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Report on Progress

U. S. Department of Energy

Grant Number DE-FG02-86ER13529

"Molecular Orbital Studies of the Bonding in Heavy Element Organometallics"

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I. Progress During the Past Year

Much of our progress during the past year has been tied to our procurement of a Digital Equipment DECstation 3100 UNIX-based workstation, purchased with DOE funds. The access to this extremely powerful stand-alone computer, as well as its facility in tying into the Cray supercomputer at the Ohio Supercomputer Center, has allowed us to expand our computational vistas greatly. We have, until this year, been largely restricted to using the $X\alpha$ scattered-wave ($X\alpha$-SW) molecular orbital method for our investigations of actinide electronic structure. While this method has been, and continues to be, very useful to us, it does employ some severe approximations that have been necessary due to computational limitations. The access to more powerful computers has allowed us to use more powerful, albeit more complex, electronic structure methods in our investigations.

We have invested a great amount of time learning how to use the DECstation 3100 and adapting our computational codes to run within its UNIX environment. We have also spent a large portion of time benchmarking our programs for computational accuracy and efficiency. Nevertheless, we have made good progress on several new projects in actinide chemistry. The highlights of these projects are as follows:

The bonding in Np, Pu, and transplutonium organometallic compounds. We have continued our investigation into the bonding in cyclopentadienyl-containing actinide complexes by using $X\alpha$-SW molecular orbital calculations with quasi-relativistic corrections. Our most recent focus has been on the Cp_3An compounds, where An = U through Cf, which represent the only homologous series of organometallic compounds for these elements. We have found that Cp_3An compounds of the early actinides are more covalent than those of the later actinides. Furthermore, we have carried out comparison calculations on the electronic structure of the corresponding lanthanide (Ln) and transition

metal (M) complexes. Differences exist between the Cp_3An compounds and the Cp_3Ln compounds, but most of these occur in orbitals that are not primarily responsible for the bonding of ligands. Major differences exist between the Cp_3An compounds and Cp_3M, largely because of the role of the 5f orbitals in the bonding of the Cp rings to the actinide center. A manuscript on these results is currently being written, for submission in mid-1990.

Applications of the discrete variational Xα method to actinide chemistry. As part of our effort to bring more sophisticated electronic structure methods into application in actinide chemistry, we have begun to use the discrete variational Xα (DV-Xα) method of Ellis. The DV-Xα method, while more expensive than the Xα-SW method, involves fewer approximations. It incorporates a fully relativistic treatment of the molecular Hamiltonian, including the effects of spin-orbit coupling, and employs the correct double group representation of the one-electron wavefunctions.

As a first test of the DV-Xα method on the types of systems in which we are interested, a large number of calculations have been performed on the simple model compound UH_3. The results are in qualitative agreement with Xα-SW, but some important differences are apparent. Of particular significance, the DV-Xα calculations reveal the importance of spin-orbit coupling in the f manifold. While the Xα-SW method places the f manifold in a tight block about the HOMO, DV-Xα splits it into two manifolds, of mostly $f_{5/2}$ and $f_{7/2}$ character, the former containing the three orbitals that make up the HOMO, and the latter approximately 0.75 eV higher in energy. Our results suggest that three-coordinate uranium(III) compounds will be strong σ and π acids.

We have also performed preliminary DV-Xα calculations on the series of compounds UR_3 (R = CH_3^-, NH_2^-, OH^-, and $C_5H_5^-$), although at a lower level of theory than for UH_3. We find that the f orbitals become progressively more important in ligand bonding as one moves from H^- to CH_3^- to NH_2^- to OH^- to Cp^-,

as reflected by their ligand field splitting. In all of these molecules we anticipate the ground electronic state to be a quartet corresponding to three half-filled $f_{5/2}$ orbitals. We anticipate the Cp_3U compound to be a particularly strong Lewis acid, based on the availability of a low-lying acceptor orbital, and for the other compounds to be progressively weaker acids.

Ab initio calculations on actinide molecules. Access to the Cray supercomputer has allowed us to pursue first-principles, correlated electronic structure calculations on actinide molecules. As a prototype molecule for these investigations, we are investigating the bonding in the "naked dimer" of uranium, U_2. This is a molecule that is attracting increased experimental attention. We have begun to study the bonding in this molecule via multi-configuration self-consistent-field (MCSCF) and configuration interaction (CI) calculations, with the hope that spin-orbit effects will be properly included in the near future. Our preliminary results are proving to be extremely interesting and, we believe, provocative: The diuranium molecule may possess a maximum-spin ground state.

Experimental comparisons of organoactinide and organotransition metal chemistry. We have undertaken a detailed experimental comparison of the bonding and energetics of Cp_3AnX and Cp_3MX complexes. Results from our laboratories and those of our collaborators are being used to compare the molecular structures, electrochemistry, and photoelectron spectroscopy of homologous thorium, zirconium, and hafnium complexes. The results are providing, for the first time, an experimental gauge of the importance of the 5f orbitals in the bonding in organoactinide complexes.

II. Related Activities During the Past Year

Our progress on this proposal has been assisted by a number of other

developments in the past year. In addition, our research on actinide complexes has received significant recognition in the form of invited lectures and review papers. Highlights of these activities are:

Ancillary funding. We have successfully sought additional funds that directly or indirectly have a positive effect on the completion of our actinide research. On the basis of a competitive proposal, in November, 1989 we were granted 240 hours of computing time on the Cray Y-MP supercomputer at the Ohio Supercomputer Center. The commercial value of this grant-in-time is $300,000. Approximately 60% ($180K) is being used to complete calculations directly related to our DOE grant. We also obtained a grant from the Petroleum Research Fund in support of a research project unrelated to our DOE-sponsored research. Part of these funds were used to purchase a $25K inert-atmosphere box for chemical synthesis. We are using this apparatus in part for the preparation of compounds used in our experimental studies of organoactinide chemistry.

Invited papers. We have been asked to contribute review articles on our work on organoactinide chemistry by two very prestigious journals, Angewandte Chemie and Chemical Reviews. Both reviews will be submitted in the next several months. In addition, some of our actinide research will appear as part of an invited chapter we wrote for a book, "Metal-Metal Bonds and Clusters in Chemistry and Catalysis."

Invited presentations. The PI has been invited to present our results in actinide chemistry at a number of prestigious meetings during 1990. These include the Symposium on Computational Chemistry at the ACS Great Lakes Regional meeting, the Canadian Institute of Chemistry Meeting, and the World Congress of Theoretical Organic Chemistry. The PI is also an invited lecturer at the International Conference on Organometallic Chemistry, where he will talk in part on actinide research. In addition, the PI maintains Collaborator

status at Los Alamos National Laboratory, and has been invited to present a seminar and discuss collaborative possibilities by Oak Ridge National Laboratory.

III. Plans for the Forthcoming Year

As is evident from Section I of this report, the past year has been one of transition for us. We are beginning to utilize more sophisticated theoretical methods, an activity that requires extensive training and testing. Much of our activity in the coming year will serve to complete some projects that we began this year. The DV-Xα method shows tremendous promise as a tool for studying the bonding in organoactinide complexes. In the next year we hope to implement a total-energy package for the method, which will allow us to calculate geometries of molecules. Ultimately, we hope to use this implementation to calculate reaction pathways for organoactinide reactions.

The ab initio calculations on actinide complexes also appear very promising. The MCSCF and CI calculations are extremely complex and difficult to interpret in terms of simple bonding pictures. We hope to develop the means for "translating" these results into conclusions that will be meaningful to experimental actinide chemists. We plan to complete our studies on U_2, and follow these with an investigation of UH_3, which will provide a nice comparison of the ab initio methods with our apporximate ones. Finally, we plan to investigate the dimerization of UH_3 to U_2H_6, a prototype of the unknown class of molecules that contain a direct actinide-actinide bond.

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U.S. Department of Energy

Grant Application Budget Period Summary

(See Reverse for Definitions and Instructions)

OMB Approval
No. 1910-1400

Please Print or Type

Organization:	Period Covering:	FOR DOE USE ONLY
The Ohio State University Research Foundation	From: 7/1/90	Proposal No:
Principal Investigator (P.I.)/Project Director (P.D.): Bruce E. Bursten	To: 6/30/91	Award No.:

A. SENIOR PERSONNEL PI/PD Co PIs, Faculty and Other Senior Associates (List each separately with title. A.6 show number in brackets. Attach separate sheet, if required.)	DOE Funded Person-Mos. Cal.	Acad.	Sumr.	Funds Requested By Applicant $
1 Bruce E. Bursten		1.35		WOC
2. " " "			2	10,585
3.				
4				
5.				
6 (1) TOTAL SENIOR PERSONNEL		1.35	2	10,585
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)				
1. (1) POST DOCTORAL ASSOCIATES	11			19,250
2. ( ) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)				
3. ( ) GRADUATE STUDENTS				
4. ( ) UNDERGRADUATE STUDENTS				
5. ( ) SECRETARIAL-CLERICAL				
6. ( ) OTHER				
TOTAL SALARIES AND WAGES (A + B)				29,835
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)				4,400
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)				34,235
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM)				
TOTAL EQUIPMENT				
E. TRAVEL 1. DOMESTIC (INCL. CANADA AND U.S. POSSESSIONS)				2,180
2. FOREIGN				
F. OTHER DIRECT COSTS				
1. MATERIALS AND SUPPLIES				2,000
2. PUBLICATION COSTS/PAGE CHARGES				450
3. CONSULTANT SERVICES				
4. COMPUTER (ADPE) SERVICES				
5. CONTRACTS AND SUBGRANTS				
6. OTHER Service contract for workstation				1,380
TOTAL OTHER DIRECT COSTS				3,830
G. TOTAL DIRECT COSTS (A THROUGH F)				40,245
H. INDIRECT COSTS (SPECIFY RATE AND BASE) 47% of Modified Total Direct Costs (less Equipment) TOTAL INDIRECT COSTS				18,915
I. TOTAL DIRECT AND INDIRECT COSTS (G & H)				59,160
J. APPLICANT'S COST SHARING (IF ANY)				
K. TOTAL AMOUNT OF THIS REQUEST (ITEM I LESS ITEM J)				59,160

PI/PD TYPED NAME & SIGNATURE	DATE
INST. REP. TYPED NAME & SIGNATURE	DATE