

PROJECT ADMINISTRATION DATA SHEET

ORIGINAL REVISION NO. _____

Project No. G-41-675 (R6011-OA0) GTRC/~~OT~~ DATE 8/26/85

Project Director: J. L. Cole School/~~Lab~~ Phy

Sponsor: ~~Petroleum Research Fund~~ AMERICAN CHEMICAL SOCIETY

Type Agreement: Grant PRF # 17174-AC1

Award Period: From 9/1/85 To 8/31/86 (Performance) 8/31/87 (Reports)

Sponsor Amount: This Change Total to Date

Estimated: \$ _____ \$ 35,000

Funded: \$ _____ \$ 35,000

Cost Sharing Amount: \$ N/A Cost Sharing No: N/A

Title: Characterization of Ligand-Free Copper and Silver Clusters and Their Reactions to the Form Metal Cluster Oxides and Halides

ADMINISTRATIVE DATA

OCA Contact John Schonk x4820

1) Sponsor Technical Contact:

2) Sponsor Admin/Contractual Matters:

Joseph E. Rodgers, Jr.

American Chemical Society

Petroleum Research Fund

1155 Sixteenth St., SW

Washington, DC 20036

202/872-4481

Defense Priority Rating: N/A Military Security Classification: N/A

(or) Company/Industrial Proprietary: N/A

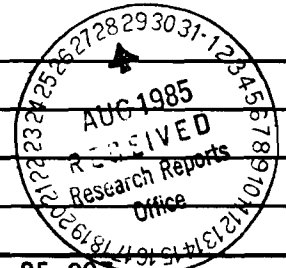
RESTRICTIONS

See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval - Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with _____

COMMENTS:



COPIES TO: SPONSOR'S I. D. NO. 02.500.009.85.007

Project Director
Research Administrative Network
Research Property Management
Accounting

Procurement/GTRI Supply Services
Research Security Services
Reports Coordinator (OCA)
Research Communications (2)

GTRC
Library
Project File
Other A. Jones

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

10-1
SR-781

Date November 5, 1987

Project No. G-41-675

School/Dept Physics

Includes Subproject No.(s) N/A

Project Director(s) J. L. Gole GTRC / ~~EXX~~

Sponsor Petroleum Research Fund

Title Characterization of Ligand-Free Copper and Silver Clusters and Their Reactions to the Form Metal Cluster Oxides and Halides

Effective Completion Date: 10/1/87 (Performance) 10/1/87 (Reports)

Grant/Contract Closeout Actions Remaining:

- None
- Final Invoice or Final Fiscal Report
- Closing Documents
- Final Report of Inventions
- Govt. Property Inventory & Related Certificate
- Classified Material Certificate
- Other _____

Continues Project No. _____ Continued by Project No. _____

COPIES TO:

- Project Director
- Research Administrative Network
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- Legal Services

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- GTRC
- Research Communications (2)
- Project File
- Other Russ Embry
- Angela DuBose
- Duane Hutchison

G-41-615

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 17322-A6

Page 1 of 3 pages.

PREPARED BY

James L. Gole

Date 9/19/86

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

17322-A6 Characterization of Ligand-Free Copper and Silver Clusters and Their Reactions to Form Metal Cluster Oxides and Halides

James L. Gole, Georgia Institute of Technology

Metal clusters represent unique intermediate states of matter, the analysis of whose properties should reveal much about the growth of atoms into small metal particles, the development of features in the bulk metallic phase, and, within themselves, a very intriguing dynamic behavior. Further, sufficient evidence now exists to demonstrate that metal clusters are of importance to the fundamental mechanisms of catalysis and numerous chemical conversions. Thus, the basic properties (geometry, bond strength, reactivity) of small metallic clusters, $M_n (2 < n < 6)$, have become the subject of intense theoretical and experimental study.¹

As a contribution to the understanding of these intermediate and unique states of matter, the goal of our experimental research effort has been to (1) develop intense cluster sources² and characterize the molecular electronic structure and hence bonding in select small metal aggregates and (2) study the nature of the oxidation processes which small metal aggregates undergo.

We have developed a source configuration which lies intermediate to a low pressure effusing molecular beam and a high pressure flow device, generating substantial concentrations of small metal clusters which are then exposed to an oxidizing environment. This "high flux" non-effusive source has been combined with those techniques which have proven invaluable for the study of highly exothermic chemiluminescent reactive processes across a wide pressure range^{3,4} to probe the optical signatures of those reaction products associated with the oxidation of small copper ($Cu_x + O_3$)⁵ and silver ($Ag_x + O_3$)^{3,5} clusters with further extension to select

THE PETROLEUM RESEARCH FUND

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Page 2 of 3 pages.

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transition (Mn_x+O_3, Cr_x+O_3)⁶ metals. From these studies we have obtained the first quantal information on the energy levels and optical signatures of several metal cluster oxides, M_nO_y ($n \geq 2$). These studies serve to outline the potential for chemiluminescent probes of polyatomic metal cluster oxide quantum levels,⁵ not only within themselves but also as a means of suggesting future laser fluorescent probes of the metal cluster oxides. In addition, they are beginning to reveal a rather unique dynamics associated with the oxidation of small metal clusters.

The most extensive work on copper and silver cluster oxidation has yielded a wealth of information on the vibrational level structure of Cu_2O and Ag_nO (esp. Ag_2O) and demonstrated an expected red shift in spectral emission features upon traversal of the series M_nO as n increases from two. This work has also focused our attention on the rather unique molecular electronic structure of the excited states of silver dimer.

Our research effort has also focused on the formulation of intense continuous sources producing small cold metal clusters in supersonic expansion at concentrations up to $10^{12}/cc$ ($Na_3, Cu_3, (Ag_3)$).^{2,7} The products of expansion are studied using a combination of cw dye lasers and mass spectrometry. While the application of these sources has focused primarily on the study of copper clusters, their potential extension to the transition metals, specifically to nickel trimer,⁷ is now well underway and initial results have now been obtained on the gas phase nickel trimer spectrum. The development of these intense sources is necessary for the observation of the internal mode structure associated especially with polyatomic metal clusters or the polyatomic products of metal cluster oxidation, in many instances, may be plagued by the rapid depletion of excited state populations via either non-radiative processes, photodissociation, or predissociation, either before the emission of a monitoring photon can occur or before an appropriate spectroscopic probe can be made operative (for example, TPI spectroscopy). The metal cluster sources are formulated in order to overcome inherent loss mechanisms.

- (1) "Metal Clusters", edited by M. Moskovits, John Wiley and Sons, New York (1986).

THE PETROLEUM RESEARCH FUND

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GRANT, PRF # 17322-A6

Page 3 of 3 pages.

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James L. Gole

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- (2) W. H. Crumley, J. S. Hayden, and J. L. Gole, J. Chem. Phys. 84, 5250 (1986). "Formation and Oxidation of Intense Metal Cluster Beams and Flows," in Proceedings of the International Workshop on Ionized Cluster Beam Techniques (ICBT) '86, Tokyo and Kyoto, Japan, pg. 85.
- (3) R. Woodward, J. S. Hayden, J. L. Gole, and D. A. Dixon, J. Phys. Chem. 89, 4905 (1985).
- (4) For example: G. J. Green and J. L. Gole, Chemical Physics 100, 133 (1985), R. Woodward, J. S. Hayden and J. L. Gole, *ibid.* 100, 153 (1985).
- (5) R. Woodward, P. N. Le, M. Temmen, M. McQuaid, and J. L. Gole, "Potential Probes of Metal Cluster Oxide Quantum Levels - Optical Signatures for the Oxidation of Small Metal Clusters M_x ($M = Cu, Ag, Si, Ge, B$)," J. Phys. Chem., in press.
R. Woodward, M. Temmen, R. C. Oldenberg, T. C. Devore, and T. Burkeholder, "A Comparative Study of the Oxidation of Atomic Copper and Higher Copper Clusters Under Single and Multiple Collision Conditions," in preparation.
- (6) T. C. Devore, T. Burkeholder, and J. L. Gole, work in progress.
- (7) R. Woodward, S. H. Cobb, and J. L. Gole, work in progress.

FINANCIAL STATEMENT
(Insert "ANNUAL" or "FINAL", as appropriate)

AMERICAN CHEMICAL SOCIETY - THE PETROLEUM RESEARCH FUND

For the Period: October 1, 1985 to August 31, 1986
(The preferred closing date for the reporting period is August 31)

Balance Carried Forward from Previous Reporting Period (from Same or Earlier Grant)	0	
Received from PRF During This Reporting Period (Include Summer Research Supplements)	19,500	
Stipends to:		
a. Principal Investigator (Contribution Toward Summer Salary)*	0	
b. Undergraduate Students	0	
c. Graduate Students	0	
d. Postdoctoral Fellows	15000	
e. Summer Research Fellows (Only if funded by Summer Research Supplement) Faculty <input type="checkbox"/> Student <input checked="" type="checkbox"/> (check one).	1500	
f. Other (Specify)	0	
tuition	0	
aterials and Supplies	2000	
quipment	0	
omputer Time Charges	500	
ravel (Explain if in excess of budget).	0	
ther Expenses (Attach itemized list)	0	
epartmental Allocation*	500	
 *If provided in grant agreement		
Total Expenditures During Reporting Period.	8,160.65	
Balance on Hand at End of Period		11339.35
Total of PRF Grant Payments Received to Date		

Complete this section ONLY for a Financial Statement which shows a balance in the grant account at the termination date of the current grant agreement.

- The balance in the grant account will be liquidated:
- By refund of unspent and uncommitted funds. The check should be drawn to the order of American Chemical Society - The Petroleum Research Fund, and identified by the PRF grant number.
- By use in the completion of the grant project. We hereby request approval by the American Chemical Society of an extension of the grant agreement, without commitment of additional funds, until _____ (Period up to one year, renewable).

I hereby certify that the expenses reported herein were incurred for education and research in accordance with the terms of the approved ACS-PRF grant-in-aid.

Georgia Institute of Technology
(Grantee Institution)

Financial Officer (typed name)	(Signature)	(Telephone)	(Date)
James L. Gole		17322-AC6	
Principal Investigator (typed name)		PRF Number	

PERSONNEL STATEMENT

PRF# 17322-AC6 REPORTING PERIOD OCTOBER 1, 1985 TO August 31, 1986

GRANTEE INSTITUTION Georgia Institute of Technology DEPARTMENT Physics-Chemistry

PRINCIPAL INVESTIGATOR(S) James L. Gole

GRANT PROJECT TITLE Characterization of Ligand-Free Copper and Silver Clusters and Their Reactions to Form Metal Cluster Oxides and Halides

List undergraduate, graduate, and postdoctoral co-workers receiving stipends under the above named grant:

NAME	TITLE OR ACADEMIC APPOINTMENT	PREVIOUS EDUCATION & DEGREES*	COUNTRY OF PERMANENT RESIDENCE	PERIOD OF SUPPORT (MONTHS)	PERCENT OF SUPPORT FROM PRF **	DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD
Robert Woodward	Research Sci.	B.S., M.S. Furman Univ.	U.S.	10 months	25%	-----
Christian Pettyjohn	Research Assistant	Undergraduate	U.S.	Full Summer Supplement	83%	-----

List other co-workers on grant project not directly supported with ACS - PRF funds:

NAME	SOURCE OF SUPPORT	DATES ASSOCIATED WITH GRANT PROJECT
Thomas Devore	N.S.F. Research Undergrad. Inst.	June 1, 1986 - present
Thomas Burkholder	N.S.F. Research Undergrad Inst.	May 15, 1986 - August 1, 1986
Mark Temmen	(Masters Degree) Physics Department	Oct. 1, 1985- April 1, 1986

* For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph. D. granting institution.

** (during the period stated in preceding column)

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 17322-A6

Page 1 of 3 pages.

PREPARED BY

James L. Gole

Date 9/29/87

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

17322-A6 Characterization of Ligand-Free
Copper and Silver Clusters and Their Reac-
tions to form Metal Cluster Oxides and
Halides

James L. Gole, Georgia Institute of
Technology

Metal clusters represent unique intermediate states of matter whose basic properties (geometry, bond strength, reactivity) have become the subject of intense theoretical and experimental study.¹ As a contribution to the understanding of these intermediate and unique states of matter, the goal of our experimental research effort has been to (1) develop intense cluster sources allowing the mapping of the molecular electronic structure and hence bonding in select small metal aggregates and (2) study the nature of the oxidation processes which these small aggregates undergo. These studies have not only revealed a unique reaction dynamics but also the manifestation of an intriguing temperature dependent dynamic behavior associated with the clusters themselves.

We have developed two source configurations which lie intermediate to a low pressure effusing molecular beam and high pressure flow device, generating substantial concentrations of small metal clusters which are then exposed to an oxidizing environment. In one configuration, an intense near supersonic metal flow expands into a low pressure environment where it is bathed by a concentric flow of a given oxidant. In a second configuration, a non-effusive metallic flow is bathed in an entrainment gas at room to LN₂ temperature to induce clustering, the clusters then being oxidized in a multiple collision intermediate pressure environment. These "high flux" noneffusive sources have been combined with those techniques which have proven invaluable for the study of highly exothermic chemiluminescent reactive processes across a wide pressure range² to probe the optical signatures of those reaction products associated with the oxidation of small copper

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 17322-A6

Page 2 of 3 pages.

PREPARED BY

James L. Gole

Date 9/29/87

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($\text{Cu}_x\text{O}_3, \text{Cl}_2, \text{Cl}$)^{3,5} and silver ($\text{Ag}_x\text{O}_3, \text{Cl}_2$)^{3,6} clusters with further extension to select transition metals ($\text{Mn}_x\text{O}_3, \text{Cr}_x\text{O}_3$)^{3,7,8}. From these studies we have obtained the first quantal information on the energy levels and optical signatures of several metal cluster oxides, M_nO_y ($n \geq 2$) and preliminary data on the copper cluster chlorides. In addition it has been possible to study the manifestations of ultrafast energy transfer among known excited electronic singlet states and previously uncharacterized triplet states of CuCl .⁵ These studies serve to outline the potential for chemiluminescent probes of polyatomic metal cluster oxide and halide quantum levels^{3,5} not only within themselves but also as a means of suggesting future laser fluorescent probes of the metal cluster oxides and halides.

From these studies, we have obtained quantal information on several previously uncharacterized metal cluster oxides. This work includes the analysis of two and possibly three low-lying electronic states of Ag_2O ,^{3,6} allowing an evaluation of the ground state vibrational constants for the asymmetric AgAgO isomer. We have obtained a plethora of information on the vibrational level structure of the CuCuO ^{3,4} and Cu_xO ($x \geq 3$)⁴ copper cluster oxides. Further, in studying the multicentered Cu_x ($x \geq 3$) + Cl_2 reactions, we have tentatively identified the chemiluminescent emission spectrum of the Cu_2Cl molecule formed in the multicentered $\text{Cu}_3 + \text{Cl}_2 \rightarrow \text{Cu}_2\text{Cl} + \text{CuCl}$ reactive encounter. We have also studied the reactions of small manganese clusters, obtaining the first Mn_2O emission spectrum which demonstrates that this molecule takes on an ionic form corresponding to $(\text{Mn}_2^{\delta+})^{(0)\delta-}$ where the $\text{Mn}_2^{\delta+}$ stretch frequency is found to fall between that of Mn_2 and Cr_2 . Finally, additional data obtained on the copper and silver systems has demonstrated an expected red shift in spectral emission features upon traversal of the series M_nO as n increases from two. This work has also focused our attention on the rather unique molecular electronic structure of the excited states of silver dimer and trimer.

- (1) "Metal Clusters", edited by M. Moskovits, John Wiley and Sons, New York (1986).

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Page 3 of 3 pages.

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James L. Gole

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- (2) For example: G. J. Green and J. L. Gole, Chemical Physics 100, 133 (1985), R. Woodward, J. S. Hayden and J. L. Gole, *ibid.* 100, 153 (1985).
- (3) "Potential Probes of Metal Cluster Oxide Quantum Levels - Optical Signatures for the Oxidation of Small Metal Clusters M_x (M=Cu,Ag,Mn,B)", with R. Woodward, P. N. Le, and M. Temmen, Jour. Phys. Chem. Cluster Symposium Issue 91, 2637 (1987). "Quantum Level Probes of Small Metal Clusters and Their Oxidation", American Institute of Physics Conference Proceedings, Advances in Laser Science - in press.
- (4) "A Comparative Study of the Oxidation of Atomic Copper and Higher Copper Clusters Under Single and Multiple Collision Conditions", with R. Woodward, T. C. Devore, and T. Burkeholder, submitted.
- (5) "Evidence for Ultrafast Energy Transfer Among the Singlet and Triplet States of CuCl", with L. Mathews.
- (6) "Formation of Electronically Excited Ag_xO from the Oxidation of Small Silver Clusters", with R. Woodward, P. N. Le, T. C. Devore, and D. A. Dixon, submitted.
- (7) "Formation of Electronically Excited Mn_xO from the Oxidation of Small Manganese Clusters", with T. C. Devore and J. R. Woodward.
- (8) "Formation of the Low-Lying Electronic States of CrO in Highly Exothermic Reactive Oxidation, - Assessment of New States and Resolution of Previous Observations", with T. C. Devore.

PERSONNEL STATEMENT

PRF# 17322-AC6 REPORTING PERIOD September 1, 1986 TO September 30, 1987

GRANTEE INSTITUTION Georgia Institute of Technology DEPARTMENT Physics-Chemistry

PRINCIPAL INVESTIGATOR(S) James L. Gole

GRANT PROJECT TITLE Characterization of Ligand-Free Copper and Silver Clusters and Their Reactions to Form Metal Cluster Oxides and Halides.

List undergraduate, graduate, and postdoctoral co-workers receiving stipends under the above named grant:

NAME	TITLE OR ACADEMIC APPOINTMENT	PREVIOUS EDUCATION & DEGREES*	COUNTRY OF PERMANENT RESIDENCE	PERIOD OF SUPPORT (MONTHS)	PERCENT OF SUPPORT FROM PRF **	DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD
Robert Woodward	Research Sci.	B.S., M.S., Furman Univ.	U. S.	12	65%	-----
Derek Vargo	Research Assistant	Undergrad.	U. S.	Full Summer Supplement	100%	-----
James L. Gole	PI	Ph.D., Rice Univ.	U. S.	3/4	5.5%	-----
M. McQuaid	Grad. Student	B.S. U. of Virginia	U. S.	12	10.8%	-----

List other co-workers on grant project not directly supported with ACS - PRF funds:

NAME	SOURCE OF SUPPORT	DATES ASSOCIATED WITH GRANT PROJECT
Thomas Devore	N.S.F. Research Undergrad. Inst.	September 1, 1986 to present
Kevin Morris	N.S.F. Research Undergrad. Inst.	June 1, 1987 - August 15, 1987

* For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph. D. granting institution.

** (during the period stated in preceding column)

Revised 6/82

See Reverse Page
for Instructions

FINANCIAL STATEMENT

PRF # 17322-AC6

(Insert "ANNUAL" or "FINAL", as appropriate)

AMERICAN CHEMICAL SOCIETY - THE PETROLEUM RESEARCH FUND

For the Period: September 1, 1986 to September 31, 1987
(The preferred closing date for the reporting period is August 31)

Balance Carried Forward from Last Reporting Period (for This or Previous Grant)	<u>11339.35</u>
Total Payments Received from PRF During This Reporting Period (Include Summer Research Supplements)	<u>19500.</u>
Stipends to:	
a. Principal Investigator (Contribution Toward Summer Salary)*	<u> </u>
b. Undergraduate Students	<u> </u>
c. Graduate Students	<u> </u>
d. Postdoctoral Fellows	<u>15000</u>
e. Summer Research Fellows (Only if funded by Summer Research Supplement)	
Faculty <input type="checkbox"/> Student <input checked="" type="checkbox"/> (check one).	<u>1500</u>
f. Other (Specify)	<u>0</u>
Tuition	<u>0</u>
Materials and Supplies	<u>2000</u>
Equipment	<u>0</u>
Computer Time Charges	<u>500</u>
Travel (Explain if in excess of budget. Identify costs for field work, if any)	<u>0</u>
Other Expenses (Attach itemized list)	<u>0</u>
Departmental Allocation*	<u>500</u>

*If provided in grant agreement

Total Expenditures During Reporting Period	<u>28848.32</u>
Balance on Hand at End of Period	<u>1991.03</u>

DO NOT complete this section unless there is a balance in the grant account at the termination date of the current grant agreement.

The balance in the grant account will be liquidated:

By refund of unspent and uncommitted funds. The check should be drawn to the order of American Chemical Society-The Petroleum Research Fund, and identified by the PRF grant number.

By use in the completion of the grant project. We hereby request approval by the American Chemical Society of an extension of the grant agreement, without commitment of additional funds, until (already granted for (Period up to one year, renewable).
~~one year~~)

This is to certify that the expenses reported herein were incurred for education and research in accord with the terms of the approved ACS-PRF grant-in-aid.

Georgia Institute of Technology
(Grantee Institution)

James L. Gole
Name of Principal Investigator

Financial Officer (typed name) (Signature)

(Telephone)

(Date)

Please submit to The Petroleum Research Fund, American Chemical Society
1155 Sixteenth Street, N.W., Washington, D.C. 20036 Telephone (202) 872-4481

FINANCIAL STATEMENTS

1. This form, which is reproduced on the reverse page, should be completed by the business office of your institution and signed by a financial officer. The signature of the principal investigator is not required. The statement is "Final" if the grant terminates this August 31. It is "Annual" if the grant terminates after this August 31, or if a time extension is being requested.
2. Please include an institutional grant reference number, if any, on the statement.
3. DO NOT include funds received from Project SEED when reporting funds received from PRF during the period.
4. Funds expended for Summer Research Fellowship supplements should be reported on line e. Please do not include these expenditures with stipends to "undergraduate students" or "other".
5. If expenses reported for "Travel" include field work, please specify the amount for field work.
6. All costs reported as "Other Expenses" MUST be itemized. Failure to provide this detailed information may delay the processing of your request, if any, for a no-cost time extension.
7. Costs incurred for membership fees or dues are not allowable research-related expenses.