MASTER

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

Progress Report
for Period March 1, 1975 - November 20, 1975

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November 1975

Prepared For

THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. E(11-1)-2569

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Abstract

We discuss the formulation and development of versatile oven systems for high temperature metal vaporation at temperatures in excess of 2000°C. The construction of an apparatus appropriate to the production and study of small metal aggregates M_n ($2 \leq n \leq 6$) is discussed at length. This includes a consideration of the construction and operation of an argon ion pumped dye laser system. The dye laser system will be used to induce fluorescence from the small metal aggregates, and thereby will lead to the study of their molecular electronic structure. The production of carbon vapor and the reaction of this vapor with metal atoms and metal dimers to form metal carbides is outlined.

We outline a thorough study of the luminescence process leading to a new understanding of those chemiluminescent phenomena occurring as a result of the "single collision" bimolecular reaction of metal atoms and metal dimers with select oxidants. This study presents methods for the determination of upper bounds to the heats of sublimation and vaporization of those metals which can be strongly oxidized in a "single collision" bimolecular reaction. In addition, extremely simple methods by which one can infer the radiative lifetimes of metastable product chemiluminescing molecules are discussed. We outline beginning efforts toward the

formulation of new and novel catalytic surfaces via aggregate deposition. Current studies of the titanium oxide system are presented. These chemiluminescence studies allow the determination of a lower bound to the TiO dissociation energy and a determination of the heat of vaporization of titanium metal.

Our focus during the first grant period can be grouped into five main efforts

(1) The formulation and development of versatile oven systems for high temperature metal vaporization and the construction of an apparatus appropriate for the study of small metal aggregates M_n ($2 \leq n \leq 6$) at temperatures in excess of 2000°C .

(2) The investigation of various carbon sources to be used in the production of carbon vapor whose constituency is primarily C_1 , C_2 and C_3 . These carbon sources are to be 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.

(3) The construction of a dye laser module for use in the study of the molecular electronic structure of those metal aggregates formed in the newly devised high temperature ovens.

(4) Beginning efforts on the construction of an apparatus appropriate for the study of new and novel catalytic surfaces produced via aggregate deposition.

(5) A thorough study of the luminescence process leading to a new understanding of those chemiluminescent phenomena occurring as a result of the "single collision bimolecular reaction of metal atoms and metal dimers with select oxidants. From these studies we have determined the method by which one can extract upper bounds for the latent heats of vaporization and sublimation of those metals which can be oxidized in a "single collision" bimolecular reaction giving rise to chemiluminescent emission from excited electronic states. In addition, we have arrived

at a formulation which allows us to deduce the activation energy for formation of product molecules in a selected excited state populated through single collision bimolecular reaction. The above mentioned quantities can be deduced from the temperature dependence of the observed chemiluminescent spectrum. A preprint describing this work is enclosed.

In a tandem effort directly related to our activation energy studies, we consider the influence of excited state radiative lifetime on the molecularity of the chemiluminescent emission which emanates from product molecules formed in long lived excited electronic states. A manuscript is in preparation entitled "The kinetics of metastable excited state products in a beam-gas chemiluminescent reaction--the definition of a single collision process in a beam-gas experiment." If the radiative lifetime of an excited state product molecule exceeds the mean time between collisions in the pressure range over which the chemiluminescent emission is studied, we will observe an effect in the pressure dependence of the chemiluminescent intensity. We find that processes which are expected to be bimolecular and first order in both metal and oxidant display a "faster than first order" dependence on oxidant pressure. This phenomena coupled with activation energy studies serves to signal the presence of a metastable excited state.

As an example we consider the reaction

discussed in the enclosed preprint (pgs 14-18). We have monitored the temperature dependence of the chemiluminescent emission from the $\text{SrF}^* \text{C}^2\Pi$ and $\text{D}^2\Sigma^+$ states and have deduced that the activation energy for formation in these states is equal within experimental error. Yet there is a considerable difference in the emission intensity from the two states both of which are easily accessible by virtue of the exothermicity of the $\text{Sr} + \text{F}_2$ reaction. We suspect that the much weaker emission from the $\text{D}^2\Sigma^+$ state results from a much smaller oscillator strength and hence much longer radiative lifetime. Figures 1 and 2 (following), which display the dependence of the $\text{C}^2\Pi$ and $\text{D}^2\Sigma^+$ SrF^* emission features on oxidant pressure, support this conclusion. The $\text{SrF}^* \text{C}^2\Pi$ emission is characterized by a linear onset while the $\text{D}^2\Sigma^+$ emission is characterized by a "faster than first order" (sometimes wrongly equated with quadratic) pressure dependence.

This work is of fundamental importance to the present ERDA research effort. In deducing metal carbide bond energies, we must know the kinetics of those processes leading to metal carbide chemiluminescent emission. The group of studies which we have outlined under effort (5) serves as a means of unraveling the complex relations between molecular dynamics and molecular electronic structure. This work provides us with a means of deducing, very rapidly, whether or not an excited state is metastable. We believe that this result will represent an important practical tool. In summary, we have laid the framework for the study of metal carbide formation and metal aggregate oxidation. This work is being submitted for publication in the Journal of Chemical Physics.

Figure 1

Figure 2

Metal Aggregates Apparatus

The apparatus which we have constructed to study metal aggregates is depicted in Figure 3. The figure includes our Model I all tungsten oven. The system features a radiator constructed from woven tungsten. This radiator is capable of extended operation at temperatures in excess of 3000 K. The radiator heats tungsten or tungsten carbide crucibles, the former obtained through vapor deposition techniques (dissociated WF_6) and the latter through a delicate pressing and sintering process. These crucibles are relatively unique. Present plans call for the construction of tantalum, titanium, and zirconium carbide crucibles. We expect to obtain crucibles of these materials before the end of the present grant period (February 29, 1976). This grouping gives us a good arsenal with which to approach the high temperature vaporization of the metals of interest. At present, the radiator and crucible are surrounded by three layers of tungsten shielding and a copper cooling jacket. The oven system (Model I) is currently assembled in our vacuum chamber; however we do not expect to use this oven for an extended period and a new oven (Model II) is currently under construction in the chemistry department shops. The present system should be operable to 2400 K, while the Model II version will be operable to 3000 K. The Model II includes revision of present cooling jacket and heat shielding as well as the facility for larger and more versatile ovens. In addition, more shielding can be added over and above that necessary to obtain 3000 K temperatures and we hope to reach an operating limit of 3300 K. In order to operate the present

METAL AGGREGATION APPARATUS

Figure 3

systems, we have purchased a 12KVA variac (\$395) and a 12KVA transformer (\$487) under the category of oven facilities. We are currently testing our system using the model I oven facility. A thermostat to be used to control the high temperature oven systems is being constructed. It will consist of a feedback loop from a thermocouple in the oven. The BCD output from a DVM is fed into a comparator circuit to determine whether more or less power to the oven is needed. A logic pulse from the comparator will trigger a triac to shut off the power to the oven for 16 msec at a time if the oven temperature is too high. (At maximum oven power, the oven will cool by about .5K in 16 msec.) The unit is capable of switching 50 amps at 240 volts.

Once the metal vapor is generated, it can be expanded effusively (typical oven pressures 10^{-1} to 1 torr, typical exit slits ~ 100 mils) or hydrodynamically (typical oven pressures ~ 10 to 100 torr) through a nozzle opening (diameter ~ 16 mils or less) into a vacuum of about 10^{-6} torr. In principle, a hydrodynamic expansion should lead to a tremendous cooling of the internal degrees of freedom for those molecules formed in the beam and to a collapse of the Maxwellian velocity distribution along the beam axis (resulting in a relatively low beam divergence). This hydrodynamic expansion should give rise to a super-saturated metal vapor which undergoes nucleation leading to the production of polyatomic species. As is apparent from Figure 3, the metal beam expands into the scattering chamber where it can be probed with the output of an argon ion laser or the output of a cw dye laser. The laser beam is directed through the top of

the scattering chamber via a micrometer mounted prism arrangement. The motor driven micrometer facilitates the scanning of the beam divergence. This is important since we expect to induce a spatial distribution in the hydrodynamic expansion with heavier aggregates located closer to the beam axis. For our initial experiments, we have fit the chamber with a two inch circular window; however, an appropriate 1"x8" rectangular window is constructed and ready for use. The effective operation of this system requires extensive light baffling (alleviation of scattered laser light) as indicated in Figure 3.

In order to facilitate the reliable operation of the oven system, we have purchased a 6" diffusion pump which has been installed below the oven. Because of the nature of nozzle expansions, we require extensive pumping in order to insure the desired system characteristics and to lessen the probability of oven blockage. The diffusion pump has been purchased under oven facilities at a cost of \$884.

We have purchased and installed the quadrupole mass analyzer indicated in the figure. This mass analyzer can detect masses up to 400 amu with a resolution of 1 amu. Both digital and analogue outputs facilitate interfacing with recording equipment. Details concerning the installation are as follows.

- 1) An in-line valve, and a 25 l/sec ion pump allow the system to be kept at a pressure of 10^{-9} torr when not in use.
- 2) A movable aperture was built to stop down the metal beam,

thereby minimizing the tendency to plate out metal on the elements in the analyzer probe.

- 3) The metal beam is directed normal to the quadrupole field so that neutral metal atoms passing through the ionizer will plate out on the chamber wall, and not on the quadrupole field rods in the probe.

The cost of this mass analyzer system increased substantially over the period in which the grant was considered for funding. The total cost was \$14,000.

The complete aggregates apparatus can now be used to carry out simultaneous mass analysis and laser induced excitation spectroscopy on small metal aggregates, M_n ($2 \leq n \leq 6$).

Carbon Vapor Source

We are investigating several possible sources for the production of carbon vapors (C_1 , C_2 , C_3). Our present carbon vapor source is depicted in Figure 4. This device has been used to heat the dumbbell shaped carbon insert to temperatures in excess of 2400 K. The stainless steel flexible tubing has recently been inserted to allow for the relief of strain in the very hot carbon source. We are presently preparing to test this device and feel that it will be superior to traditional arc-furnace systems. The entire carbon source is water cooled. It will be placed in an insert above the spectrometer window in the apparatus shown schematically in Figure 5. The system requires cautious masking of the black-body radiation emanating from both the carbon source and the metal oven. In our initial studies, using the present carbon source, we will also use the oven system depicted in Figure 6 and will attempt to form the vanadium carbides VC and VC_2 .

CARBON VAPOR SOURCE

Figure 4

Figure 5

Figure 6

Dye Laser System

A. Dye Module

A cw dye laser was constructed. The 200 cm folded cavity is partially corrected for astigmatism. The optics which define the cavity length are supported by four invar rods. The dye jet is pumped by a cw argon ion laser in a near-longitudinal configuration in which the argon laser beam makes about a 5° angle with the dye laser cavity. Frequency selection is accomplished by a three stage Lyot filter, and one or two tilt tuned, solid, intra-cavity etalons. The solid etalons are to be replaced by two pressure tuned air gap etalons (now under construction). The total cost of the module includes all associated optics and mounts, the dye pump and flow system, and a 2' x 8' x 4" stainless steel breadboard (\$1120) which supports both the dye laser and an argon ion laser. Total cost $\approx$ \$4000.

B. Argon Ion Pump Laser

As indicated in our original proposal, we have been the "proud" possessors of an argon-ion laser produced by Control Laser Inc. Considerable work was done on this laser in order to achieve acceptable performance in pumping the dye laser module. A change in the wiring in the power supply increased the ion laser power output at $5145\text{\AA}$ from 900 mw to 2.5 watts (specified power at $5145\text{\AA}$ --3.5 watts). The efficiency initially obtained in pumping the dye laser was about 1%. (The expected optimum efficiency for broad band operation is 20-25%.) Replacing the dye laser jet and realigning the optics increased the efficiency to 3%. Rotating the polarization of the argon laser output with a half wave plate increased the efficiency to 11%. The discrepancy between this efficiency and the optimum expected efficiency suggested that the argon laser was operating in higher radial modes than TEM_{00} (specified to lase in TEM_{00} only). A quantitative measurement of the beam intensity profile indicated that for any reasonable output power of the argon laser (greater than 1 w at $5145\text{\AA}$) about half of the power was in the 1-0 radial mode (doughnut mode) and was not available for pumping the dye laser. We contacted the company and they openly admitted that their carbon-bore design did not perform up to specifications after several hours of run time. They suggested that we buy one of their new tungsten bore lasers or that we attempt to correct the defect in our laser by purchasing appropriate materials so as to increase the radius of the argon ion laser beam. This adjustment effectively amounted

to the insertion of an aperture in the laser cavity, that is a device which causes losses in high order radial modes and thus allows only amplification of the TEM_{00} radial mode removing higher order radial mode structure. This, however, must be compensated by severe losses in TEM_{00} as well.

In addition to the problems encountered with the mode structure of the laser, we found it to be thermally unstable. That is, the optical mounts required constant alignment whenever the plasma tube and hence the optics changed in temperature (operation at different power levels). In summary, we found that the laser was a very inferior product.

Mr. Donald Preuss attempted to insert an aperture into the control laser cavity. His efforts resulted in irreparable damage to the laser tube. We were left with the choice of purchasing a new tube for \$2800 or trading in our laser to Control and purchasing their tungsten bore laser for \$6300 (\$2000 for the carbon-bore laser in trade). At the time this offer was proposed, the President of Control Laser admitted that they had sold us an inferior product. Shortly after our discussions with Control Laser, we received a very good offer from Spectra Physics for a comparable laser system. We felt that Spectra Physics produced a much more reliable product. They offered to sell us a demonstrator laser for \$9000. We contacted our contract monitor, Dr. Robert Epple, and he agreed to a transfer of \$4500 from salaries and wages to permanent equipment. This transfer was accompanied by a similar transfer in our NSF grant. Hence we are in the process

of purchasing the much more reliable Spectra Physics laser.

The now nonexistent excess of funds in salaries and waves resulted from delays in the arrival of a budgeted postdoctoral fellow.

The appropriate transfer of funds is currently being processed through the institute.

Catalysis Apparatus

An undergraduate in our laboratory is engaged in the construction of an apparatus which we hope will lead to the formulation of new and versatile (heterogeneous) catalytic surfaces. This work is in large part based on the development of new high temperature oven facilities. The apparatus is shown in Figure 7. Here a metal beam expanded hydrodynamically, flows upward from an oven within the reaction chamber and coats an alumina screen to form a catalytic surface. We hope to take advantage of the low internal energy which characterizes polyatomic species produced via hydrodynamic expansion. We hope to test whether this method of production will minimize "surface migration" and the formation of large metallic surface clusters, hence allowing for formation of larger effective catalytic surface areas. In other words, we are asking whether we can improve on the presently available commercial catalytic surfaces.

After a short period of deposition the alumina screen will be rotated to a vertical position to become an interface in a vacuum line through which various species of interest can be passed. The experiments will be carried out in the pressure range $\approx 10^{-6}$ torr. The specificity, selectivity, and applicability of these newly generated surfaces will be tested for catalytically enhanced oxidation, reduction, hydrogenation, hydrogenolysis, isomerization, and polymerization.

figure 7: Heterogeneous Catalysis Apparatus

Figure 7

The Titanium Oxide System

We are currently applying the beam-gas chemiluminescent technique to the titanium-oxygen system. These studies allow us to determine $D_0^0(\text{TiO})$ and an upper bound to ΔH vaporization (Ti). This work is warranted for several reasons.

- (1) Considerable interest has centered on the value of the dissociation energy of $\text{TiO}(\text{g})$ since titanium oxides are important in many commercial applications.
- (2) The vaporization of titanium and hence the development of reliable titanium sources is of primary importance to both our metal carbide and metal cluster studies.
- (3) The previous determinations of the TiO bond strength fall across a considerable range from 157 to 168 kcal/mole.
- (4) Preliminary studies in this laboratory indicate that the actual bond energy is somewhat higher than the upper limit of the range of values quoted in the literature.

Figure 8 represents a tracing of the emission spectrum which emanates from the Ti-O_2 reaction. The visible chemiluminescence is dominated by the $\text{C}^3\Delta\text{-X}^3\Delta$ band system of TiO . We are currently studying this emission spectrum and the detailed kinetic mechanism leading to the formation of $\text{TiO}(\text{C}^3\Delta)$. This work should be completed by the end of the initial contract period.

Figure 8

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

Dr. Derek Lindsay is a postdoctoral research associate who has been supported on the project since September 1, 1975. Other graduate students working on this project, but supported by fellowships or teaching assistantships include Mr. Donald Preuss and Mr. Carl Chalek. In addition, Mr. Brian Silverman, Mr. David Niver, and Mr. Larry Dubois are undergraduate research participants on this project.

Public Relations

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

Yale University, 4/14/75

Rochester University, 11/12/75

Publications Submitted

"Determination of Latent Heats of Sublimation, Latent Heats of Vaporization, and Selected State Activation Energies from Intensity Measurements of Beam-Gas Chemiluminescent Reactions. D. R. Preuss and J. L. Gole--submitted to J. Chem. Phys.

Publications in Preparation

1. "The Kinetics of Metastable Excited State Products in a Beam-Gas Chemiluminescent Reaction--The Definition of a Single Collision Process in a Beam-Gas Experiment."
D. R. Preuss, J. L. Gole, and C. Chalek.
2. "Determination of $D_{O}^O(TiO)$ and $\Delta H_{\text{vaporization}}(Ti)$ from a Beam-Gas Chemiluminescent Experiment." J. L. Gole.