RadChem 2014



Contribution ID: 264

Type: Verbal

Higher oxides, peroxides, and superoxides of early transuranium elements: a relativistic density functional study

Tuesday, 13 May 2014 09:06 (18 minutes)

The results of relativistic electronic structure calculations on simple molecules of higher oxides (actinide oxidation state VI through VIII), peroxides, and superoxides of Pu, Am, and Cm are reported. The calculations employed accurate "small-core" two-component pseudopotentials derived from the outer (valence) shell solutions of the atomic Dirac–Fock–Breit equations with the Fermi nuclear model; the optimal description of the valence (rather than semicore) shells appears essential for reproducing the chemical properties. The molecular semicore/valence many-electron problem was solved by the two-component non-collinear relativistic DFT technique with the fully unrestricted optimization of Kohn–Sham one-electron spinors expanded in weakly contracted Gaussian basis sets; the bases were optimized for spin-orbit-coupled calculations. Ground-state equilibrium structures, vibrational frequencies and charge and spin magnetization density distributions were analyzed in order to characterize the different isomers in chemical terms.

The stability of higher oxidation states in oxygen compounds rapidly decreases from Pu to Am and further to Cm. All "true"An tetroxides (An = Pu, Am, Cm), were predicted to be thermodynamically unstable in realistic gas-phase conditions with respect to the decay into lower oxides (An2O6 or An2O7) and molecular oxygen as well as to the conversion into dioxosuperoxides AnO2 which appear to be the most stable An·4O species in all cases. Structural and magnetization-density features of the tetroxides indicate that Pu and Am are octavalent while Cm is only hexavalent. No structural similarities between higher oxides of Pu-Am and Os-Ir was found. A variety of bis-dioxygen species of different nature (An(O2)2, AnO22) is discussed. The stability of some heterooxide molecules (PuAmO6 and especially PuAmO7) with respect to the transformation to the mixture of the corresponding pure oxides is noticed. Implications for the chemistry of the transuranium element – oxygen systems and the identification of volatile An-oxygen compounds are discussed.

The work is partially supported by the RFBR (grant # 13-03-01234). Thanks are due to Prof. C. van Wüllen for providing us with his relativistic DFT code. The calculations were performed at MCC NRC "Kurchatov Institute" (http://computing.kiae.ru/).

Primary author: Prof. ZAITSEVSKII, Andrei (Petersburg Nuclear Physics Institute / NRC Kurchatov Institute)

Co-authors: TITOV, Anatoly V. (Petersburg Nuclear Physics Institute); Dr MOSYAGIN, Nikolai S. (Petersburg Nuclear Physics Institute); SCHWARZ, W. H. Eugen (Department of Chemistry, Tsinghua University, Beijing / Theoretical Chemistry, University Siegen)

Presenter: SCHWARZ, W. H. Eugen (Department of Chemistry, Tsinghua University, Beijing / Theoretical Chemistry, University Siegen)

Session Classification: Chemistry of Actinide and Trans-actinide Elements 2

Track Classification: Chemistry of Actinide and Trans-actinide Elements