

PROJECT ADMINISTRATION DATA SHEET

ORIGINAL

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This ChangeTotal to DateEstimated: \$ 202,900Funded: \$ 58,900Cost Sharing Amount: \$ 2,021Cost Sharing No: G-41-364Title: Characterization of Small Metal Clusters and Their Unique Oxidation Processes.ADMINISTRATIVE DATAOCA Contact John B. Schonk ext. 48201) Sponsor Technical Contact:2) Sponsor Admin/Contractual Matters:William H. CramerDonald R. MitchellNational Science FoundationNational Science FoundationMPS/CHEDGC/MPSWashington, DC 20550Washington, DC 20550202/357-7951202/357-9671Defense Priority Rating: N/AMilitary Security Classification: N/A(or) Company/Industrial Proprietary: N/ARESTRICTIONSSee Attached NSF 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 GITCOMMENTS:* Include a 6 month unfunded flexibility period.It is expected that this project will be funded for an additional 2 years.COPIES TO:SPONSOR'S I. D. NO. 02.107.000.86.051Project Director
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OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Date 10/26/89

Project No. G-41-630

Center No. R6190-OA0

Project Director J. L. Gole

School/Lab Physics

Sponsor National Science Foundation

Contract/Grant No. CHE-8604471

GTRC GIT

Prime Contract No. N/A

Title Characterization of Small Metal Clusters & Their Unique Oxidation Processes

Effective Completion Date 7/31/89 (Performance) 10/31/89 (Reports)

Closeout Actions Required:

- ☐ None
- ☐ Final Invoice or Copy of Last Invoice
- ☐ Final Report of Inventions and/or Subcontracts
- ☐ Government Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Release and Assignment
- ☐ Other

Includes Subproject No(s).

Project Under Main Project No.

Continues Project No. Continued by Project No.

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Research Progress Report

and

Grant Renewal Request
submitted to the

NATIONAL SCIENCE FOUNDATION

Proposed Amount: \$72,000 Proposed Effective Date: 2/1/87

Proposed Duration: 12 months

Characterization of Small Metal Clusters
and Their Unique Oxidation Processes

Grant Number: CHE-8604471

Principal Investigator: James L. Gole

Social Security Number: 551-74-2508

Department: Physics - Chemistry

Institution: Georgia Institute of Technology
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Atlanta, Georgia 30332

Endorsements:

Principal Investigator

James L. Gole

Department Head

Edward W. Thomas

Institutional Administrative Official

Lynn Boyd

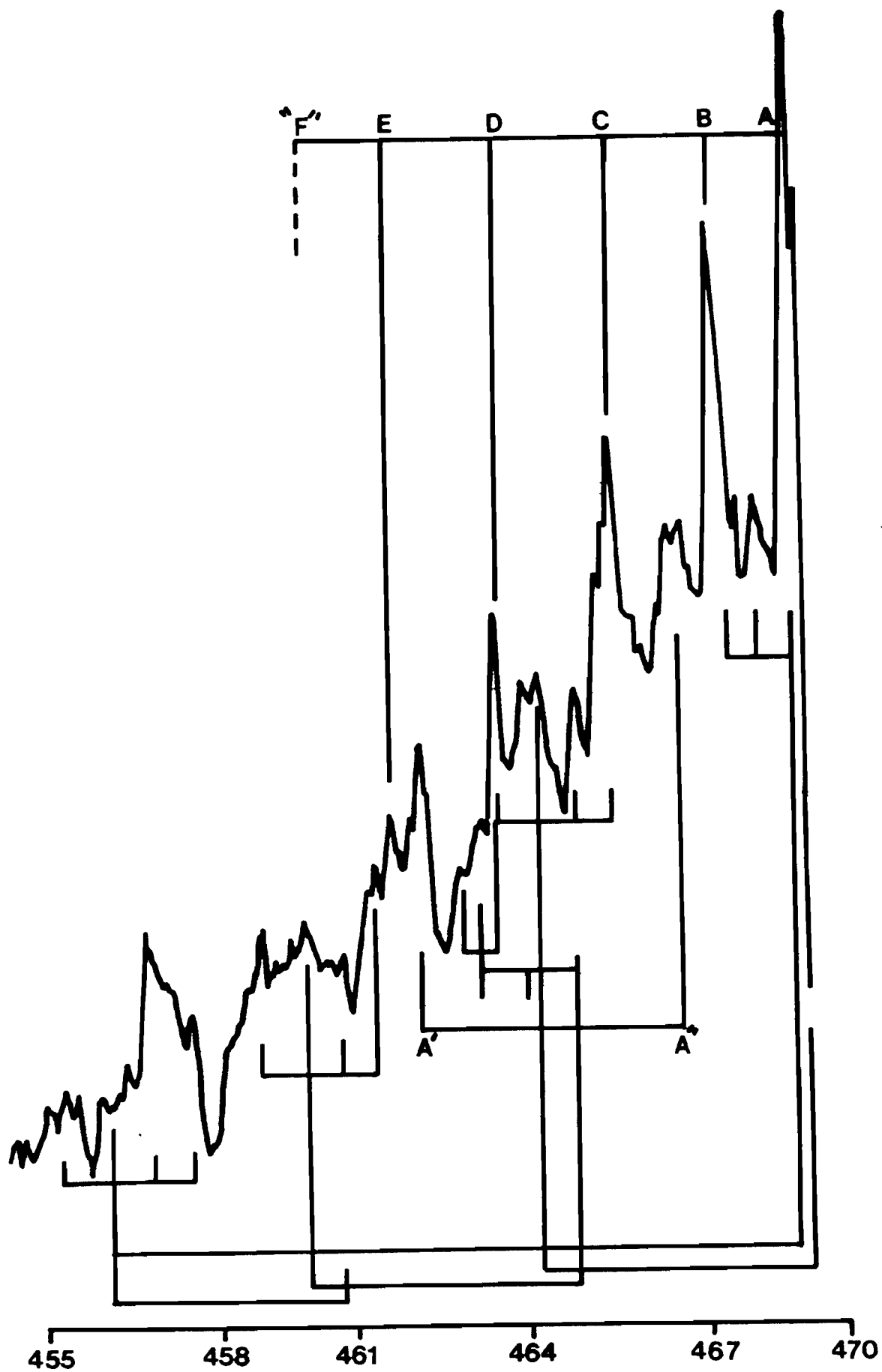
The research effort during the period June 1, 1986 - November 23, 1986 has involved several projects focused on the experimental and theoretical treatment of small metal clusters, their unique dynamic behavior, and the unique nature of the oxidation processes which they undergo. Our research effort during the past 6 months has included the following:

1) We have extended our studies with the high intensity supersonic refractory metal vapor expansion source developed in our laboratory to obtain the first gas phase fluorescence spectra for the nickel trimer molecule. Previously we noted¹ that one of the most exciting aspects of this new source was the attainment of intensities comparable to that produced in a pure sodium supersonic expansion and three to six orders of magnitude greater than that obtained with laser vaporization techniques. The development of this source and the attainment of the first gas phase nickel trimer excitation spectrum in our laboratory demonstrates an important extension of our previous and continuing studies of the copper trimer molecule.

Although it is clear that the electronics and reactive properties of small metal clusters lie intermediate to those of the atom and those of the bulk metallic phase, the detailed aspects of this picture especially with respect to internal mode structure have not yet been colored. Quantum level probes which have already indicated the need for models including vibronic coupling as well as demonstrating the unique dynamic behavior of small metal clusters as a function of temperature are slowly emerging.² It is now apparent that it will be difficult to probe resultant quantum levels even with extremely sensitive laser spectroscopic techniques. If intense cluster beam sources are developed, however, it may be possible to overcome some of these difficulties.^{2,3} Thus cluster sources must be designed to overcome the substantial loss mechanisms including predissociation and rapid intramolecular

conversion and relaxation which deplete excited state populations at a rate competing effectively with those spectroscopic probes that can be applied to the analysis of quantum level structure.

A portion of the nickel trimer excitation spectrum is displayed in Figure 1. This excitation spectrum was obtained using an argon ion pumped stilbene 3 dye laser operating at 0.5 cm^{-1} resolution to excite Ni_3 produced in a moderate supersonic expansion of the pure metal at a stagnation pressure of 30 torr. The cooling obtained is such that vibrational features which can be correlated with (1) ground ($\nu_1'' \approx 230 \pm 5 \text{ cm}^{-1}$, $\nu_2'' \approx 105 \pm 5 \text{ cm}^{-1}$) and excited state ($\nu_1' \approx 200 \pm 5 \text{ cm}^{-1}$, $\nu_2' \approx 95 \pm 5 \text{ cm}^{-1}$) stretching and bending modes can be identified. This spectrum, which will be extended to longer wavelength in the near future, correlates well with the 480 nm absorption system observed by Moskovits and Hulse in rare gas matrices and with the laser Raman spectrum obtained by the Moskovits' group. It is significant that this gas phase Ni_3 spectrum is lost to the resonant two photon ionization (R2PI) technique; that is, loss mechanisms which may include strong predissociation and/or rapid intramolecular energy redistribution apparently deplete the excited state population before the requisite R2PI two-photon pump-probe scheme can be made operative. It is apparent that the single photon nickel trimer excitation spectrum is obtained as a result of overcoming those loss mechanisms which have plagued other extremely sensitive spectroscopic techniques. Thus an initial aspect of the promise of our copper trimer excitation spectral studies,¹ which have yielded spectra for strongly predissociating excited state levels of the copper trimer molecule, is now undergoing the extension envisioned when this approach was formulated. We are afforded a unique opportunity to probe systems where photodissociation and nonradiative processes are competitive with fluorescence.



The gas phase Ni_3 spectrum and its correlation with (1) the matrix isolation results of Moskovits et al. and (2) recent theoretical studies on both Cu_3 and Ni_3 by Dr. Steven Walsh (Nasa Ames Laboratory, Moffett Field) have lead us to formulate a potentially fruitful approach to the unraveling of a least of portion of transition metal cluster quantal structure. Although there are a plethora of possible states which must be associated with the transition metal clusters, it is apparent that both the spectra of matrix isolated and gas phase copper and nickel trimers are strongly dominated by the absorption and/or emission from only a few states. We believe that this results from very dominant transition moments associated with only a few of the transition metal states. This can be determined at a relatively moderate level of quantal calculation and, at our suggestion, Dr. Walsh will soon attempt to carry out such a study for several of the first row transition metal trimers. We believe that the combination of a high transition moment coupled with a large cluster concentration affords the most appealing means to overcome the loss mechanisms which must plague not only transition metal but also other metal and metalloid cluster quantal probes. We envision a strong collaborative effort in both experiment and theory in order to exploit this possibility.

(2) We have continued our efforts to study the metal cluster photodissociation process through the application of the technique of "laser induced atomic fluorescence" (LIAF) where a metal cluster M_n is dissociated with a cw dye laser to yield the fragments M_{n-1} and an electronically excited metal atom, M^* . By monitoring the emission from this electronically excited M^* , we have been able to elucidate many features of the bonding and energy levels of sodium and potassium trimer, determine upper and lower bounds for the difficult to measure $\text{M}_2\text{-M}$ metal cluster bond energy, and assess the behavior of these clusters under a variety of perturbing conditions. In order to

clarify certain ambiguities in the bound-free spectroscopy of sodium and potassium trimer, we are also extending our efforts to the characterization of the lithium trimer LIAF spectrum. The high reactivity of liquid lithium makes this extension a difficult one. We have constructed a variety of low-carbon stainless steel and molybdenum oven systems in order to formulate an appropriate source with which to study the Li_3 LIAF spectrum. Thusfar, we have obtained extensive Li_3 excitation spectra which demonstrate extensive cooling, however, we have not yet operated our systems at temperatures commensurate to the formation of sufficiently high lithium trimer concentrations. Here, we must overcome the problem of an apparently catalytically induced melting and vaporization of those tantalum heating elements which must be used to bring the oven to a temperature of 1100-1150°C! Thusfar, we are able to operate the system consistently at temperatures which do not exceed 1050°C.

The apparent low temperature vaporization of the tantalum heating elements is under study by both our laboratory and the Cabot Corporation which manufacture the tantalum wire used in the elements. When the solution to this problem is found, we will continue these experiments. However, in the interim, it is to be noted, that the present oven design is currently in duplication at both the Pennsylvania State and Johns Hopkins Universities.

(3) In order to study metal cluster oxidation 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" noneffusive 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^{3,6,7} to probe the optical signatures of those reaction products associated with the oxidation of small

copper (Cu_xO_3)^{3,8} and silver (Ag_xO_3)^{3,6} clusters with further extension to select transition ($\text{Mn}_x\text{O}_3, \text{Cr}_x\text{O}_3$)^{9,10} metals and Group IVA ($\text{Si}_x, \text{Ge}_x\text{O}_3, \text{N}_2\text{O}, \text{NO}_2$) metalloids. From these studies we have obtained the first quantal information on the energy levels and optical signatures of several metal cluster oxides, $\text{M}_n\text{O}_y (n \geq 2)$. These studies serve to outline the potential for chemiluminescent probes of polyatomic metal cluster oxide quantum levels,³ 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.

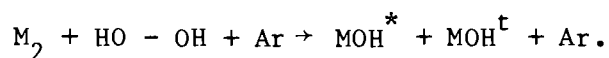
The most extensive work on copper and silver cluster oxidation has yielded a wealth of information on the vibrational level structure of the ground electronic states of Cu_2O and Ag_nO (esp. Ag_2O) and demonstrated an expected red shift in spectral emission features upon traversal of the series M_nO 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. This study is discussed in more detail in the enclosed preprint.

A particularly intriguing aspect of our studies of metal cluster oxidation thusfar has been the initiation of an experimental-theoretical collaborative-interaction with the Los Alamos Scientific Laboratory Theory Group (Ag_2O) and Dr. Charles Bauschlicher (NASA Ames Laboratory - Moffett Field) (Cu_2O). In conjunction with the Los Alamos Scientific Laboratory theory group, we have embarked on a collaborative effort to study several of the small silver oxides (Ag_xO). Silver surfaces are known to catalyze the epoxidation of ethylene. As with many metal catalyzed processes, an aspect of the catalytic cycle involves the need to understand the influence of surface oxidation. The Los Alamos group has modeled silver surfaces and the oxidation

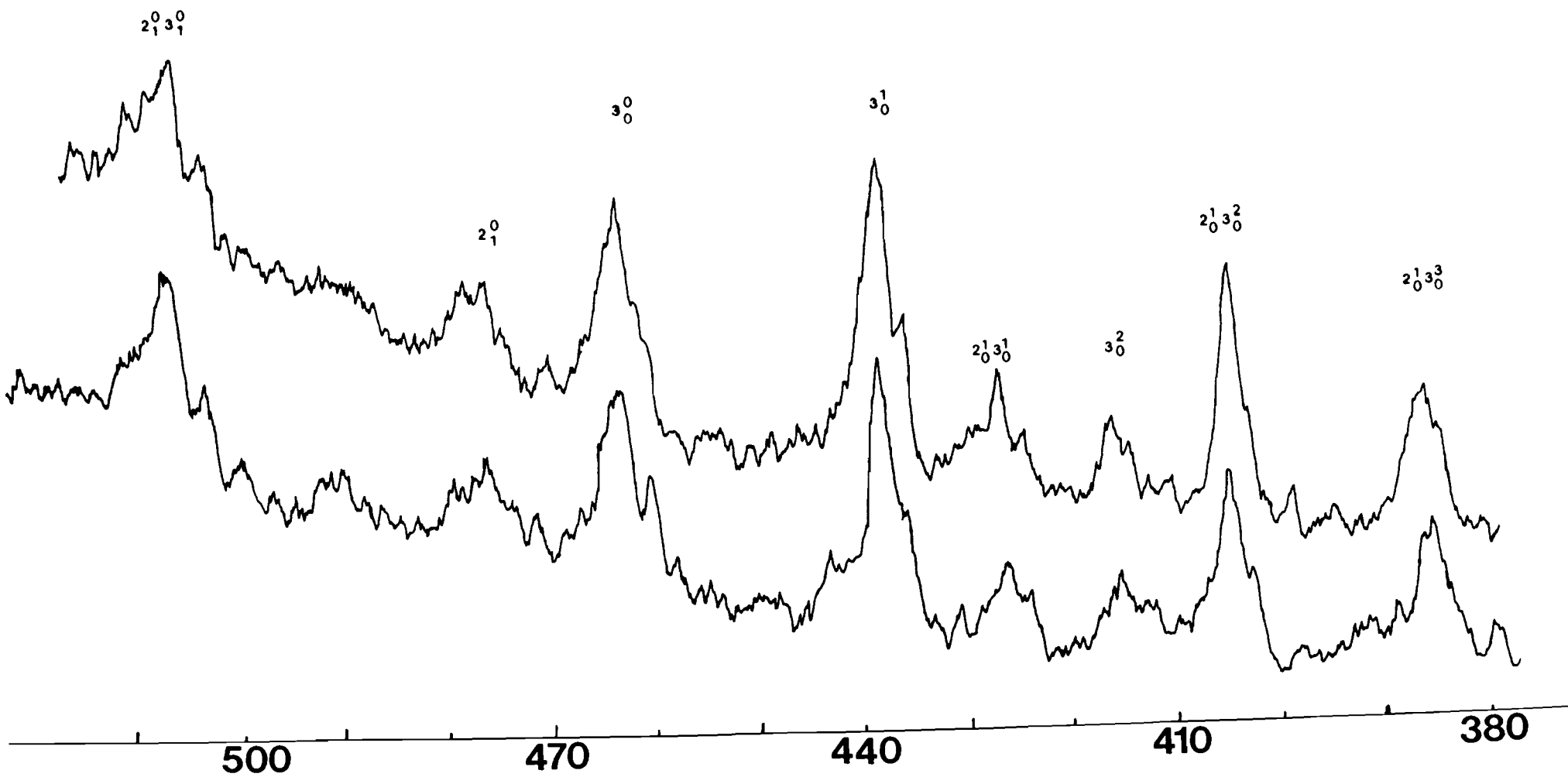
of these surfaces using pseudo-potential techniques. One of the fundamental building blocks of their model involves a two-fold binding site for oxygen atoms bound to the silver surface. Hence they have carried out detailed calculations on Ag_2O . We have obtained the first electronic emission spectrum for Ag_2O . This result has sparked an effort to model the low-lying electronic states of the oxide. Detailed quantum calculations will serve to aid our interpretation of the spectrum while, simultaneously, the experimental spectrum furnishes a benchmark on which to further refine the silver surface model.

Sparked by our recent experimental results (see attached preprint), and several mutually stimulating discussions, Dr. Charles Bauschlicher is now carrying out detailed quantum calculations on the ground and low-lying excited electronic states of the Cu_2O molecule. These will, of course be invaluable as an aid to the understanding of Cu_xO spectroscopy.

(4) By virtue of the metal cluster oxidation entrainment source, we have been able to extrapolate and extend our studies of alkali metal hydroxide spectroscopy and dynamics to several additional MOH species. We have obtained the first electronic emission spectra for the technologically important boron, aluminum, and silicon monohydroxides, these species being formed under multiple collision conditions primarily in the pseudo-"four-center" process



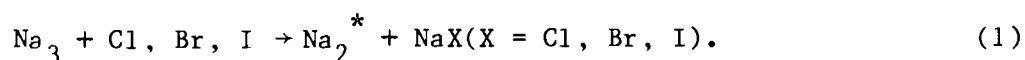
The boron hydroxide spectrum (depicted in Figure 2), which is currently under study, appears dominated by a combination of ground and excited state B-OH stretch and bending modes. The nature of this spectrum and a general description of the BOH molecule contributes to our understanding of trends in the bonding of the only moderately characterized HAB molecules. This is parti-



cularly intriguing for the boron system since it is thought that the stability of the isomeric HBO molecule (previously matrix isolated) considerably exceeds that of BOH. This is in sharp contrast to the aluminum hydroxides where AlOH is considerably more stable than HAlO. As we unravel the BOH spectrum more thoroughly through isotropic substitution, we hope to test and provide a reasonable explanation for these observed trends.

A further exciting aspect of our characterization of the metal hydroxides is the collaboration developing between our research group and that of Professor John Parson of the Ohio State University. We envision that our mutual interest will provide a strong inroad into the understanding not only of the spectroscopy but also of (1) the dynamics of formation of the hydroxides and (2) the dynamics of the hydroxides behavior, once formed.

(5) We have continued our studies of the sodium cluster - halogen atom reactions ($\text{Na}_n + \text{Cl}, \text{Br}, \text{I}$) in the single collision pressure regime. The major impetus of our present effort involves the study of the Na_2 chemiluminescent emission from the reactions



Completed and continuing studies in our laboratory now demonstrate a very unique gas phase oxidation chemistry associated with these reactions. The Na_2 chemiluminescent emission originates in large part from an only recently analyzed double minimum state of Na_2 ($C' \ ^1\Pi_u$) which has now been demonstrated to be the source of the dominant feature contributing to the well-known sodium "violet" bands. Based on a recently completed high resolution analysis of this low-lying electronic state, a reasonable set of Franck-Condon factors has now been computed to be used in a first order fit of the emission spectrum.

Spectral simulations of the emission from the Na_2 $A^1\Sigma_u^+ - X^1\Sigma_g^+$, $B^1\Pi_u - X^1\Sigma_g^+$, and $C^1\Pi_u - X^1\Sigma_g^+$ band systems as well as the newly discovered $C'^1\Pi_u - X^1\Sigma_g^+$ band system can be used to establish the distribution of Na_2 produced as the nascent product of reaction (1). However, when one attempts to fit the observed fluorescence spectra, one finds that the observed spectral distributions are considerably sharper than those which would be predicted on the basis of a simple fluorescence phenomena. The sharp nature of the Na_2 emission features may well indicate possible population inversions with respect to the ground state and stimulated emission analogous to that observed in alkali dimer optical pumping experiments. There are several dynamical factors which could lead to this phenomena which must first be further experimentally demonstrated through laser gain experiments (to be carried out shortly in the laboratory).

At this point, we may state that the considerable cross correlation of spectral data from all three reactions (1) and the appropriate spectral simulations indicate a rich chemistry including (1) a clear bimodal distribution of Na_2^* product vibrational levels correlating with the dynamics of Na_2 formation, (2) the clear effect of the molecular electronic structure of Na_2 on the dynamics of the reaction $\text{Na}_3 + X \rightarrow \text{Na}_2^* + \text{NaX}$, and (3) the possible observation of stimulated emission associated with the Na_2^* formed in reaction.

In order to characterize and correctly model the observed emission features, we are modifying a normal fluorescence spectral program to include the effects of "small signal gain" as it distorts the fluorescence features.

(6) Having received the necessary equipment, we are now in the latter stages of implementing important transient signal processing and averaging capabilities for our laser photoionization - time-of-flight mass spectrometer system. This installation will facilitate the attainment of mass spectra

and/or the measurement of other transient signals at a considerably greater signal to noise.

(7) In collaboration with Dr. David Dixon (E. I. Dupont), we have now begun extensive ab-initio studies of the structure of metal ion - CO, N₂, and H₂ adducts as a first step in the approach to the spectroscopy of metal cluster ion-molecular complexes.

Principal Investigator

The principal investigator has devoted 30% of his time to the present research efforts outlined in this proposal. This amounts to approximately 25 or more hours per week.

Personnel

Graduate students working on and supported in part by this project include Mr. Steven Cobb and Mr. Michael McQuaid. Collaborative efforts which continue with Dr. David Dixon (E. I. Dupont Nemours), Dr. V. E. Bondybey (Ohio State University - Bell Laboratories), and Dr. Thomas Devore (James Madison University) also benefit this project. Further collaborations as outlined in the progress report are also envisioned.

Public Relations

Seminars, talks and invited papers describing NSF sponsored work were given at the following locations:

International Workshop on Ionized Cluster Beam Techniques, Tokyo and Kyoto, Japan (1986) - Invited Talk, "Formation and Oxidation of Intense Metal Cluster Beams and Flows".

20th Mid Atlantic ACS Meeting, Symposium on Clusters and Cluster Ions, Baltimore, Maryland (1986) - Invited Talk, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

Optical Society: OSA Annual Meeting and APS/OSA International Laser Science Conference

1. Invited Talk, "Preparation, Characterization, and Oxidation of Small Metal Clusters".
2. "Possible Chemically Pumped Alkali Dimer Diffuse Band Lasers", P. W. Kleiber, W. C. Stwalley, and J. L. Gole.

Publications

"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.

"Self-Flushing Optical Window to Prevent Collection of Condensates", with W. H. Crumley, Rev. Sci. Instruments, 57, 1692 (1986).

"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, in press.

"Bound-Free Transitions in Molecular Metal Trimers", in Proceedings of the International Laser Science Conference, American Institute of Physics Conference Proceedings No. 146, Advances in Laser Sciences - [age 522 (1986).

"The Binding of Li^+ and Na^+ to Small Molecules", with D. A. Dixon, submitted.

Publications in Preparation

"Gas Phase Laser Induced Excitation Spectrum of Nickel Trimer", with R. W. Woodward and S. H. Cobb.

"A Comparative Study of the Oxidation of Atomic Copper and Higher Copper Clusters Under Single and Multiple Collision Conditions", with R. Woodward, J. S. Hayden, T. C. Devore and T. Burkeholder, in preparation.

"Electronic Emission Spectra and Bonding of the Alkali Hydroxides, NaOH CsOH", with J. S. Hayden, R. Woodward and C. Pettyjohn, in preparation.

"Chemiluminescent Emission from the Oxidation of Small Silver Clusters", with R. Woodward, P. N. Le, and D. A. Dixon, in preparation.

References:

1. W. H. Crumley, J. S. Hayden and J. L. Gole, J. Chem. Phys. 84, 5250 (1986). R. Woodward, S. H. Cobb, and J. L. Gole, work in progress.
2. "Metal Clusters", edited by M. Moskovits, John Wiley and Sons, New York (1986).
3. See discussion in 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 ($M = Cu, Ag, Mn, B$)", J. Phys. Chem., in press.
4. G. J. Green, S. A. Pace, D. R. Pruess, and J. L. Gole, J. Chem. Phys. 76, 2247 (1982).

5. J. S. Hayden, R. Woodward and J. L. Gole, J. Phys. Chem. 90, 1799 (1986).
6. R. Woodward, J. S. Hayden, J. L. Gole, and D. A. Dixon, J. Phys. Chem. 89, 4905 (1985).
7. 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).
8. R. Woodward, M. Temmen, R. C. Oldenberg, T. C. Devore, and T. Burkholder, "A Comparative Study of the Oxidation of Atomic Copper and Higher Copper Clusters Under Single and Multiple Collision Conditions", in preparation.
9. T. C. Devore, T. Burkholder, and J. L. Gole, work in progress.
10. T. C. Devore and J. L. Gole, work in progress.

Statement on Funding

All funds currently provided by the National Science Foundation will be expended at the end of the period for which NSF is currently providing support.

Delineation of Other Research Efforts and Support

The research on metal aggregates which is proposed to the National Science Foundation is not supported in any way by other government agencies. In addition, no proposal involving only metal aggregate characterization has been submitted to any agency.

"Characterization of Ligand-Free Copper and Silver Clusters and Their Reactions to Form Metal Cluster Oxides and Halides", - American Chemical Society, Petroleum Research Fund \$37,000.00 October 1, 1985 - October 1, 1987.

A delineation of other research proposals submitted or in preparation is as follows:

Office of Naval Research and Army Research Office, Durham, "The Chemistry and Kinematics of the Photoenhanced Etching of Silicon", with E. W. Thomas - Proposed Amount \$560,224/3 years.

"The Photophysics and Kinetics of Boron Cluster Compounds", Air Force Office of Scientific Research - with M. Duncan - in preparation.

APPENDIX A

Potential Probes of Metal Cluster Oxide Quantum Levels -
Optical Signatures for the Oxidation of Small Metal Clusters

M_x (M = Cu, Ag, B, Mn)

Potential Probes of Metal Cluster Oxide Quantum Levels -
Optical Signatures for the Oxidation of Small Metal Clusters

M_x (M = Cu, Ag, B, Mn)

R. Woodward, P. N. Le, M. Temmen, and J. L. Gole

High Temperature Laboratory
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and

School of Physics

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Atlanta, Georgia 30332

Abstract

Using a source configuration which lies intermediate to a low pressure effusing molecular beam and a high pressure flow device, we generate large concentrations of small metal clusters in a highly oxidizing environment. Clusters are formed from a high metal flux source ($K_{\text{Knudsen}} < 1$), which creates the seed for the initial phases of a cluster forming environment, and are further agglomerated in a controlled argon or helium flow at room to liquid nitrogen temperature. The high flux non-effusive source has been combined with techniques which have proven valuable in studying chemiluminescent processes across a wide pressure range to probe the chemiluminescent emission from several processes including the oxidation of small copper ($\text{Cu}_x + \text{O}_3$), silver ($\text{Ag}_x + \text{O}_3$), boron ($\text{B}_x + \text{NO}_2, \text{N}_2\text{O}$), Group IVA, and early transition metal clusters. 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 . The present study outlines the potential for chemiluminescent probes of metal cluster oxide quantum levels, not only within themselves but as a means of suggesting future laser fluorescent probes of the metal cluster oxides.

Introduction

As the current volume demonstrates, there is now widespread interest and a growing effort to understand several aspects of the structure and properties of atomic, molecular, and ionic clusters. Within this grouping, 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,¹ the development of features in the bulk metallic phase,² 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.³ Thus, the basic properties (geometry, bond strength, reactivity) of small metallic clusters, M_n ($2 \leq n < 6$), have become the subject of intense, theoretical and experimental study.^{4,5}

While it is clear that the electronic and reactive properties of small metal clusters lie intermediate to those of the atom and those of the bulk metallic phase, the detailed aspects of this picture especially with respect to internal mode structure have not yet been colored. Quantum level probes which have already indicated the need for models including vibronic coupling⁶ as well as demonstrating the unique dynamic behavior of small metal clusters as a function of temperature are slowly emerging.⁷ It is now apparent that it will be difficult to probe resultant quantum levels even with extremely sensitive laser spectroscopic techniques. If intense cluster beam sources are developed, however, it may be possible to overcome some of these difficulties.^{7,8} These cluster sources must be designed to overcome the substantial loss mechanisms including predissociation and rapid intramolecular conversion and relaxation which deplete excited state populations at a rate competing effectively with those spectroscopic probes that can be applied to

the analysis of quantum level structure.

We have been concerned with the development of intense sources producing cold metal clusters and with the characterization of cluster molecular electronic structure,^{7,9,10} dynamic behavior,⁷ and oxidation.¹¹⁻¹³ Studies of gas phase metal cluster oxidation afford the opportunity to characterize the intermediate region bordered on the one side by the gas phase oxidation of metallic atoms and dimers and on the other by the surface oxidation of the bulk metallic phase. It has been suggested that these studies may provide information useful for the assessment of short and long range factors affecting surface oxidation.¹⁴ The products of metal cluster oxidation may be studied using a combination of chemiluminescent (product formation in excited electronic states for highly exothermic oxidation) and laser fluorescent techniques, although observations of the internal mode structure associated especially with the polyatomic products of metal cluster oxidation may be plagued by the rapid depletion of excited state populations, either before the emission of a monitoring photon (chemiluminescence) can occur or before an appropriate, usually multiphoton, laser spectroscopic probe can be made operative (for example quantum level probes by TPI spectroscopy¹⁵). Here again, the development of intense metal cluster sources offers a viable means for overcoming these loss mechanisms.^{7,13} Although the results may be complex, the potential value of such studies, as a means of evaluating the local environments which characterize surface oxidation, provides an impetus for the development of sources appropriate for the study of metal cluster oxidation products and their internal state distributions.

Quantum level probes of the products of metal cluster oxidation have been carried out in at least two distinct configurations. In one configuration a stream of metal clusters formed through the "supersonic expansion" of the metallic element of interest is made to intersect a tenuous atmosphere of a

given oxidant (beam gas configuration), the products of reaction being studied using a combination of chemiluminescent and laser fluorescent techniques. As a prototype the $\text{Na}_n + \text{X}$ (Cl, Br, I) reactions has been under study in our laboratory.¹¹ The $\text{Na}_3 - \text{X}$ (Cl, Br, I) metathesis are found to produce Na_2^* (electronically excited products) with sharp bimodal excited state vibrational distributions, the emission from these states resembling that characterizing optically pumped alkali dimer lasers.¹⁶ In this discussion, we will focus on a second and possibly more versatile source configuration which lies intermediate to a low pressure molecular beam and high pressure flow device.¹² Clusters are formed from a high metal flux source and further agglomerated by an entraining argon or helium flow at room to liquid nitrogen temperature. Using this source, we have successfully obtained the first quantal information on the energy levels and optical signatures of several metal cluster oxides and select halides (M_nO , M_nX), the qualitative nature of which we now wish to consider. Our focus is to be distinguished from recent very exciting studies in which small to intermediate size clusters have been generated in flow systems,¹⁷ reacting with reagents in another continuous or pulsed flow stream under high pressure (~ 300 -500 torr) conditions in a modified merged flow environment. The products in the flow have been measured mass spectrometrically; however, this technique has yet to provide a direct measure of structural or dynamic properties although important kinetic information has been extracted. Here, we focus on both spectroscopic information and the intriguing dynamic behavior which appears to characterize the oxidation reactions of small metal clusters.

The purpose of the following discussion is to summarize (1) the experimental techniques for generating large concentrations of small metal clusters in a highly exothermic oxidizing environment and (2) information

which we have garnered on the quantum levels of metal cluster oxide compounds, M_xO_y . We suggest that the present studies outline the potential for chemiluminescent probes of metal cluster oxide quantum levels, not only within themselves but also as a means of suggesting future laser fluorescent probes of the metal cluster oxides.

Experimental Considerations

To approach the study of the internal mode structure of metal cluster oxides and halides, we extrapolate experience gained in the study of chemiluminescent metal atom oxidation reactions,¹⁸ focusing on the development of "high flux" continuous metal flow sources. We use this high flux continuous metal flow to create large concentrations of small metal clusters by forming an environment which is intermediate to that of a low "source" pressure effusive device, producing primarily atoms, a small percent diatomics and, in some cases, small percentages of polyatomics,¹⁹ and those conditions which prevail subsequent to the agglomeration of the metallic plasma formed in laser vaporization as it is entrained in a continuous or pulsed rare gas flow at high pressures. The latter technique, especially when operated in the pulsed supersonic expansion mode, produces a wide diversity of much larger clusters (vs. effusive source) although at small ($\sim 10^7/\text{cm}^3$) concentration.²⁰ In operating a metal source at temperatures or through containment designs such that the Knudsen number associated with the source is much less than one, we create the seed for the initial phases of a cluster forming environment. The high metal flux, which within itself can lead to agglomeration to form clusters, is further agglomerated to small clusters by an entraining argon or helium flow at room to liquid nitrogen temperature.

The agglomeration-entrainment device is depicted schematically in Figure 1(a). Here, using a tungsten basket heater (R. D. Mathis), a metal is heated in a particularly designed crucible to a temperature producing a vapor pressure between one and three orders of magnitude greater than that employed for effusive operation. The basket heater is wrapped in zirconia cloth (Zircar, Florida, N. Y.) and surrounded concentrically by (1) a tantalum heat shield and (2) a cylindrical heavy-walled zirconium tube (Zircar). Both the top and

bottom of the basket heater zone are heavily insulated with zirconia cloth. This extra insulation allows the ready operation of the tungsten basket heater at temperatures consistently at the upper limits of its performance specifications.

The metal flux issuing from the lower crucible chamber is entrained in a rare gas (He or Ar - Airco 99.998%) flow ranging in pressure from 100 to 3000 millitorr, dependent upon the metal under study and the optimization of the chemiluminescent oxidation processes which are of interest, the agglomeration of the metal to form small clusters occurring both as a result of the high metal flux and as the metal flow is cooled by the variable temperature entrainment gas. In order to vary the temperature of the entrainment gas which, as it enters the device depicted in Fig. 1(a), is brought to the desired operating condition, the entire upper assembly depicted in the Figure, with which the gas is in intimate contact, is maintained at the desired temperature. This is accomplished with the systems depicted in Figure 1(b). For cooling to temperatures approaching 196K, methanol is continuously pumped through all cooling lines after passing through a dry ice slush bath. For cooling to lower temperatures, liquid nitrogen is allowed to flow at varying rates through these cooling lines. The choice of a cooling system is dictated by several parameters which will be considered in following discussion.

At a suitable point above the flow, an oxidant intersects the entrained metal clusters, entering either from a concentric ring injector inlet as depicted in Figure 1(a) or from a nozzle perpendicular to the flow and elevated above the cooled upper region of the oven assembly (Figure 1(b)). Typical oxidant pressures ranged from 10 to 100 millitorr. Here, for metatheses which are sufficiently exothermic, a chemiluminescent flame may be formed.

In the studies which we will outline here, concentrations of metal, carrier gas, and oxidant are adjusted in a controlled manner to maximize or minimize the intensities of various potential emitters over the spectral region 2300- 8000 Å. The "multiple collision" flames vary in shape with a base diameter of 12mm and a height ranging from 1 to 5 cm. They are adjusted primarily by varying four parameters: 1) metal flux, 2) entrainment gas cooling, 3) pumping speed, and 4) oxidant configuration and concentration. On the basis of previous studies,¹⁸ the final internal rotational temperatures of the clusters before reaction will be considerably lower than the oven source from which the metal flow exits ($\sim T_{\text{Rot}} \leq 200\text{K}$ for cold entrainment). Where readily characterized for a diatomic emitters,¹⁸ the rotational temperatures for room temperature entrained emitters are found to vary from 500 to 700 K.

The mode of operation might better be gauged so as to clearly assess the nature of the "multiple collision" conditions under which the results reported here are obtained. We have previously exemplified the utility of studying chemiluminescent processes across a wide pressure range from single to multiple collision conditions.¹⁸ For processes which are chemiluminescent at low pressures where excited states are populated due strictly to a well-defined reaction exoergicity and photons are emitted from the reaction products before subsequent collisions, extremely complex spectra may result; the controlled extension of these studies to the multiple collision regime can provide useful spectral simplification as a result of differences in rotational, vibrational, and electronic relaxation rates. Multiple collision scans serve two primary purposes: (1) They allow the controlled study of relaxation and quenching phenomena and (2) they allow the study of rapid energy transfer among the excited states of high temperature molecules. Extensions from single to multiple collision conditions must be made under conditions such that only

relaxation and rapid energy transfer characterize the spectra. We maintain a readily assessed and well defined energy conservation. With the exception of light emitting processes which are readily ascribed to a combination of the dynamics of product formation and rapid energy transfer, a reaction which is dark under single collision conditions remains dark under multiple collision conditions as energy is conserved. This is an important touch-stone for the experiments to be considered.

Here, we focus on highly exothermic copper, silver, and boron cluster oxidations and touch on transition metal reactions which produce the metal cluster oxides and result in a considerable modification of those spectral features which are found to characterize the oxidation of effusively generated atomic fluxes. For the present studies, the oven source parameters summarized in Table 1 correspond to a gas phase metal flux between 3×10^{16} and 5×10^{18} particles/cm²-sec at the oven orifice, the concentrations at the upper limit being well in excess of that generated from an effusive source. The commercially available oxidants NO₂ (Matheson, 99.5%) and N₂O (Matheson > 98%) have been used in these studies. Ozone was generated and used as previously described.²¹

Spectra were taken with a 1m Czerny-Turner scanning spectrometer operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 5000 Å. A dry ice cooled EMI 9880 photomultiplier tube was used to obtain the majority of the spectra depicted in the following discussion. In addition, a dry ice cooled RCA 4840 phototube was used. The photomultiplier signals have been detected with a Keithley 417 fast picoammeter whose output signal (partially damped) drove a Leeds and Northrup stripchart recorder. All spectra were wavelength calibrated.

Table I

Parameters Associated with the Generation of Metal Cluster Flows

Metal (Purity, Source)	Metal Source Operating Temperature (Vapor Pressures)	Effusive Operation
Ag(99.99, Cerac)	1400-1700K (10^{-1} -5 Torr)	\leq 1400K (10^{-1} Torr)
Cu(99.9, Fisher)	\sim 1650-1960K (10^{-1} -2 Torr)	\leq 1650K (10^{-1} Torr)
B(99.7, Alfa)	2520-2800K (10^{-1} -1 Torr)	\leq 2520K (10^{-1} Torr)
Mn(99.95, Fisher)	1350-1600K (10^{-1} -5 Torr)	\leq 1300K ($<10^{-1}$ Torr)

Results and Discussion

Influencing Parameters

There are a number of factors in addition to metal flux, entrainment gas cooling rate, pumping speed, and oxidant configuration which determine the nature of the fluorescence spectra that can be generated using the techniques described herein. A process must be of sufficient exothermicity to populate the excited electronic states of the products of a given metathesis, be they polyatomic and/or diatomic emitters. A significant limiting factor on the success of the present experiments is the magnitude of the quantum yield for fluorescence once the excited electronic states of the polyatomic molecules on which we focus are populated. How large can a metal cluster be in order that we are able to observe its chemiluminescent oxidation to form a metal cluster oxide or halide? At some point, even with the requisite reaction exoergicity,²² quantum yields will drop to zero as non-radiative processes strongly dominate the system. This will be influenced by transition moments, the strength of coupling to non-radiative channels, and the density of states associated with a given system, as it increases with atomic mass. We monitor the competition between radiative and non-radiative channels and through this effort also assess those systems which will, in the future, be amenable to laser fluorescent probes.

In a given system, there will be a variety of conditions under which cluster distributions optimal for oxidation to form strongly emitting metal cluster oxides will be produced. As experimental conditions are varied, shifting cluster distributions, we proceed through optimal regions for the excitation of a given metal cluster oxide fluorescence spectrum. We thus engage in a search for those experimental conditions optimizing a given metal cluster oxide spectrum. Given sufficient exothermicity we must gradually shift

the metal source cluster distributions through either a buildup of metal flux or increased (entrainment) cooling rate. In the following examples, we contrast results obtained upon the oxidation of effusive metal atom flows and those changes which occur as agglomeration ensues.

"Cu_x + O₃"

Depicted in Figure 2 is the emission spectrum obtained when the output from a high flux copper source (operating at $K_{\text{Knudsen}} < 1$) is entrained in room temperature argon, this mixture being subsequently oxidized with ozone. The spectrum displays features which can be associated with several excited states of diatomic copper oxide (CuO) but is, in fact, dominated by a number of other band systems in the range 5200-5500 (I), 5700-6200 (II), 6900-7100 (III), and 6500-7800 Å (IV). In addition, we find a moderately sharp emission feature (V) extending from 6300 to 6450 Å. This is in contrast to the situation at lower copper fluxes where emission from the CuO $A^2\Sigma^+ - X^2\Pi$, $A'^2\Sigma^+ - X^2\Pi$, and $\delta^2\Sigma - X^2\Pi$ band systems²³ is much more pronounced, the $A^2\Sigma^+$ and $\delta^2\Pi$ emission features dominating the spectrum.²⁴

Systems I, II, and III (Fig. 2) are characterized by what appear to be short progressions in low frequency ~ 120 -150 cm⁻¹ modes or sequence structure. We favor the former interpretation for sequence frequency separations of this magnitude imply that extended progressions in the modes with which they are associated will be observed. These are apparently absent and systems I, II, and III do not appear to extend over wide spectral regions. Based on the behavior which we will now exemplify, we assign systems I - V to metal cluster oxide emitters.

The Cu + O₃ → CuO + O₂ metathesis is 1.76 ± 0.05 eV exothermic.²⁵ This corresponds to 14198 cm⁻¹ which does not represent a sufficient energy to populate the CuO $A^2\Sigma^+$ state ($\nu_{00}(A^2\Sigma^+ - X^2\Pi_{3/2}) = 16492$ cm⁻¹;²³ $\nu_{00}(A - X^2\Pi_{1/2})$

$= 16213 \text{ cm}^{-1}$)²³ unless the $\sim 2000 \text{ cm}^{-1}$ of additional energy necessary can be obtained from internal energy in O_3 and atomic copper ($E_{\text{int}}(\text{O}_3) + E_{\text{int}}(\text{Cu})$) or the relative initial translational energy of the copper-ozone encounter.²⁶ Similarly, the reaction of room temperature copper dimer (Cu_2) with ozone in a multicenter reaction producing CuO and CuO_2 is not expected to increase the reaction exoergicity substantially since the Cu_2 dissociation energy (2.03 eV)²⁷ and the CuO_2 bond strength are expected to be similar.²⁸ The formation of the $\text{CuO } A^2\Sigma^+$ and $A'^2\Sigma^+$ states must therefore result from a more complex process which, under the conditions of Figure 2, involves the reaction of vibrationally hot copper dimer or larger copper clusters. The Cu_3 bond energy ($D(\text{Cu}-\text{Cu}_2)$) is substantially smaller than that of the dimer ($D(\text{Cu}-\text{Cu}_2) = 1.02 \text{ eV}$,^{19(a)} and a multicentered process involving the trimer could yield the excited $A^2\Sigma^+$ and $A'^2\Sigma^+$ states of CuO . In contrast to the $A^2\Sigma^+$ and $A'^2\Sigma^+$ states, the $\text{CuO } \delta^2\Sigma^+$ state can be formed as a result of the $\text{Cu} - \text{O}_3$ metathesis. The chemiluminescence from the $\text{Cu}_x + \text{O}_3$ metathesis has now been characterized across a wide pressure range extending from single collision conditions (beam-gas configuration) to the intermediate pressure range exemplified in Figures 2 and 3. The single collision results, which will be considered in more detail at a latter time, bear summary here.

Under single collision conditions, the chemiluminescent spectrum resulting from the reaction of a copper beam with ozone displays a weak but clearly structured feature in the green²⁹, a moderately structured and dominant feature in the region $5700 - 6400 \text{ \AA}$, and a weak emission feature at $\sim 7700 \text{ \AA}$. A portion of the structured features in the green region of the spectrum extending from 5200 to 5600 \AA appear to correspond to system I in Figure 2, whereas the $5700\text{-}6200 \text{ \AA}$ feature appears to correlate with system II. The 7700 \AA feature most certainly correlates with the $\delta^2\Sigma^+ - X^2\Pi$ emission system of CuO .

The single collision chemiluminescent features all display a first order ozone reactant dependence. However, while the temperature dependence of the 7700 \AA feature indicates that it results from the reaction of a ground state copper atom, the features observed at wavelengths shorter than 6200 \AA appear to increase in intensity at a rate too fast for the chemiluminescence to depend solely on ground state copper atoms. It appears that the emitter may be formed in the bimolecular reaction of metastable copper atoms which form a very small percentage of the beam or, more likely, vibrationally hot copper molecules.

The single collision results correlate with and compliment our multiple collision agglomeration studies. Under the conditions by which the spectra in Figure 2 were obtained, the copper beam is thermalized to a temperature between 500 and 700 K. Thus, the reaction of copper atoms at sufficiently high thermal energies to populate observed band systems at wavelengths shorter than 7000 \AA seems unlikely. Metastable 2D copper atoms might be present under the conditions associated with Fig. 2, however, the absence of band systems below 5200 \AA and the observation of some emission in the $4600 - 5200\text{ \AA}$ region²⁹ under certain single collision conditions casts doubt on this possibility. On the other hand, vibrationally hot copper dimers and higher copper n-mers are ideally suited to form copper oxide in a multicentered process with ozone to produce CuO and CuO_2^* or higher order Cu_xO_2 species. If Cu_2 , vibrationally hot, reacts to form $\text{CuO } A^2\Sigma^+$ and $A'^2\Sigma^+$, a decrease in vibrational excitation should result in the quenching of the $\text{CuO } A^2\Sigma^+ - X^2\Pi$ and $A'^2\Sigma^+ - X^2\Pi$ features as subsequent studies with LN_2 cooled argon entrainment demonstrate.

Given that clusters are formed in high metal flux entrainment cluster agglomeration should be enhanced as the temperature of the argon entrainment gas is decreased. Figure 3 demonstrates the effect of such a cooling process for a moderate and effectively constant copper flux. In Figures 3(a)-(c), the

liquid nitrogen flow and cooling rate are increased. In Fig. 3(a), the $\text{CuO } A^2\Sigma^+ - X^2\Pi$ and $A'^2\Sigma^+ - X^2\Pi$ emission bands observed in Fig. 2 are again monitored, however, the $A^2\Sigma^+$ features are muted somewhat relative to $A'^2\Sigma^+$; the $\delta^2\Sigma^+ - X^2\Pi$ system is readily observed. As the LN_2 flow rate and cooling are increased (Figure 3(b)), a condition which should (1) enhance the cooling of vibrationally hot species in the copper beam and (2) increase agglomeration, the $\text{CuO } A^2\Sigma^+$ and $A'^2\Sigma^+$ emission features virtually disappear while the $\delta^2\Sigma^+ - X^2\Pi$ emission system is still apparent. In contrast, systems I-V are enhanced. As the LN_2 cooling is further increased, the $\delta^2\Sigma^+ - X^2\Pi$ and system I emissions are virtually quenched and the spectrum is dominated by systems II - IV which have not been observed previously. The most significant change resulting from the transformation from single to multiple collision conditions observed in the $\text{Cu}_x + \text{O}_3$ system is the continual growth of the 6500-7800 Å emission region relative to other spectral features. In fact, these systems (III, IV) are rather muted under low copper flux multiple collision conditions and virtually absent under low copper flux single collision conditions. That the observed behavior is coincidental with increased agglomeration suggests that band systems II-V and probably system I³¹ should be associated with the formation of excited states of the metal cluster oxide via metathesis with small copper agglomerates.

* Although the origin of a CuO_2 emission system can be found in the region of system II,³⁰ it corresponds to a transition from the B state to a low-lying A state and is characterized by the dominance of a long progression in a Cu-O stretch at $\sim 600 \text{ cm}^{-1}$. Further, if the 5700-6200 Å feature corresponds to CuO_2 , we find no indication of the CuO_2 B-X system at $T_0 \sim 20700 \text{ cm}^{-1}$ which should be observed.

"Ag_x + O₃"

We have previously reported the initial phases of a study of the silver-ozone system in the multiple collision agglomeration mode. Here, we briefly summarize these results and outline the extension of initially reported efforts.

In contrast to the chemiluminescence observed when a copper beam intersects a tenuous atmosphere of ozone in a beam-gas configuration, the corresponding silver-ozone interactions do not populate excited electronic states of the products of metathesis. This is not surprising for an effusive silver beam, containing predominantly silver atoms and a small concentration of silver dimer, can react with ozone in a process whose exoergicity is ~ 1.25 eV for the reaction of ground state atoms ($D_0^0(\text{AgO})^{32} - D(\text{O-O}_2)^{25}$) excluding the internal energies of ozone and silver and the relative initial translational energy, E_T^i , of the reactants.³³ The sum of all available energy is insufficient to produce excited states of the metal monoxide. In contrast to atomic copper which has a low-lying metastable 2D state ($^2D_{5/2}$, 11203 cm⁻¹, $^2D_{3/2}$, 13245 cm⁻¹), the lowest-lying metastable 2D state of the silver atom ($^2D_{5/2}$, 30242, $^2D_{3/2}$, 34714) will not be sufficiently populated at the temperatures associated with effusive beam conditions (Table I), and therefore need not be considered. Further, even the multicentered reaction of silver dimer with ozone viz.



is also not sufficiently exothermic to form the excited states of AgO since the AgO₂ (Ag-O₂)³⁴ bond strength is approximately equal to or slightly less than the Ag₂ (1.63 eV)³⁵ dissociation energy. Thus, based strictly on thermodynamic

considerations, the interaction of an effusive silver beam with ozone produces no electronically excited products.

Figure 4 demonstrates results obtained as the silver-ozone system is taken in a controlled manner from single to multiple collision conditions and we operate in the metal agglomeration mode. The spectra in Figure 4 were obtained when a moderate silver flux ($K_{\text{Knudsen}} < 1$) entrained in room temperature argon in the pressure range 150-700 millitorr is oxidized with ozone. The observed emission corresponds to AgO in the region 4000-4200 Å (some continuation (weak features) in 4200-4400 Å range) and is believed to correspond to Ag₂O in the region ~ 4300-4800 Å. The AgO bands correspond to (0,0) transitions originating from predissociating excited $A^2\Pi$ spin-orbit components and terminating in ground state $X^2\Pi$ spin-orbit levels.^{36,37} The band at 4096 Å is assigned to the $^2\Pi_{3/2} - ^2\Pi_{3/2}$ transition and that at 4125 Å is assigned to the $^2\Pi_{1/2} - ^2\Pi_{1/2}$ transition.

Although the AgO excited electronic state cannot be formed from the reaction of silver atoms or dimers with ozone, the multicentered reaction of silver trimer



can be sufficiently exothermic to populate excited states of AgO if the formation of Ag₂O₂ from Ag₂ and O₂ releases 3.0 eV of energy. A large energy release is possible because of the low trimer, Ag-Ag₂ bond strength^{19(a)} (0.99 eV) and because of the possibility of some vibrational excitation in the trimer.³⁸ The major consideration is that the formation of AgO $A^2\Pi$ requires a metathesis involving silver clusters, Ag_x, $x \geq 3$.³⁸

The spacings between the resolved vibrational peaks in the region

4400-4800 \AA do not follow a regular progression increasing to a maximum of $\sim 260 \text{ cm}^{-1}$. The number of observed features indicates a substantial change in at least one molecular parameter (bond angle or bond length) upon transition. We tentatively correlate the emission with a transition from an excited state of Ag_2O to what is thought to be a linear ground state.³⁹

As the silver flux is increased, the features emanating from the pre-dissociating A^2_{Π} state of AgO are quenched⁴⁰ and features tentatively associated with the silver cluster oxides become more pronounced.⁴¹ Simultaneously, a similar behavior characterizes the monitored chemiluminescence corresponding to the AgO 3500 \AA band system ($\text{B}^2_{\Pi} - \text{X}^2_{\Pi}$) depicted in Figure 5. In an ozone rich environment,⁴¹ the spectral features depicted in the 3200 - 3700 \AA region are dominated by the AgO emission feature. However, in a silver rich environment, this emission feature is strongly quenched relative to both the Ag^* emissions and those features which dominate the spectrum at longer wavelength.

A further increase of the silver flux (the generation of higher-order clusters) leads to some quenching of the features observed in the 4400-4800 \AA region⁴⁰ and an enhancement of spectral features in the range 5000 - 7500 \AA . Figure 6 depicts a portion of the spectra over the range 5500 - 7400 \AA now obtained in the high silver flux configuration. While the spectrum in Fig. 6(a) is complex in the region 5500-6340 \AA it clearly simplifies to a series of bands separated by between 150 and 175 cm^{-1} . The overall frequency separations in the range 5500-7000 \AA are indicative of silver-silver stretch, bending, or torsional modes, however, more definitive statements will require considerable further evaluation under a wider variety of conditions leading to the generation of the observed spectral features. Finally we note that as the silver flux is again increased (Figure 6(b)) further spectral complication

arises with the definite emergence of a new red shifted feature at $\lambda > 6800 \text{ \AA}$.

The results outlined here in conjunction with previous studies of the 5000 - 6000 \AA region suggest that the observed features result, at least in part, from Ag_xO , $x \geq 3$, although considerable further experiments and analysis will be necessary to establish definitive correlations. As one might anticipate, the observed emission features appear to red shift as the size of the metal cluster oxide increases.

" $\text{B}_x + \text{NO}_2, \text{N}_2\text{O}$ "

The results obtained for copper and silver represent specific examples of a general trend. In Figure 7, we provide a further comparison of the significant changes which can be observed using the agglomeration technique in conjunction with the much higher temperature boron system. We have studied the B-NO_2 and $\text{B-N}_2\text{O}$ systems across a wide pressure range from single to multiple collision conditions.⁴² Under both single and multiple collision conditions ($\text{B+NO}_2+\text{Ar}$), the boron- NO_2 reaction leads to the formation of BO_2^* ($\text{A}^2\Pi$, $\text{B}^2\Sigma^+$) and BO^* ($\text{A}^2\Pi$) excited electronic states as we exemplify in Figures 7(a) and (b). When an intense boron beam is agglomerated in dry ice cooled argon and subsequently reacts with NO_2 , the spectrum is found to consist largely of a modified " BO_2 " emission system⁴³ which overlaps BO emission features ($\text{BO } \text{A}^2\Pi - \text{X}^2\Sigma$) emanating from $v' = 0, 1, 2, \text{A}^2\Pi$, and what appears to be a new system at $\lambda > 5900 \text{ \AA}$ which begins to dominate the total chemiluminescent spectrum as the boron flux is increased substantially. The spectrum is apparent in Figure 7(c) taken under conditions such that first order light at wavelengths below 3700 \AA has been filtered (second order features absent to 7400 \AA). A closer view of the new emission system is presented in Figure 8. At least two $\Delta v = 40 \text{ cm}^{-1}$ sequence groupings separated by $\sim 440 \text{ cm}^{-1}$ and a second long progression (or sequence grouping) with $\Delta v \sim 142 \text{ cm}^{-1}$ are observed and tentatively correlated with emission from the asymmetric BBO molecule.⁴⁴

"Mn + O₃"

In Figure 9 we summarize one further comparison which again emphasizes the significant changes induced using the agglomeration technique. We have studied the manganese-ozone reaction ($\text{Mn} + \text{O}_3 \rightarrow \text{MnO} + \text{O}_2$) across a wide pressure range from single to multiple collision conditions.⁴⁵ Under both single and multiple collision conditions ($\text{Mn} + \text{O}_3 + \text{Ar, He}$), the Mn-O₃ reaction leads to the formation of the lowest-lying $\text{MnO}^* \text{A}^7\Sigma^+$ excited electronic state⁴⁶ and the observation of a strong chemiluminescent signal corresponding to the $\text{MnO} \text{A}^7\Sigma - \text{X}^7\Sigma$ band system. When an intense manganese beam is agglomerated in LN₂ cooled helium and subsequently interacts with O₃, the intense MnO A-X emission system which extends from ~500 to 700 nm is accompanied by a new system extending from ~670 to at least 1000 nm which grows relative to the MnO A-X system with increased entrainment gas cooling. This new system, whose first order spectrum is depicted in Figure 9, is tentatively associated with moderate progressions in two modes of the ground electronic state of Mn₂O ($\text{Mn}_2^+ \text{O}^-$).⁴⁵

Summary and Conclusions

We have emphasized the development of a new source for the study of metal cluster oxidation and the analysis of metal cluster oxide internal mode structure. The results which we have outlined are very new and much work remains to be done to clarify the band systems and dynamics responsible for the observed metal cluster oxide emissions. In contrast to a preliminary mass spectrometric analysis of the silver system which is also characterized by a much more readily defined thermodynamics, only limited mass spectrometry has

yet been performed on the copper, boron, and manganese systems to clarify precisely the cluster distributions characterizing these systems. In addition, the more complex Group IV A cluster oxide systems are also under study. These studies are in their infancy, however, we believe that we have implemented a general approach for the aggregation of atoms to small metallic agglomerates which can subsequently be oxidized to form the metal cluster oxides. These examples provide a flavor for the broad approach to the formation of the metal cluster oxides of a variety of metals ($M = \text{Cu, Ag, Si, Ge, B, Al, early transition metals...}$) and the characterization of their quantum level structure. Further, we have now obtained preliminary chemiluminescent data on the Ag_x , $\text{Si}_x + \text{Cl}_2$, Br_2 systems. Here, the $\text{Ag, Si} + \text{Cl}_2$, Br_2 reactions are dark (no chemiluminescence) whereas the high metal flux metal cluster-halogen molecule interactions are the source of emission. We intend to study this emission and, in correlation with an available technology for forming halogen atoms will definitely extend our efforts to investigate the Ag_x , $\text{Si}_x + \text{Cl, Br, I}$ reaction system.

It is hoped that these studies will provide information which will be useful for the assessment of short and long-range factors affecting surface oxidation as well as aiding the characterization of those metal cluster oxides which play an important role in catalytic systems. Finally we should note that the internal structure which we are mapping using chemiluminescence should subsequently be studied using laser vaporization techniques to generate and interrogate the metal cluster oxides.

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25. Based on a CuO bond energy of 2.79 eV (S. Smoes, F. Mandy, A. Vander Auwera-Maheiu, and J. Drowart, Bull. Soc. Chim. Beig., 81, 45 (1972)) and an O₃ bond energy of 1.03 eV (F. D. Rossini, "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards, Washington, DC).
26. 2000 cm^{-1} of excitation easily exceeds the sum $E_{\text{int}}(\text{Cu}) + E_{\text{int}}(\text{O}_3) + E_{\text{T}}$ which one can readily associate with a copper beam at 1600K interacting with room temperature ozone in a non-thermalized beam-gas environment.
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28. We estimate the Cu-O₂ bond strength to be 1.8 - 2 eV based on the bond strength for NaO₂ $\text{Na} + \text{O}_2$ of 1.6 - 2.0 eV and the ionic character associated with CuO₂ (C. W. Bauschlicher, private communication).
29. Under certain circumstances, the copper-ozone system displays structured features in both the blue and green spectral regions extending from 4600 to 5600 Å. The extension of spectral emission to wavelengths shorter than 5200 Å is believed due to an electric discharge in the region of the oven source.
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31. It is noteworthy that the emission from System I at first increases in intensity with increasing liquid nitrogen flow (Figure 3) and then decreases. This would seem to indicate its formation via reaction with a small copper cluster that is subsequently lost as the distribution shifts to larger cluster sizes.
32. Based on an AgO bond strength of 2.29 eV - see reference 25.
33. $E_{\text{int}}(\text{O}_3) + E_{\text{int}}(\text{Ag}) + E_{\text{T}}$ will not exceed 0.15 eV even at the highest temperatures (1800 K) associated with an effusive oven system operating in a beam-gas configuration.
34. We estimate the bond strength of AgO₂ $\text{Ag} + \text{O}_2$ as 1.5 eV based on the bond strength for NaO₂ $\text{Na} + \text{O}_2$ of 1.6-2.0 eV and the ionic character observed for CuO₂ (C. W. Bauschlicher, private communication).
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38. The formation of Ag_2O can occur directly from the reaction of the dimer with O_3 , $\text{Ag}_2 + \text{O}_3 \rightarrow \text{Ag}_2\text{O} + \text{O}_2$, however, even if we assume that a symmetrical species is formed and that the two Ag-O bond strengths in symmetrical Ag_2O are the same as that in Ag-O it is unlikely that the reaction will lead to the formation of Ag_2O in the excited electronic state from which emission is observed unless an unlikely substantial vibrational excitation in Ag_2 (~ 1.0 eV) is transferred into electronic excitation. The reaction in the absence of vibrational excitation releases ~ 1.92 eV of energy which is clearly not sufficient to form Ag_2O with enough energy to luminesce in the observed range. The trimer can also react via

$$\text{Ag}_3 + \text{O}_3 \rightarrow \text{Ag}_2\text{O} + \text{AgO}_2 \quad (5)$$
 to form Ag_2O with enough internal energy to account for the observed chemiluminescence.
39. Based on comparison with Li_2O or Na_2O we would predict a linear ground state of $D_{\infty h}$ symmetry. One might conceive of a C_v configuration, AgAgO ; however, the formation of this species is difficult to rationalize on energetic grounds. Detailed quantum chemical calculations are now in progress at Los Alamos Scientific Laboratory (R. L. Martin and P. J. Hay) to evaluate these states and assess whether the ground state is in fact linear.
40. See reference 12(a) also R. Woodward, P. N. Le, and J. L. Gole, to be published.
41. The observed AgO emission features are found to be strongly dependent on the relative silver flux and ozone concentration (through a series of experiments monitoring the effect of changing ozone concentrations). Some contribution to the observed spectral features in the range 4200-4400 Å may result from short progressions in the previously identified Ag_2 A-X band system; however, a definitive statement will await further spectral analysis.
42. "A Comparative Study of the Boron- NO_2 and Boron- O_3 Reactions I - Chemiluminescent Processes, Ultrafast Energy Transfer, and the Nature of Population Buildup in Curve-Crossing Regions," Bengt Ohlsson, Edward Greene, and J. L. Gole, Chem. Phys., to be submitted. See also G. J. Green and J. L. Gole, Chem. Phys. Lett. 69, 45 (1980). A. W. Hanner and J. L. Gole, J. Chem. Phys. 73, 5025 (1980).
43. It is not clear that all of the features associated with the region of the BO_2 spectrum in Figure 10(c) can readily be associated with BO_2 ; however, at significantly higher NO_2 concentrations, there appears to be a convergence to a spectrum strongly dominated by the same features associated with BO_2 emission in Figures 10(a) and (b).
44. R. Woodward, T. C. Devore, and J. L. Gole, work in progress.

45. T. C. Devore, T. Burkholder, and J. L. Gole, work in progress.
46. Both experiment and theory indicate that the $A^7\Sigma$ excited state is the lowest-lying excited state of manganese oxide - T. C. Devore, private communication.

Figure Captions

Figure 1. (a) Schematic of metal entrainment - agglomeration oxidation device showing tungsten basket heater, insulation, entrainment region, and oxidation region. (b) Outline of entraining gas cooling system.

Figure 2. (a) Chemiluminescent spectrum resulting from the oxidation of a moderate copper flux ($K_{\text{Knudsen}} < 1$) entrained in room temperature argon. The $\text{CuO } A^2\Sigma^+ - X^2\Pi$, $A'^2\Sigma^+ - X^2\Pi$, and $\delta^2\Sigma^+ - X^2\Pi$ emission features are identified in the figure. Systems I-V do not correlate with CuO and are believed associated with metal cluster oxide emission systems. Spectral resolution is 8 \AA . (b) Expanded views as indicated. See text for discussion.

Figure 3. (a) - (c) Chemiluminescent spectra resulting from the oxidation of a moderate copper flux ($K_{\text{Knudsen}} < 1$) entrained in liquid nitrogen cooled argon at various stages of cooling increasing from (a) to (c) where LN_2 cooling is at a maximum. In (a) the $\text{CuO } A^2\Sigma^+ - X^2\Pi$, $A'^2\Sigma^+ - X^2\Pi$, and $\delta^2\Sigma^+ - X^2\Pi$ band systems are apparent although the A-X and A'-X band systems are muted relative to Figure 2. Systems I-V are assigned to Cu_xO ($x \geq 2$). Spectra (b) and (c) indicate that the CuO A-X and A'-X band systems are lost and the $\delta^2\Sigma^+ - X^2\Pi$ band system is muted relative to systems I-V. Spectral resolution is 14 \AA . See text for discussion.

Figure 4. Chemiluminescent spectra resulting from the ozone oxidation of a moderate silver flux ($K_{\text{Knudsen}} < 1$) entrained in room temperature argon showing emission corresponding to the $\text{AgO } A^2\Pi - X^2\Pi$ band system ($4000\text{--}4300 \text{ \AA}$) and what is believed to be an Ag_2O emission system ($4400\text{--}4800 \text{ \AA}$). Spectral resolution is 5 \AA . See text for discussion.

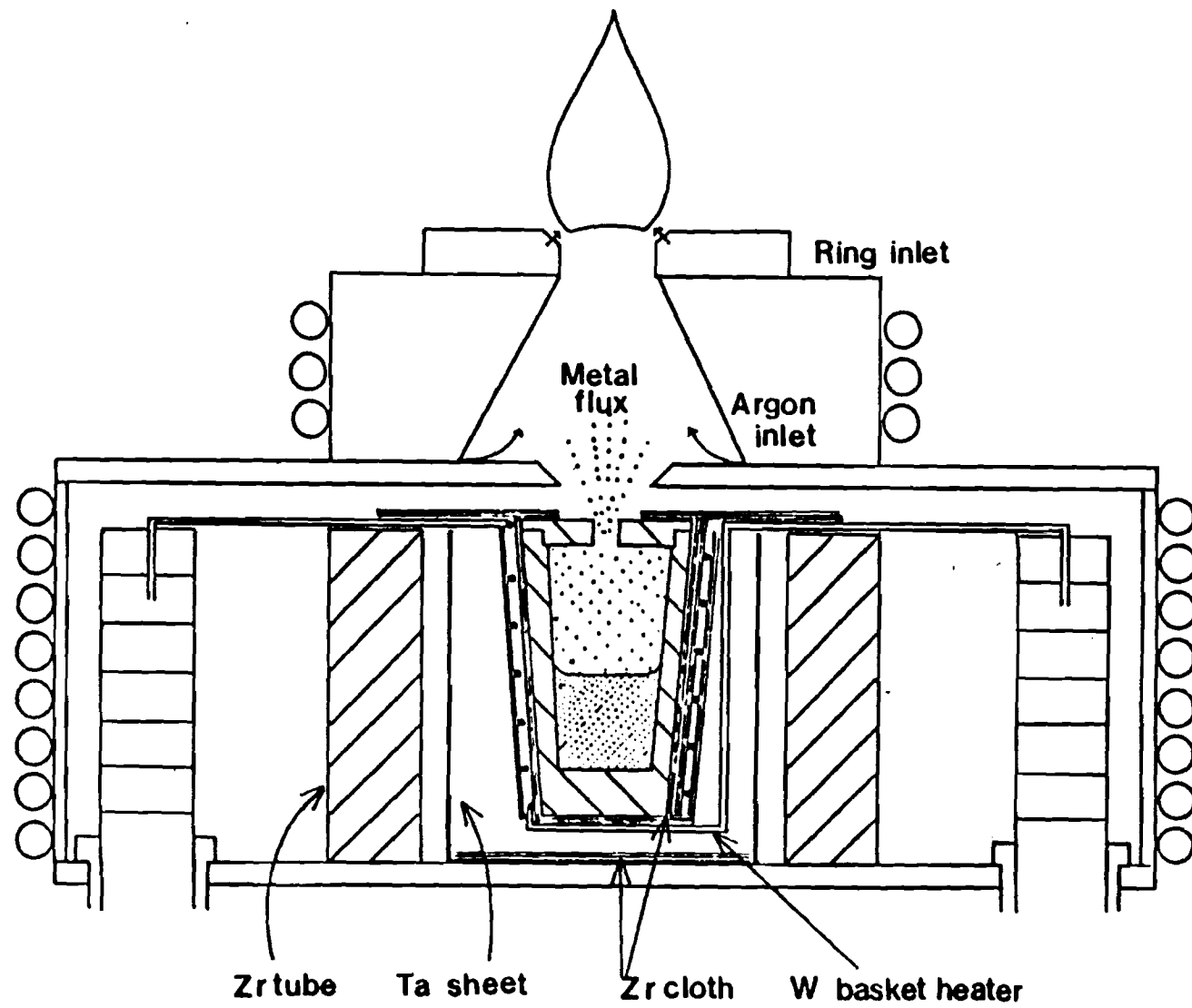
Figure 5. Chemiluminescent spectra resulting from the ozone oxidation of (a) a moderate silver flux ($K_{\text{Knudsen}} < 1$) entrained in room temperature argon and (b) a high silver flux entrained in room temperature argon. Both spectra consist of the $\text{AgO } B^2_{\Pi} - X^2_{\Pi}$ band system and certain silver atom emission features. At high silver flux the AgO emission system is considerably quenched relative to the atomic emission features and the Ag_2O emission features in Figure 4. Spectral resolution is 5\AA . See text for discussion.

Figure 6. Portion of the chemiluminescent emission spectra from the oxidation of high silver fluxes ($K_{\text{Knudsen}} < 1$) entrained in room temperature argon showing a closeup of the observed emission in the region $5500\text{--}7300\text{\AA}$ believed to correlate with the metal cluster oxides Ag_xO_y ($x \geq 2$). The upper spectrum (b) is obtained at considerably higher silver flux vs. spectrum (a). Spectral resolution is 7\AA . See text for discussion.

Figure 7. (a), (b) Chemiluminescent spectra resulting from the multiple collision oxidation of boron with NO_2 showing the $\text{BO } A^2_{\Pi} - X^2_{\Sigma^+}$ and BO_2 A-X and B-X emission systems. (c) Chemiluminescent spectrum resulting from the oxidation of a high boron flux ($K_{\text{Knudsen}} < 1$) entrained in dry ice cooled argon. The spectrum (c) which is characterized by a complete absence of $\text{BO } A^2_{\Pi, v' \geq 3}$ emission and the presence of a new emission feature at $\lambda > 5900\text{\AA}$ is correlated with the reaction of boron agglomerates B_x ($x \geq 3$). Spectral resolution is 8\AA for (a), 5\AA for (b), and 6\AA for (c). See text for discussion.

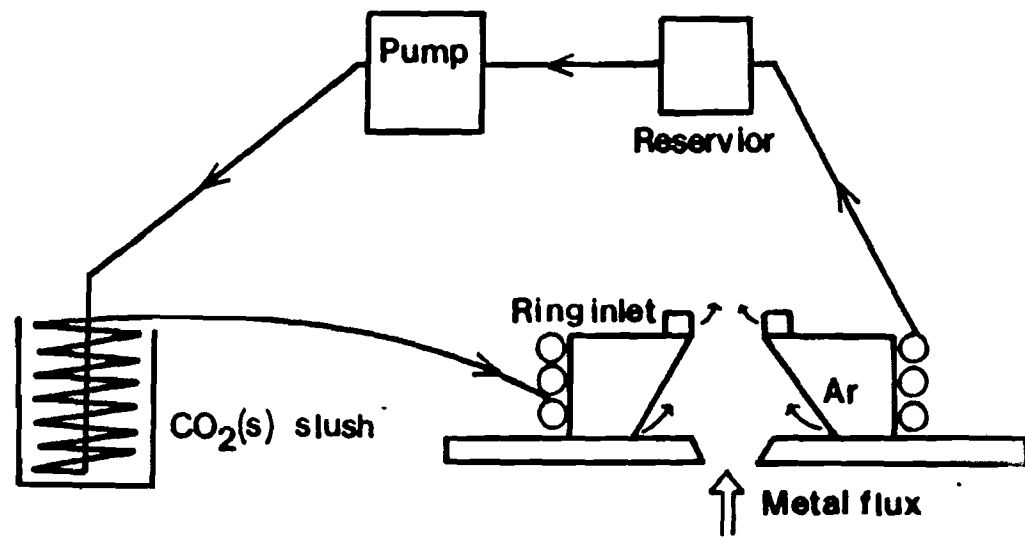
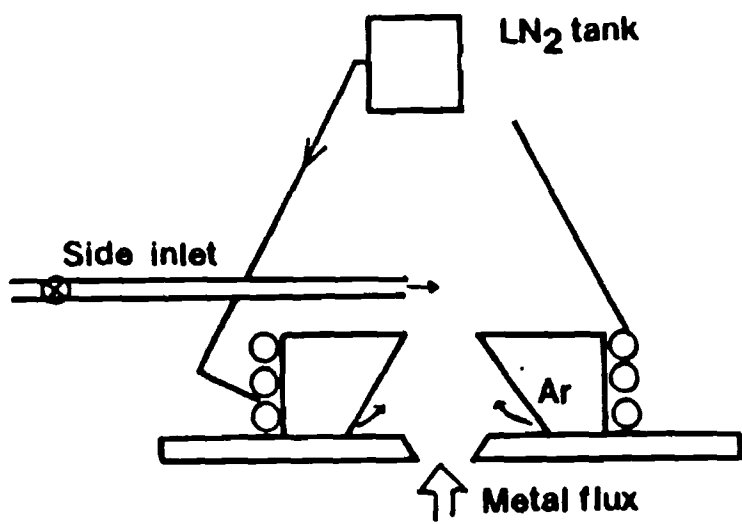
Figure 8. Closeup of $\lambda > 5900 \text{ \AA}$ emission region associated with the reaction of boron agglomerates with NO_2 . The spectrum appears to be a combination of both sequential structure and a long progression (or sequence) in a low frequency ($\sim 150 \text{ cm}^{-1}$) vibrational mode. Spectral resolution is 5 \AA . See text for discussion.

Figure 9. Chemiluminescent spectra resulting from the multiple collision ozone oxidation of manganese atoms to form MnO^* and manganese molecules to form Mn_xO^* where x is most likely 2. Spectral resolution is 3 \AA . See text for discussion.



a

Figure 1



b

Figure 1

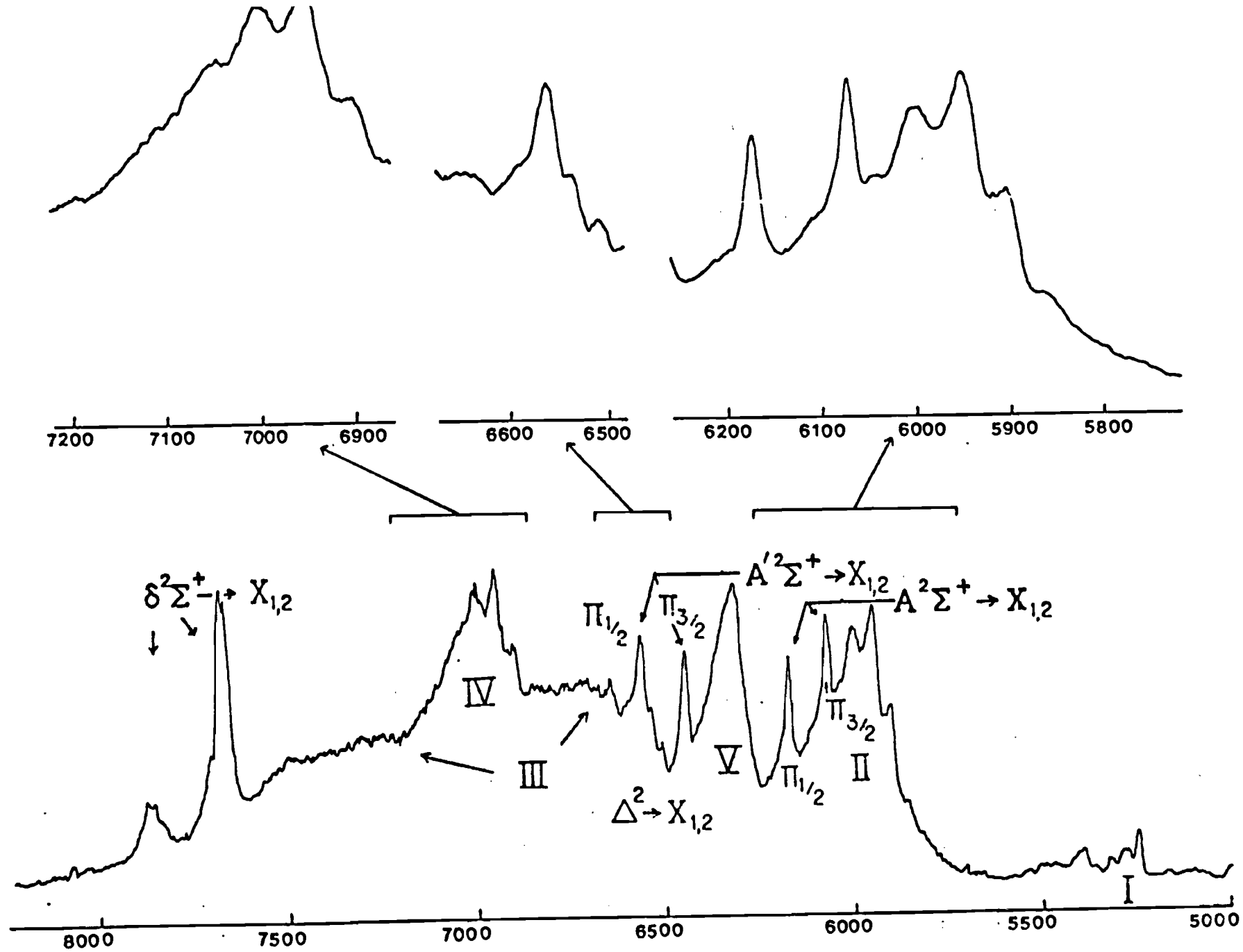


Figure 2

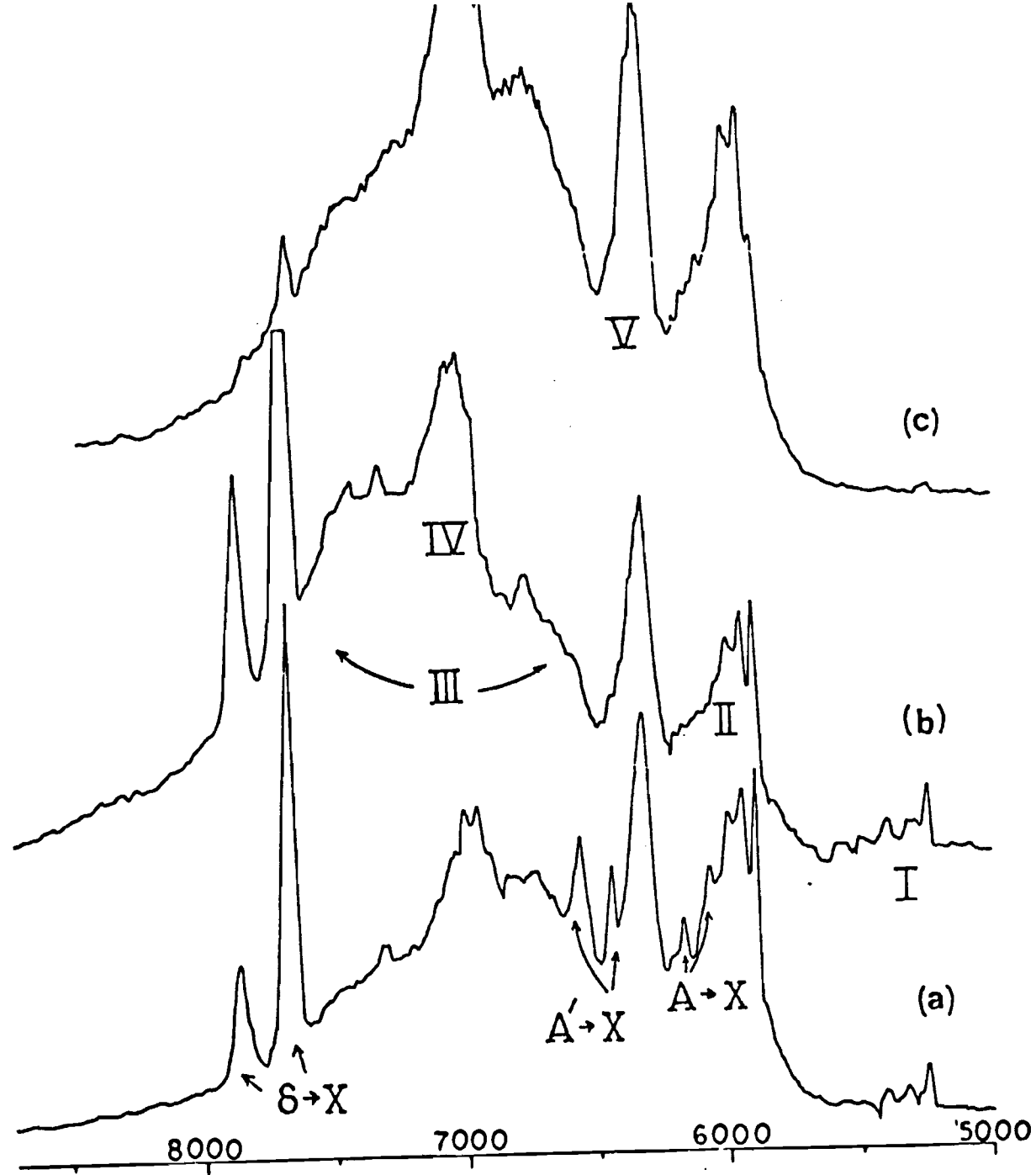


Figure 3

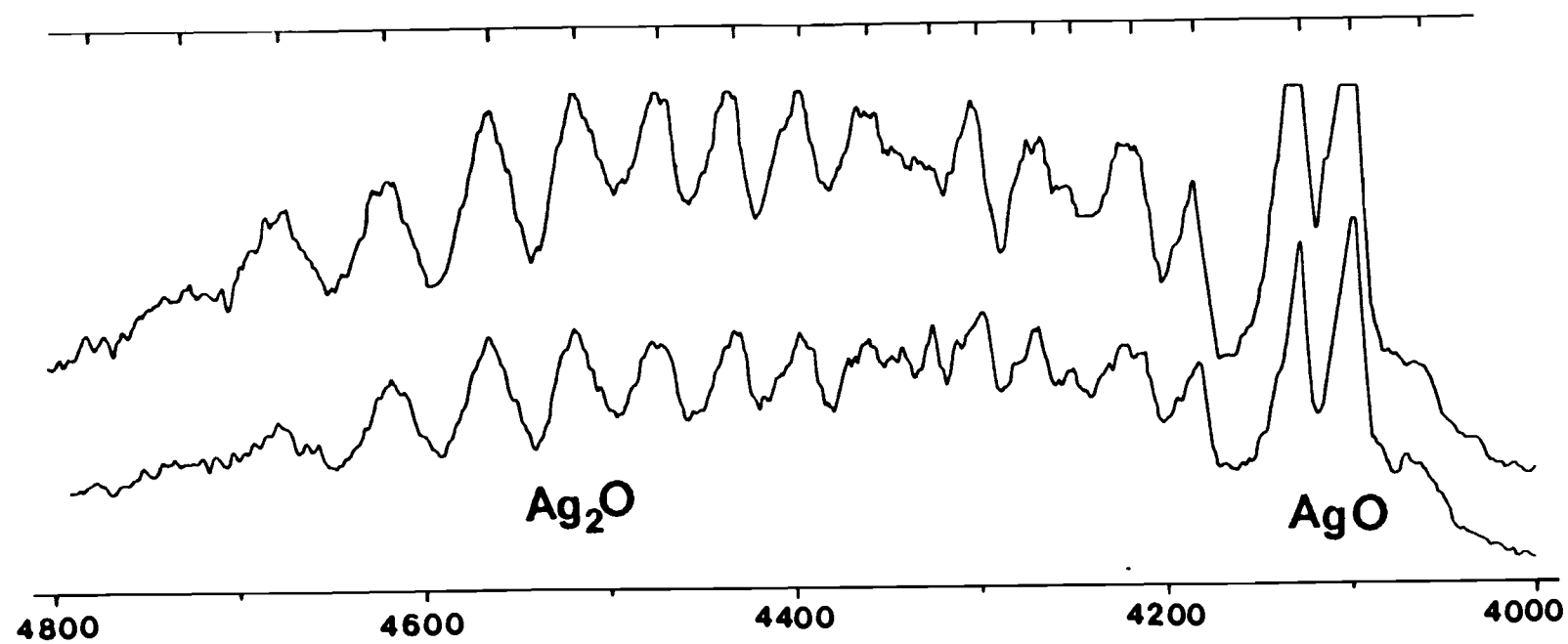


Figure 4

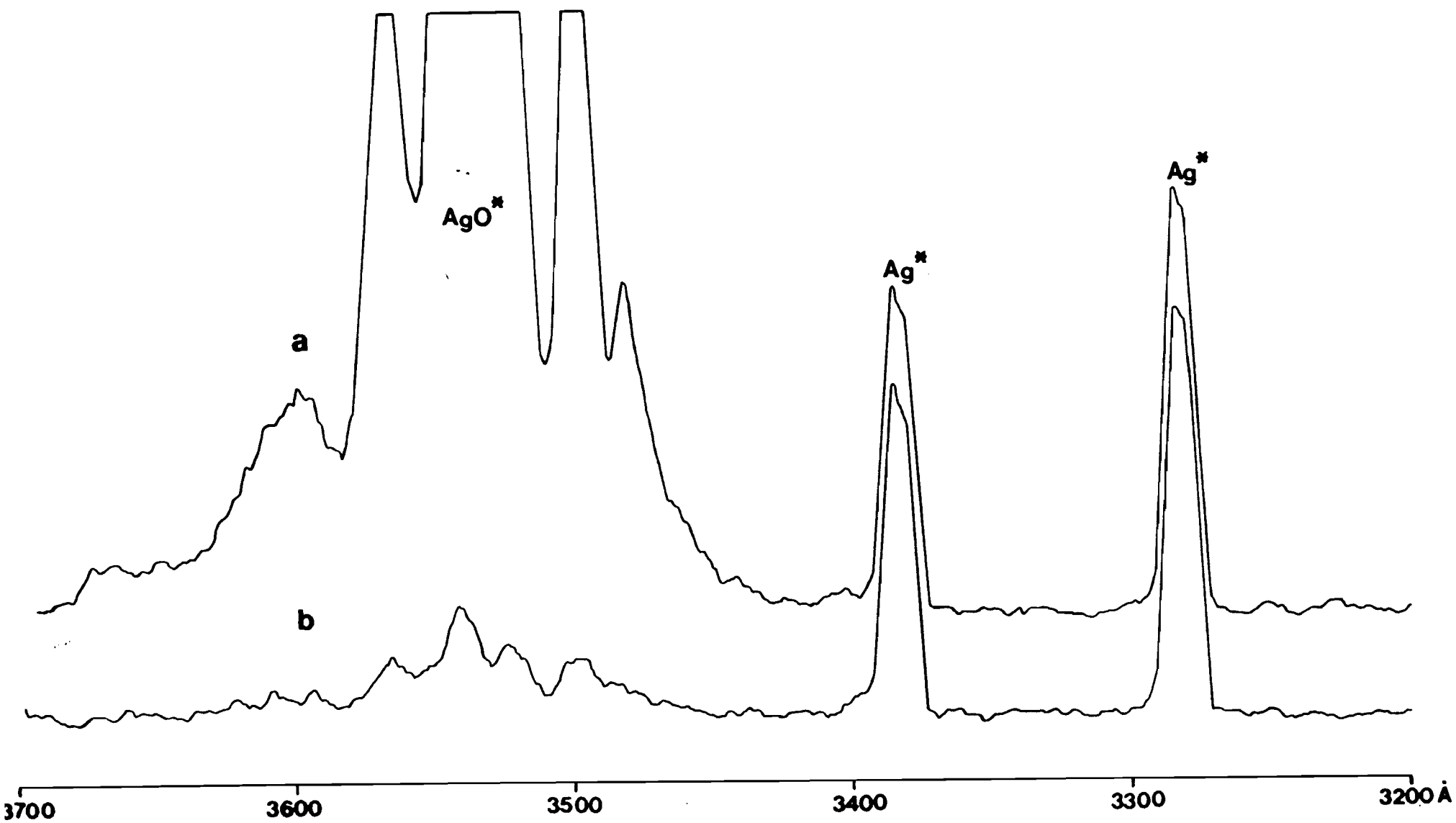


Figure 5

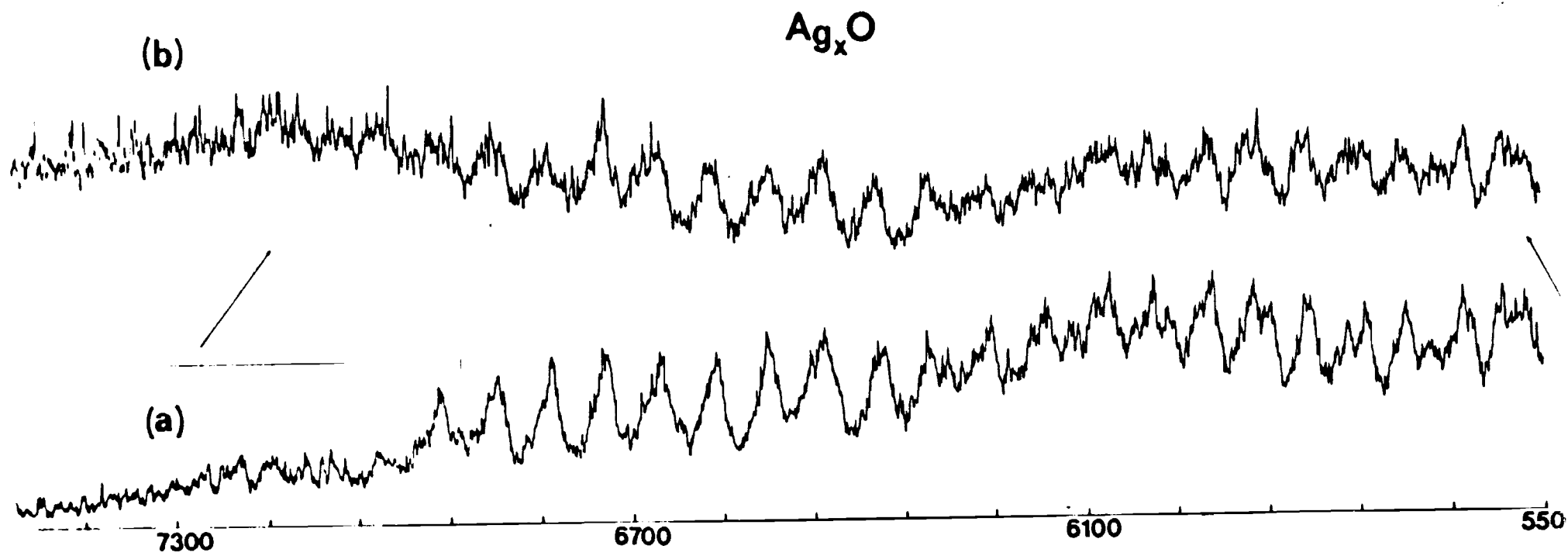


Figure 6

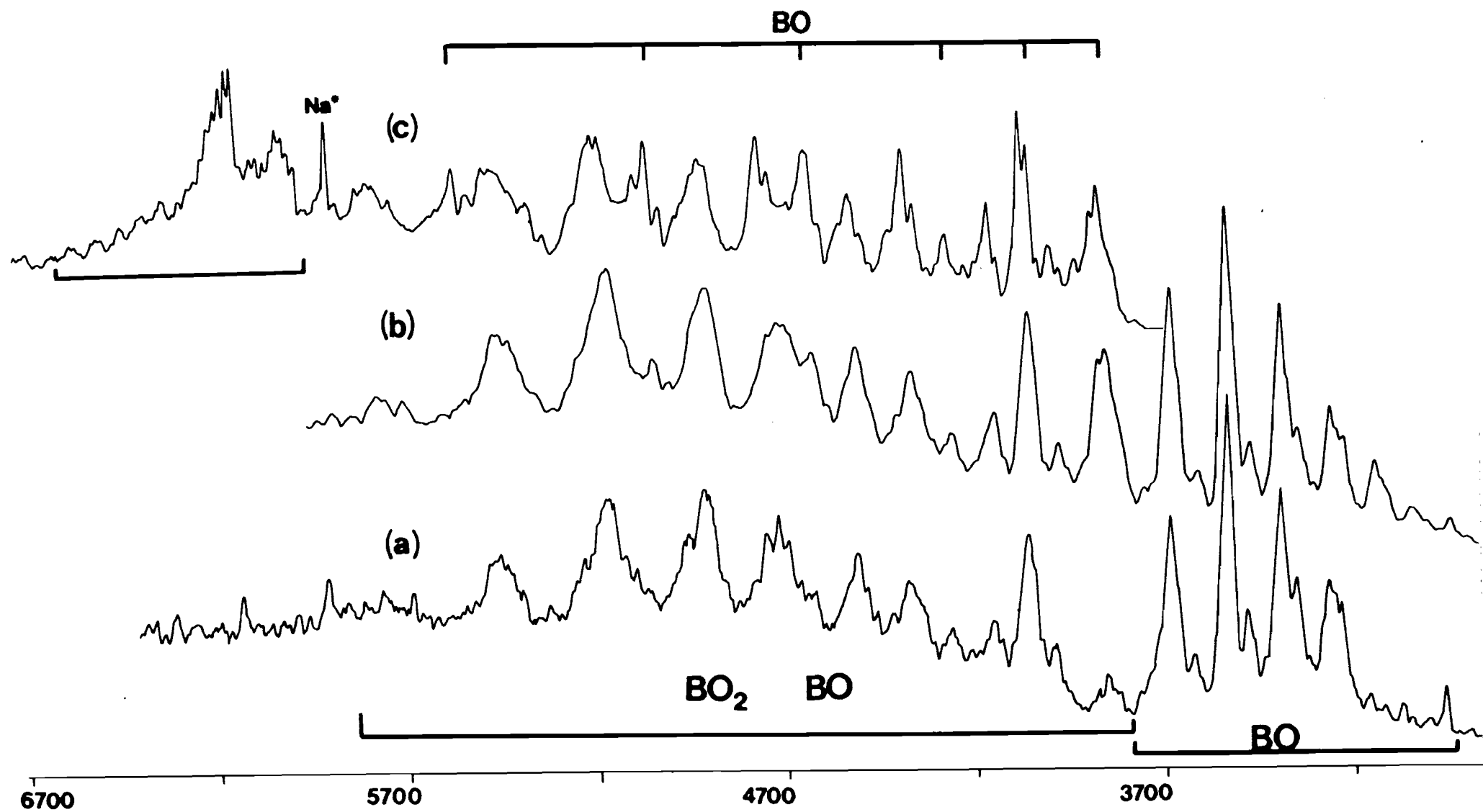


Figure 7

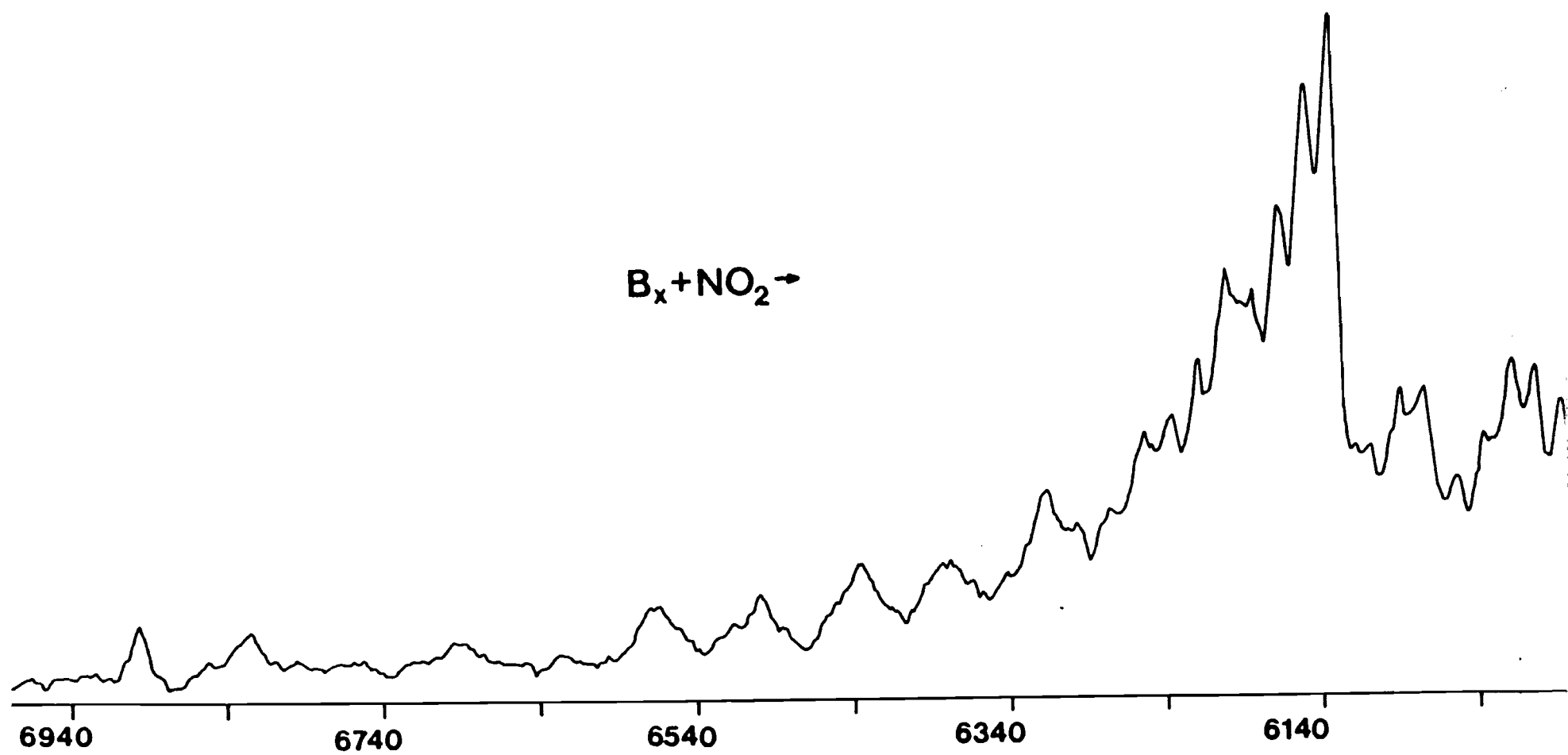


Figure 8

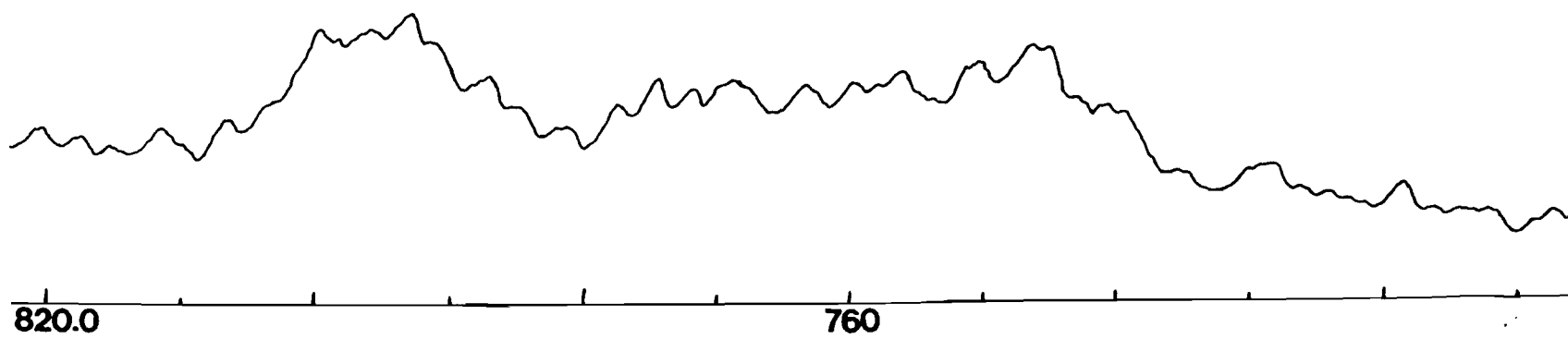
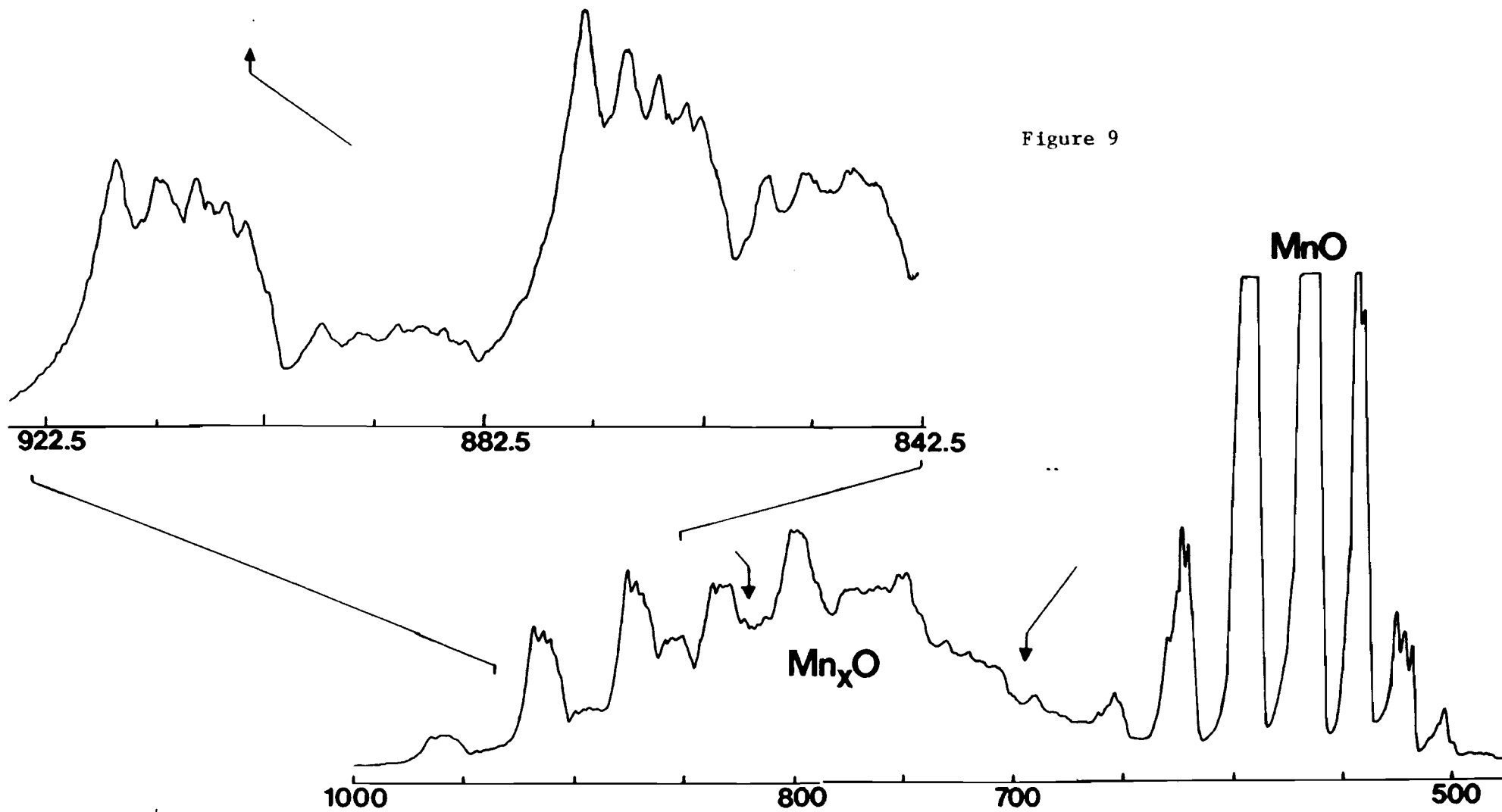


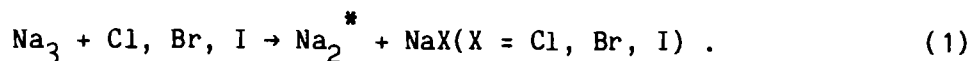
Figure 9



The research effort during the period November 24, 1986 - September 28, 1987 has involved several projects focused on the experimental and theoretical treatment of small metal clusters, their unique dynamic behavior, and the unique nature of the oxidation processes which they undergo. Included in this effort have been two major breakthroughs: (1) the demonstration of the first chemically pumped continuous laser amplifier in the visible spectral region, based on a characterization of the $\text{Na}_3 + \text{X}$ reaction and (2) the development of a source configuration which has allowed the first analysis of middle transition metal cluster (Ni_3) quantal structure. We have completed the first phase of a group of studies in which we have observed and analyzed the optical signatures for the products of metal cluster oxidation, this work yielding important information on the kinetically controlled formation of the asymmetrical cluster oxides M_2O and M_xO ($x \geq 3$) (vs. the thermodynamically more stable species). We have also begun the extension of these studies to obtain quantal information on the metal cluster halides. We have developed techniques which have allowed the initiation of studies whose focus has been on the formation of metal based CO and CO_2 complexes and the corresponding metal-ligand binding energies. Finally, we have initiated studies of the proton affinities of Li_2 , Na_2 , LiH , and NaH and the alkali cation affinities of N_2 , CO , and H_2 .

(1) The Na_3 - Halogen Atom Reactions - Development of a Visible Chemical Laser Amplifier

We have been engaged in a major study of the sodium cluster - halogen atom reactions ($\text{Na}_n + \text{Cl}, \text{Br}, \text{I}$) primarily in the single collision pressure regime. The major impetus of our effort has involved the study of the Na_2 chemiluminescent emission from the reactions



Completed and continuing studies in our laboratory now demonstrate a very unique gas phase oxidation chemistry associated with these reactions. The Na_2 chemiluminescent emission originates in large part from an only recently analyzed double minimum state of Na_2 ($C' \ ^1\Pi_u$) which has now been demonstrated to be the source of the dominant feature contributing to the well-known sodium "violet" bands. Based on a recently completed high resolution analysis of this low-lying electronic state, we have now obtained a reasonable set of Franck-Condon factors which have been computed to be used in a first order fit of the chemiluminescent emission spectrum.

Spectral simulations of the emission from the Na_2 $A \ ^1\Sigma_u - X \ ^1\Sigma_g^+$, $B \ ^1\Pi_u - X \ ^1\Sigma_g^+$, and $C \ ^1\Pi_u - X \ ^1\Sigma_g^+$ band systems as well as the newly discovered $C' \ ^1\Pi_u - X \ ^1\Sigma_g^+$ band system can be used to establish the distribution of Na_2 produced as the nascent product of reaction (1). However, when one attempts to fit the observed fluorescent spectra, one finds that the observed spectral distributions in certain spectral regions are considerably sharper than those which would be predicted on the basis of a simple chemiluminescent-fluorescence phenomena. The sharp nature of the Na_2 emission features in the Na_2 B-X spectral region has now been demonstrated to result from population inversions of the Na_2 B and C state levels with respect to the ground $X \ ^1\Sigma_g^+$ state. This leads to stimulated emission analogous to that observed in alkali dimer optical pumping experiments. There are several dynamical factors which could lead to this phenomena which has now been experimentally demonstrated through laser gain experiments. The nature of these results is summarized in the following abstract and a more detailed description is given in Appendix A.

A CHEMICAL PROCESS PRODUCING A CONTINUOUS LASER AMPLIFIER IN THE VISIBLE REGION

S. H. Cobb, R. Woodward, and James L. Gole

In a study of the reaction dynamics characterizing the $\text{Na}_3 - \text{X}(\text{Cl}, \text{Br}, \text{I})$ metatheses, we form Na_2^* in several excited electronic states, the fluorescence from these states resembling in some respects that characteristic of optically pumped alkali dimer lasers. Optical gain through stimulated emission demonstrates the presence of a population inversion involving several excited state levels of Na_2 and hence an amplifying medium for a visible chemical laser. An explanation is provided for this extremely efficient inversion process at low pressures and comparisons are made with optically pumped laser systems.

At this point, we may also state that the considerable cross correlation of spectral data from all three reactions (1) and the appropriate spectral simulations indicate a rich chemistry including (1) a clear bimodal distribution of Na_2^* product vibrational levels correlating with the dynamics of Na_2 formation and (2) the clear effect of the molecular electronic structure of Na_2 on the dynamics of the reaction $\text{Na}_3 + \text{X} \rightarrow \text{Na}_2^* + \text{NaX}$. We are now engaged in a detailed fit of the spectra for all three reactions (1).

(2) High Intensity Metal Cluster Sources - The Laser Induced Excitation

Spectrum of Nickel Trimer

We have extended our studies with the high intensity supersonic refractory metal vapor expansion source developed in our laboratory to obtain the first gas phase fluorescence spectra for the nickel trimer molecule. Previously we noted¹ that one of the most exciting aspects of this new source was the attainment of intensities comparable to that produced in a pure sodium supersonic expansion and three to six orders of magnitude greater than that obtained with laser vaporization techniques. The development of this source and its application to the nickel trimer molecule is significant for, although it is clear that the electronic and reactive properties of small metal clusters lie intermediate to those of the atom and those of the bulk metallic phase, the detailed aspects of this picture especially with respect to internal mode structure have not yet been colored. Quantum level probes which have already indicated the need for models including vibronic coupling as well

as demonstrating the unique dynamic behavior of small metal clusters as a function of temperature are slowly emerging.¹ It has now become apparent that it will be difficult to probe resultant quantum levels even with extremely sensitive laser spectroscopic techniques. Intense cluster beam sources once developed, however, can overcome these difficulties.^{2,3} Thus cluster sources must be designed to overcome the substantial loss mechanisms including predissociation and rapid intramolecular conversion and relaxation which deplete excited state populations at a rate competing effectively with those spectroscopic probes (such as TPI spectroscopy) which other researchers have attempted to apply to the analysis of quantum level structure. The nature of our current and continuing studies of the nickel trimer molecule are summarized in the following abstract and a more detailed description is given in Appendix B.

GAS PHASE LASER INDUCED EXCITATION SPECTRUM OF NICKEL TRIMER

J. R. Woodward, S. H. Cobb, and J. L. Gole

The first gas phase nickel trimer laser induced excitation spectrum has been generated from the supersonic expansion of pure nickel vapor. The spectrum, which correlates well with that observed in matrix isolation studies, appears to be dominated by a combination of symmetric stretch and bending mode frequencies. On the basis of the results obtained we suggest an approach to the evaluation of ground state transition metal cluster quantal structure.

(3) Metal Cluster Oxidation - Optical Signatures for the Metal Cluster Oxides and Halides

In order to study metal cluster oxidation we have developed two source configurations which lie 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. 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 LN_2 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 range⁴ to probe the optical signatures of those reaction products associated with the oxidation of small copper ($\text{Cu}_x + \text{O}_3, \text{Cl}_2, \text{Cl}$)^{3,5,6} and silver ($\text{Ag}_x + \text{O}_3, \text{Cl}_2$)^{3,7,8} clusters with further extension to select transition metals ($\text{Mn}_x + \text{O}_3, \text{Cr} + \text{O}_3$).^{9,10} 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 . 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.

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 , 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 and Cu_xO ($x \geq 3$) 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 $(\text{Mn}_2^{\delta+}(\text{O})^{\delta-})$ 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.

Our focus is to be distinguished from recent very exciting studies in which small to intermediate size clusters have been generated in flow systems,¹¹ reacting with reagents in another continuous or pulsed flow stream under high pressure (300-500 torr) conditions in a modified merged flow environment. The products in the flow have been measured mass spectrometrically; however, the technique has yet to provide a direct measure of quantum levels or dynamic properties although important kinetic information has been extracted. While we have been concerned with both spectroscopic information and the intriguing dynamic behavior which appears to characterize oxidation reactions of small metal clusters, there are other clear contrasts which need be noted.

In this project we wish to deal not only with metal cluster oxidation but also with the properties of the metal cluster oxides. Because metal cluster oxide bonding likely differs from that of the bare metal clusters and their positive and negative ions, this research effort complements the ongoing studies of neutral and ionic cluster reactivity now underway in a number of research groups.¹¹ Further, it is appropriate that we note that most transition metal catalysts are in the oxide form. Therefore studies which characterize the transition metal oxides can provide valuable insights. In

fact our current studies of the silver cluster oxides may contribute to our understanding of the behavior of silver oxides in the catalytic epoxidation of ethylene. The results obtained thusfar have lead to a collaboration with the Los Alamos Scientific Laboratory theory group currently studying the epoxidation process. Finally, it is significant that the metal cluster oxides we generate represent the nonsymmetrical isomers, M_xO , rather than those compounds which might be synthesized through thermochemical means. We believe that through a study of the unsymmetrical isomers, we provide a closer parallel to the nature of reactions on a metallic surface and the catalytic action of such surfaces. The nature of these current and continuing studies is summarized in the following abstracts of submitted papers and in some greater detail in Appendix C.

OXIDATION OF SMALL BORON CLUSTERS - FORMATION OF AND CHEMILUMINESCENT EMISSION FROM BBO

T. C. Devore,[†] J. R. Woodward, and J. L. Gole

A source configuration which lies intermediate to a low-pressure effusing molecular beam and a high-pressure flow device is used to form boron cluster molecules in a highly oxidizing environment. Using this source operating in an NO_2 or N_2O oxidative environment, a chemiluminescent emission spectrum for the asymmetric BBO molecule is generated. The observed spectrum is characterized by a strong $\Delta v = 0$, $\Delta v = 40\text{ cm}^{-1}$, sequence grouping and a weaker $\Delta v = +1$ sequence ($\Delta v = 40\text{ cm}^{-1}$), 440 cm^{-1} to higher energy. A second sequence with $\Delta v \sim 142\text{ cm}^{-1}$ is also observed. Combining the 440 cm^{-1} upper state frequency with the 142 cm^{-1} sequence structure implies a lower state frequency of $\sim 582\text{ cm}^{-1}$ for the B-B stretch, consistent with ab-initio calculation.

FORMATION OF ELECTRONICALLY EXCITED Ag_xO FROM THE OXIDATION

OF SMALL SILVER CLUSTERS

T. C. Devore, J. R. Woodward, P. N. Le, D. A. Dixon, and J. L. Gole

The chemiluminescent reactions of silver clusters, M_n , $n \geq 3$, with ozone

have been studied under multiple collision conditions. As a function of variations in the silver flux, a minimum of five distinct electronic emissions associated with AgO, Ag₂O, and Ag₂ are observed as well as features which are tentatively associated with the higher silver cluster oxides. The energetics of the observed spectral features combined with supplementary thermodynamic and kinetic information demonstrates that all of the monitored products with enough energy to account for the observed chemiluminescence cannot be produced through the reaction of either Ag or Ag₂ with O₃. The smallest cluster whose reaction can yield the observed AgO emission features is the trimer. The formation of Ag₂O* can also be achieved through reaction of the trimer, however, it might better be accounted for via the reaction of higher clusters. At moderate silver fluxes, the observed chemiluminescence is dominated by the AgO A²Π-X²Π (400-420 nm) and B²Π-X²Π (320-370 nm) emission features. At still higher silver fluxes, leading to greater agglomeration, both the AgO A-X and B-X emissions are quenched and the spectrum is dominated by a combination of Ag₂O and Ag₂ emission features extending from 420 to 700 nm. At stills higher silver flux further spectral features at λ > 680 nm emerge.

The chemiluminescent spectrum between 500 and 700 nm contains two emission band systems assigned as the A-X and B-X band systems of Ag₂O. The A-X transition which onsets at ~630 nm is well fit by the expression

$$\nu(\text{cm}^{-1}) = 15670 - 165\nu_3'' + (0.4)\nu_3''^2.$$

The B-X transition which originates at 506 nm is well fit by the expression

$$\nu(\text{cm}^{-1})_{\nu_1'', \nu_2'', \nu_3''} = 19766 - 442\nu_1'' - 256\nu_2'' - 165\nu_3'' + 6\nu_1''^2 + 6(\nu_1'')(\nu_2'') + 25(\nu_1'')(\nu_2'')$$

The observed frequencies are consistent with an Ag-Ag-O structure, emission from the asymmetric cluster oxides characterizing these kinetically controlled oxidation experiments in contrast to the thermodynamically more stable symmetrical species. Assuming a linear Ag₂O molecule, the vibrational frequencies are assigned as

$$\begin{array}{ll} \nu_1 \approx 442 \text{ cm}^{-1} & \text{Ag-O stretch} \\ 2\nu_2 \approx 256 \text{ cm}^{-1} & \text{AgAgO bend} \\ \nu_3 \approx 165 \text{ cm}^{-1} & \text{Ag-Ag stretch} \end{array}$$

FORMATION OF ELECTRONICALLY EXCITED Mn_xO FROM THE OXIDATION

OF SMALL MANGANESE CLUSTERS

T. C. Devore, J. R. Woodward, and J. L. Gole

The chemiluminescent reactions of manganese atoms and clusters with ozone have been studied under multiple collision conditions. Manganese atoms entrained in room temperature argon or helium react with ozone to form the

lowest-lying $\text{MnO}^* A^7\Sigma^+$ excited electronic state ($\text{Mn} + \text{O}_3 + \text{Ar}(\text{He}) \rightarrow \text{MnO}^* (A^7\Sigma^+) + \text{O}_2 + \text{Ar}(\text{He})$) producing a strong chemiluminescent signal corresponding to the $\text{MnO } A^7\Sigma^+ - X^7\Sigma^+$ band system. A high flux of manganese vapor is entrained in LN_2 cooled argon to induce clustering. This entrained mixture subsequently reacts with ozone to produce a new complex emission system (which accompanies the $\text{MnO } A-X$ system) containing at least 72 bands and extending from 720 to 970 nm. The new system which is not present unless the carrier gas is cooled increases precipitously with entrainment gas cooling and increased metal flux. The observed bands are fit within experimental error by the expression

$$\nu_{v'_1, v''_1, v'_3, v''_3} = 12512 + 600v'_1 - 534v''_1 + 360v'_3 - 306v''_3$$

where all values are in cm^{-1} . The ground state spacing of 306 cm^{-1} is assigned as an Mn-Mn stretch. The 534 cm^{-1} spacing is assigned to an MnO stretch and the emitting molecule is believed to be the asymmetrical Mn-Mn-O isomer.

The Mn-Mn stretch frequency is in excellent agreement with the frequency estimated for Mn_2^+ by averaging the derived force constants for Mn_2 and Cr_2 .

The MnO stretching frequency is considerably lower than the 840 cm^{-1} diatomic frequency, lying intermediate to those of KO (384 cm^{-1}) and CaO (733 cm^{-1}). This suggests that the bonding in this molecule is similar to the bonding in the alkali oxides and that it may reasonably be represented as $(\text{Mn-Mn})^+\text{O}^-$.

A COMPARATIVE STUDY OF THE OXIDATION OF ATOMIC COPPER AND HIGHER COPPER CLUSTERS UNDER SINGLE AND MULTIPLE COLLISION CONDITIONS

J. R. Woodward, T. C. Devore, T. Burkeholder, and J. L. Gole

The chemiluminescent reactions of copper atoms and clusters with ozone have been studied across a wide pressure range from single to multiple collision conditions. Under single collision conditions, the exothermicity of the Cu-O_3 reaction allows formation of the $\text{CuO } \delta^2\Sigma^+$ state as monitored by the $\text{CuO } \delta^2\Sigma^+ - X^2\Pi$ band system. At high copper fluxes two additional band systems attributable to the copper cluster oxides (Sys. II,V) are found to dominate the observed single collision emission spectrum.

A high copper flux, entrained under multiple collision conditions in room temperature argon, is oxidized to produce emission from several excited states of CuO and from a number of metal cluster oxide emitting states with band systems in the range 5700 - 6200 Å (II), 6900 - 7100 Å (III), and 6500 - 7800 Å (IV). A moderately sharp emission feature extending from 6300 to 6450 Å is also found. This behavior contrasts to that found under conditions of low copper agglomeration where emission from the $\text{CuO } A^2\Sigma^+ - X^2\Pi$, $A'^2\Sigma^+ - X^2\Pi$, and $\delta^2\Sigma^+ - X^2\Pi$ band systems is more pronounced, the $A^2\Sigma^+$ and $\delta^2\Sigma^+$ emission features being considerably more dominant. With increased cooling of the

argon entrainment gas, the CuO emission bands with the exception of the $\delta^2\Sigma^+ - X^2\Pi$ system are lost while systems II, III, and IV are enhanced. CuO band systems (I) in the region 5200 - 5500 Å are at first enhanced and then quenched in the cooling cycle signaling the formation of the $\beta^2\Delta_1$ and $\lambda^2\Pi_1$ upper states from a shifting copper cluster distribution. With increased copper flux and cooling, the 6500 - 7800 Å emission region (Sys. III and IV) is enhanced relative to that from all other spectral regions, a behavior coincidental with increased copper agglomeration. The system II fluorescence observed under both single and multiple collision conditions consists of 5 bands whose spacing of $132 \pm 10 \text{ cm}^{-1}$, associated with a bending mode, is consistent with that expected in a transition from a bent excited state to a linear ground state of the asymmetric CuCu-O molecule. The asymmetric isomer is formed via the $\text{Cu}_3\text{-O}_3$ reaction ($\text{Cu}_3 + \text{O}_3 \rightarrow \text{Cu}_2\text{O}^* + \text{CuO}_2$). The system V emission feature, observed under both single and multiple collision conditions shows little structure and is tentatively associated with the formation of electronically excited Cu_2O_2 or Cu_3O formed via Cu_3 oxidation ($\text{Cu}_3 + \text{O}_3 \rightarrow \text{Cu}_2\text{O}_2^* + \text{CuO}$, $\text{Cu}_3 + \text{O}_3 \rightarrow \text{Cu}_3\text{O}^* + \text{O}_2$). The conditions for formation of that metal cluster oxide excited state leading to system IV, consisting of four bands whose spacing is 100 cm^{-1} , and the overall shape of the band grouping suggests a bending mode excitation involving a bent and linear state or a non-planar-non-planar transition in a molecule Cu_xO_y with at least C_3 symmetry.

FORMATION OF THE LOW-LYING ELECTRONIC STATES OF CrO IN HIGHLY EXOTHERMIC REACTIVE OXIDATION - ASSESSMENT OF NEW STATES AND RESOLUTION OF PREVIOUS OBSERVATIONS

T. C. Devore and J. L. Gole

The highly exothermic reactions of chromium atoms with O_3 and N_2O have been studied over a pressure range extended in a controlled manner from a single collision bimolecular reactive environment ($\text{Cr} + \text{XO}^2 \rightarrow \text{CrO}^* + \text{X}(\text{O}_2, \text{N}_2)$) with $P_{\text{Total}} \leq 10^{-4}$ Torr to multiple collision conditions ($\text{Cr} + \text{XO} + \text{Ar} \rightarrow \text{CrO}^* + \text{X} + \text{Ar}$) with $P_{\text{Total}}(\text{Ar}) \sim 1$ Torr. The multiple collision environment prompts rotational relaxation and allows the study of strong coupling and rapid energy transfer among CrO excited states. The combination of these studies provides further information on the CrO electronic state manifold and allows an independent determination of the CrO bond energy, $D_0^0(\text{CrO}) \geq 4.45 \text{ eV}$. Emission is observed from two and possibly three excited states of CrO including the well-known 600 nm system ($\text{B}^5\Pi - \text{X}^5\Pi$), a system at $\sim 850 \text{ nm}$

($T_0 = 11800 \text{ cm}^{-1}$, $\Delta G'_{1/2} = 820 \text{ cm}^{-1}$) tentatively associated with an $A'^5\Delta - X'^5\Pi$ transition, and a newly observed blue system in the range $\lambda\lambda$ 510-420 nm

($E_{\text{onset}} \sim 22163$, $\Delta G_{1/2} = 575 \text{ cm}^{-1}$) emanating either from a new electronic

state or from higher vibrational levels of a strongly inflected $B'^2\Pi$ state.

Features associated with the $v' = 2, 3, 4$, and 5 levels of the $\text{CrO } B'^5\Pi$ state display an apparent doubling into two components (bands) whose average frequency corresponds closely to that anticipated vibrational level structure for the $B'^5\Pi$ state. This dual level structure is attributed to the interaction between two closely lying excited electronic states of CrO , one being $B'^5\Pi$.

The mixing is of such a magnitude that perturbations of the $B'^5\Pi$ state extend across a large manifold of rotational levels leading to the observed shift of these levels due to the interaction with a perturber state. The perturber state which borrows intensity from $B'^5\Pi$ becomes the second component of the doublet structure.

(4) The Optical Signatures of Metal Based CO and CO_2 Complex Oxidations - The Metal Monocarbonyl Binding Energies

The volatile metal carbonyls ligated with several carbonyl groups exhibit a variety of molecular structures. These structures have created much previous interest and the vibrational spectroscopy of the multiply ligated species, primarily those of the transition metals which play an extremely important role in chemistry, has been the subject of considerable investigation. Both M-C and C-O stretching modes have been well studied.⁹ While there has been considerable research in the volatile multiply ligated metal carbonyls, relatively little experimental work has focused on the basic metal monocarbonyl, M-CO, binding energies and MCO spectroscopy.¹³ This gap in understanding is significant for, without doubt, the most celebrated and studied gas-surface interaction is that of carbon monoxide on metal surfaces.¹⁴ Similarly, there has been relatively little information garnered on M- CO_2 complexes.

We are developing a research effort whose focus is to improve our understanding of these sparsely characterized yet fundamental building blocks of metal-carbon-oxygen chemistry. A number of unique source configurations

are being developed to study $M\text{-CO}_x$ and $M(\text{CO}_2)_x$ complexes, where M corresponds to a transition metal atom, and their oxidation under a variety of conditions to form long-lived excited electronic state (metal oxide)-carbonyl or (metal-oxide)- CO_2 complexes. We employ a combination of chemiluminescence and continuous or pulsed laser induced fluorescence techniques, correlated with photoionization quadrupole or time-of-flight mass spectrometry in order to characterize (1) $M\text{-CO}$ and $M\text{-CO}_2$ binding energies, (2) study the long-lived (metal-oxide)-carbonyl and (metal-oxide)- CO_2 complexes which are the products of the highly exothermic oxidation of $M\text{-(CO)}_x$ and $M(\text{CO}_2)_x$, and (3) develop an electronic spectroscopy of $M\text{-CO}$ and $M\text{-CO}_2$ complexes. Although our primary focus has been on the metal atom -CO and CO_2 complexes and their oxidation, at a later stage we will extend these efforts to the corresponding metal compounds $M_x(\text{CO})_y$ and $M_x\text{CO}_2$ ($x = 2, 3$, $Y = 1, 2$). This effort will be a strong consideration once a firm framework is established with the metal atom systems. The nature of these current and continuing studies is summarized in the following abstracts of submitted papers.

FORMATION AND OXIDATION OF METAL BASED CO AND CO_2 COMPLEXES:

CHARACTERIZATION OF $\text{Al}(\text{CO})_x$, $\text{Al}(\text{CO}_2)_x$ AND THEIR OXIDATION

M. McQuaid, J. R. Woodward, and J. L. Gole

In a comparative study, aluminum atoms entrained in argon, CO, and CO_2 are oxidized with ozone to study the nature of aluminum complexation with CO and CO_2 to form $\text{Al}(\text{CO})_x$ ($x = 1, 2$) and AlCO_2 . The optical signatures corresponding to the chemiluminescent oxidation of these complexes with ozone to form the $\text{AlO B}^2\Sigma^+$ state or a polyatomic complex are compared to that $\text{AlO B}^2\Sigma^+$ emission associated with the chemiluminescent oxidation of nonbonded aluminum atoms in argon. We (1) establish a method for evaluating $M(\text{CO})_x$ binding energies and (2) observe the optical signature for a potentially long-lived ($\sim 10^{-7}$ s) metal oxide-carbon dioxide solvation complex formed in metal- CO_2 complex oxidation. From these studies, we estimate a lower bound to the total $\text{Al}(\text{CO})_2$ binding energy (to $\text{Al}+2\text{CO}$) of 0.7 eV. The current study suggests a method for studying the spectra of MCO , $M(\text{CO})_2$, and $M\text{-CO}_2$ complexes.

TRENDS IN THE OPTICAL SIGNATURES FOR TRANSITION METAL OXIDE
CARBONYL COMPLEXES - EVALUATION OF TRANSITION METAL CARBONYL,
 $M(CO)_x$ BINDING ENERGIES

M. J. McQuaid, K. Morris, and J. L. Gole

Transition metal atoms entrained in argon, helium and CO are oxidized with ozone (O_3) and nitrogen dioxide (NO_2) to study the nature of the metal atom complexation with CO. We establish a method for evaluating MCO binding energies through comparison of the chemiluminescent emission from the oxidation of argon and CO entrained transition metal atoms. These studies have thusfar yielded E binding ($TiCO$) ~ 1.75 eV and E binding ($NiCO$) ~ 1.10 eV, the latter in excellent agreement with previous experimental and theoretical evaluations of the Ni-CO bond energy. We identify the optical signatures for transition metal carbonyl (MOCO) complexes formed in the oxidation of $M(CO)$ complexes. We outline trends in the nature of the observed metal oxide complex emissions. The current study suggests a method for obtaining the spectra of transition metal carbonyl $(M(CO)_x, x = 1,2)$ complexes.

(5) Spectroscopy and Molecular Structure of Metal Ion Complexes

In collaboration with Dr. David Dixon (E. I. Dupont), we have now completed extensive ab-initio studies on the structure of alkali metal ion - CO, N_2 , and H_2 adducts as a first step in the approach to the spectroscopy of metal cluster ion-molecular complexes. Further we have studied the proton affinities of Na_2 , Li_2 , NaH, and LiH. The nature of these current and continuing studies is summarized in the following abstracts of submitted papers.

THE LITHIUM AND SODIUM CATION AFFINITIES OF H_2 , N_2 AND CO

D. A. Dixon, J. L. Gole, and A. Komornicki

The Li^+ and Na^+ affinities of H_2 , N_2 and CO have been calculated by ab-initio molecular orbital theory with extended basis sets. Geometries were gradient optimized at the SCF level. Force fields were calculated at the SCF level at stationary points as were correlation corrections at the CI(SD) level with a correction for higher order excitations where appropriate. The optimum

geometries for MH_2^+ are C_{2v} (bent) and for MCO^+ , MOC^+ and MN_2^+ are $\text{C}_{\infty v}$ (linear). The Li^+ affinities (ΔH at 300 K) for H_2 , CO (at O), CO (at C) and N_2 are 4.8, 12.0, 14.6 and 11.8 kcal/mol, respectively, at the correlated level. The Na^+ affinities (ΔH at 300 K) for H_2 , CO (at O), CO (at C) and N_2 are 2.8, 7.6, 9.6 and 7.4 kcal/mol, respectively, at the correlated level.

THE ABSOLUTE PROTON AFFINITIES OF Li_2 , Na_2 , LiH , AND NaH

D. A. Dixon, J. L. Gole, and A. Komarnicki

The proton affinities of LiH , NaH , Li_2 and Na_2 have been calculated by ab-initio molecular orbital theory with extended basis sets. Geometries were gradient optimized and force fields were calculated at the SCF level. Correlation corrections were calculated at the CI(SD) level for the valence electrons. The proton affinities are calculated to be 244.2, 261.8, 277.8 and 274.1 kcal/mol and the Na^+ affinity of NaH is calculated to be 49.7 kcal/mol.

We have completed studies of a low-lying electronic state of the alkali oxides. The nature of these studies is summarized in the following abstract of the submitted manuscript.

FORMATION AND CHARACTERIZATION OF A LOW-LYING ELECTRONIC STATE OF THE ALKALI MONOXIDES $\text{LiO} \dots \text{CsO}$ AT THE FRINGES OF THE VISIBLE REGION

R. Woodward, J. S. Hayden, and J. L. Gole

In studying a variety of highly exothermic alkali oxidation chemiluminescent processes, a significant body of evidence has been obtained to indicate that the alkali monoxides LiO , NaO , KO , RbO , and CsO possess a weakly bound low-lying predominantly covalent excited electronic state thought to be of $^2\Pi$ symmetry ($^2\Pi^2$). The emission from this state for the heavier alkali oxides lies at the fringes of the visible region whereas the LiO emission system extends through the entire visible range to the near infrared. Alkali atoms react with ozone (O_3) and nitrous oxide (N_2O) under both "single collision" beam-gas and "multiple collision" conditions to yield the chemiluminescent spectra ascribed to the alkali monoxides. Under "single collision" conditions, the observed emission spectra resulting from an oxidation process first order in metal and first order in oxidant are almost entirely continuous. The "single collision" studies are extended in a controlled manner to higher pressure by entraining the alkali atoms in Ar, He, N_2 , or CO and subsequently carrying out the oxidation of this mixture at

background pressures ranging from 0.15 to 1 Torr in order to study relaxation and rapid intramolecular energy transfer. Partially rotationally relaxed spectra obtained for LiO, NaO, and KO demonstrate considerable structure associated predominantly with the vibrational levels of the ground and very low-lying ionic states of the alkali oxides. Temperature dependence studies (T_{beam}) under single collision conditions demonstrate that the O_3 reactions proceed with a much lower activation energy for excited state formation versus the N_2O reactions. Through energy conservation, the bond energies for LiO, NaO, KO, and CsO are extracted. While those bond energies determined for NaO, KO, and CsO are in good agreement with previous workers, the determined bond energy for LiO is notably higher than that determined mass spectrometrically. This study correlates well with the recent evaluation of $\text{M}_2 + \text{O}_2$ alkali oxidation processes where weak emission from an MO_2 ($\text{M} = \text{Na-Cs}$) species appears to be observed. The significance of the low-lying alkali oxide state as it pertains to the detection of the alkali oxides is considered.

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PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Institute of Technology 225 North Avenue Atlanta, Georgia 30332	2. NSF Program Experimental Physical Chem	3. NSF Award Number CHE-8604471
	4. Award Period From 8/1/86 To 7/31/89	5. Cumulative Award Amount \$216.500
6. Project Title Quantum Level Probes of Metal Clusters and Their Oxidation to form Unique Metal Clustered Oxides and Halides		

PART II—SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

The project has focused on the experimental and theoretical treatment of small metal clusters and their ions and the unique oxidation processes which they undergo.

We have demonstrated the first chemically pumped continuous laser amplifier in the visible spectral region, based on the characterization of the $\text{Na}_3 + \text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) reactions. We have developed a source configuration which has allowed the first analysis of middle transition metal cluster (Ni_3) quantal structure. We are completing the first phases of a group of studies in which we have observed and analyzed the optical signatures for the products of metal cluster oxidation, this work yielding important information on the kinetically controlled formation of the asymmetrical cluster oxides M_2O and M_xO ($x \geq 3$). It is significant that the metal cluster oxides we generate represent the non-symmetrical isomers, M_xO , rather than those compounds which might be synthesized through thermochemical means. The study of the unsymmetrical isomers provides a closer parallel to the nature of reactions on a metallic surface and the catalytic action of such surfaces and complements the ongoing studies of neutral and ionic cluster reactivity now underway in a number of research groups. We have completed initial studies of the formation of metal based CO and CO_2 complexes and the determination of the corresponding metal-ligand binding energies. These species can serve as prototype models for CO chemisorption on metal surfaces. We have completed theoretical studies of the proton affinities of Li_2 , Na_2 , LiH , and NaH and the alkali cation affinities of N_2 , Co , and H_2 . These studies represent the lead to the future study of the Li_2H^+ and Na_2H^+ cations which may serve as the basis for 21st century hydrogen based propellants.

Using the technique of Electric Field Enhanced Laser Induced Plasma Spectroscopy we have initiated the study of the internal mode structure and dynamics of small copper, aluminum, carbon and silicon metal and metalloid clusters, their ions and the hydrides of these metal clusters and their ions.

PART III—TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
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a. Abstracts of Theses					
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c. Data on Scientific Collaborators					
d. Information on Inventions					
e. Technical Description of Project and Results					
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2. Principal Investigator/Project Director Name (Typed)	3. Principal Investigator/Project Director Signature			4. Date	

PART IV - SUMMARY DATA ON PROJECT PERSONNEL

NSF Division Chemistry

The data requested below will be used to develop a statistical profile on the personnel supported through NSF grants. The information on this part is solicited under the authority of the National Science Foundation Act of 1950, as amended. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. NSF requires that a single copy of this part be submitted with each Final Project Report (NSF Form 98A); however, submission of the requested information is not mandatory and is not a precondition of future awards. If you do not wish to submit this information, please check this box ☐

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*U.S. Citizens/ Permanent Visa	PI's/PD's		Post- doctorals		Graduate Students		Under- graduates		Precollege Teachers		Others	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
American Indian or Alaskan Native												
Asian or Pacific Islander												
Black, Not of Hispanic Origin							1					
Hispanic												
White, Not of Hispanic Origin					6		3	1				
Total U.S. Citizens					6		4	1				
Non U.S. Citizens					0		0	0				
Total U.S. & Non- U.S. . .					6		4	1				
Number of individuals who have a handicap that limits a major life activity.												

*Use the category that best describes person's ethnic/racial status. (If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)

AMERICAN INDIAN OR ALASKAN NATIVE: A person having origins in any of the original peoples of North America, and who maintains cultural identification through tribal affiliation or community recognition.

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Final Technical Report

National Science Foundation
Grant CHE-8604471

"Characterization of Small Metal
Clusters and Their Unique Oxidation Processes"

James L. Gole

School of Physics
Georgia Institute of Technology

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Summary of Research Effort

Our research effort under NSF Grant CHE-8604471 has focused on the experimental and theoretical treatment of small metal clusters and their ions and the unique oxidation processes which they undergo. Included in this effort have been several breakthroughs.

We have demonstrated the first chemically pumped continuous laser amplifier in the visible spectral region, based on the characterization of the $\text{Na}_3 + \text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) reactions. We have developed a source configuration which has allowed the first analysis of middle transition metal cluster (Ni_3) quantal structure. We are completing the first phases of a group of studies in which we have observed and analyzed the optical signatures for the products of metal cluster oxidation, this work yielding important information on the kinetically controlled formation of the asymmetrical cluster oxides M_2O and M_xO ($x \geq 3$). It is significant that the metal cluster oxides we generate represent the nonsymmetrical isomers, M_xO , rather than those compounds which might be synthesized through thermochemical means. The study of the unsymmetrical isomers provides a closer parallel to the nature of reactions on a metallic surface and the catalytic action of such surfaces and complements the ongoing studies of neutral and ionic cluster reactivity now underway in a number of research groups. In addition, we initiated studies whose focus has been on the formation of metal based CO and CO_2 complexes and the determination of the corresponding metal-ligand binding energies. These species can serve as prototype models for CO chemisorption on metal surfaces. We have also completed a theoretical study of the proton affinities of Li_2 , Na_2 , LiH , and NaH and the alkali cation affinities of N_2 , CO, and H_2 . These studies represent the lead to the future study of the Li_2H^+ and Na_2H^+ cations using laser vaporization plasma spectroscopy.

Finally, in developing the technique of Electric Field Enhanced Laser Induced Plasma Spectroscopy we have initiated the study of the internal mode structure and dynamics of small copper, aluminum, carbon and silicon metal and metalloid clusters, their ions and the hydrides of these metal clusters and their ions.

Publications

"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.

"Self-Flushing Optical Window to Prevent Collection of Condensates", J. L. Gole, W. H. Crumley, Rev. Sci. Instruments, 57, 1692 (1986).

"Bound-Free Transitions in Molecular Metal Trimers", in Proceedings of the International Laser Science Conference, American Institute of Physics Conference Proceedings No. 146, Advances in Laser Science - page 522 (1986).

"Potential Probes of Metal Cluster Oxide Quantum Levels - Optical Signatures for the Oxidation of Small Metal Clusters M_x ($\text{M} = \text{Cu}, \text{Ag}, \text{Mn}, \text{B}$)", J. L. Gole, 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 Oxidations", American Institute of Physics Conference Proceedings, No. 160, Advances in Laser Science II - Optical Science and Engineering Series 8, pg. 439.
- "A Chemical Process Producing a Continuous Laser Amplifier in the Visible Region", J. L. Gole, S. H. Cobb and R. Woodward, Chem. Phys. Lett. 143, 205 (1988).
- "The Lithium and Sodium Cation Affinities of H_2 , N_2 and CO ", J. L. Gole, D. A. Dixon, and A. Kormornicki, J. Phys. Chem. 92, 1378 (1988).
- "The Proton Affinities of LiH , NaH , Li_2 , and Na_2 ", J. L. Gole, D. A. Dixon, and A. Kormornicki, J. Phys. Chem. 92, 2134 (1988).
- "Oxidation of Small Boron Clusters - Formation of and Chemiluminescence from BBO ", J. L. Gole, T. C. Devore and R. Woodward, J. Phys. Chem. 92, 6919 (1988).
- "Gas Phase Laser Induced Excitation Spectrum of Nickel Trimer", J. L. Gole, R. W. Woodward and S. H. Cobb, J. Phys. Chem. 92, 1404 (1988).
- "Formation and Oxidation of Metal Based CO and CO_2 Complexes - Characterization of $Al(CO)_x$ and $Al(CO_2)_x$ and Their Oxidation", J. L. Gole, M. McQuaid, and J. R. Woodward, J. Phys. Chem. Letts. 92, 252 (1988).
- "Trends in the Optical Signatures for Transition Metal Oxide Carbonyl Complexes - Evaluation of Transition Metal Carbonyl $M(CO)_x$ ($x = 1,2$) Binding Energies", J. L. Gole, M. McQuaid, J. Am. Chem. Soc., 110, 5280 (1988).
- "Formation of Electronically Excited Mn_xO from the Oxidation of Small Manganese Clusters", J. L. Gole, T. C. Devore and J. R. Woodward, Journal of Physical Chemistry, 93, 4920 (1989).
- "Formation of Electronically Excited Ag_xO from the Oxidation of Small Silver Clusters", J. L. Gole, R. Woodward, P. N. Le, T. C. Devore, and D. A. Dixon, Jour. Phys. Chem. in press.
- "Formation and Characterization of a Low-Lying Electronic State of the Alkali Monoxides $LiO...CsO$ at the Fringes of the Visible Region", J. L. Gole, R. Woodward and J. S. Hayden, Chem. Phys., 134, 395 (1989).
- "Chromium Cluster Fluorination - Three New States of CrF and the Observation of the First Cr_xF Emission Spectra", T. C. Devore, M. McQuaid, and J. L. Gole, High Temperature Science, in press.
- "Continuous Chemical Amplification of Single and Multimode Lasers in the Visible Region", with S. H. Cobb and J. R. Woodward, Chem. Phys. Lett., 156, 197 (1989).
- "Electric Field Enhanced Laser Induced Plasma Spectroscopy of Jet Cooled Metal Clusters and Their Hydrides", with K. X. He, M. Diestler, M. Xu, E. Daykin, and K. Everett, Bull. Am. Phys. Soc.

"Formation of the Low-Lying Electronic States of CrO in Highly Exothermic Reaction Oxidation, - Assessment of New States and Resolution of Previous Observations", with T. C. Devore, Chemical Physics, 133, 95 (1989).

"Electric Field Enhanced Laser Induced Plasma Spectroscopy of Jet Cooled Metal Clusters and Their Ions", with K. X. He, M. Diestler, M. Xu, and E. Daykin, Chemical Physics Letters, submitted.

"Stability and Oxidation of Metal Based CO and CO₂ Complexes", with M. J. McQuaid, Proceedings of the Fourth International Laser Science Conference, in press.

"Continuous Chemical Laser Amplifiers in the Visible Region", with S. H. Cobb and J. R. Woodward, Proceedings of the Fourth International Laser Science Conference, in press.

"Oxidation of Small Metal Clusters", with T. C. Devore, Proceedings of the Sixth International Conference on High Temperature Materials, in press.

"Spectroscopy of the AlAr Van der Waals Complex: Rotationally Resolved $B^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ Electronic Transitions", with M. McQuaid and M. C. Heaven, J. Chem. Phys., in press.

SELF-FLUSHING OPTICAL WINDOW TO PREVENT COLLECTION OF CONDENSATES

W. H. Crumley and J. L. Gole

As an aid to the characterization of nominally condensible and/or high-temperature molecules using optical techniques, a self-flushing optical window operating at room temperature and requiring no external heating has been designed to prevent the collection of these condensates. The optical design allows the unobstructed transmittance of light into and out of several devices to which it is readily adopted.

POTENTIAL PROBES OF METAL CLUSTER OXIDE QUANTUM LEVELS. OPTICAL SIGNATURES FOR THE OXIDATION OF SMALL METAL CLUSTERS M_x ($M = Cu, Ag, B, Mn$)

R. Woodward, P. N. Le, M. Temmen, and J. L. Gole

A source configuration which lies intermediate to a low-pressure effusing molecular beam and a high-pressure flow device is used to generate large concentrations of small metal clusters in a highly oxidizing environment. Clusters are formed from a high metal flux source ($K_{\text{Knudsen}} < 1$), which creates the seed for the initial phases of a cluster-forming environment, and are further agglomerated in a controlled argon or helium flow at room to liquid nitrogen temperature. The high-flux noneffusive source has been combined with techniques which have proven valuable in studying chemiluminescent processes across a wide pressure range to probe the chemiluminescent emission from several processes including the oxidation of small copper ($Cu_x + O_3$), silver ($Ag_x + O_3$), boron ($B_x + NO_2, N_2O$), group IVA (group 14), and early transition-metal clusters. 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 . The present study outlines the potential for chemiluminescent probes of metal cluster oxide quantum levels, not only within themselves but as a means of suggesting future laser fluorescent probes of the metal cluster oxides.

A CHEMICAL PROCESS PRODUCING A CONTINUOUS LASER AMPLIFIER IN THE VISIBLE REGION

S. H. Cobb, R. Woodward and James L. Gole

In a study of the reaction dynamics of the Na_3-X (Cl, Br, I) metatheses, Na_2 is formed in several electronic states, the fluorescence from these states resembling in some respects that characteristic of optically pumped alkali dimer lasers. Optical gain through stimulated emission demonstrates population inversion involving several excited state levels of Na_2 and hence an amplifying medium for a visible chemical laser. A maximum laser gain of 1% of the input laser power has been observed at 5270 Å, corresponding to a gain coefficient of $\approx 2 \times 10^{-3} \text{ cm}^{-1}$. An explanation is provided for this efficient inversion process and comparisons are made with optically pumped laser systems.

LITHIUM AND SODIUM CATION AFFINITIES OF H₂, N₂, AND CO

David A. Dixon, James L. Gole, and Andrew Komornicki

The Li⁺ and Na⁺ affinities of H₂, N₂, and CO have been calculated by ab initio molecular orbital theory with extended basis sets. Geometries were gradient optimized at the self-consistent field (SCF) level. Force fields were calculated at the SCF level at stationary points as were correlation corrections at the CI(SD) level with a correction for higher order excitations where appropriate. The optimum geometries are C_{2v} (bent) for MH₂⁺ and C_{∞v} (linear) for MCO⁺, MOC⁺, and MN₂⁺. The Li⁺ affinities (ΔH at 300 K) for H₂, CO (at O), CO (at C), and N₂ are 4.8, 12.0, 14.6, and 11.8 kcal/mol, respectively, at the correlated level. The Na⁺ affinities (ΔH at 300 K) for H₂, CO (at O), CO (at C), and N₂ are 2.8, 7.6, 9.6, and 7.4 kcal/mol, respectively, at the correlated level.

ABSOLUTE PROTON AFFINITIES OF Li₂, Na₂, AND NaH

David A. Dixon, James L. Gole, and Andrew Komornicki

The proton affinities of LiH, NaH, Li₂, and Na₂ have been calculated by ab initio molecular orbital theory with extended basis sets. Geometries were gradient optimized and force fields were calculated at the SCF level. Correlation corrections were calculated at the CI-SD level for the valence electrons. The proton affinities are calculated to be 244.2, 261.8, 277.8, and 274.1 kcal/mol for LiH, NaH, Li₂ and Na₂. The Li⁺ affinity of LiH is calculated to be 56.4 kcal/mol, and the Na⁺ affinity of NaH is calculated to be 49.7 kcal/mol.

OXIDATION OF SMALL BORON AGGLOMERATES: FORMATION OF AND CHEMILUMINESCENT EMISSION FROM BBO

T. C. Devore, J. R. Woodward, and J. L. Gole

A source configuration that lies intermediate to a low-pressure effusing molecular beam and a high-pressure flow device is used to generate boron cluster molecules in a highly oxidizing environment. Using this source operating in an NO₂ or N₂O oxidative environment, we generate a chemiluminescent emission spectrum which we attribute to the asymmetric BBO molecule. The observed spectrum is characterized by a strong Δv = 0, Δv = 40 cm⁻¹ sequence grouping and a weaker Δv = +1 sequence (Δv = 40 cm⁻¹), 440 cm⁻¹ to higher energy. A second sequence with Δv ~ 142 cm⁻¹ is also observed. Combining the 440-cm⁻¹ upper-state frequency with the 142-cm⁻¹ sequence structure implies a lower-state frequency of ~582 cm⁻¹ for the B-B stretch, consistent with ab initio calculation.

GAS-PHASE LASER-INDUCED EXCITATION SPECTRUM OF NICKEL TRIMER

J. R. Woodward, S. H. Cobb, and J. L. Gole

The first gas-phase nickel trimer laser-induced excitation spectrum has been generated from the supersonic expansion of pure nickel vapor. The spectrum, which correlates well with that observed in matrix isolation

studies, appears to be dominated by a combination of symmetric stretch and bending mode frequencies. On the basis of the results obtained we suggest an approach to overcome the substantial loss mechanisms which plague metal cluster spectroscopy and evaluate ground-state transition-metal cluster quantal structure.

FORMATION AND OXIDATION OF METAL-BASED CO AND CO₂ COMPLEXES: CHARACTERIZATION OF Al(CO)_x AND Al(CO₂)_x AND THEIR OXIDATION

M. McQuaid, J. R. Woodward, and J. L. Gole*

In a comparative study, aluminum atoms entrained in argon, CO, and CO₂ are oxidized with ozone to inspect the nature of aluminum complexation with CO and CO₂ to form Al(CO)_x (x = 1,2) and AlCO₂ adducts. The optical signatures corresponding to the chemiluminescent oxidation of these complexes with ozone to form the AlO B²Σ⁺ state or, in the case of CO₂, a polyatomic complex are compared to that AlO B²Σ⁺ emission associated with the chemiluminescent oxidation of nonbonded aluminum atoms in argon. We (1) establish a method for evaluating M(CO)_x binding energies and (2) observe the optical signature for a potentially long-lived (~10⁻⁷s) metal oxide-carbon dioxide solvation complex formed in metal-CO₂ complex oxidation. From a comparison of these studies, with results obtained for Al-N₂O oxidation, we estimate a lower bound to the total Al(CO)₂ binding energy (to Al + 2CO) of ~0.7 eV. The current study in conjunction with parallel efforts involving the transition metals suggests a method for studying the spectra of MCO, M(CO)₂, and M-CO₂ complexes.

TRENDS IN THE OPTICAL SIGNATURES FOR TRANSITION-METAL OXIDE CARBONYL COMPLEXES. EVALUATION OF TRANSITION-METAL CARBONYL, M(CO)_x, BINDING ENERGIES

M. J. McQuaid, K. Morris, and J. L. Gole*

Transition-metal atoms entrained in argon, helium, and CO are oxidized with ozone (O₃) and nitrogen dioxide (NO₂) to study the nature of the metal atom complexation with CO. We establish a method for evaluating M-CO binding energies through comparison of the chemiluminescent emission from the oxidation of argon- and CO-entrained transition-metal atoms. These studies have thus far yielded E_{binding}(Ti(CO)_x) ≈ 1.75 eV and E_{binding}(NiCO) ≈ 1.10 eV, the latter in excellent agreement with previous experimental and theoretical evaluations of the Ni-CO bond energy. We identify the optical signatures for transition-metal oxide carbonyl (MOCO) complexes formed in the oxidation of M(CO) complexes. We outline trends in the nature of the observed metal oxide complex emissions. The current study suggests a method for obtaining the spectra of transition-metal carbonyl (M(CO)_x, x = 1,2) complexes.

FORMATION OF ELECTRONICALLY EXCITED Mn_xO FROM THE OXIDATION OF SMALL MANGANESE CLUSTERS

T. C. Devore, J. R. Woodward, and J. L. Gole

The chemiluminescent reactions of manganese atoms and clusters with ozone have been studied under multiple collision conditions. Manganese atoms entrained in room temperature argon or helium react with ozone to form the

lowest-lying $\text{MnO}^* \text{A}^7\Sigma^+$ excited electronic state ($\text{Mn} + \text{O}_3 + \text{Ar}(\text{He}) \rightarrow \text{MnO}^* (\text{A}^7\Sigma^+) + \text{O}_2 + \text{Ar}(\text{He})$) producing a strong chemiluminescent signal corresponding to the $\text{MnO} \text{A}^7\Sigma^+ - \text{X}^7\Sigma^+$ band system. A high flux of manganese vapor is entrained in LN_2 cooled argon to induce clustering. This entrained mixture subsequently reacts with ozone to produce a new complex emission system (which accompanies the $\text{MnO} \text{A-X}$ system) containing at least 72 bands and extending from 720 to 970 nm. The new system which is not present unless the carrier gas is cooled increases precipitously with entrainment gas cooling and increased metal flux. The observed bands are fit within experimental error by the expression

$$\nu_{v'_1, v''_1, v'_3, v''_3} = 12512 + 600v'_1 - 534v''_1 + 360v'_3 - 306v''_3$$

where all the values are in cm^{-1} . The ground state spacing of 306 cm^{-1} is assigned as an Mn-Mn stretch. The 534 cm^{-1} spacing is assigned to an MnO stretch and the emitting molecule is believed to be the asymmetrical Mn-Mn-O isomer.

The Mn-Mn stretch frequency is in excellent agreement with the frequency estimated for Mn_2^+ by averaging the derived force constants for Mn_2 and Cr_2 . The MnO stretching frequency is considerably lower than the 840 cm^{-1} diatomic frequency, lying intermediate to those of KO (384 cm^{-1}) and CaO (733 cm^{-1}). This suggests that the bonding in this molecule is similar to the bonding in the alkali oxides and that it may reasonably be represented as $(\text{Mn-Mn})^+\text{O}^-$.

FORMATION OF ELECTRONICALLY EXCITED Ag_xO FROM THE OXIDATION OF SMALL SILVER CLUSTERS

T. C. Devore, J. R. Woodward, P. N. Le, D. A. Dixon, and J. L. Gole

The chemiluminescent reactions of silver clusters, M_n , $n \geq 3$, with ozone have been studied under multiple collision conditions. As a function of variations in the silver flux, a minimum of five distinct electronic emissions associated with AgO , $\text{Ag}_x\text{O}(x \geq 2)$, and Ag_2 are observed as well as features which are tentatively associated with the higher silver cluster oxides. The energetics of the observed spectral features combined with supplementary thermodynamic and kinetic information demonstrate that it is unlikely that electronically excited products with enough energy to account for the observed chemiluminescence can be produced through the reaction of either Ag or Ag_2 with O_3 . The smallest cluster whose reactions can readily yield the observed AgO emission features is the trimer. The formation of Ag_2O^* can also be achieved through reaction of the trimer, however, it may better be accounted for via the reaction of higher clusters. At moderate silver fluxes, the observed chemiluminescence is dominated by the $\text{AgO} \text{A}^2\Pi - \text{X}^2\Pi$ ($400\text{-}420\text{nm}$) and $\text{B}^2\Pi - \text{X}^2\Pi$ ($320\text{-}370\text{nm}$) emission features. At higher silver fluxes, leading to greater agglomeration, both the $\text{AgO} \text{A-X}$ and B-X emissions are quenched and the spectrum is dominated by a combination of $\text{Ag}_x\text{O}(x \geq 2)$ and Ag_2 emission features extending from 420 to 700 nm. At even higher silver flux further spectral features at $> 680 \text{ nm}$ emerge.

The chemiluminescent spectrum between 500 and 700 nm has been found to contain two distinct emission band regions which have been assigned as the A-X and B-X band systems of Ag_2O . The A-X transition which onsets at $\sim 630 \text{ nm}$ is well fit by the expression

$$\nu(\text{cm}^{-1}) = 15670 - 165v''_2 + (0.4)v''_2{}^2.$$

The B-X transition which originates at 506 nm is well fit by the expression

$$\nu(\text{cm}^{-1})_{v''_1, v''_2, v''_3} = 19766 - 442v''_1 - 165v''_2 - 256v''_3 + 6v''_1^2 + 6(v''_1)(v''_3) = 25(v''_1)(v''_2)$$

The observed frequencies are consistent with a non-linear Ag-Ag-O structure, emission from the asymmetric cluster oxides characterizing these kinetically controlled oxidation experiments in contrast to the thermodynamically more stable symmetric species.

FORMATION AND CHARACTERIZATION OF A LOW-LYING ELECTRONIC STATE OF THE ALKALI MONOXIDES LiO...CsO IN THE RED AND NEAR INFRARED

J. R. Woodward, J. S. Hayden and J. L. Gole

In studying a variety of highly exothermic alkali oxidation chemiluminescent processes, a significant body of evidence has been obtained to indicate that the alkali monoxides LiO, NaO, KO, RbO, and CsO possess a weakly bound, low-lying predominantly covalent excited electronic state thought to be of 2π symmetry ($B^2\pi$). The emission from this state for the heavier alkali oxides lies at the fringes of the visible region whereas the LiO emission system extends through the entire visible range to the near infrared. Alkali atoms react with ozone (O_3) and nitrous oxide (N_2O) under both single collision beam-gas and multiple collision conditions to yield the chemiluminescent spectra ascribed to the alkali monoxides. Under single collision conditions, the observed emission spectra resulting from an oxidation process first order in metal and first order in oxidant are virtually continuous. The single collision studies are extended in a controlled manner to higher pressures ranging from 0.15 to 1 Torr in order to study the internal relaxation and rapid intramolecular energy transfer characteristic of the metal monoxide. Partially rotationally relaxed spectra obtained for LiO, NaO, and KO demonstrate considerable structure associated predominantly with the vibrational levels of the ground and very low-lying ionic states of the alkali oxides. Temperature dependence studies (T_{beam}) under single collision conditions demonstrate that the O_3 reactions proceed with much lower activation energy for excited state formation versus the N_2O reactions. Through energy conservation, the bond energies for LiO, NaO, KO, and CsO are extracted. While those bond energies determined for NaO, KO, and CsO are in good agreement with previous workers, the determined bond energy for LiO is notably higher than that determined mass spectrometrically. This study correlates well with the recent evaluation of M_2+O_2 alkali oxidation processes where weak emission from an MO_2 ($M=\text{Na...Cs}$) species appears to be observed. The significance of the low-lying alkali oxide state as it pertains to the detection of the alkali oxides in combustion streams is considered.

FLUORINATION OF COMPLEXED CHROMIUM ATOMS AND MOLECULES - THREE NEW STATES OF CrF AND THE POSSIBLE OBSERVATION OF Cr_xF EMISSION SPECTRA

T. C. Devore, M. McQuaid, and J. L. Gole

Three new electronic states of CrF and two electronic transitions tentatively assigned to a polyatomic " Cr_xF " (Cr_2F) emitter are observed in the chemiluminescent flame resulting from the reaction between entrained (He, CO) chromium vapor and molecular fluorine under multiple collision conditions. The CrF transitions are vibrationally analyzed and term symbols

assigned. Each of the new transitions correlates well with a previously observed transition in the "pseudo-isoelectronic" molecules MnO, CrH, or CrCl. This correlation provides a basis for determining the electronic configuration of the CrF states and a guideline for predicting unobserved electronic transitions in the "pseudo-isoelectronic" molecules.

CONTINUOUS CHEMICAL AMPLIFICATION OF SINGLE AND MULTI-MODE LASERS IN THE VISIBLE REGION

S. H. Cobb, J. R. Woodward, and J. L. Gole

The chemiluminescent spectrum for the $\text{Na}_3 + \text{Br} \rightarrow \text{Na}_2^* + \text{NaBr}$ reaction has been analyzed to determine that optical gain through stimulated emission characterizes certain distinct visible spectral regions. Broadband (0.5 cm^{-1}) laser gain measurements performed across the spectral region extending from 420 to 600 nm demonstrate gain in the regions of ~ 527 , ~ 492 , and ~ 460.5 nm, the maximum gain at ~ 527 nm being 1% of the input laser power. Single mode (0.007 cm^{-1}) laser gain measurements extending from 527.03 to 526.63 nm demonstrate that amplification involves four to seven rovibronic levels in this region. A maximum gain close to 3% is recorded in the single mode studies.

ELECTRIC FIELD ENHANCED LASER INDUCED PLASMA SPECTROSCOPY OF JET COOLED METAL CLUSTERS AND THEIR IONS

K. X. He, M. Diestler, M. Xu, E. Daykin and J. L. Gole

Electric Field Enhanced Laser Induced Plasma Spectroscopy is developed as a relatively simple and general first order approach to a mapping of electronic states and internal mode structure in small metal clusters and their ions. Neutral and ionic emission features are distinguished with a sorting procedure based on field enhancement. Results obtained for Cu_x ($x = 1-3$) and Cu_x^+ ($x \geq 1$) emission systems are used to exemplify the approach which has now also been applied to the aluminum, carbon, and iron systems. It is also suggested that this approach will be useful for a study of the corresponding metal hydrides in systems where the chemisorption of hydrogen is prevalent.

FORMATION OF THE LOW-LYING ELECTRONIC STATES OF CrO IN HIGHLY EXOTHERMIC REACTIVE OXIDATION - ASSESSMENT OF NEW STATES AND PARTIAL RESOLUTION OF PREVIOUS OBSERVATIONS

T. C. Devore and J. L. Gole

The highly exothermic reactions of chromium atoms with O_3 and N_2O have been studied over a pressure extended in a controlled manner from a single collision bimolecular reactive environment ($\text{Cr} + \text{XO} \rightarrow \text{CrO}^* + \text{X} (\text{O}_2, \text{N}_2)$) with $P_{\text{Total}} \leq 10^{-4}$ Torr to multiple collision conditions ($\text{Cr} + \text{XO} + \text{Ar} \rightarrow \text{CrO}^* + \text{X} + \text{Ar}$) with $P_{\text{Total}} (\text{Ar}) \approx 2000 \mu$. The multiple collision environment promotes rotational relaxation and allows the study of strong couplings and rapid energy transfer among CrO excited states. The combination of these studies provides further information on the CrO electronic state manifold. Emission is observed from two and possibly three different excited states of CrO including the well-known 600 nm system ($B^5\pi - X^5\pi$), a system at ~ 850 nm

($T_0 = 11800 \text{ cm}^{-1}$, $\Delta G_{1/2}' = 820 \text{ cm}^{-1}$) tentatively associated with an $A'^5\Delta - X^5\Pi$ transition, and a newly observed blue system in the range $\lambda\lambda 510\text{-}420 \text{ nm}$ ($E_{\text{onset}} \approx 22163$, $\Delta G \approx 575 \text{ cm}^{-1}$) which emanates either from a new electronic state or from higher vibrational levels of a strongly inflected $B^5\Pi$ state. Features associated with the $v' = 2, 3, 4$ and 5 levels of the $\text{CrO } B^5\Pi$ state display an apparent doubling into two components (bands) whose average frequency corresponds closely to that anticipated vibrational level structure for the $B^5\Pi$ state. This dual level structure is attributed to the interaction between two closely lying excited electronic states of CrO , one being $B^5\Pi$, the mixing being of such a magnitude that perturbations of the $B^5\Pi$ state extend across a large manifold of rotational levels leading to an apparent shift of this bundle of levels due to the interaction with a perturber state. The perturber state which borrows intensity from $B^5\Pi$ becomes the second component of the doublet structure.

**SPECTROSCOPY OF THE AlAr VAN DER WAALS COMPLEX:
ROTATIONALLY RESOLVED $B^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ ELECTRONIC TRANSITIONS**

Michael J. McQuaid, James L. Gole, Michael C. Heaven

Rotationally resolved spectra were recorded for six bands of the $\text{AlAr } B^2\Sigma^+ - X^2\Pi_{1/2}$ transition. Vibrational and rotational constants derived from these spectra were used to determine the upper and lower state potential energy curves. The accuracy of these potentials was assessed through calculations of the spectroscopic constants and Franck-Condon factors. Dissociation energies of $D_e = 440_{-8}^{+35} \text{ cm}^{-1}$ and $D_e = 180_{-10}^{+40} \text{ cm}^{-1}$ were obtained for the B and X states, respectively. The interaction between $X^2\Pi_{1/2}$ and the low-lying $A^2\Sigma^+$ state has been characterized by analysis of the ground state lambda doublet splitting.

Seminars and Invited Talks on NSF Sponsored Research

International Workshop on Ionized Cluster Beam Techniques, Tokyo and Kyoto, Japan (1986) - Invited Talk, "Formation and Oxidation of Intense Metal Cluster Beams and Flows".

20th Mid Atlantic ACS Meeting, Symposium on Clusters and Cluster Ions, Baltimore, Maryland (1986) - Invited Talk, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

Optical Society: OSA Annual Meeting and APS/OSA International Laser Science Conference - Seattle (1987) - Invited Talk, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

Department of Chemistry, University of Georgia (1987) "Formation and Oxidation of Metal Based CO and CO₂ Complexes".

Gordon Research Conference on Metal and Semiconductor Clusters (1987), "The Varied Dynamics of Metal Clusters and Their Oxidations".

Quarterly PICO Seminar - School of Physics, Georgia Tech (1987), "Chemically Driven Visible and Ultraviolet Lasers".

Gaseous Electronics Conference, Atlanta, Georgia (1987) - Invited Talk in Symposium on Molecular Clusters, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

E. I. Dupont Nemours, Wilmington, Delaware (1987), "Metal Atom and Cluster Oxidations - What Are They Good For".

Third International Laser Science Conference, Atlantic City, New Jersey (1987), Invited Talk in Symposium on Molecular and Cluster Spectroscopy "Characterization of Cluster Formation in Metal Atom and Cluster Based Systems".

Third International Laser Science Conference, Atlantic City, New Jersey (1987), "A Chemical Process Showing Laser Gain in the Visible Region".

Southeast Regional A.C.S. Meeting, Orlando, Florida (1987) - Invited Talk, in Symposium on Optical and Dynamical Properties of Metal Clusters, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

University of Iowa - Departments of Chemistry and Physics and Iowa Laser Facility (1987), Invited Talk, "Developing a Visible Chemical Laser".

Gordon Conference on High Temperature Chemistry (1988) - "The Varied Dynamics of Metal Clusters and Their Oxides".

196th ACS Meeting, Symposium on the Chemistry of Isolated Atoms and Clusters, Los Angeles (1988) - Invited Talk - "Metal Atoms and Cluster Based Complex Oxidation".

Fourth International Laser Science Conference, Atlanta, Georgia (1988) - "Formation, Characterization, and Oxidation of Metal Based CO and CO₂ Complexes".

Fourth International Laser Science Conference, Atlanta, Georgia (1988) - " A Chemical Process Producing a Continuous Laser Amplifier in the Visible Region".

40th Southeast Regional ACS Meeting, Atlanta, Georgia (1988) - Symposium on Metal Clusters - Invited Talk - "Metal Atom and Cluster Based Complex Oxidation".

Emory University Department of Physics, Atlanta, Georgia (1988) - Invited Talk - "Chemically Pumped Visible Lasers".

Furman University, Department of Chemistry, (1989) - Invited Talk - "Chemically Pumped Visible Lasers".

Short Wavelength Chemical Laser Workshop - Atlanta, Georgia (1989) - Invited Talk, "The SiO, GeO - Tl and Na₃ - X(Cl,Br,I) Laser Systems".

METAL CLUSTERS AND THEIR UNIQUE REACTION DYNAMICS

Because they represent bridging regions of molecular bonding, structure and reactivity, clusters of several atoms and metal clusters in particular are attracting the attention of physicists, chemical physicists, and chemists alike.¹ Not only can these species and their interactions be used to model the manner in which atoms and molecules come together to form bulk matter, but also they possess a unique and useful chemistry onto themselves. Sufficient evidence now exists to indicate that an increased knowledge of the behavior and reactivity of metal clusters heightens and elucidates our understanding of the fundamental mechanisms of catalysis, as bulk metals and metal clustered oxides influence and enhance the rate of many significant processes for the chemical production of widely used materials such as methanol. Further evidence is now accumulating to suggest that the concepts developed for the formation and characterization of metal clusters can be extended to the modification of the bulk metallic phase so as to create novel materials of low density combined with unusual hardness and unexpectedly low resistivity.¹ These materials, whose formation is controlled by kinetics or the rate at which chemical conversions occur rather than thermodynamics or the relative stability of reactant and product molecules, may prove useful in a variety of applications ranging from airplane construction to the development of improved electrical circuit components.

Although a number of elegant studies have emerged thusfar in this burgeoning field, these efforts have largely neglected the complex movements of groups of several metal atoms and the way in which this behavior influences the products formed in metal cluster reactions. The limited information which is available demonstrates that metal clusters undergo a very unique and in many instances totally unexpected reactive branching. Not only is the study of this reactive branching fundamental to the development of rules required to extrapolate from simple $A + BC$ reactions but also the study of the specific energy framework of the product metal clustered oxides and halides provides

detailed and fundamental information on molecular structure and bonding. The entire realm of cluster studies currently underway benefits from an analysis of this energy framework. In correlation with computer simulations of the forces which define molecular movement this data provides a benchmark for the generation of reliable descriptions which can be used to (1) model and improve the behavior of highly exothermic combustion processes such as those involving boron (see also following) which can provide more than twice the volumetric energy density of conventional and currently used hydrocarbon fuels, (2) model those local cooperative phenomena between metal atoms which influence reactivity and mobility and whose description can be very useful in the modeling at the interface of metal cluster oxide surfaces where, for example, catalytic behavior is most likely influenced, and (3) model the nature of metal cluster based interactions which influence the quality of a surface etch ($\text{Si}_n + \text{X}(\text{Cl}, \text{Cl}_2, \text{F}, \text{F}_2)$) as one fabricates microelectronic circuitry in this rapidly expanding industry or enhance understanding of the new class of high temperature superconductors (see also following). We wish to develop a description of the intimate environment associated with the metal cluster-oxygen or metal cluster-halogen interaction, determining (1) how clusters of metal atoms interact with the oxygen or halogen atom and (2) the dynamic behavior which these clustered atoms may exhibit as they move about the oxygen or halogen atom.

The major research impetus in our laboratory focuses on the experimental and theoretical treatment of metal clusters and the unique oxidation processes which they undergo. This research effort has included several breakthroughs.

We have demonstrated (see attached) the first chemically pumped continuous laser amplifier in the visible spectral region (green, blue, and purple light) based on the characterization of the sodium trimer (Na_3) + halogen atom ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) reactions. This effort, which stemmed from our laboratories study of sodium polymer - halogen atom reactions within the

general framework of exploring metal cluster oxidation, marks the end of a long (~ 20 year) and frustrating effort to push chemical lasers from the infrared into the visible region. Lasers which operate in the visible region are more easily focused, require simpler equipment, and can be more compact. They hold the further advantage of greater efficiency verses commercially available electrical lasers and provide the ability to work in space or remote locations where a portable energy source is necessary.

It is noteworthy that before this detailed study of the $\text{Na}_3\text{-X}$ reactive system was undertaken, no available theories or previous experiments predicted the unique reactive branching leading to the formation of this visible chemical laser amplifier. A full understanding of this system will surely lead to new insights into molecular bonding and reactivity.

In extending our study of metal cluster oxidation, we are completing the first phases of a group of studies in which we have observed and analyzed the optical signatures for the products of metal cluster oxidation, this work yielding important information on the kinetically controlled formation of the asymmetrical cluster oxides M_2O and M_xO ($x \geq 3$). It is significant that the metal cluster oxides and halides we generate represent the nonsymmetrical isomers, M_xO and M_xF (ex. $\text{Ag}_x\text{O}(\text{Ag}_2\text{O}), \text{Cu}_x\text{O}(\text{Cu}_x\text{O}), \text{B}_x\text{O}(\text{B}_2\text{O}), \text{Cr}_x\text{F}, \text{Al}_x\text{F}$) where a metal atom grouping is bound to the oxygen or halogen, rather than those compounds which might be synthesized through thermochemical means.

Not only do we study a new class of interactions, generating a new class of metal clustered compounds but the study of the asymmetrical isomers provides a closer parallel to the nature of reactions on a metallic surface and the catalytic action of such surfaces and complements the ongoing studies of neutral and ionic cluster reactivity now underway in a number of research groups. We establish structures and determine, through bond angle and vibrational frequency determinations, the manner in which metal clusters

interact with an oxygen or halogen atom when they are formed in a unique kinetically controlled environment. While these are difficult experiments, the bounty on success is high and can well be considered in terms of the individual systems chosen for investigation. It is appropriate that we detail the importance of these studies for a few systems involving the boron, copper, and silver cluster oxides.

Boron combustion can provide more than twice the volumetric energy density of conventional hydrocarbons. While the emphasis in boron combustion and fuel research has been largely on boron particle ignition, it is also recognized that as much as half of the potential energy content of boron rocket fuels can be released in gas phase oxidation processes which might be exemplified by the conversion of $\text{BO}(\text{g})$ to $\text{B}_2\text{O}_3(\text{g})$. With a focus on homogeneous combustion chemistry, elegant studies are now in progress to assess the specific details of the gas phase oxidation of $\text{BO}(\text{g})$ to $\text{B}_2\text{O}_3(\text{g})$. Here, the key BO oxidation step in dry atmospheres is thought to be the rate limiting oxidation $\text{BO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{BO}_2(\text{g}) + \text{O}(\text{g})$, followed by the subsequent reaction of BO_2 with additional BO molecules, the two step process producing $\text{B}_2\text{O}_3(\text{g})$. If $\text{BO}(\text{g})$ is a major constituent in dry atmospheres, it is likely that this molecule strongly influences the homogeneous combustion chemistry associated with boron oxidation. However, it is not certain that gaseous BO is the prime gas phase constituent liberated in the ignition of boron particulates, and several important gas phase compounds released as boron combusts might be neither gas phase $\text{BO}(\text{g})$ nor solid boron but rather intermediate species. It has been suggested that one of these species might be B_2O . If so, it is feasible that the process $\text{B}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$ can compete with the two-step mechanism indicated above for $\text{B}_2\text{O}_3(\text{g})$ formation. It is up to the modern kineticist to assess this possibility, however, he can only be in a position to make this assessment with information on the energetics and energy level structure characterizing these boron clustered oxide molecules.

This is especially significant in the boron system where our studies of boron cluster oxidation have already demonstrated that the molecular electronic structure of the asymmetric and symmetric boron cluster oxides (BBO vs. BOB) and their energy level framework are quite different for even these "simplest" of cluster oxide isomers. This behavior is not readily discerned from simple molecular structure concepts. This data is now proving quite valuable to the boron kinetics group at the Naval Research Laboratory.

Our studies of the copper cluster oxides have now provided the impetus for the generation of models for the copper-oxygen interactions in these molecules. The models being generated for CuOCu and CuCuO are indicating that these molecules are bent but extremely floppy. These models are gauged by their fit of experimental vibrational frequencies generated in our initial studies. This modeling effort may well be relevant to the assessment of the role which the copper oxide lattice plays in high T_c superconductors. Here the movement of the copper and oxygen atoms as dictated by the Cu_xO potential function, especially the vibrational modes associated with the out-of-plane bending of these species, is thought to play an important role in the high T_c mechanism.

The chemistry of silver derives its technological importance from its use in photography and catalytic processes. The epoxidation of ethene is catalyzed by supported silver while the dehydrogenation of methanol is catalyzed by bulk silver both of which contribute extremely important industrial processes and products. In both systems, the silver catalyst must be in the form of a silver clustered oxide as are most metal catalysts. Studies which characterize these metal clustered oxides can be used to provide valuable insights into molecular structure, bonding, and atomic mobility in the Ag_xO constituents as an aid to their modeling in the bulk configuration. Valuable data for this modeling effort is gained from the study of Ag_2O and from the extension of these Ag_2O studies to the higher metal clustered oxides

Ag_xO ($x \geq 3$). In fact our current studies of the silver cluster oxides, which have been cited by the Silver Institute, appear to be contributing to our understanding of the behavior of these atomic groupings in the catalytic epoxidation of ethene. The results obtained thusfar have been communicated to the Los Alamos Scientific Laboratory theory group currently studying the ethene epoxidation process. Our studies of the Ag_xO system have now also sparked a collaborative extension to the corresponding Ag_xS sulfides. These compounds are believed to play an important role, through sulfide-halide interactions in film emulsions, thus they are of significant interest to the Eastman Kodak company.

Finally, we note that we have recently observed the optical signatures associated with the formation and oxidation of metal atom based CO and CO_2 solvation complexes. These complexes are representative of a virtually unstudied intermediate bonding region spanning the range, both as a function of the metal atom under study and experimental conditions, from weak binding Van der Waals interactions to the establishment of significant chemical bonds. The metal atom based CO complexes form a subset of the $\text{M}_x(\text{CO})_x$ ($1 \leq x \leq 3$) complexes whose properties also are expected to span this intermediate region. These compounds bear a greater significance as potential models for enhancing our understanding of one of the outstanding questions in heterogeneous catalysis. This question concerns the role of precursor states and the kinetics of transformation between these states and the chemisorption regime. With a focus on the metal surface carbonyl interaction, the $\text{M}_n(\text{CO})_x$ ($1 \leq n \leq 3$) clusters are pertinent to this question since they encompass a series of model compounds for which detailed microscopic information describing the intimate environment of the metal-carbonyl interaction can be extracted. It is precisely this information which can provide the productive tension between experiment and theory required for the development of systematically constructed and meaningful model systems representing the nature of ligand-

metal surface interactions.

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This Week

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some aspect that all...
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their structure or in how they...
humans, the only natural hosts of the
cold viruses.

In the recent work, scientists at the University of Virginia in Charlottesville and Johns Hopkins University in Baltimore report that, regardless of the rhinovirus involved, proteins called kinins appear to be the primary cause of painful nasal congestion. Released from plasma proteins activated by enzymes, kinins in the blood cause expansion of blood vessels, which allows fluid to leak into surrounding tissue. This fluid accumulation and its pressure on nerve endings is responsible for characteristic cold symptoms. Although these effects were already known, the researchers were surprised by the close relationship between kinin levels and symptoms.

The study, to be published in the January JOURNAL OF INFECTIOUS DISEASES, shows that kinin levels increase as cold symptoms appear and then decrease as symptoms fade. "The striking thing was that the kinins reached a peak on day two or three [after infection], which coincided with the peak of symptoms," J. Owen Hendley of Virginia told SCIENCE NEWS.

Using nasal discharges from 40 volunteers infected with rhinoviruses, the researchers found that kinin levels increased 20- to 80-fold in the two-thirds who developed symptoms. What the scientists did not find, Hendley says, is a similar rise in the level of histamines, proteins released from tissue cells during allergic attacks that also dilate blood vessels. "Antihistamines have been used in common cold remedies for years," says Hendley. "But the evidence from studies in the past 10 years saying that they work [for colds] is marginal at best."

"Antikininins," however, may be more promising, says Hendley. Because there is a time gap between infection of nasal passages and the influx of kinins into tissues, he suspects that the viruses may be activating kinin production. Drugs to

260	Meningitis Vaccine Stirs Controversy
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and foot-and-mouth disease viruses.

After making synthetic peptide structures that included these amino acid sequences, McCray and Werner injected them into rabbits. Antibodies produced

protection against infection, she says. Palmenberg and colleague Michael G. Rossmann discovered the surface cleft about two years ago while studying the structures of viruses. — D.D. Edwards

Chemical power for visible-light lasers

Energy generated directly by chemical reactions may soon power lasers capable of producing intense visible light. The recent development of the first visible-light chemical amplifiers marks the end of a two-decade search by scientists throughout the world for such systems. It also opens up the possibility of using lasers in remote locations such as space stations or satellites.

Conventional lasers rely on strong bursts of electricity to excite materials into emitting coherent light. Notoriously inefficient, such lasers require large quantities of electrical power to operate. Chemically powered lasers promise a more efficient way to generate intense light.

"It was a long road," says physicist James L. Gole of the Georgia Institute of Technology in Atlanta, who led the research. "What we have done so far is to demonstrate that these lasers amplify radiation." The next step, he says, is to build an oscillator consisting of a mirrored cavity that bounces light back and forth through the reaction zone.

"It's a significant development," says Terry A. Cool of Cornell University in Ithaca, N.Y., who years earlier had developed the first chemically powered infrared laser. Until Gole's persistence paid off, he says, scientists, despite trying many different approaches, had a long record of failure in their search for chemical reactions leading to molecules in excited states that would per-

mit light amplification.

In Gole's pulsed amplifier, thallium atoms pick up energy from collisions with excited molecules formed by a reaction between ozone and silicon or germanium. The collisions pump the thallium atoms up to an excited state. The atoms can then be stimulated to emit their radiation in a coordinated fashion to produce light amplification. The emitted light is green. When developed, says Gole, the system could turn out to be so powerful that it may be difficult to control.

Gole and his team have also developed a less powerful, continuous light amplifier based on the reaction between three-atom sodium clusters and halogen atoms. When a halogen such as chlorine reacts with a three-atom sodium cluster, the result is the formation of sodium chloride and an excited two-atom sodium cluster. The new cluster emits light, dropping to a lower energy level, and immediately reacts with any excess chlorine. Because this reaction is so rapid, the population of excited sodium clusters is always higher than that of low-energy clusters, allowing the laser to operate continuously.

Potential applications of chemically powered lasers depend not only on the possibility of achieving high powers but also on the fact that visible light requires simpler optics and is easier to focus than infrared radiation. Visible-light lasers are also likely to be quite compact.

— I. Peterson

TECHNOLOGY IN PERSPECTIVE

Optical chemical lasers take a quantum leap

Recent work at Georgia Institute of Technology has brought the chemically powered optical laser one step closer. Researchers have been looking for 20 years for visible laser amplifiers powered by chemical reaction. Now Georgia Tech researchers have discovered two laser amplifier systems—one continuous and one pulsed—which operate in the visual range. The work is an offshoot of research into chemical reactions being done for the National Science Foundation.

Chemical lasers could have a number of applications, particularly in space, the battlefield or any other environment where electricity is not readily available.

In laser action atoms or molecules in the laser medium are excited. When the number of excited atoms or molecules is greater than those in the lower energy levels, there is population inversion which gives the potential for the laser effect. With sufficient excited atoms or molecules there is the possibility that one atom or molecule falling back to a lower energy level and emitting a photon will stimulate another atom or molecule to do so also, giving amplification, a cascade of photons of the same frequency and in phases.

What the Georgia group has done is to produce this amplification in a chemical system. They have yet to oscillate this cascade of photons between two parallel mirrors to build up the sort of beam normally associated with conventional lasers.

In the continuous system the population inversion is produced by gas-phase molecules made up of three sodium atoms reacting with atoms of the halogens chlorine, bromine or iodine. The reaction gives a sodium halide molecule and an excited molecule of two sodium atoms. The excited molecule has the excess energy for a population inversion.

As the excited sodium molecules release their photons they react with excess halogen atoms. This reaction takes them out of the system and helps maintain the population inversion.

As explained by the leader of the research team James

ponent of the process is the fact that the excited sodium molecules emit light faster than they can react with the excess halogen atoms.

In the pulsed system there is rapid transfer of energy from a highly excited metastable metal oxide molecule to a thallium atom. The metal oxide molecule is formed by reacting silicon or germanium with ozone.

Thallium has an energy ground state which is split into two widely separated levels. When thallium is vaporised its atoms are in the lower of the

two ground states. The metal oxide molecules which are highly excited pass over their energy and pump the thallium atoms up to an excited state with respect to the upper level of the thallium ground state, creating the necessary population inversion.

These two initial systems produce green light but the team is working on similar chemical systems with the hope of light in the blue and violet sectors of the spectrum.

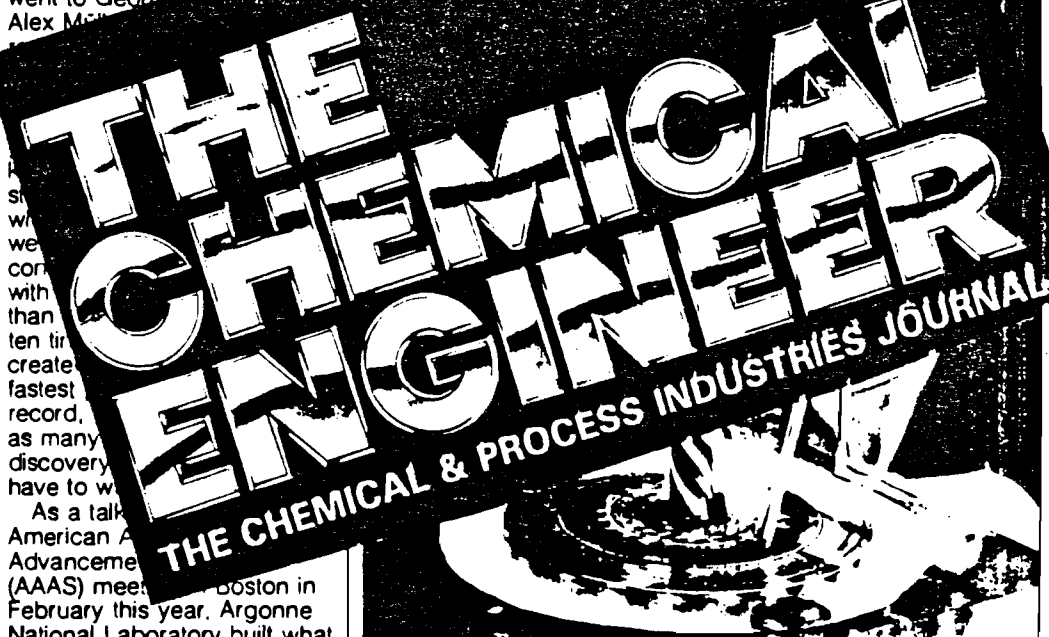
Dr Gole points out that these chemical lasers make more efficient use of energy

than conventional electrical lasers. "When you calculate how much energy you can channel into a system with a chemical reaction versus what you can put in with normal electrical means, you are much better off with the chemical approach," he says.

Chemical lasers operating in the lower energy infrared region of the spectrum already exist but they require large optical systems. Dr Gole points out that visible light lasers when developed will be easier to focus and will operate with simpler equipment.

Electric motor demonstrates superconductivity

As anyone who reads the scientific press must know superconductivity is the "hot topic" of the moment. Last year's Nobel Prize for physics went to Georg Bednorz and Alex Müller.



As a talk at the American Association for the Advancement of Science (AAAS) meeting in Boston in February this year, Argonne National Laboratory built what it claims is the first electric motor based on the new high-temperature superconductors. The simple motor rotates at around 50 rpm. Although it produces little power it demonstrates some of the properties of superconductors rather elegantly.

Below the critical temperature superconductors show perfect diamagnetism. In a magnetic field a diamagnetic substance becomes magnetised in the opposite direction to the field and thus opposes it.

To exploit this effect the motor consists of a circular aluminium plate about 22cm

Richard McDaniel, a researcher in the ceramics section at Argonne, pours liquid nitrogen on the motor

edge are mounted 24 small electromagnets about 4 cm by 1.2 cm in size. The electromagnets are energised via a commutator on the plate and a carbon brush. This plate rotates above two discs made of yttrium-barium-copper oxide. These disks become superconducting at 94K.

As an electromagnet circles over a superconductor it is switched on, producing a magnetic field which induces the superconductor to produce an opposing mag-

netic field and pushing it.

Roger B Poeppel, manager of the ceramics section of Argonne's division of materials and components technology, claims, "We built it to show that simple, operating motors can be made with new superconducting ceramics. It is too small for practical use... but it demonstrates for the first time that these motors are possible."

After the AAAS in Boston the motor is going on show in the Museum of Science and

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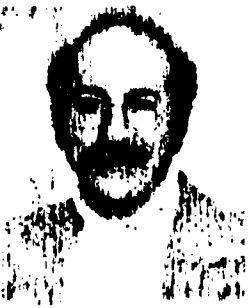
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♥ The International Newspaper of Optical and Optoelectronic Applied Science and Engineering

Medical imaging applications

An interview with Martin A. Afromowitz: Multispectral imaging of burn wounds

Martin A. Afromowitz received BS, MS, and PhD degrees in electrical engineering from Columbia University. He spent five years at Bell Labs in Murray Hill, working on III-V semiconductor LEDs and laser structures. In 1974 he joined the Center for Bioengineering at the University of Washington. He is now an associate professor of electrical engineering and an adjunct associate professor of bioengineering. His research interests include medical instrumentation, microfabrication, and optical fiber sensors. Afromowitz is coauthor of a paper to be presented in the Digital Medical Photography session of the Medical Imaging II: Image Formation, Detection, Processing, and Interpretation conference this month in Newport Beach, CA. He was interviewed recently by Robert Sol, SPIE Technical Consultant.



First of all, what do you mean by multispectral imaging of burn wounds?

Afromowitz: Multispectral imaging, to me, means taking a series of images simultaneously, or as simultaneously as possible, of a burn wound, in narrow wavelength ranges. We take images in the red, the green, and the near infrared.

Do you use a laser source?

Afromowitz: No, we use a white light source and a CCD camera with a filter wheel spinning in front of it to acquire the different wavelength images. The white light source is a standard photo flood

light source. On further inspection, they found out that that particular area of the burn turned out to be a third degree burn—a deep or full-thickness burn, which eventually needed to be grafted, whereas the other areas of the burn healed. So there was some suspicion that infrared photography can detect anomalous regions underneath the surface, and that there was some correlation of these anomalous regions with the burn-healing mechanism. Because the infrared image was also affected by the surface features of the burn, Anselmo and Zawacki also examined images in red and green light. Images were taken simultaneously through three different cameras, using filters in front of panchromatic film for the visible images and

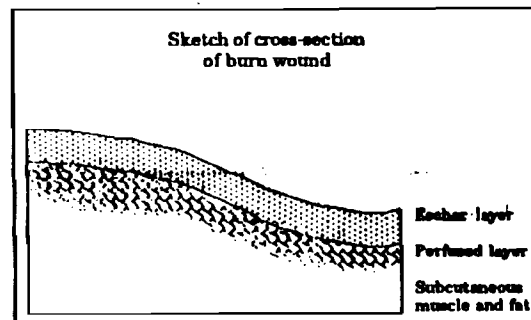


Figure 1. Sketch of cross-section of a burn wound.

infrared film and filters for the infrared images. The negatives of the three images of the burn—in the red, in the green, and in the near infrared—were digitized using a computer, and the ratios of intensities were calculated at each digitized pixel: red to infrared, green to infrared.

This issue's Focus

Medical Imaging

(see pages 4 and 5)

New visible light chemical lasers offer space applications

For 20 years, scientists have been searching for chemically powered visible lasers. Now physicists at the Georgia Institute of Technology have developed what are believed to be the first two chemical laser amplifiers operating in the visible spectral region.

The new laser amplifiers could have applications in space or in any environment where electricity to operate conventional lasers is not readily available, said James Gole, who heads the research group that

The group has succeeded in producing both continuous and pulsed visible laser amplifiers running solely on energy produced by chemical reaction..

developed the lasers. Conventional lasers require large electrical currents to generate the molecular changes that produce the laser effects.

The Gole group points out that these chemical lasers, developed in the Georgia Tech School of Physics, also make more

Fromowitz: Multispectral imaging, to me, means taking a series of images simultaneously, or as simultaneously as possible, of a burn wound, in narrow wavelength ranges. We take images in the red, the green, and the near infrared.

Q: Do you use a laser source?

Fromowitz: No, we use a white light source and a CCD camera with a filter wheel spinning in front of it to acquire the different wavelength images. The white light source is a standard photo flood quartz halogen lamp.

Q: How did interest in this procedure arise?

Fromowitz: Back in the mid-70s, I became aware of some work that

The ratios of red to infrared, red to green, green to infrared seemed to correlate with the depth of the burn. It was the first indication that a colorimetric analysis of a burn would be useful.

was published in the Proceedings of the SPIE by two researchers in California—Victor Anselmo, of the Jet Propulsion Laboratory, and Bruce Zawacki, a burn surgeon in Los Angeles. Their first article showed that, by using infrared photography, they were able to detect dark amorphous regions on a burn wound which had no surface correlate. They saw a darker region on an infrared image of a burn on a child's back; the surface features were not especially different at that point. They assumed they were seeing something underneath the surface, because infrared light can transmit through tissue farther

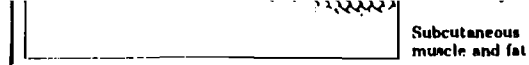


Figure 1. Sketch of cross-section of a burn wound.

infrared film and filters for the infrared images. The negatives of the three images of the burn—in the red, in the green, and in the near infrared—were digitized using a computer, and the ratios of intensities were calculated at each digitized pixel: red to infrared, green to infrared, and red to green. They were able to show, on a very limited number of patients, that these ratios seemed to correlate with the depth of the burn. And that was very exciting. It was the first indication that a colorimetric analysis of a burn would be useful at all.

The digitization of the negatives took several weeks to accomplish and was a fairly expensive process in those days. Because of the time lag in getting information back from photographic processing and computer densitometry, the patient had to be dealt with in the clinic before any information came back from this method; so it wasn't a useful clinical tool.

Q: So what was needed was a real-time measurement tool?

Fromowitz: Yes. But I started looking into the development of a bedside, real-time instrument that would take the same measurements, just to see what kind of information such a method would give. And since Anselmo and Zawacki's work was terminated by NASA at the time there wasn't any more information forthcoming from that source. So I built a small instrument, basically a spot meter, with a hand-held probe that illuminated a small selected

(continued on page 4)

duced by chemical reaction..

developed the lasers. Conventional lasers require large electrical currents to generate the molecular changes that produce the laser effects.

The Gole group points out that these chemical lasers, developed in the Georgia Tech School of Physics, also make more efficient use of energy than electrical lasers.

"When you calculate how much energy you can channel into a system with a chemical reaction versus what you have to put in with normal electrical means, you are much better off with the chemical approach," Gole said. The Georgia Tech group has succeeded in producing both continuous and pulsed visible laser amplifiers running solely on the energy produced by chemical reaction.

Although the researchers had been searching for a visible chemical laser on and off for a decade, the discovery of the continuous laser amplifier came as an offshoot of research on chemical reactions being done for the National Science Foundation.

"We recognized that we had observed the earmark of stimulated emission when

(continued on page 2)

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65149
Dr. Donald C. O'Shea
Georgia Institute of Technology
Department of Physics
Atlanta, GA 30332

oer2

dynamic raster or medical imaging.

On another topic, we note with pride the publication of the 50th issue of *OE Reports*. Just over four years ago, SPIE published the first issue, and it's been a period of growth for the paper and for everyone involved. We are grateful for your readership and support, and look forward to continued progress over the next 50 issues!

Robert E. Fischer, Editor of OE Reports, is manager of U.S. operations for Ernst Leitz Canada Ltd. He is a past president of SPIE and currently serves as chairman of SPIE's Long Range Planning Committee, and as a member of the Education Committee.

Visible light chemical lasers

(continued from page 1)

"we studied these chemical reactions," Gole explained. "We probably would not have recognized that very easily if we had not been familiar with the chemical laser work."

Chemical lasers operating in the lower energy infrared spectral region already exist, but Gole said visible lasers, once developed to their full capacity, will be easier to focus and operable with simpler equipment.

The group, which also includes Stephen H. Cobb and J. Robert Woodward, is now attempting to convert the amplifier systems to laser oscillators. The two initially discovered Georgia Tech lasers produce green light, but Gole reports that additional research underway on similar chemical systems indicates the promise of blue and violet light.

The operation of any laser depends on creating a substantial population of highly excited molecules. When the number of highly excited molecules exceeds the number of molecules in lower energy levels, a population inversion exists which creates the potential for the lasing effect.

The continuous laser amplifier creates a population inversion by reacting molecules composed of three sodium atoms (Na_3) with atoms of halogen (chlorine, bromine or iodine). This reaction forms sodium halides (NaX), which possess the excess energy required to place them in the higher energy levels needed for a population inversion.

As the excited sodium molecules release light, they relax to their lower energy ground state, where they immediately react with excess halogen atoms. This reaction takes these molecules out of the system, maintaining the population inversion and allowing the laser to operate continuously.

An important aspect of this process, Gole explains, is that the excited sodium (Na_3) molecules emit light at a rate faster than they

can react with the excess halogen atoms.

The pulsed amplifier relies on the rapid transfer of energy from a highly excited metastable metal monoxide molecule to a thallium atom. The excited metal oxide molecule is formed through the reaction of silicon or germanium with ozone. Thallium was chosen because its ground state is split into two widely separated levels.

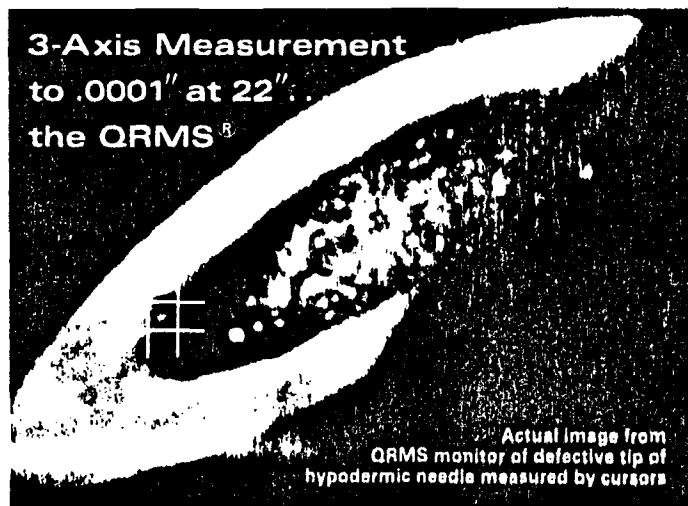
Upon vaporization, the thallium atoms are in the lower of the two energy levels. When they receive energy from the highly excited metal oxide molecules, the thallium

atoms are pumped to an excited state with respect to the upper level of the thallium atom ground state, creating the necessary population inversion.

The search for chemically driven visible lasers has occupied researchers for two decades, Gole noted.

"The number of approaches that have been taken in attempts to make this laser would probably take about seven pages to list," he added. "There have been many possibilities, but until now, they all had some flaw."

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Correction

Dr. Robert Alfano, featured in an article in last month's *OE Reports*, was honored as Distinguished Professor of Science and Engineering, not physics as reported, at City College of the City University of New York.

OE Reports

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LASERS

High efficiency keys interest in visible chemical lasers

PHYSICISTS AT Georgia Institute of Technology, Atlanta, have developed two chemical laser amplifiers that produce visible laser light. The work marks the first time that researchers have been able to generate visible laser light by a chemical method.

Chemical lasers operating in the lower-energy infrared spectral region already exist, but research has been geared toward chemical lasers operating in the visible spectral region because they promise to be easier to focus and operate. Primary uses for such systems are space and military applications, but the benefits that the laser could provide may translate into more uses than this, said Dr. James Gole, who directed the research.

Robert Woodward who, along with Stephen Cobb, also worked on the project, said, "The importance of a chemical process for a visible laser is that it is going to be extremely efficient.

"All of the commercial lasers now use some sort of large electrical supply to power them and they are not efficient—less than 1% normally. But in a chemical process most of your energy is going to be channeled into producing the light that you want to see," he told *R&D*.

The Georgia Tech group succeeded in producing continuous and pulsed chemical-laser amplifiers. Their discovery actually was an offshoot of research into chemical reactions they were doing for the National Science Foundation.

"We were initially studying these [compounds] from a chemical reactions standpoint, and noticed that situations

were arising where we expected to see laser emissions, and then we pursued it ourselves," Woodward said.

Creating a laser amplifier requires achieving a population inversion—a state where highly excited molecules outnumber the molecules in lower-energy states. For the continuous laser amplifier, a population inversion was created by reacting molecules composed of three sodium atoms (Na_3) with atoms of a halogen (chlorine, bromine, or iodine).

This reaction forms sodium halide molecules and molecules consisting of two sodium atoms (Na_2), which possess the excess energy required to put them in the higher-energy levels needed for a population inversion. As the excited sodium molecules release light, they relax to their low-energy ground state where they immediately react with excess halogen atoms.

This reaction takes these molecules out of the system, maintaining the population inversion and providing continuous laser operation.

The pulsed laser amplifier relies on the rapid transfer of energy from a highly excited metastable metal-monoxide molecule to a thallium atom. The excited metal-oxide molecule is formed through the reaction of silicon or germanium with ozone.

Upon vaporization, the thallium atoms are in the lower of their two energy levels. When they receive energy from the highly excited metal-oxide molecules, the thallium atoms are pumped to an excited state with respect to the upper level



Georgia Tech researchers Dr. James Gole, Robert Woodward, and Stephen Cobb (l to r) developed a chemical laser amplifier that produces visible (green) light.

of the thallium atom ground state, creating the necessary population inversion.

The researchers now are developing oscillator systems for the observed chemical reactions to make the light coherent. They also are experimenting with other possible chemical amplifiers, Woodward said.

"We are working on other chemical reactions involving the same idea, the same theory, to make light in different regions. Right now we can make green laser light, but by selecting a slightly different compound and doing analogous experiments, we might be able to produce blue and violet lights, which are more energetic than green light," Woodward explained.

"This will allow more applications or a wider range of wavelengths to choose from" for the chemical laser, he added.

—Skip Derra □

COMPUTERS

Advances in electronics spur interest in neurocomputers

THE EMERGENCE of a new computer concept that may have a dramatic effect on information processing techniques of the future was evident at the First Intl. Conference on Neural Networks. As indicated by the papers presented at the symposium, an increasing amount of R&D is being devoted to computer systems that attempt to mimic neural networks of the human brain.

The idea of doing this is not new, with pioneering work having been performed more than 30 years ago. However, the state of the art being what it was at that time, more progress toward practical computing techniques could be made by following other avenues, and neurocomputing essentially remained dormant until around 1982.

It was at this time that researchers,

such as Dr. John Hopfield of Caltech and AT&T Bell Labs, and Dr. Stephen Grossburg of Boston Univ. (both of whom presented papers at the conference), helped spawn new interest among scientists in physics and optics which resulted in an upsurge of work in the field.

A contributing factor was the great increase in the past 10 years in understanding the brain's way of working. As one conference speaker, Dr. Carver Mead of Caltech, recalled, the picture that biologists had of the brain 20 years ago "was much more simplistic and much less analog in nature. At the time, neurobiologists were preoccupied with nerve impulses and the way they were generated in neurons.

"Now they are looking more deeply at the principles on which neural compu-

tation is based, and there are some surprises here. Nerve impulses, which are quasi-digital, play a surprisingly small role in the actual computation process," Mead said.

"Most of the computation is analog and it's done at the very tips of the dendritic tree of the neuron. Throughout the brain there is a distributed feedback from these dendritic tips to the nerves that are driving them."

Such findings, he stressed, caused computer experts to look into synthesizing systems with some neural-type properties. The timing proved right, not only because of new insights into brain functions, but also because of advances in digital technology, such as the ability to make 6-in. chips with 1×10^9 transistors.

In typical digital use, many of the

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THE WEEKLY REPORT ON TECHNICAL INNOVATION

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December 23, 1987

New Sensor Measures Sub-picosec Electrical Pulses: Noninvasive probe for testing and designing integrated circuits measures pulses 100 times faster than conventional electronic sensors. AT&T researcher developed the electrooptic technique to work with any kind of circuit material, from Si and GaAs to ceramics and hybrids. Sensor resolves signals of less than 0.3 picosec. No specialized circuit designs are needed to accommodate testing, as with commonly-used sampling oscilloscope technique.

Key element is electrooptic crystal of lithium tantalate with a tip only 40 μ dia. Crystal is mounted below a high-resolution microscope on a quartz support rod that positions it near test point on the IC. Local electric field corresponding to voltage variations in conducting lines of the circuit affects crystal's optical properties. Subpicosec laser directed through the crystal translates optical changes into voltage data. Sensor lets chip designers zero in on electrical properties of features only microns wide to test and refine circuits.

Details: Janis Valdmanis, AT&T Bell Laboratories, 600 Mountain View, Murray Hill, NJ 07974. Phone: To reach Dr. Valdmanis, call Kevin Compton, 201-564-4097.

Heterojunction Transistor Promises to Double Speed: New type of bipolar transistor developed by IBM, silicon-germanium base heterojunction transistor, has potential to significantly extend performance limits of silicon bipolar technology. Bipolar transistors use both positive and negative charge carriers and are intrinsically faster than other transistor types, such as the field-effect transistor. They are used in supercomputers and large main-frame computers. With new design speed will be increased further.

SiGe alloy forms the middle (base) layer through which charge carriers travel. Alloy gives new transistor better electronic control compared to conventional homojunction (Si only) base transistors. Advantages include lower base resistance, higher emitter injection efficiency, and ability to operate at very low temperatures. New circuits work at 77°K (liquid nitrogen temperature).

Researchers use molecular beam epitaxy (MBE) to build the heterojunction and align crystalline structure. Technique is being used to grow SiGe crystals less than 1000 Å thick.

Details: S. S. Iyer or G. L. Patton, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598. Phone: To reach Iyer or Patton, call Tom Murphy, 914-945-3036.

Visible Chemical Lasers: Georgia Tech researchers have developed chemical laser amplifiers that operate solely on energy from chemical reaction. Previous designs for chemical lasers operated only in the infrared spectrum. New lasers produce green light, so are easier to focus and can be operated using simpler equipment. Other advantages are greater efficiency, compared with electrical lasers, and ability to work in space or other remote locations where portable energy source is a plus.

Researchers made two types of chemical lasers -- continuous and pulsed. Continuous laser creates population inversion by reacting sodium trimers with halogen atoms (chlorine, bromine, or iodine). Sodium dimers and sodium halides are formed, releasing light energy. Pulsed system relies on rapid transfer of energy from an excited metastable metal monoxide molecule to a thallium atom. Energized thallium creates the population inversion.

Current goals are to expand capabilities to include emission of blue and violet light, and convert the amplifiers to laser oscillators.

Details: James Gole, School of Physics, Georgia Institute of Technology, Atlanta, GA 30332. Phone: 404-894-3444.

NEWS

with full electron shells are neodymium-like ions, with 60 electrons, and there are no stable elements with atomic numbers high enough to produce short wavelengths. In essence, you run out of electrons to remove.

Hagelstein, who left Livermore in early 1987 to join the faculty at the Massachusetts Institute of Technology, is more interested in scaling to longer wavelengths. The reason is that comparatively modest power levels should suffice to remove enough electrons to produce gain. He says nickel-like molybdenum could emit near 20 nm; that would require stripping only 14 electrons from the molybdenum atoms. He thinks a \$250,000 benchtop system might be able to do the job, putting extreme ultraviolet sources within the reach of small laboratories. He is waiting to get equipment he needs to begin experiments.

Personal experience makes Hagelstein sympathetic to the needs of "little science." It took a couple of years to

get time on Nova for the nickel-like laser experiments. He believes more smaller-scale short-wavelength sources would encourage more research in the field.

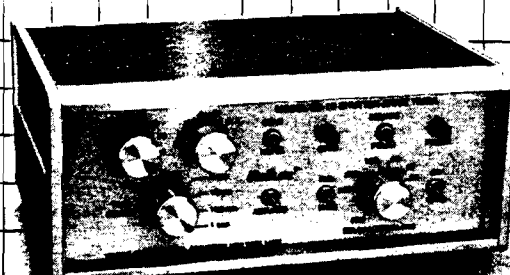
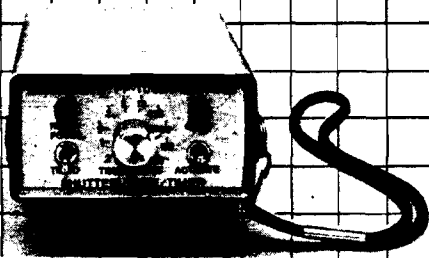
—Jeff Hecht

Chemical Laser Amplifies In Visible

After two decades, the search for visible-wavelength chemical lasers is starting to pay off. James L. Gole, Stephen H. Cobb and J. Robert Woodward of the Georgia Institute of Technology have measured laser gain at visible wavelengths in two chemically-driven systems. Although they have yet to demonstrate oscillation—which most observers consider a prerequisite for using the word "laser"—their experiments appear to mark the

end of a long and frustrating effort to push chemical lasers from the infrared into the visible region.

Visible chemical lasers have long been near the top of the military's laser wish list because of the prospects of greater portability and more efficient operation than electrically powered lasers. The infrared wavelengths of present-day chemical lasers have limited their practical applications. Large optics are needed to focus the beams tightly, and most target materials have low absorption at infrared wavelengths. Nonetheless, years of sponsoring futile projects led military agencies to write off the quest, although the Strategic Defense Initiative included visible chemical lasers on its long list of possible "Innovative Science and Technology" research. Ironically, the Georgia Tech results were the outgrowth of basic research into reactions of sodium trimers with halogens, sponsored by the National Science Foundation, and was not the

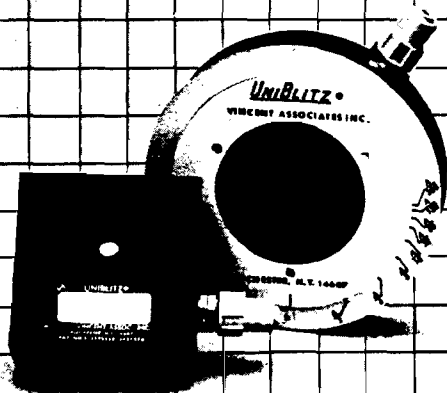


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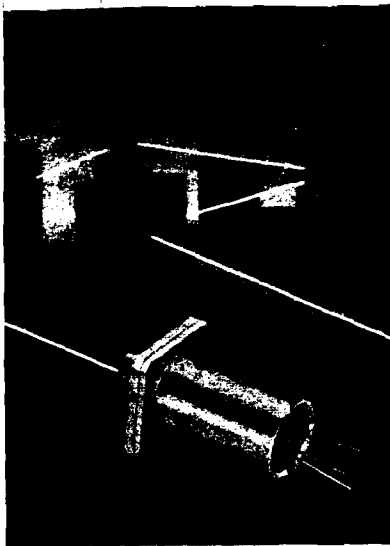
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NEWS

result of a systematic effort to develop chemical lasers.

Both systems operate on green transitions in metal vapors. The first system demonstrated relies on the reaction of a halogen atom with a sodium trimer, Na_3 . Chlorine, bromine, or iodine atoms react with the Na_3 molecules to form a sodium halide and an excited sodium dimer, Na_2 . The highly exothermic reaction between the sodium molecules and halogen atoms in crossed beams produced bright fluorescence from Na_2 with sharp emission regions. By passing a dye laser beam through the reaction zone, Gole, Cobb, and Woodward detected a population inversion. They measured maximum laser gain at 527 nanometers of up to 1 percent of the probe beam power, corresponding to a gain coefficient of 0.002 per centimeter. They also observed superradiant emission from 524 to 530 nm.

The Georgia Tech group vaporizes metallic sodium in an oven operating at 950 to 1100 K, then passes the vapor through a supersonic nozzle into a reaction chamber at pressures of 10^{-5} to 10^{-6} torr. The rate of trimer production is low; at best, the ratio of sodium atoms, dimers, and trimers is about 1:1:0.03. However, Gole reports the reaction had an "extremely efficient inversion process," and that laser amplification was observed for 20 to 40 minutes. Reaction of halogen atoms with sodium dimers effectively depopulates the lower laser level, maintaining the population inversion.

In their second system, chemically produced silicon or germanium monoxide transfers energy to atomic thallium vapor. Reaction of ozone with atomic silicon or germanium atoms forms excited SiO or GeO molecules. These excited molecules are mixed with thallium atoms evaporated from an oven, and transfer energy from the excited SiO and GeO molecules to thallium's resonant $7^2_{1/2}$ level. This produces a population inversion, with the lower level being the upper of two levels of thallium's split ground state.

The thallium system produces bright green pulses at 535 nm. Because no fast mechanism removes atoms from the lower laser level, stimulated emission reduces the population inversion.

Like the nitrogen laser, the thallium emission is self-terminating.

Gole's group is exploring ways to extend their chemical pumping schemes to different systems and wavelengths. They believe the sodium-dimer system might work at shorter wavelengths, with the most attractive regions near 412.5, 395, 365, and 350 nm. They also are investigating prospects of extending the energy-transfer scheme to produce 451- and 417-nm emission from gallium and indium atoms.

Other efforts include trying to move beyond their present laser amplification experiments to demonstrate laser oscillators, and to scale to higher powers. "I would be very loathe to say there would be no problems," Gole said. However, he is optimistic that oscillation is possible as long as design and engineering "can be carried off as we think it can."

The Georgia group has yet to wrap up contracts for follow-up research, but Gole says they are exploring possibilities. One plan is a research partnership with the Tetra Corp. of Albuquerque to seek research contracts to raise power levels by scaling production of metastable SiO and GeO states.

— Jeff Hecht

ENTERTAINMENT & DISPLAY

Holographic Museum Opens In Los Angeles

Los Angeles now has its first holographic museum—the third in the nation. The new museum is called Holographic Visions and was officially opened on December 9, 1987 by Mayor Thomas Bradley. Mayor Bradley presented a plaque to the museum's founders, Chris Outwater and Jerry Preston, and proclaimed it Holographic Vision Day in Los Angeles. During the ceremony, Mayor Bradley also unveiled a large animated rainbow hologram of himself that was shot just the week before the opening.

Holographic Visions has a prime location in downtown Los Angeles, right next to the Museum of Contemporary