

## Gas-Phase Actinide Ion Chemistry—Reaction Kinetics and Molecular Thermodynamics\*

John K. Gibson

Oak Ridge National Laboratory

gibsonjk@ornl.gov

http://www.ornl.gov/sci/csd

Collaborators:

R. G. Haire, D. C. Duckworth—ORNL

J. Marçalo, M. Santos, A. Pires de Matos—Instituto Tecnológico e Nuclear, Portugal

### Overall research goals

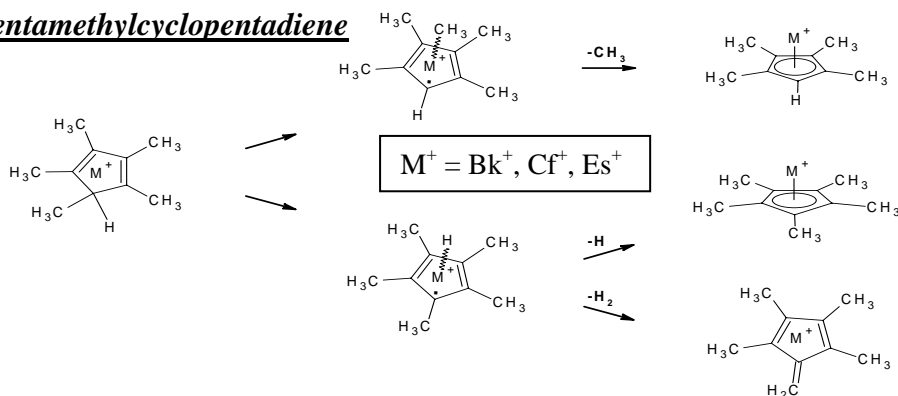
The program's central objective is to perform basic experimental research to provide information for the overall understanding of the underlying science, properties and behavior of actinides.

Gas-phase actinide ion chemistry is a valuable approach for obtaining such fundamental information and insights. These studies focus on experimental molecular actinide chemistry, but also provide a basis to develop and validate theoretical concepts of actinide chemistry. An underlying theme is the role of the 5f electrons/orbitals in molecular chemistry.

### Selected recent accomplishments

- Gas-phase actinide ion reactions have revealed new transcurium organometallic chemistry.<sup>3</sup>

#### Activation of Pentamethylcyclopentadiene



- Ionization energies of  $AnO_2$  ( $An = Np, Pu, Am$ ) were determined by electron transfer.<sup>1,8</sup> Substantial corrections to previously available values.<sup>10</sup>

	IE[ $AnO_2$ ] / eV	
U	6.13 <sup>a</sup>	5.5±0.5 <sup>c</sup>
Np	6.33±0.18 <sup>b</sup>	5.0±0.5 <sup>c</sup>
Pu	7.02±0.12 <sup>b</sup>	9.4±0.5 <sup>c</sup>
Am	7.23±0.15 <sup>b</sup>	-

<sup>a</sup> Ref. 9—photoionization

<sup>b</sup> This project—electron transfer<sup>1,8</sup>

<sup>c</sup> Ref. 10—electron impact

- Synthesis and characterization of bare actinyls:  $UO_2^{2+}(g)$ ,  $NpO_2^{2+}(g)$ ,  $PuO_2^{2+}(g)$ .<sup>2</sup> Determined  $AnO_2^{2+}$  hydration enthalpies of ca.  $-1670 \text{ kJ mol}^{-1}$  (same as from DFT<sup>11</sup>).
- Assessment of bonding in monoxides indicated a requirement for two metal d-electrons at the actinide metal center.<sup>6</sup>

### Selected objectives for 2005-2006

- Study the oxidation chemistry of  $\text{Pa}^+$  and  $\text{Pa}^{2+}$ , and determine bond energies and ionization energies of Pa oxides. Examine organometallic reactions of bare and oxo-ligated Pa ions.
- Determine ionization energies of  $\text{UF}_2$  and  $\text{UF}_3$ , and the reactivities of  $\text{UF}_2^+$  and  $\text{UF}_3^+$ . These fluorides are of particular interest for comparison with uranium oxides.
- Systematic examinations of reactions of  $\text{An}^{2+}$  with organic molecules (An = Th through Cm).
- Perform electrospray ionization mass spectrometry studies with transuranics to explore actinide solution speciation and gas-phase complexation.
- Carry out the first quantitative studies of gas-phase curium ion chemistry by FTICR-MS. Establish thermodynamics of molecular curium oxides.
- Explore comparative chemistries of particular ligated actinide ions to experimentally probe the concept of “autogenic isolobality”.<sup>12</sup>

### References of work supported by this project

1. J. K. Gibson, R. G. Haire, J. Marçalo, M. Santos, J. P. Leal (2005), “Determination of the Ionization Energy of  $\text{NpO}_2$  and Comparative Ionization Energies of Actinide Oxides,” *J. Nucl. Materials* (in press).
2. J. K. Gibson, R. G. Haire, M. Santos, J. Marçalo, A. Pires de Matos (2005), “Oxidation Studies of Dipositive Actinide Ions,  $\text{An}^{2+}$  (An = Th, U, Np, Pu, Am) in the Gas Phase: Synthesis and Characterization of the Isolated Uranyl, Neptunyl and Plutonyl Ions  $\text{UO}_2^{2+}(\text{g})$ ,  $\text{NpO}_2^{2+}(\text{g})$  and  $\text{PuO}_2^{2+}(\text{g})$ ,” *J. Phys. Chem. A*, web-published March 03, 2005.
3. J. K. Gibson, R. G. Haire (2005), “Activation of Pentamethylcyclopentadiene by  $\text{Bk}^+$ ,  $\text{Cf}^+$  and  $\text{Es}^+$  Ions in the Gas Phase: A Probe of the Electronic Structures of Heavy Actinides,” *Organometallics*, **24**, 119-26.
4. G. P. Jackson, J. K. Gibson, D. C. Duckworth (2004), “Gas-Phase Reactions of Bare and Ligated Uranium Ions with Sulfur Hexafluoride,” *J. Phys. Chem. A*, **108**, 1042-51.
5. J. K. Gibson, R. G. Haire (2004), “Ternary Gas-Phase Plutonium Oxide Cluster Ions,  $\text{Pu}_x\text{M}_y\text{O}_z^+$ : Exploring the Oxidation Behavior of Pu,” *J. Alloys Compds.*, **363**, 112- 21.
6. J. K. Gibson (2003), “The Role of Atomic Electronics in f-Element Bond Formation: Bond Energies of Lanthanide and Actinide Oxide Molecules,” *J. Phys. Chem. A*, **107**, 7891-99.
7. J. K. Gibson, R. G. Haire (2003), “Einsteinium Ion Chemistry in the Gas Phase: Divalent Character of the Heavy Actinides,” *Radiochimica Acta*, **91**, 441-48.
8. M. Santos, J. Marçalo, J. P. Leal, A. Pires de Matos, J. K. Gibson, R. G. Haire (2003), “FTICR-MS Study of the Gas-Phase Thermochemistry of Americium Oxides,” *Int. J. Mass Spectrom.*, **228**, 457-65.

### Other references

9. J. Han, L. A. Kaledin, V. Goncharov, A. V. Komissarov, M. C. Heaven (2003), “Accurate Ionization Potentials for  $\text{UO}$  and  $\text{UO}_2$ : A Rigorous Test of Relativistic Quantum Chemistry Calculations,” *J. Am. Chem. Soc.*, **125**, 7176-77.
10. D. L. Hildenbrand, L. V. Gurvich, V. S. Yungman (1985), “The Chemical Thermodynamics of Actinide Elements and Compounds. The Gaseous Actinide Ions,” IAEA: Vienna.
11. L. V. Moskaleva, S. Krüger, A. Spörl, N. Rösch (2004), “Role of Solvation in the Reduction of the Uranyl Dication by Water: A Density Functional Study,” *Inorg. Chem.*, **43**, 4080-90.
12. L. Gagliardi, P. Pyykkö (2004), “Theoretical Search for Very Short Metal-Actinide Bonds:  $\text{NUIr}$  and Isoelectronic Systems,” *Angew. Chem. Int. Ed.*, **43**, 1573-76.

\*Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC

**"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."**