(NASA-CR-168391) THEORETICAL STUDIES OF THE ELECTRONIC STRUCTURE OF SMALL METAL CLUSTERS Final Report, 1 Oct. 1979 - 31 Mar. 1981 (Pittsburg Univ., Pa.) 7 p HC A02/MF A01 CSCL 20L G3/76

N82-23032

Unclas 18846

Theoretical Studies of the Electronic Structure of Small Metal Clusters

Final Report covering the Period October 1, 1979 - March 31, 1982

NASA Grant NSG - 2407*

by

Kenneth D. Jordan, Principal Investigator
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

---

* The NASA technical officer for this grant is David M. Cooper, Materials Science Division, NASA Ames Research Center, Moffett Field, CA 94035.

The main thrust of our research efforts during the period of the NASA grant involved theoretical studies of the electronic structure of metal clusters, in particular clusters of Group IIA and IIB atoms. Early in the project it became clear that electron correlation involving d orbitals plays a more important role in the binding of these clusters than had been previously anticipated. This necessitated that we replace our computer codes for calculating two electron integrals and for constructing the resulting CI Hamiltonions with newer, more efficient procedures. Hence, considerable time was spent on program modification, interfacing, and testing. (See Appendix A)

I. Group II A metal atom clusters

Perhaps the most significant finding resulting from our studies is that although Mg_4 is essentially unbound at an SCF level of treatment[2] the inclusion of electron correlation effects involving d functions gives rise to appreciable ($\sim$ 0.8 eV) binding.[1] This is the first example of strong binding originating from correlation effects alone. This work was performed in collaboration with Professor C. Dykstra and utilized the CEPA and SCEPA methods for treating electron correlation. These calculations on Mg_4 included explicitly all electrons and represents one of the largest (in terms of the number of electrons treated explicitly and number of basis functions employed) calculations on a metal cluster to date.

During the course of our study of Mg_4, Pople and coworkers[3] published a paper on the electronic structure of beryllium clusters. These authors also found that correlation effects involving d functions plays an important role in the cluster binding. However, a fundamental difference exists between the Be_4 and Mg_4 cases in that Be_4 displays appreciable binding even in the absence of correlation effects. The discoveries that d functions play a fundamental role in the binding of beryllium and magnesium clusters has led us to perform new calculations on Be_2^- and Be_3^-. Here we have found that it is essential to include both d functions and correlation effects to obtain the correct ordering of the pi and sigma anion states.[4]

We are presently carrying out a new set of calculations on Mg_4 utilizing a local potential to model the $1s^2 2s^2 2p^6$ atomic cores. If these local potential calculations successfully reproduce the results of the all-electron calculations, then, we can confidently employ local potentials to study the larger clusters.

As part of our continuing effort to understand electron attachment to group IIA metal clusters, we have also calculated[5] electron affinities of atomic Be, Mg, and Ca. For the atoms the anion states lie energetically above the ground states of the neutral atoms, requiring scattering calculations for their investigation. Using the Harris-Michels method, we have shown that all three atoms have low-lying ^2P anions. For Mg a broad feature due to ^2D Mg^- is found near 2.5 e.V in the scattering cross section. For Ca the ^2D anion is found to lie only 0.7 ev above the ^2P anion.

II. <u>Cu_2 and CuH</u>.

During the course of the grant we began calculations on Cu_2 and CuH and their anions[6]. In these studies we have utilized the effective potential of Topiol <u>et.al.</u>[7] for the copper atoms. The first challenge was to find a compact Cu basis set suitable for the $d^{10}s$ and d^9s^2 states of Cu as well as the $d^{10}s^2$ state of Cu^-. After much experimentation, we arrived at a [4s3p5d/4s3p2d] basis set. With this basis we are able to obtain a SCF $d^{10}s \rightarrow d^9s^2$ excitation energy of 0.59 eV in fair agreement with the all-electron value of 0.34 eV and a SDCI (single and double excitation configuration interaction) excitation energy of 1.41 eV in excellent agreement with the experimental value of 1.49 eV. A SDCI with this basis yields a dissociation energy of Cu_2 of 1.87 eV compared with the 2.05 eV experimental value. The above results are noteworthy since other investigators have concluded that a 5d/3d contraction is required to describe the $d^9s^2 \rightarrow d^{10}s$ atomic excitation energy and presumably also to describe the bonding in the Cu_2 molecule. The calculations on the Cu_2 and the Cu_2^- potential energy curves as well as on CuH and CuH^- are near completion. We expect to submit this work in the near future to the Journal of Chemical Physics for publication.

III. Reactions of Metal Atoms with H_2O.

The second major thrust of our research program has been the investigation of the reactions of metal atoms with small molecules, especially H_2O. In particular, we have characterized the $M{\cdot}OH_2$ and HMOH species for M= Be, B, C, Mg, Al, Si.[9,10] For each of these species the geometries, stabilities, and vibrational frequencies have been determined. Perhaps the most interesting finding of these calculations is that for the B, C, Al, and Si insertion products both cis and trans isomers exist. Experimental evidence for the existence of cis/trans isomers of HSiOH has recently been found.[11]

IV. Other Work Carried Out Under the NASA Grant

Theoretical investigations of several other systems were also completed during the course of our NASA grant. Using 2nd order many-body perturbation theory we have determined the polarizabilities of LiF and BeO,[12] BF,[13] and LiCl.[14] The results for LiF and BeO [12] and those for

BF have been published.[13] Those for LiCl are near completion.[14] The calculations on LiCl are of particular interest since in this case we have determined several properties using different pseudopotentials for the chlorine atom. Finally, we have utilized[15] both the configuration interaction and many-body perturbation theory (through fourth-order) to calculate the electron affinities of C_2 and C_3. We plan to extend these studies to include larger carbon clusters.

Appendix A: Program Implementation and Development

During the course of the NASA grant we implemented the Pitzer-Schaefer integral program, which is considerably faster for integrals over d functions than the MOLECULE program we had been using. A significant gain in speed resulted from a switch over to Shepard's Unitary-group multiconfigurational self-consistent field (MCSCF) and configuration interaction (CI) programs. These programs were modified to allow for the use of local potentials to model the core electrons and to use input vectors from Purvis' SCF program.

REFERENCES

*1. R. A. Chiles, C.E. Dykstra, and K.D. Jordan, "Bonding in the Mg_4 Cluster: An Example of Chemical Bonding Originating from Electron Correlation Effects", J. Chem. Phys, 75, 1044 (1981).

2. K. D. Jordan and J. Simons, J. Chem. Phys. 72, 2889 (1980).

3. R. A. Whiteside, M. B. Krogh - Jesperson, R. Khrishnan, G. Wenke, J. A. Pople, and P.V.R. Schleyer, J. Comp. Chem. 1, 307 (1980).

*4. K. D. Jordan and J. Simons, "On the Lowest Sigma and Pi Anion States of Be_2 and Be_3", submitted to J. Chem. Phys.

*5. H. A. Kurtz and K. D. Jordan, "Cross Sections for Electron and Positron Scattering from Be, Mg, and Ca", J. Phys. B. 14, 4361 (1981).

*6. K. K. Sunil and K. D. Jordan, unpublished results.

7. S. Topiol, J. W. Moskowitz, C. F. Melius, M.D. Newton, and J. Jafri, Courant Institute of Mathematical Sciences Report (00-3077-105).

*8. P. J. Hay, J. Chem. Phys. 66, 4377 (1977)

*9. K. D. Jordan and H. A. Kurtz, "Theory of Metal Atom-Water Interactions and Alkali Halide Dimers", published in "High Temperature Chemistry", editors, J. L. Gole and W. C. Stwalley, ACS Symposium Series, 179, pp.-378-393, 1982.

*10. S. Sakai, H. A. Kurtz, and K. D. Jordan, "Structure and Vibrational Frequencies of $B.OH_2$, $Al{\cdot}OH_2$, HBOH, HALOH", to be submitted to Chem. Phys. Letters.

11. R. Hauge, personal communication.

*12. Y. Yoshioka and K. D. Jordan, "Many-body Perturbation Theoretical studies of the Dipole Moments, Polarizabilities and Electron Affinities of LiF and BeO", J. Chem. Phys. 73 5899 (1980).

*13. H. A. Kurtz and K. D. Jordan "Properties of the $X^1\Sigma^+$ State of BF", Chem. Phys. Letters 81 104 (1981).

*14. K. K. Sunil and K. D. Jordan, unpublished results.

*15. A. Orendt, K. K. Sunil, and K. D. Jordan, "Theoretical Study of the Vertical Excitation Energies, Ionization Potentials, and Election Affinities of C_3", to be submitted to Chem. Phys. Letters.

---

* Denotes papers funded totally or in part under the present NASA grant.