

# UniCat Colloquium

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Lecturer: **Prof. emer. Lester S. Andrews**, Department of Chemistry, University of Virginia, USA

Title: **Metal Bearing Molecules**

Abstract: The terminal oxo species  $\text{OUF}_2$  and  $\text{OThF}_2$  have been prepared via the spontaneous and specific  $\text{OF}_2$  molecule reactions with laser ablated uranium and thorium atoms in solid argon. These isolated molecules are characterized by one terminal M-O and two F-M-F (M = U or Th) stretching vibrational modes observed in matrix isolation infrared spectra, which are further supported by density functional frequency calculations and CASPT2 energy and structure calculations. Both molecules have pyramidal structures with singlet (Th) and triplet (U) ground states. The molecular orbitals and metal-oxygen bond lengths for the  $\text{OUF}_2$  and  $\text{OThF}_2$  molecules indicate triple bond character for the terminal oxo groups, which are also substantiated by NBO analysis at the B3LYP level and by CASPT2 molecular orbital calculations. Interestingly, dative bonding involving  $\text{O}_{2p} \rightarrow \text{Th}_{6d}$  or  $\text{U}_{5f}$  interactions contributes to these oxo systems. A normal six-electron triple bond was likewise characterized using the same methods for the terminal nitride bearing  $\text{NUF}_3$  molecule prepared by reaction of U atom and  $\text{NF}_3$ <sup>1</sup> and for the first uranium methylidyne  $\text{HCUF}_3$ .<sup>2</sup> Finally, the weak O-F bond in  $\text{OF}_2$  as well as the strong U-O, U-F and Th-O, Th-F bonds make reaction to form the  $\text{OUF}_2$  and  $\text{OThF}_2$  molecules highly exothermic for these very stable actinide oxyfluoride products.

Experiments with mercury amalgams as a source for laser ablated Hg atoms as reaction partners with  $\text{OF}_2$  gave strong  $\text{HgF}_2$  absorptions<sup>3</sup> and new bands for  $\text{OHgF}$  and  $\text{FOHgF}$ . Assignment of the new bands to the first oxyfluoride of mercury,  $\text{OHgF}$ , and to the  $\text{FOHgF}$  insertion product is supported by density functional and CCSD(T) calculations of electronic structure and vibrational frequencies. The <sup>18</sup>O isotopic shifts in these two differently mixed Hg-O, Hg-F vibrational modes matches the calculated shifts for each product and provides diagnostic information for these two new mercury bearing oxyfluoride molecular species.

<sup>1</sup> Andrews, L.; Wang, X. F.; Lindh, R.; Roos, B. O.; Marsden, C. J. *Angew. Chem. Int. Ed.* 2008, 47, 5366-5370.

<sup>2</sup> Lyon, J. T.; Hu, H. S.; Andrews, L.; Li, J. *Proc. Natl. Acad. Sci.* 2007, 104, 18919-18924.

<sup>3</sup> X. Wang, L. Andrews, S. Riedel, and M. Kaupp, *Angew. Chem. Intl. Ed.* 2007, 46, 8371-8375.

Date: **Wednesday, July 4, 2012**

Time: **5:15 pm - around 6:45 pm**

Location: **TU Berlin, Institute of Chemistry  
Straße des 17. Juni 115, 10623 Berlin  
Building C, Lecture Hall C 264**

Organizer: **Prof. Martin Kaupp (TUB)**

Coffee and tea will be served thirty minutes prior to the lecture start.  
**Guests are cordially invited to attend!**

Prof. Dr. Matthias Driess, Chair of the Cluster of Excellence UniCat