MASTER

C00-2569-3

THE LUMINESCENCE PROCESS, REFRACTORY STABILITIES, AND
NEW AND NOVEL ELECTRONIC STATES--SCANNING CHEMICAL
REACTIONS AND NOVEL PRODUCTS FOR LASER INDUCED
ISOTOPE SEPARATION

Progress Report
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Special Note

For the past two years, Professor James Gole has carried on research on the "Luminescence process, refractory stabilities, and new and novel electronic states" at the Massachusetts Institute of Technology. We submit this progress report at the present time because the principal investigator Professor James Gole, will shortly join the chemistry faculty at the Georgia Institute of Technology. The work currently carried out at M.I.T. will be continued at Georgia Tech. The project must therefore be terminated at M.I.T. A renewal proposal is being submitted from the Georgia Institute of Technology.

Abstract

We discuss the formulation, development, and use of versatile oven systems for high temperature metal vaporization at temperatures in excess of 2000°C. Refinements of an apparatus appropriate for the production and study of small metal aggregates $M_n (2 \leq n \leq 6)$ are discussed at length. We discuss improvements in our argon ion and nitrogen pumped dye laser systems, and necessary additions for effective interfacing of these dye lasers to the aggregates apparatus. Internal calibration standards are discussed. Progress on the production of carbon vapor and the reaction of this vapor with metal atoms and metal dimers to form metal carbides is outlined. Metal sulfide chemistry is discussed.

We outline several specific studies of the luminescence process. Included in these studies are completed work on aluminum oxidation. Studies of germanium and silicon oxidation are outlined and new investigations of inorganic hydride oxidation are presented.

We outline the status of our efforts to form new and novel surfaces via aggregate deposition. Quantum chemical calculations on small metal aggregates are discussed. The first applications of dynamic laser induced fluorescence to the AlO molecule are presented.

Our focus during the present grant period can be grouped into six main efforts. In addition we comment on the status of additional projects outlined in progress report C00-2569-2.

(1) We have continued our extensive studies of the luminescence process. This work has already resulted in several inroads and a considerable increase in our understanding of chemiluminescent phenomena occurring as a result of the "single collision" bimolecular reaction of metal atoms and metal dimers. We have also extended our studies to the "multiple collision" pressure regime as a tool for both elucidating "single collision" phenomena and approaching more closely the pressures characterizing normally observed combustion phenomena. Work has centered on aluminum oxidation, germanium oxidation as a prelude to studies of silicon oxidation and the study of inorganic hydride oxidation. This research opens the way for the study of higher metal n-mer oxidation.

(2) We have continued formulation and development of versatile oven systems for high temperature metal vaporization. This work has included a substantial effort to develop efficient data acquisition systems for use in conjunction with our apparatus for the study of small metal aggregates, M_n ($2 \leq n \leq 6$) at temperatures in excess of 2000°C . Much of this effort focuses on efficient filtering of black body radiation and scattered laser light. The major modification of our oven sources has involved the completion of "nozzle" sources constructed of tungsten carbide and carbon.

(3) We have developed and are improving a carbon source for the production of carbon vapor whose constituency is primarily C_1 , C_2 , and C_3 . This carbon source is being used for the characterization of metal carbides MC and MC_2 produced via reaction of M or M_2 with C_1 , C_2 , and C_3 in a "single collision" chemiluminescent reaction. Thus far it appears that we have produced VC , VC_2 , and TiC .

(4) We have continued the improvement of our cw dye laser module and our pulsed nitrogen pumped dye laser. Both dye lasers are being used to study the molecular electronic structure and radiative lifetimes of those compounds and aggregates formed in our newly devised high temperature ovens.

(5) Quantum chemical calculations are proceeding on lithium and boron clusters as well as their negative ions. This work is being done in conjunction with Dr. David Dixon.

(6) We have successfully observed "dynamic" laser-induced fluorescence in aluminum oxide. The excitation spectrum will be discussed in a following section.

Additional Projects:

- A. We have now completed the oven source system for our analysis apparatus. The apparatus will be utilized once the characterization and control of aggregate formation is established. We are still working on a method of deposition which involves a simultaneous beam chopping and support vibrating mechanism.
- B. We are well along the construction of a apparatus appropriate for the study of chemiluminescence on surfaces. Here, we will deposit appropriate metals and attempt to observe fluorescence upon highly exothermic oxidation of freshly deposited surfaces.
- C. We are continuing our efforts in metal sulfide chemistry and are searching for new "well-defined" sources for excited state metal sulfide production. Recent work using ethylene sulfide has not proved as successful as we had hoped. The importance of the work cannot be underestimated since our understanding of high temperature sulfur compounds is extremely sparse.

The Luminescence Process

A. Aluminum Oxidation

1. In order to better understand the low lying $A^2\Pi_i$ state of AlO, we have investigated the $A^2\Pi_i - X^2\Sigma^+$ "multiple collision" chemiluminescent emission from the reaction $Al + O_3 \rightarrow AlO^* + O_2$. Surprisingly, we have found that the constants extracted for the $A^2\Pi_i$ state by McDonald and Innes adequately describe the vibrational structure of this state to high (~ 29) vibrational levels, the behavior being indicative of a Morse oscillator. Perturbations previously observed in the $X^2\Sigma^+$ state are explicitly analyzed in terms of $A^2\Pi_{1/2} - X^2\Sigma^+$ spin-orbit interactions, and a comparison with $A^2\Pi_{1/2} - X^2\Sigma^+$ perturbations is made. Approximate populations N_v , for the $A^2\Pi_i$ vibrational levels are determined, the population distribution being dramatically non-Boltzmann. This analyzed peaking is fundamentally important to future dynamic laser induced fluorescence work and correlates closely with recent AlO results presented in a later section. The population distribution peaks at an energy just below the $v = 0$ level of the $B^2\Sigma^+$ state. This peaking can be explained in terms of efficient collisional transfer from the A state to the B state. These results are fundamentally important to our understanding of the role played by low lying electronic states in the luminescence process and hence in chemical reaction. They also should be fundamental to the study of chemiluminescence from surfaces as the enclosed preprint demonstrates.

2. For many years several researchers have concerned themselves with upper atmospheric studies of turbulence, cloud formation and numerous other phenomena. A great many of these studies have involved upper atmospheric seeding with aluminum and its compounds. The emission from exploding aluminum grenades and the oxidation of released $Al(CH_3)_3$ results in a broad continuum extending across the visible region of the spectrum. In an effort to elucidate the nature of

of this continuum (the subject of much conjecture) we have carried out several studies which we believe clarify the source of the continuum.

The reactions of aluminum with water and ozone have been studied under "single collision" conditions. We have also examined the reactions of aluminum with water, sea level air, and ozone under "multiple collision" rotationally relaxed conditions. Under multiple collision conditions the aluminum-ozone reaction is found to yield resolvable vibronic levels in the spectrum of AlO, whereas reactions with water and sea level air yield a broad emission continuum, due to a polyatomic emitter. The combination of single and multiple collision studies indicates that the continuous emission results from the formation of a metal hydrate. Quenching of the observed emission with H_2O , CO_2 , and O_2 has been examined and found to be rather efficient.

This work is of fundamental importance to our understanding of those processes which characterize seeding studies with aluminum and its compounds. There is no doubt the substantial revision of current models and several new kinetic studies will result from the present discovery. A preprint will be available shortly.

B. Germanium Oxidation (Initial Silicon Studies)

We have studied both the single and multiple collision chemiluminescence from the $Ge-F_2$, and $Ge-O_3$ reactions yielding GeF and GeO . In addition we have studied the $Ge-N_2O$ and $Si-N_2O$ reactions under single collision conditions. The analysis of the single collision spectrum is greatly facilitated through use of the multiple collision results. Both GeO and SiO spectra appear to be characterized by emission from three excited states. We observe the $a^3\Sigma^+ - X^1\Sigma^+$, the $b^3\Pi - X^1\Sigma^+$, and the $A^1\Sigma^+ - X^1\Sigma^+$ band systems. The analysis of the multiple collision GeO ($Ge + O_3$) spectrum is almost complete and confirms our observation of these states. Combining the multiple collision studies with

our single collision work we are analyzing interactions and collisional transfer between excited electronic states in a manner similar to that used for AlO and have determined a lower bound to the GeO dissociation energy from the single collision spectrum. The SiO chemiluminescence from the Si-N₂O reaction will be studied under multiple collision conditions and single and multiple collision studies of the Si-O₃ reaction will be carried out shortly from which we will deduce state interactions and determine the SiO dissociation energy (renewal proposal 2).

The GeF chemiluminescent spectrum is identified with emission from the A²Σ⁺ state and we observe emission from levels v' = 0 → 12. The luminescence observed corresponds to the A²Σ⁺ - X²Π band system. The germanium oxidation studies should be in preprint form shortly. The analysis is being carried out by Dr. E. Weinstock in our laboratory.

Inorganic Hydride Oxidation

We have studied the chemiluminescent reaction between hydrogen telluride and fluorine. This reaction produces an intense emission spectrum in the region 3900-5200 Å due to the previously unobserved TeF radical. The structure of the vibronic bands arising from transitions between ²Π_i states has been assigned by analogy with the similar spectrum of SF. From the extrapolated convergence limits of the emission spectrum the dissociation energy of the ground X(²Π_{3/2}) state of TeF is shown to be 97.7 ± 19.5 kcal/mole. A preprint of this work which involves the initial phases of inorganic hydride combustion studies will be available shortly.

Additions to the Aggregates Experiment - Continuous Wave and Pulsed Dye Laser Systems

The aggregates apparatus is quite similar in design to that presented schematically in progress report C00-2569-2 however there have been several significant changes.

1. High resolution scanning capability has been added to the dye laser. A solid etalon (typically 1 mm thick with 58% reflective coatings) is positioned by a galvanic scanner (General Scanning Inc.). Subsequent to modification, the scanner responds to a dc voltage in order to tilt the etalon by an angle which is reproducible to 5 micro-radians (1 arc sec).

2. A digital ramp generator was built in order to supply a highly linear, reproducible voltage ramp (or fixed level) to drive the galvanic scanner.

3. Several sets of output couplers and etalons were purchased for the dye laser. Using 2 1/2 watts of "all lines" from the argon laser, approximately 100 mW of single frequency ($\Delta\nu \approx 50\text{MHz}$) emission was obtained.

4. A cell containing I_2 vapor was built, along with a suitable detector and housing. This is intended to supply an accurate calibration for excitation spectra carried out on the metal clusters.

5. The copper nozzle (coherent radiation) which forms the dye jet in the dye laser was replaced by a stainless steel nozzle (coherent radiation). The latter should be less susceptible to corrosion and other deleterious effects caused by the dye solution.

6. The spectrometer (spex 3/4 meter) was outfitted with a stepping motor to allow it to be controlled synchronously with the other recording equipment.

7. Two inexpensive power-supplies (0-1500V, 0-1 MA) were assembled in order to power various detectors (i.e. PMT in I_2 cell).
8. We have been unsatisfied with the performance of the spark gap in our nitrogen laser. Therefore, we are in the process of replacing this device with a commercially available EG & G grounded grid thyatron in order to obtain more reliable pulse to pulse operation. The nitrogen laser was discussed in our previous progress report.

Metal Carbide Chemistry

With suitable modifications, it appears that the carbon source outlined in progress report C00-2569-2 can be used for the study of metal carbides MC and MC₂. Thus far we have observed what we believe to be emission from VC and VC₂ and from TiC. We are currently working simultaneously on increasing the V₂ and Ti₂ concentrations in our metal beams as well as modifying the vaporization kinetics from our carbon source. Future work will involve a analysis of the state distribution for the carbon atoms produced and necessary analysis of the metal dimers produced in a low Knudsen number environment (expansion which is intermediate between effusive and hydrodynamic).

Quantum Chemical Calculations

We are currently studying Li_3 and its negative ion. A reprint of our work on Li_2 and its negative ion is enclosed. It is important to note that the nature of electron attachment to small metallic clusters must be clarified. Such clarification may be useful in understanding the importance of charge transfer processes in catalysis as well as in determining the convergence of the properties of small metal clusters to the metallic phase.

Although we are making some progress, calculations on boron clusters are considerably more difficult. We have completed initial SCF calculations; however, these studies are not definitive because of the need for large scale configuration interaction studies. This problem is not unknown in previous studies of the B_2 molecule. We are currently transferring our SCF programs and output to the Georgia Tech computer and expect to begin further SCF and CI calculations shortly.

We are beginning calculations on larger lithium atom clusters. Currently, we will be able to study clusters up to M_8 using the PRDDO method. Here, ab-initio calculations employing a minimal basis set can be done very rapidly with minimal computer cost. These calculations will be the most accurate to date on small lithium clusters (M_n , $n \geq 4$) and will provide a strong test for future treatment of larger clusters as well as clusters composed of larger atomic entities.

A10 Excitation Spectrum

In Figure 1 we present an excitation spectrum for the A10 molecule. As our original proposal discusses, this spectrum is obtained by scanning our cw dye laser and monitoring fluorescence perpendicular to the laser beam. This spectrum is taken using only a phototube. The corresponding photoluminescence spectrum obtained with simultaneous use of a spectrometer and phototube requires further optimization of the system. Briefly, the signal levels required are considerably (10^3 to 10^5) higher and hence it is necessary to achieve optimal conditions. By adjusting the laser to the corresponding transitions in Figure 1, we have observed weak photoluminescence from the $v' = 11, 12, 25,$ and 27 levels of the $C^2\Pi$ state of A10. The system will be optimized further; however this optimization can be greatly facilitated and improved with the acquisition of an optical multichannel analyzer. We discuss this point further in our renewal proposal.

Figure 1
 AlO Excitation Spectrum
 $C^2\Pi - A^2\Pi$
 $C^2\Pi - X^2\Sigma^+$

Principal Investigator

The principal investigator has devoted $\approx$ 40% of his research time to the present research efforts outlined in this proposal. This amounts to approximately 25 or more hours per week.

Personnel

Mr. Donald Preuss is a graduate student currently working on and supported by this project. Mr. Preuss will continue working with the group for at least one year as a technician-graduate student at Georgia Tech. Mr. Michael Sayers and Mr. Roger Jones have worked on the project but will remain at M.I.T. Graduate students working on this project but supported by other sources include Mr. Carl Chalek and Mr. Donald Newlin. Professor Elliott Weinstock has participated in this work over the summer and has been supported as a part time researcher. In addition Mr. Gary Brennen and Mr. Steve Oblath have been supported as undergraduate research participants on the project.

Public Relations

Seminars and invited papers describing ERDA sponsored research were given at the following locations

University of Michigan	10 February 1977
University of Iowa	11 March 1977
Aerospace Corporation	15 March 1977
Exxon Central Research	30 March 1977
Georgia Institute of Technology	20 April 1977
	21 April 1977

The principal investigator will be the guest of the Union of Soviet Socialist Republics where he will present a series of lectures.

Preprints Removed

Cumulative List of Publications

1. "The Temperature Dependence of Single Collision Chemiluminescent Reactions - I- Theory, D.R. Preuss and James L. Gole - J. Chem. Phys. 66, 2994 (1977) (copy enclosed).
2. "The Temperature Dependence of Single Collision Chemiluminescent Reactions - II - Experimental Studies, James L. Gole and D.R. Preuss - J. Chem. Phys. 66, 3000 (1977) (copy enclosed).
3. "Single Collision Oxidation of Vanadium with NO_2 and O_2 ", Roger W. Jones and James L. Gole, J. Chem. Phys. 65, 3800 (1976) (copy enclosed).
4. "Bimolecular, Single Collision Reaction of Ground and Metastable Excited States of Titanium O_2 , NO_2 and N_2O - Confirmation of $\text{D}_0^0(\text{TiO})$." Lawrence H. Dubois and James L. Gole, J. Chem. Phys. 66, 779 (1977) (copy enclosed).
5. "Kinetics of Metastable Excited State Products in a Beam-Gas Chemiluminescent Reaction," J.L. Gole, D.R. Preuss, and C.L. Chalek, J. Chem. Phys. 66, 548 (1977)(copy enclosed).
6. "High Temperature Chemistry - Modern Research and New Frontiers", J.L. Gole, Annual Review of Physical Chemistry, 27, 525 (1976) (copy enclosed).
7. "The Use of Temperature Dependent Reaction Rates to Correct Metal Oxide (Halide) Dissociation Energies as Determined from Chemiluminescent Reactions, D.R. Preuss and James L. Gole, J. Chem. Phys. 66, 880 (1977) (copy enclosed).
8. "Single Collision Chemiluminescent Studies the La-OCS Reaction - Vibrational Analysis of the $\text{LaS } C^2\Pi - X^2\Sigma^+$ System and Determination of $\text{D}_0^0(\text{LaS})$, Roger W. Jones and James L. Gole, Chem. Phys. - 20, 311 (1977) (copy enclosed).

9. "Ab-Initio Study of the Structure of Li_2^- ", D.A. Dixon, J.L. Gole, and K.D. Jordan, J. Chem. Phys. 66, 567 (1977) (copy enclosed).

Publications Submitted

1. "Chemiluminescence from $\text{Al} + \text{O}_3$: Perturbations, Populations, and Vibrational Analysis for the $\text{AlO } A^2\Pi - X^2\Sigma^+$ Transition", Michael J. Sayers and James L. Gole. (copy enclosed)

Publications in Preparation

1. "A Correlation of Activation Energies and Mechanisms for Group IIIB- (Sc,Y,La) Metal Oxidation with O_2 , NO_2 , and N_2O ", James L. Gole.
2. "Single and Multiple Collision Chemiluminescent Studies of the Ge-F_2 and Ge-O_3 Reactions", Elliott M. Weinstock, Steven Oblath and James L. Gole.
3. "On the Upper Atmospheric Emission Observed Upon Oxidation of Aluminum and Its Compounds" Steven Oblath and James L. Gole.
4. "Chemiluminescence from Oxidation of Inorganic Hydrides' Spectrum of TeF ", Donald Newlin, Gerald Stewart and James L. Gole.