also yielded a value for the second ionization energy of PaO₂, 16.61 eV, in very close agreement with the experimental estimate [9] (see Tab. 2).

The bond energies and ionization energies of the several neutral, monpositive and dipositive AnO and AnO₂ molecules studied directly lead to estimated values of formation enthalpies, such as through the following relationships: $\Delta_f H[\text{AnO}^+] = \Delta_f H[\text{An}^+] + \Delta_f H[\text{O}] - \text{D}[\text{An}^+-\text{O}]$; and $\Delta_f H[\text{AnO}] = \Delta_f H[\text{AnO}^+] - \text{IE}[\text{AnO}]$. Moreover, together with available literature data, the bond and ionization energies may also be assessed using equations (5) to (8), a type of analysis currently under way [10],

$$\text{D}[\text{An}^+ - \text{O}] = \text{D}[\text{An} - \text{O}] + \text{IE}[\text{An}] - \text{IE}[\text{AnO}] \quad (5)$$

$$\text{D}[\text{OAn}^+ - \text{O}] = \text{D}[\text{OAn} - \text{O}] + \text{IE}[\text{AnO}] - \text{IE}[\text{AnO}_2] \quad (6)$$

$$\text{D}[\text{An}^+ - \text{O}] = \text{D}[\text{An}^{2+} - \text{O}] + \text{IE}[\text{AnO}^+] - \text{IE}[\text{An}^+] \quad (7)$$

$$\text{D}[\text{OAn}^+ - \text{O}] = \text{D}[\text{OAn}^{2+} - \text{O}] + \text{IE}[\text{AnO}_2^+] - \text{IE}[\text{AnO}^+]. \quad (8)$$

As a final note to this section, we point out that recent theoretical calculations of the enthalpies of formation of UO₂²⁺ [22] and of PuO₂²⁺ [23] showed close agreement with the values derived for these species from our experimental results [7]. These gas-phase thermodynamic data obtained for the “bare” AnO₂²⁺ ions (An = U, Np, Pu) were also employed in conjunction with the known aqueous thermochemistry of these actinyls to derive “experimental” hydration enthalpies, that were found to be approximately constant for these three actinyls — $\Delta_{hyd} H[\text{AnO}_2^{2+}] \approx -1670$ kJ/mol [7]. The “experimental” hydration enthalpies for uranyl, neptunyl, and plutonyl showed close agreement with recent theoretical studies of the solvation of these actinyls by water [24–27].

3 Reactions of actinide ions with hydrocarbons — Probing the role of 5f electrons in actinide chemistry

Some types of reactions illuminate electronic structures and energetics for actinide atoms, as well as the multiple

roles of valence electrons in molecular chemistry. Of particular interest is the chemical role of the actinides' $5f$ electrons. An effective approach for probing the chemical nature of a metal ion's valence electrons is to examine hydrocarbon activation products and efficiencies. Such activation frequently proceeds by oxidative insertion into a C–H or C–C bond, which requires two chemically active valence electrons at the metal center, such as in a $\{C-M^+-H\}$ activated intermediate. Therefore, product distributions and efficiencies of the reactions of An^+ , AnO^+ and An^{2+} with alkanes and alkenes can be interpreted in the context of the electronic configurations of the ground state and low-lying excited states of the ions, and may elucidate the role of the $5f$ electrons at the actinide metal center.

Previous studies of the reactivity of An^+ ions with alkenes, for An^+ from Th^+ to Es^+ , carried out with the LAPRD technique, permitted a qualitative assessment of the relative reactivities of these An^+ [3,4]. As LAPRD does not allow the measurement of reaction kinetics, we have used FTICR/MS to study reactions of An^+ with alkanes and alkenes, for An^+ from Th^+ to Cm^+ , and have basically confirmed the LAPRD results and quantified the relative reactivities of the early An^+ ions [11]. The LAPRD and FTICR/MS studies have indicated that the reactivity of An^+ ions towards hydrocarbons correlates inversely with the promotion energies necessary to excite the ions from their ground states to "divalent" electronic configurations with two unpaired non- $5f$ outer valence electrons, of the type $[Rn]5f^{n-2}6d7s$ (where $[Rn]$ represents the closed radon electronic core) [28]. From this correlation it is concluded that for the An^+ from Pu^+ to Es^+ promotion to a "divalent" configuration with two unpaired non- $5f$ valence electrons is necessary for reactions to proceed. However, it cannot be immediately ascertained from the An^+ reactivity results if direct $5f$ -electron participation in the bonding in a $\{C-An^+-H\}$ intermediate is occurring for the early An^+ ions, Th^+ to Np^+ , as these all have ground states or low energy (≤ 0.1 eV) excited states with at least two non- $5f$ unpaired electrons [28].

To more effectively probe the participation of the $5f$ electrons in molecular bond activation for the first half of the actinide series, we have examined hydrocarbon activation by the oxo-ligated actinides, AnO^+ ($An = Th, Pa, U, Np, Pu, Am, Cm$) [11]. Addition of an oxo-ligand to a metal ion necessarily transforms the electronic structure of the metal center and, as a result, the reactivities of AnO^+ ions can provide additional information to that obtained for the bare An^+ ions. It was found that ThO^+ and UO^+ are relatively inert and the heavier AnO^+ ($An = Np, Pu, Am, Cm$) are completely inert (to within our detection limit) toward activation of small alkanes and alkenes. Conversely, PaO^+ exhibited a distinctive and remarkably high propensity to activate hydrocarbons by an oxidative insertion type of mechanism, which implies a $\{C-Pa^+-H\}$ intermediate even after attachment of an O atom to Pa^+ . To a first approximation, two outer valence electrons at the metal center are engaged in formation of the $An^+ = O$ double bond. The inert nature of ThO^+

can be attributed to the availability of only one valence electron at the metal center: Goncharov and Heaven [29] used the pulsed field ionization — zero kinetic-energy photoelectron spectroscopy (PFI-ZEKE) technique to show that the ground electronic state of ThO^+ originates from $Th^{3+}(7s)O^{2-}$ and the low-lying excited states correspond to $Th^{3+}(6d)O^{2-}$. Whereas the ground state of bare U^+ is $5f^37s^2$ [28], that of UO^+ is formally $U^{3+}(5f^3)O^{2-}$ and the low-lying states up to 0.65 eV originate from $U^{3+}(5f^3)O^{2-}$, with the exception of a $U^{3+}(5f^27s)O^{2-}$ state at 0.62 eV, as demonstrated by Goncharov et al. [30] using PFI-ZEKE, so that the relatively inert character of UO^+ suggests that the $5f$ electrons at the U center are ineffective at oxidative insertion. The same interpretation is presumed to apply to the later, inert AnO^+ ions, for which the electron density at the metal centers can be assumed to be of primarily $5f$ atomic orbital character. The ground state of bare Pa^+ is $5f^27s^2$ [28], but this does not necessarily indicate that the ground state of PaO^+ is formally $Pa^{3+}(5f^2)O^{2-}$. Therefore, to understand the distinctively high reactivity of PaO^+ , we performed theoretical calculations of its electronic structure, the results of which indicate that the ground state is instead $Pa^{3+}(5f6d)O^{2-}$ and all of its excited states up to 1.8 eV have a $5f$ -orbital occupancy of ≥ 0.8 [11]. In view of the ground and low-lying electronic states of PaO^+ indicated by the calculations, the reactivity of PaO^+ by insertion of the Pa metal center into C–H bonds concomitant with formation of two bonds then indicates participation of the $5f$ electrons in organometallic bond activation.

In another attempt to probe the participation of the $5f$ electrons in bond activation for the early actinides, we have studied the reactions of doubly charged actinide ions, An^{2+} ($An = Th, Pa, U, Np, Pu, Am, Cm$) with alkanes and alkenes [12]. The reaction products generally consisted of multiple doubly charged organometallic ions that formed via metal ion induced elimination of dihydrogen and/or alkanes from the hydrocarbons, and/or singly charged ions that resulted from electron, hydride, and/or methide transfers from the hydrocarbons to the metal ions. The observation of the latter charge-separation reaction channels with some of the hydrocarbons is in accord with the fact that the second ionization energies of the actinides are higher than the first ionization energies of the hydrocarbons. The type of doubly charged product ions formed via activation of the hydrocarbons revealed that Pa, here as Pa^{2+} , was again a candidate for possible participation of the $5f$ electrons in the observed chemistry. By comparing the products of the An^{2+} reactions with those obtained by us in reactions of lanthanide dications [12] and by Freiser and co-workers in reactions of d -transition metal dications [31], it was demonstrated that Th^{2+} and Pa^{2+} reacted similarly to d -transition metal ions with d^2 or d^3 ground states, while U^{2+} and Np^{2+} reacted similarly to dipositive lanthanide ions which have only one non- $4f$ valence electron and to dipositive group 3 transition metal ions which have d^1 ground states and no low-lying excited states with more than one valence electron. The rationale for the observed reactivity patterns is again

that two unpaired valence electrons are needed for a bond insertion mechanism to occur; however, for doubly charged cations there is the possibility of an alternative, radical-like electrostatic mechanism to be operative when there is only one valence electron available [31]. As both U^{2+} and Np^{2+} have $5f^n$ ground states, $5f^{n-1}6d$ or $5f^{n-1}7s$ states at low to moderate energies (0.03 to ~ 1 eV), and $5f^{n-2}6d^2$ states only at rather high energies (> 2 eV) [28], their radical-like reactivities suggest that the $5f$ electrons are inactive in bond activation. In contrast, Th^{2+} has a $5f6d$ ground state and a $6d^2$ state at a very low energy (0.01 eV) [28], whereas Pa^{2+} has a $5f^26d$ ground state, $5f^27s$ and $5f^3$ states at moderate energies (~ 0.5 eV), and a $5f6d^2$ state at higher energy (1.2 ± 0.7 eV) [28]. While in the case of Th^{2+} the low-energy $6d^2$ state presumably accounts for the observed reactivity, in the case of Pa^{2+} it appears conceivable that a state or states with only one non- $5f$ electron is/are determining the observed reactivity. As the reactivity of Pa^{2+} suggests two chemically active electrons at the metal center, this latter interpretation would indicate that a $5f$ electron participates in organometallic bond activation. However, the regrettably large uncertainty in the $5f^26d$ -to- $5f6d^2$ promotion energy for Pa^{2+} , somewhere in the range of 0.5–2 eV [28], precludes a definitive interpretation of its observed reactivity. Ab initio theoretical calculations are being performed to obtain a refined value for this Pa^{2+} promotion energy [12].

4 Conclusion — Late actinides and beyond

The currently available experimental data on the gas-phase reactivity of actinide ions, with both the LAPRD and FTICR/MS techniques, have permitted systematizations based on the electronic structures of the ions that can provide a guide for predicting the chemistry of the last part of the actinide series, Fm to Lr. This was attempted in regard to the stability of the oxidation states of the actinides in condensed phase [32]. Regarding physical properties of the “bare” actinide ions, recent experimental observations have indicated that the spectroscopically determined $5f^{10}7s$ -to- $5f^96d7s$ promotion energy for Cf^+ [28] does not correspond to the lowest-lying such excited-state configuration [33]. As regards neutral and singly charged actinide monoxides, an assessment of the known bond dissociation energies of these species in relation to the electronic structures and energetics of the isolated metal atoms and ions has provided a basis for estimating unknown bond dissociation energies, including in the later part of the actinide series [34].

Another interest in the study of fundamental physical and chemical properties of actinide species in the gas phase lies in its direct relevance to theoretical studies [35,36]. These theoretical studies generally employ gas-phase results as a reference and existing experimental results for actinide ion chemistry provide a basis to both develop and validate advanced theoretical approaches for the heavy elements.

On the experimental side, it is apparent that the types of FTICR/MS studies employed to understand fundamen-

tal aspects of the chemistry of the first half of the actinide series should also be applicable to some late actinide and early transactinide isotopes. Among the later actinides, it may ultimately prove feasible to carry out experiments in our LDI-FTICR/MS instrument using sub-milligram amounts of Cf-249, which has a 351 year half-life. It is feasible that isotopes such as Bk-249 ($t_{1/2} = 320$ d), Es-253 (20 d), Fm-255 (20 h), and perhaps even Md-258 (52 d) could be studied with a “conventional” FTICR/MS facility employing a high-efficiency ion source. However, for No, Lr, and transactinides, the ICR ion trap would almost certainly need to be directly coupled to a heavy isotope production facility with the requirements that the isotope half-lives be sufficiently long, e.g. ≥ 1 s, and that enough ions can be produced and accumulated in the trap. Using the ICR image current for ion detection, it is expected that at least ca. 10–100 ions would need to be accumulated in the ion trap. However, by employing an ion counting detector external to the ion trap, it should be feasible to perform experiments with single trapped ions. This type of set-up has been implemented in the ISOLTRAP at ISOLDE/CERN [37] and, more recently, in the SHIPTRAP at SHIP/GSI [38], both based on a system developed some years ago at the Johannes Gutenberg-Universität, Mainz [39]. The SHIPTRAP may be expected to produce, in the near future, relevant experiments with the heavy actinide and transactinide ions.

As indicated by previous studies of actinide ions [3,4], by numerous studies of d -block metal ions [40–42], and by the studies summarized here, of interest for the heavy elements would be the examination of elementary metal ion oxidation reactions for evaluation of such fundamental properties as $M^{+/2+}-O$ and $OM^{+/2+}-O$ bond energies, and of hydrocarbon activation by bare and oxo-ligated M^+ and M^{2+} ions to illuminate their electronic structures.

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