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This review provides a record of research in progress, along with illustrative achievements resulting from the basic research program of the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFSC). The first section of the document contains articles written by each of the Chemistry Program managers at AFOSR plus a report on a typical in-house research project conducted at an AF lab and a survey of chemistry research in Europe. The second section contains program statistics. The third section lists research efforts completed in FY-78.

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CHEMISTRY PROGRAM REVIEW

FY78

RICHARD W. HAFFNER, EDITOR

MARCH 1979

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
DIRECTORATE OF CHEMICAL SCIENCES
BUILDING 410
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MISSION

The Directorate of Chemical Sciences of the Air Force Office of Scientific Research has the mission to encourage and support fundamental research designed to increase knowledge and understanding to stimulate the recognition of new concepts, and to provide for early exploitation of their military implications.

The Directorate obtains and maintains for the Air Force a diversified program of research at in-house laboratories as well as extramurally at university and industrial laboratories. The Directorate also functions as a dynamic interface between the Air Force and the scientific community, ensuring the free, full, and constant interchange of ideas from each to the other through publications, personal contacts, meeting attendance, and sponsored symposia. In these ways the Directorate helps the Air Force maintain technological superiority.

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DEPARTMENT OF DEFENSE
UNITED STATES OF AMERICA

TO: FRIENDS OF AFOSR

The purpose of this report is to review some selected program highlights from the past year. It is an occasion as well for an assessment of the future. Because of projected resources - in funds and personnel - our outlook can be an optimistic one.

The Program Review emphasizes the Directorate contract and grant program as it always has. It is important to realize also that the overall Air Force research program for which the Director is responsible is performed at six in-house laboratories, as well as at over a hundred extramural locations. Recently, the Directorate responsibilities were expanded to include atmospheric sciences as well as chemistry. The overall Air Force research budget is about $15,000,000 in FY 79 for these two disciplines.

Within the Directorate there have also been changes in personnel. Dr. Frank Wodorczyk left us to join private industry while Dr. Bob Osteryoung returned to Colorado State University. Lt Colonel John Viola moved to the Electronic Systems Division. Soon to move to another assignment in the Plans Office at AFOSR is our able editor, Lt Colonel Dick Haffner. Fortunately, losses in staff are matched by corresponding gains. Dr. Don Ulrich has returned from the Air University. Captain Russell Armstrong has joined us from the Air Force Weapons Laboratory. Most recently, Captain Lorelei Krebs has assumed program manager duties following completion of her advanced degree requirements. Major William McKechney transferred from the Directorate of Physics with his duties in the atmospheric sciences.

Despite the importance of an able staff, they do not achieve the real purpose of our program--namely, research of value and importance to the Air Force. We facilitate the contributions of the real performers and seek rapid transition of their results to technology. There is no way to acknowledge the individual efforts of all the hundreds of principal investigators supported over the past quarter century. I would merely close with a mention of one of the very best, Professor Herb Broida. His contributions as a researcher and as a teacher of research were truly remarkable. I am proud that his efforts were supported by this Directorate as early as 1954, at the National Bureau of Standards, and as recently as 1978, at the University of California, Santa Barbara. His passing was sudden and untimely; we all regret it very much.

Sincerely,

Donald L. Ball

DONALD L. BALL
Director, Chemical Sciences

THE SURFACE CHEMISTRY OF LOW WORK FUNCTION CATHODES

DR. T. W. HAAS*

AIR FORCE MATERIALS LABORATORY

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Whenever a television set is turned on, a process of electron emission from a low work function oxide cathode is necessary for the operation of the picture tube. This cathode is typically a 3mm diameter sleeve of nickel or nickel alloy with a small quantity of some compound of barium, strontium and calcium on the emitting surface as the active layer. This cathode, as well as other types, has been known, used, and studied for many decades. The early history of research in this area includes such names as Langmier, Shottky, Richardson, Dushman, Nottingham, and others. Despite the amount of research expended in such studies, a generally accepted model for the activation, operation, and poisoning of low work function cathodes has not been developed. Several models have been proposed and evidence in support of one or the other has been gathered; however, conclusive experiments have not as yet been reported.

As often happens, a combination of need and opportunity may resolve this situation. The Air Force is currently interested in the development and understanding of improved cathodes for spaceborne travelling wave tube (TWT) applications. TWTs are microwave power amplification devices used in our satellite systems for communications purposes. TWTs are also used in other non-space applications such as in electronic countermeasure systems. Our current interest in cathodes stems from a need for higher power and higher frequency TWTs, requirements which cannot be met with current cathodes. The laws of electron optics impose limits on power and frequency domains for these tubes which relate directly to the emission current density of the cathode. Improved cathodes are potentially available but they will not be used in expensive satellite systems until engineers are convinced of the reliability and lifetime of these new tube elements. One step in providing such confidence is to prove conclusively the correct model for the operating cathode and, hence, provide realistic lifetime predictions. The Air Force Materials Laboratory, as well as other laboratories, particularly Navy and NASA, is currently engaged in research programs of this type and progress is being made rapidly.

DIFFERENT TYPES OF LOW WORK FUNCTION CATHODES COMMONLY IN USE TODAY

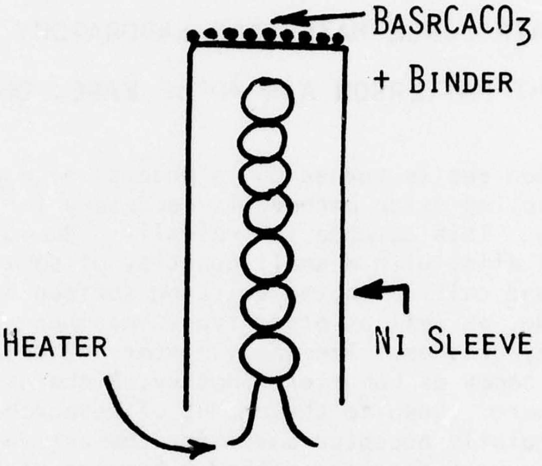


FIGURE 1-A. Oxide Cathode

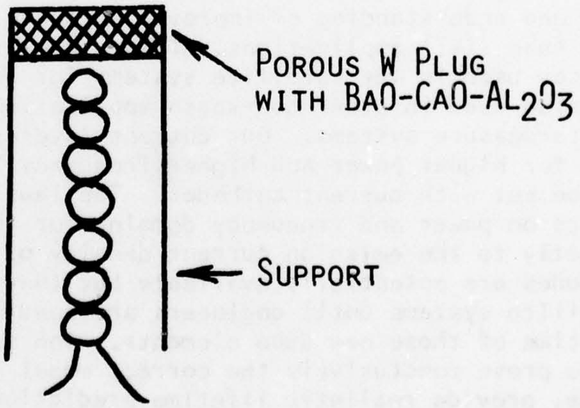


FIGURE 2-B. Dispenser Cathode

The types of low work function cathodes that I shall discuss here all have one chemical element in common: barium. Other elements present in the cathode system acting as promoters, activators, supports, etc. include strontium, calcium, aluminum, nickel, tungsten, zirconium, and others. The exact role of these elements is not known and probably varies with the type of cathode. Several types of cathodes (1) are illustrated schematically in Figure 1. The most common type and the one currently used in most Air Force spaceborne TWTs is the oxide type (figure 1-A). It generally consists of a nickel-zirconium alloy sleeve with a mixture of barium-strontium or barium-strontium-calcium carbonates. During activation the carbonates are converted to oxides and some process takes place which lowers the work function to values of 2eV or less. Continuous current densities available for such cathodes operated at about 700-800°C are 100-200mAmp/cm^2.

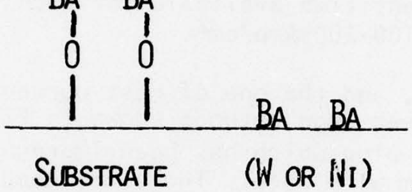
Another type cathode, and the one of most current interest to the Air Force, is the dispenser type cathode shown in Figure 1-B. It consists of a porous tungsten plug which has been impregnated with a compound of barium and calcium aluminate. The exact composition varies with claims of improvements for various starting compositions. In this cathode, during activation, a reaction occurs in the pores of the tungsten plug and barium or barium oxide is liberated which migrates to the surface resulting in a work function lowering. Typically, the dispenser cathode operated at 900-1050°C can provide continuous current densities of 1-10 Amp/cm^2, a considerable gain over the oxide type. The relation between work function and operating temperature is analogous to the case of a basketball coach who wants more players to "stuff" the ball in the basket. He may either lower the basket (work function barrier) or increase his proportion of taller players (raise the temperature).

Other types of cathodes exist as well. One of these being studied at present includes the Medicus cathode (a nickel matrix type) as well as variations of the dispenser cathodes. In all cases, barium is present and appears to be responsible for the work function lowering.

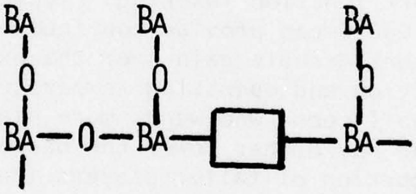
A number of models have been put forth to explain the work function lowering during activation and the subsequent operation of such cathodes. The two most accepted of these at present are the thin film model proposed first by Koller in 1925 and the semiconductor model of Eisenstein proposed in 1948. The thin film model (Figure 2) proposed that the work function lowering is due to the generation of an electro-positive element, barium in this case, on the surface by some bulk chemical reaction. This creates a strong dipole layer which lowers the potential energy barrier to the escape of electrons so that the emission takes place at lower temperatures. In this model, lifetime would be predicted by the kinetics of the reaction generated by barium, the amount of each reactant available, and the evaporation rate of barium from the surface.

THEORIES OF CATHODE ACTIVATION

THIN FILM MODEL



DEFECT MODEL



Two different models for operational low work function cathode. The thin film model postulates a work function lowering due to the strong dipole layer created by a film of Barium metal over oxygen on tungsten or on clean tungsten. The defect model proposes oxygen vacancies (square in figure) as a mechanism for adjusting the position of the Fermi level in the bulk material (in this case barium oxide).

FIGURE 2

The semiconductor model, Figure 2, suggests that the active layer on the surface is barium oxide (BaO). BaO is a semiconductor compound that has been studied by a variety of techniques. The semiconductor model proposes that activation is caused by the creation of oxygen vacancies in the lattice which adjusts the Fermi level of the material. Lifetimes would be predicted by poisoning the semiconducting layer (analogous to doping semiconductor solid state materials to produce p-n junctions, etc), evaporation of the active BaO layer, and other effects which may influence its semiconductive properties such as changes in crystallography.

At present several experimental approaches are being taken to verify a model of the operational cathode. I will not review the earlier work in this area, that is well covered by Zahm (2), but rather concentrate on the recent applications of surface analysis and characterization techniques. In one experiment, an Auger electron spectroscopic analysis of a dispenser type cathode was performed during activation and operation. (3). Considerable cleaning of the surface took place during this activation; e.g., reduction of carbon containment, sulfur removal, etc. The best semiquantitative estimates available from that work led to a model of one monolayer barium over oxygen over tungsten. The chemical states of these elements were not identified in this work. Later, Forman (4) investigated similar cathodes and, using low energy Auger spectra and chemical changes in these spectra, suggested that the barium was in a metallic-like state, something of a vote for the thin film model. However, Haas et al (5) utilizing a new technique, low energy electron reflection, investigated changes in the electron affinities of BaO films on iridium (100) surfaces and obtained evidence in favor of the semiconductor model. It is possible that different types of cathodes are best described by different models.

Experiments in progress at the Air Force Materials Laboratory will hopefully shed additional light on this controversy. It is well known that x-ray (XPS) and ultra-violet (UPS) photoelectron spectroscopies can be used to define chemical states and valence band information for solid surfaces. We are presently investigating these photoelectron spectra for various dispenser type cathodes. Line shifts in XPS have been observed in this work, but interpretation is always complicated by solid state effects. A series of experiments on carefully prepared standards will hopefully resolve this problem. Along these same lines, we are performing XPS, Auger, and LEED investigations of barium and BaO films on tungsten single crystals, the (110) plane being of primary interest. It is known from many LEED investigations that high index, less closely packed faces of tungsten single crystals tend to facet into more dense planes, with the most densely packed (110) being the most favored in the presence of oxygen. The heating of cathodes during their operation in the presence of oxygen may induce micro-facets on the small tungsten grains in the porous cathode surface so that a model for an operational cathode may be closely approximated by a layer, or layers, of barium and BaO on tungsten (110) single crystals.

From measurements and ideas such as those outlined here, I am confident that, in the near future, an answer to a very old question - "Why do low work function cathodes work?" - will finally be obtained. It is a shame that many of the famous scientists mentioned earlier who have worked on this problem are no longer alive to share the excitement.

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*Dr. Haas has been a research chemist with the Air Force since 1964. Presently, he works in the Mechanics and Surface Interactions Branch, Non-metallic Materials Division, of the Air Force Materials Laboratory. His major interest is surface chemistry and physics. Specifically, Dr. Haas has made major contributions to the field of electron spectroscopy of surfaces. The work he describes in this article is an excellent example of the high caliber research conducted "in-house" by Air Force scientists.

A STATUS REPORT FROM ABROAD

Major Charles J. LaBlonde*

In the previous AFOSR Chemistry Program Review, Lieutenant Colonel David W. Seegmiller presented a comprehensive overview of chemistry in Europe and Israel. His general observations regarding facilities and costs remain valid and are in fact borne out by the current chemistry program as monitored at EOARD. At year's end this program consisted of a healthy 21 projects, mostly in Israel and the United Kingdom which were the two areas identified as most cost effective by Lt Colonel Seegmiller. A number of interesting new projects were started this year. The following paragraphs will briefly describe projects in electrochemistry and molecular dynamics, followed by a short discussion of conference support.

Electrochemistry. There are currently four electrochemistry projects in Europe, three of which relate to solid state batteries with energy densities around 200 Wh/kg. Dr. B. C. H. Steele, Imperial College, London, is investigating lithium based anodes for potential use in solid state batteries. Initially he synthesized and characterized a number of ternary phosphides; based upon voltammetric evidence, the most promising compound to date is of the form Li_xMnP. Work is in progress to further investigate the activity of lithium and the electronic conductivity as functions of composition. A drawback noted to date is the moisture affinity of the ternary phosphides, possibly due to the high lithium activity. For this reason a small portion of the project is aimed at synthesis of new materials while the majority of the project will be directed towards investigation of lithium transport across solid anode/solid electrolyte interfaces over a temperature range of 25-300°C.

Many fast ion conductors are known in nature and a few have become very important in technological applications. But relatively little is known about the basic mechanisms of ionic transport, the point defect structure and self-diffusion parameters in these materials. Such is the basis of a study by Drs. Alan Chadwick and John Strange, University of Kent, Canterbury, who are studying fast ion transport in solids. As the project is arranged, Chadwick grows the crystals of candidate fluorides and makes the conductivity measurements; Strange, using pulsed NMR, measures F^- motion within the crystals. This dual approach allows screening of selected materials at both macroscopic and microscopic levels, the conductivity being an overall measurement while the NMR actually allows closer evaluation of individual ion dynamics within the crystals. "Atom-hopping" data obtained from the NMR may be used to calculate conductivity; such calculations are in good agreement with measured conductivity. Extensive work has been concluded on LaF_3 and work is in progress on doped rare earth fluorides.

In the laboratory of Professor John B. Goodenough, Oxford University, a two-pronged study is under way to: (1) Investigate the thermochemical, structural and basic electrochemical properties of battery cathodes. (2) Design, prepare and characterize new materials exhibiting fast ion transport for use as solid electrolytes or battery cathodes. The battery cathode materials under study thermodynamically and electrochemically are ternary oxides of the type A_xMO_n where A is an alkali metal or hydrogen capable of being inserted in variable concentration x into a transition metal oxide network MO_n to give an electrically conducting product. A number of these alkali metal oxide bronzes have already been studied by the Oxford group. Professor Goodenough has pioneered the field of fast ion transport in network structures of the type $Na_3Zr_2PSi_2O_{12}$ which can be used as a solid electrolyte. He anticipates finding superior network cathode materials also.

In direct support of the Frank J. Seiler Research Laboratory, Professor Harald A. Øye, University of Trondheim, Norway, is measuring the viscosity of the ternary molten salt system $AlCl_3$-$LiAlCl_4$-$NaAlCl_4$. This program is a classic example of international cooperation. Øye has a high temperature viscosimeter which is very likely unique in the world; Seiler requires viscosity data on chloraluminate melts for their molten salt battery program. Under AFOSR sponsoship the two were brought together in a very productive effort. In a memo of agreement dated 9 March 1978 the experimental conditions were agreed upon. While Seiler measures density, melting point, vapor pressure and specific conductivity, Øye determines the viscosity of the melts. The memo defines specific compositions to be studied.

Molecular Dynamics. This category includes five projects, two of which are EOARD Low Cost Grants. One of the latter is a study of energy transfer from $N_2(A^3\Sigma_u^+)$ and $N_2(B^3\Pi_g)$ to metal atoms being conducted by Dr. Salman Rosenwaks, Ben-Gurion University of the Negev, Israel. He is applying recently developed methods for: (1) production and monitoring of $N_2(A)$ and $N_2(B)$; and (2) production of metal atoms in low translational temperature and monitoring their excitation state. The measurements are carried out as a function of reactant concentration and total pressure. Energy transfer rates from N_2 to specific energy levels of metal atoms will be calculated from the experimental data. The information obtained by Rosenwaks will contribute significantly to understanding the dynamics of electronic energy transfer.

The other Low Cost Grant is held by Dr. A. Ben-Shaul, Hebrew University of Jerusalem, who is taking a theoretical approach to the analysis, description and prediction of vibrational relaxation patterns for non-equilibrium molecular systems, especially those in which disequilibrium is due to exoergic chemical reactions (chemical lasers) or absorption of laser radiation. Ben-Shaul is concerned mainly with molecules for which exponential gap type rate constants are available, molecules such as HF, HCl, and CO. He plans to extend the study to suitable polyatomic molecules like CH_3Cl, CF_3Cl, CCl_2Br_2, CH_3OH and NH_3; for these, "synthesized" exponential gap type rate coefficients will be used.

Dr. Ian Smith of Cambridge University has completed the first two years of a five part study of energy transfer and selective chemical reaction using tunable IR radiation. Early in the study he employed a flash lamp pumped dye laser to dissociate Br_2 and IBr at selected monochromatic wavelengths; the yield of $Br^*(^2P_{1/2})$ at each wavelength was measured to help identify the unbound electronically excited states in Br_2 and IBr which are responsible for their visible continuous absorption spectra. This work is now complete. Also complete is a determination of relaxation rate constants of HCN by HCN itself and by CO_2, CO and N_2. Work in progress includes further HCN studies utilizing two different sources of excitation for comparison purposes; NO will also be studied. Other areas slated for study include a systematic investigation of the vibrational to electronic excitation of Br atoms by transfer from CO_2, HCN, N_2O and NO; reaction and relaxation by free radical atoms; relaxation kinetics of OH(v=1).

Two projects in direct support of AFWL are being carried out in the laboratory of Dr. Michael Clyne, Queen Mary College, London. In fact Captain Steven Davis, AFWL, worked with Dr. Clyne for a period during this year. The older of the two projects involves kinetic studies of electronically excited interhalogens and halogens. One result to date has been the development of a new method, using atomic resonance, to determine absolute Br and Cl atom concentrations above 10^{13} cm^{-3}. The method has been applied to a determination of the quantum resolved dynamics of electronically excited BrCl. Whilst electronic quenching is very inefficient, internal state energy transfer is rapid and dominates lifetime measurements at pressures above 50 mTorr. A zero-pressure lifetime for BrCl was obtained by extrapolation; the same lifetime will be measured under collision-free conditions in a specially developed experimental facility. Chemiluminescence spectra of BrCl from the reaction Br_2 + OClO have been obtained with partial rotational resolution; populations of individual vibrational states of BrCl will be measured. Clyne's other project involves kinetic studies of the NF chemical laser. The excited states $a^1\Delta$ and $b^1\Sigma^+$ of NF are formed in a complex reaction between H and NF_2 radicals in a flow system; the rate constant of this reaction will be measured as a function of temperature. Preliminary work indicated that free N atoms play a role in this reaction scheme; this will be investigated. $NF(a^1\Delta)$ and $b^1\Sigma^+$ quenching rates will be determined in the presence of various quenching molecules such as NF_2 and HF. The suggested inversion of NF between $a^1\Delta$ and the ground $X^3\Sigma^-$ state will be studied; a method for monitoring NF $X^3\Sigma^-$ will be sought.

Conference Support. Each year EOARD receives a large number of requests for financial support of technical meetings. The requests are evaluated for Air Force interest and a limited number are selected for low level support. Support always involves meeting the conference organizers who, in turn, are more than happy to provide introductions to other prominent workers in the field. All in all, conference support is a very cost effective method of meeting the top European names in a given field. It should be noted that meeting support always involves waiver of conference fees for one or two Air Force attendees, free copies of all proceedings and acknowledgement of Air Force support in all conference literature. During the past year EOARD supported the following meetings:

XIth International Symposium on Rarefied Gas Dynamics, Cannes, France, 3-8 July 1978

IXth International Conference on Photochemistry, Cambridge, UK, 7-9 August 1978

International Conference on Luminescence, Paris, France, 17-21 July 1978

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*Major Charles J. LaBlonde is presently the Chemistry Liaison Officer for the European Office of Aerospace Research and Development (EOARD). EOARD is a detachment of the AFOSR located in London and, among other things, provides liaison with members of the scientific and engineering community in Europe, the Near East, India and Africa.

Major LaBlonde's experience includes a tour of duty at the Air Force Academy where he taught chemistry and served as deputy head of the Chemistry Department. Prior to his assignment at EOARD, he spent two years in Europe as a participant in the Air Force System Command exchange program for scientists and engineers.

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AFOSR RESEARCH IN MOLECULAR DYNAMICS

CAPTAIN RUSSELL A. ARMSTRONG

The molecular dynamics program has as its objective the fundamental understanding of the dynamic interaction of light, atoms, and small molecules. This is indeed a very broad objective and encompasses a large area of chemistry and physics (the distinction here being only one of semantics). The program is divided into four general categories; chemical lasers, atmospheric chemistry, plume and wake chemistry and laser assisted dynamics.

The first category is generally aimed at the development of the scientific data base from which existing lasers can be improved and new lasers can be developed. Although heavily involved with vibrational laser candidates in the past, the emphasis is now dramatically shifting to chemically pumped electronic transition lasers (CETL). The most recent breakthrough in this area was the $O_2(^1\Delta)$-I laser developed by the Air Force Weapons Laboratory (1). In the reaction scheme, $O_2(^1\Delta)$ is generated in the hypochlorite reaction of basic hydrogen peroxide and chlorine. The reactions following are (in simplified form)

$$2O_2(^1\Delta) \rightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$$

$$O_2(^1\Sigma) + I_2 \rightarrow O_2(^3\Sigma) + 2I(^2P_{3/2})$$

$$I(^2P_{3/2}) + O_2(^1\Delta) \rightarrow I(^2P_{1/2}) + O_2(^3\Sigma)$$

$$I(^2P_{1/2}) \rightarrow I(^2P_{3/2}) + 1.315\ \mu M$$

The first device was lased in December 1977 at 8 mW cw in a longitudinal flow. That has matured to cw lasing at 100 W in a transverse flow.

The area of atmospheric chemistry involves neutral-neutral, ion-neutral, ion-ion and cluster interactions. It extends from ground zero through the ionosphere and thus covers a broad spectrum of research affecting Air Force surveillance, detection and communication systems. Typical of the excellent research in this area is that of the SRI group headed by Dr. John Moseley, which is studying ion photofragment spectroscopy. Using a laser-ion coaxial beam spectrometer (2), sub-Doppler resolution studies of O_2^+, O_3^+, O_3^-, Ar_2^+ and Kr_2^+ (important in rare gas-halogen lasers) have generated new useful information of the potential surfaces of these molecular ions.

Plume and wake chemistry involves the study of species present in rocket plumes and wakes and their interaction with atmospheric species. The infrared signature of missiles at high altitude is primarily due to high velocity collisions between exhaust and atmospheric species that result in T→V energy transfer. These collisions can reach relative velocities of 10 km sec^{-1}. The cross sections for T→V excitation are known to vary with velocity but until relatively recently, reliable measurements of the absolute cross sections have been elusive. Recent experiments by Dr. John Fenn at Yale have demonstrated the technique of determining these cross sections in a beam apparatus. They have found that the CO_2 collision with the N_2 gives an excitation cross section of 0.1Å^2 at 4 km sec^{-1} and is steeply rising with velocity. Complimentary work by Dr. Al Rahbee of the Air Force Geophysics Laboratory has recently demonstrated the technique as well. This is a very fruitful area that has broad implication far beyond just the rocket plume problem.

The final area of research, laser assisted dynamics is probably the least directed and certainly the most long term oriented of all of the research areas. It is an experimental and theoretical effort probing fundamental interactions of light with molecules or light initiated interactions of molecules with molecules. Inter- and intramolecular energy transfer, energy deposition and relaxation studies are included. The impact is broad and applicable to all three of the previously mentioned areas. For example, Dr. Richard Zare has recently reported results (3) of experiments designed to study the interaction of atoms with orientation selected excited molecules that "remember" their excitation history. He has found some very interesting patterns of reactivity versus orientation that will impact the theoretical arguments of collision interactions.

Future plans in the program are, of course, dependent upon the resources available. Some particular areas for potential development are in atmospheric response to sudden perturbations; for example, persistent chemistry after nuclear airburst and laser propagation through, and effects upon the atmosphere including larger clusters and aerosols. This latter problem is principally aimed at the scattering problem and also includes the intracavity effects in high pressure laser systems, where the phenomena are similar to those in atmospheric environments. We also are interested in new work in the area of excimer lasers other than rare gas-halogen systems. In terms of chemical lasers, we would like to investigate systems that do not require the massive input of energy associated with discharges.

The outline above represents a very limited selection of the AFOSR molecular dynamics research. Many very exciting and far reaching research endeavors have not been mentioned simply due to lack of time and space. We believe our principal investigators are among the top scientists in the world. That belief is continually reinforced as the research proceeds.

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CHEMICAL TECHNIQUES

DENTON W. ELLIOTT

The subtopic of electrochemistry plays a key role in the Chemical Techniques area. Today, civilian, industrial, and military activities are all highly dependent on electrochemical energy conversion devices. The military establishment depends on these devices to perform many of its communication functions such as command, control, and information transfer, as well as power to propel and support their various vehicles. The Directorate of Chemical Sciences recognizes the relevance of electrochemistry to the Air Force and attempts to maintain a significant program in the area. A few examples of accomplishments are described below.

Professor J. T. Maloy at the University of West Virginia, collaborating with Dr. D. F. Pickett at AFAPL has been investigating the role of electrochemically coprecipitated cobalt hydroxide and nickel hydroxide at a nickel microelectrode for purposes of elucidating the effect of cobalt hydroxide on electrode reactions of battery active nickel hydroxide. Hydroxide films were deposited onto the electrode surface from boiling ethanol solutions of nickel nitrate in the presence and absence of cobalt nitrate; their behavior in thirty percent potassium hydroxide solution was studied by cyclic voltammetry, chronoamperometry, and chronocoulometry. In general, the presence of coprecipitated cobalt hydroxide appears to render the charge-discharge reaction more reversible, thereby allowing charging to occur at less positive potentials; this apparently increases the charging efficiency by minimizing concurrent oxygen evolution. The microelectrode was also used to characterize the cathode deposition process for the nickel hydroxide.

The microelectrode techniques used in this work have been shown to be useful in the study of solid film electrodes of this type. Mass transport occurring within the nickel hydroxide film has been found to determine the rate of the charge-discharge process. This observation suggests that the techniques developed may be superior to conventional (Tafel plot) methods for studying electrode kinetics in this kind of electrode.

Some insight to the improvement of nickel hydroxide electrodes through cobalt hydroxide precipitation has been provided by this work. In general, coprecipitation increases potential range over which charging may occur and also makes the electron transfer process more reversible. Thus, coprecipitated cobalt hydroxide may be viewed as an electrocatalytic agent. The mechanism of this catalysis is not known. A more detailed description of the above research may be found in Journal of the Electrochemistry Society, Vol 25, No. 7, July 1978.

At the University of Buffalo - SUNY - , Professor Stanley Bruckenstein, who pioneered the rotating ring disk electrode in this country, used this technique in his solid electrode studies, and on phenomena related to corrosion prevention. A practical and ideal candidate for a ring-disk corrosion study of a multiple-phase system was that of a simple dental amalgam which is formed by reacting mercury with Ag_3Sn.

This amalgam is known to be a three phase system consisting of a tin rich phase, $Sn_{7-8}Hg$, a silver rich phase, Ag_2Hg_3 and unreacted Ag_3Sn(1-6). Corrosion in the oral environment can take place due to electrochemical cells formed between the anodic tin-rich phase and the cathodic silver-rich phase, according to

$$\frac{1}{7-8} Sn_{7-8}Hg = Sn^{2+} + \frac{1}{7-8} Hg + 2e \qquad (1)$$

$$\frac{1}{2} O_2 + H_2O + 2e = 2OH^- \qquad (2)$$

or if the saliva is acidic, due to fermentation of carbohydrates and saccharides,

$$2H^+ + 2e = H_2 \qquad (3)$$

Any mercury formed by the anodic process is presumed to react with the excess Ag_3Sn, to form additional $Sn_{7-8}Hg$ and Ag_2Hg_3, and the corrosion continues.

Jorgensen has shown that in well condensed amalgam, the $Sn_{7-8}Hg$-phase forms a coherent network throughout the bulk, and hence tin dissolution is not limited to the surface. The literature on _in vivo_ and _in vitro_ corrosion products shows the presence of insoluble tin compounds, SnO and $SnO \cdot \frac{1}{2}H_2O$ in NaCl solution, and SnO_2 and SnS_2 in restorations taken from human mouths. Evidence for mercury and silver sulfides and silver chloride is also to be found.

Ring-disk studies were performed in 0.9% NaCl using an amalgam disk (35% Ag, 13% Sn, 51% Hg, 0.5% Cu and <0.5% Zn) and a gold ring. Only tin ions were found to leave the disk electrode providing direct proof for the selective dissolution of tin during corrosion of dental amalgam in an _in vitro_ environment.

Successive i_D-E_D curves indicate that the surface has become more noble; i.e., oxidation currents decrease at a given oxidation potential with time, in keeping with the view that surface concentration of the $Sn_{7-8}Hg$ phase is decreasing. There is only a slight affect in the cathodic branch of the i_D-E_D curve, again confirming that the corrosion reaction does not involve the Ag_2Hg_3 phase.

These results show that the mercury released by reaction (1) does not react exclusively with unreacted Ag_3Sn to produce $Sn_{7-8}Hg$. A considerable portion of the released mercury must also form Ag_2Hg_3. Since no significant amounts of silver are oxidized at the disk electrode, and tin cannot accumulate on the disk electrode surface, some of the soluble tin species may arise from the unreacted Ag_3Sn present in the dental amalgam.

This study represents the first in vitro study demonstration that soluble tin species are selectively removed from a corroding dental amalgam.

Additional information is published in the Journal of Biomedical Materials Research 12, 1 (1978).

The goal of battery modeling techniques is to relate a battery's physical characterics (electrode design, separator system, etc.) to its performance in service. Such a capability would allow battery users to select or design a battery to specific performance requirements. In addition, the enhanced understanding that is obtained will provide the battery developer with new approaches to improve battery components.

Professors D. N. Bennion and J. Newman of the University of California, Los Angeles and Berkeley, respectively, have been involved in research to identify and more clearly describe causes for failure in zinc-nickel oxide and zinc-silver oxide batteries and to propose and test ways of reducing or eliminating the negative effects. Under previous Air Force support these researchers completed an investigation on Zinc Electrode Shape Change in which they determined the cause and suggested solutions to the problems. Under AFOSR support they have made membrane transport measurements on the RAI-2291 membrane. Transference numbers of the K^+ ion and the results were recorded as shown in the following table:

Table 1

Concn. of KOH (mol/lit)	Sp. Conductivity $(\text{ohm-cm})^{-1}$
8.399	2.0059×10^{-3}
9.421	3.3259×10^{-3}
9.508	2.6886×10^{-3}
9.994	2.6335×10^{-3}

$\kappa\ (\text{av}) = 2.6635 \times 10^{-3}\ (\text{ohm-cm})^{-1}$

They have also measured the reaction profiles for pressed zinc electrodes discharged at various current densities to various depths of discharge. They found that significant errors on discharging are associated with the increase in electrode thickness by swelling. Further work on reaction profiles is being undertaken to understand and correct other failures involving the zinc electrode.

SURFACE CHEMISTRY

LT. COLONEL RICHARD W. HAFFNER

Task 2303/A2 is the official designation for the AFOSR Surface Chemistry program. The objective of this program is to provide new scientific concepts and improve basic understanding of chemical reactions occurring on surfaces and thus make valuable contributions to many materials limited technologies vital to the Air Force such as solid state, metallurgy, tribology, mechanics and propulsion.

This objective is accomplished by studying the structure and properties of surfaces and their interactions with gases, liquids and absorbed solids. The principal areas of investigation currently relate to corrosion, lubrication and adhesion.

The corrosion effort is aimed at reducing the structural damage to Air Force equipment due to corrosion, thereby saving money and improving mission capability. Generally, the AFOSR Surface Chemistry program focuses on three main facets of the corrosion problem: direct chemical attack, electrochemical phenomena, and surface protection.

More specifically, AFOSR is supporting research aimed at improving protective oxide films and inhibitors for metals such as titanium and aluminum. Also of interest is the possibility that corrosion can be controlled by using new surface modification techniques such as ion implantation and "laser glazing." Adsorption-desorption kinetics of oxygen and other species on metallic surfaces is being studied by various techniques. Understanding the mass transport of water and hostile ions through protective paint films is another research effort related to corrosion of metals.

Because the AFOSR corrosion research program was reviewed in detail last year, the remainder of this report will highlight the objectives and accomplishments of the lubrication and adhesions research programs.

At Ford Motor Company, research under the direction of Dr. Lee Mahoney is being conducted to investigate deterioration and metal corrosion phenomena occurring in lubricant systems in oxidative environments at high temperatures. The information to be gained from this work can possibly be used to formulate improved lubricants for Air Force applications that can withstand the effects of thermal aging and oxidation.

Utilizing stirred flow reactor techniques, the scientists at Ford are attempting to determine (1) the kinetics and mechanisms of the oxidative and thermal reactions of a synthetic ester lubricant, with and without antioxidants at temperatures from 180 - 220°C at various reaction times; (2) the rates of metal corrosion phenomena and the influence of corrosion products on the course of oxidative and thermal reactions of the synthetic ester over the same temperature ranges as (1)

To date, a study of the lengths of the inhibition periods caused by the addition of varying amounts of the bisphenol antioxidant, 4,4'-methylenebis (2,6-di-ter butylphenol), BPH, on the autoxidation of pentaerythrityl tetraheptanoate, PETH, in a batch reactor at 180, 220 and 220°C has been carried out. A kinetic analysis based upon these results together with preliminary results on the BPH decay and quinone methide product formation as a function of time yield the following general equation for the rate of decay of BPH:

$$-\frac{d(BPH)_t}{dt} = \frac{w_o + 2k_1\,(ROOH)_t}{2 + 2\frac{k_{QM}}{k_{BPH}}\frac{(QM)_t}{(BPH)_t} + 2\,\frac{k_P}{k_{BPH}}\frac{(P)_t}{(BPH)_t}}$$

The symbol w_o designates the rate of radical formation from the spontaneous reaction of molecular oxygen with PETH and $2k_1(ROOH)_t$ is the rate of radical production from the decomposition of organic hydroperoxides formed at high BPH concentrations from the reactions of BPH and BPH antioxidant active products, QM and P, with organic peroxy radicals and at low BPH concentrations from reactions of organic peroxy radicals with PETH. The ratios k_{QM}/k_{BPH} and k_p/k_{BPH} are the ratios of rate constants for the free radical hydrogen atom transfer reactions of WM and P to that of BPH. The general validity of this equation and the values of the various rate constants are being obtained from stirred flow reactor studies.

A study of wear rates at 100°C manifested by pure PETH and by slightly oxidized PETH has been completed. At only ca. two per cent oxidation the wear rate is increased by a factor of eight over that of pure PETH. This result together with those from various ancillary studies are consistent with the view that hydroperoxides, perhaps in combination with α,γ-substituted difunctional oxidation products, lead to a rapid corrosive wear phenomena. The separate and combined effects of model hydroperoxide and α,γ-dicarbonyl compounds on the wear of pure PETH are yet to be investigated.

For the last two and one half years, Dr. Snediker and colleagues at Battelle Columbus have been studying the effects of oxygen and water vapor on lubricant films. The approach taken in this program was to study a fundamental mechanical property of the films--the compressive rupture strength. Rupture strength measurements are made on a film-penetration apparatus developed at Battelle (Figure 1). This apparatus is so constructed that a stylus may be incrementally loaded over a wide load range until film rupture, detected by electrical continuity, occurs. Initially, films formed from a diester di-2-ethylhexyl sebacate (E-105) and the solutions of tricresyl phosphate (TCP) in the diester were studied. In addition to the film rupture strength measurements, ellipsometry and external reflection infrared spectroscopy were performed. The substrate in all cases was highly polished ARMCO iron.

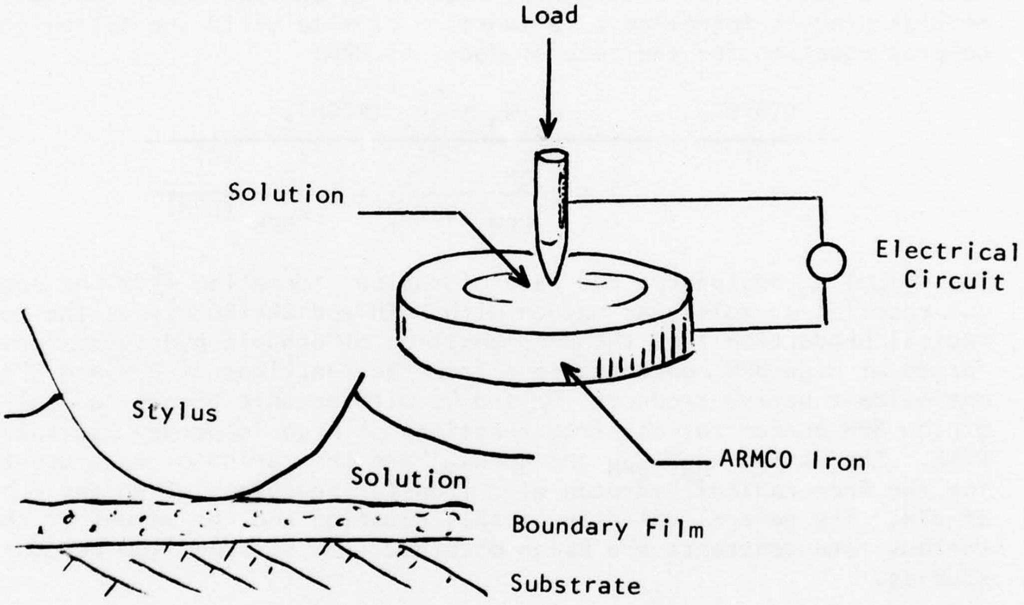


FIGURE 1

Both static and kinetic measurements were made of film strengths of E-105 and E-105 + TCP solutions. In the static measurements (performed at temperatures ranging from 20° to 204°C), it was found that the films have a low-strength component and a high-strength component and that a kind of phase transition occurs at about 93°C at which the high-strength component grows at the expense of the low-strength component. The high-strength component decomposes at about 180° Ellipsometric measurements over the same temperature range confirmed the existence of these transitions. The kinetic measurements showed that major changes in the rate of change in film strength occur in the temperature range 100° to 120°C.

During the second year of the program, the film penetration apparatus was modified to permit repeatable, routine measurements under controlled atmospheres. The apparatus was modified such that the rate of load application is automatic and reproducible.

Experiments carried out in dry and wet air environments indicate that the presence of water has a strong retarding effect on the formation of strong boundary films from both pure ester and TCP solutions. The reaction rates were observed to increase sharply at temperatures above 105° to 110°C.

Experiments carried out in dry and wet argon environments indicate that oxygen is essential to the formation of compressively strong films. Weak films found in argon gained strength with exposure to air.

More recently, experiments aimed at providing basic information in the surface chemistry of E-105/TCP film have been initiated. ESCA spectra indicated that organic phosphorus compounds may be present in the films. More ESCA work at higher resolution is needed to confirm this result. This work is now in progress. Also, infrared spectroscopy in the external reflection mode is being utilized to gain information on organic structure of the films.

Using an entirely different experimental approach, Dr. James Lauer, Rensselaer Polytechnic Institute, seeks to expand our knowledge of how and why lubricants fail when subjected to extreme boundary conditions. Dr. Lauer's basic objective can be simply stated: understand the bulk and boundary layer chemical-physical properties of lubricants in simulated elastohydrodynamic (EHD) contacts.

Although the objective of this research is simple, the approach is not. Lauer has constructed a rather unique EHD apparatus which allows him to analyze infrared radiation emitted from the contact zone. A schematic diagram of the apparatus is shown in Figure 2.

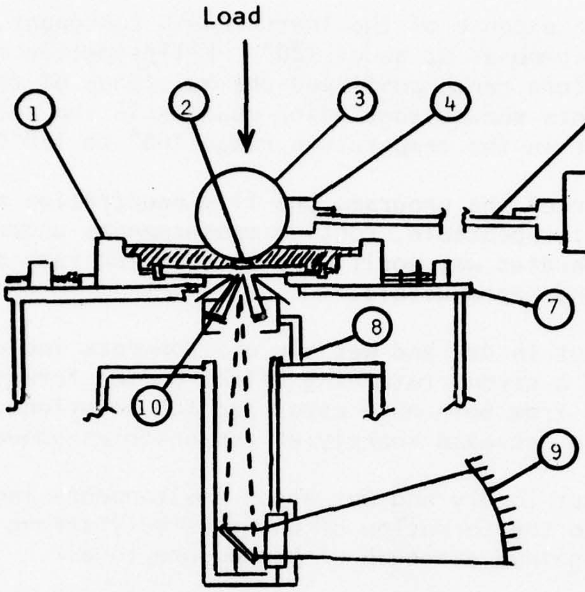


FIGURE 2

Basically, the EHD unit is an upside-down Four-Ball machine in which the gold plated test ball is rotated about a horizontal axis to form a sliding contact at a diamond window mounted in the bottom plate of a cup containing test fluid. The load (up to 50 kilobar) is applied by a lever arm (not shown) resting on top of the test ball at three point-contacts. A flexible shaft connects the ball to a constant drive motor. Diamond is an almost perfect window material for the infrared and has the mechanical strength to withstand the high contact pressure.

The radiation detecting system consists of a Beck lens, which gathers the radiation transmitted by the diamond window over a large solid angle, a Fourier spectrometer, and necessary interferometer optics. A dedicated mini-computer is interfaced with the infrared emission Fourier interferometer/spectrometer. This interface allows data collection and storage on a magnetic disc at a rate compatible with the spectrometer and data processing at the computer rate. A spectral plot is obtained in two-to-three minutes.

By analyzing the infrared spectra obtained from the contact zone, phase changes, solubility changes, changes of conformational equilibria, viscosity and temperature changes have been deduced. For the coming year, Lauer plans to investigate such things as changes of fluid composition along the conjunction line in operating bearings, influence of polar additives on the state of non-polar lubricants, fluidization of "glassy" fluids under shear, the influence of boundary surfaces on lubricants; e.g., gold or platinum plating, ceramic bearings.

There is only one adhesives research program presently ongoing in the Surface Chemistry task. Dr. Jar Mo Chen, Martin Marietta Laboratories (MML) is investigating the physical morphology, chemical composition, and crystallographic structure of aluminum alloy adherend surfaces in relation to adhesion durability under various environmental conditions.

Initially, the research is directed toward clarifying the mechanisms involved in both oxide film growth and film degradation. Hopefully, results from this work will provide useful guidelines for improving the adhesion and long term durability of aluminum adherend surfaces. Specifically, MML will investigate the factors responsible for the development of oxide protrusions and cell structures that are observed to form on aluminum surfaces treated by various chemical pretreatments such as chromic acid anodizing, Forest Products Laboratory etching and phosphoric acid anodizing. Electrolyte concentrations, anodization voltage, and treatment time will be systematically varied and the results monitored by STEM, Auger, ESA, etc., to follow the formation process from the early stages of growth to the point where the final structure is developed.

The MML scientists will also investigate crystallographic structure of the oxide films by transmission electron diffraction. Their objectives will be to: (1) clarify whether the structures are true oxides or hydroxides, and (2) determine the significance of prior observation that the structure of the protrusions is different from that of the barrier layer. An understanding of these factors is crucial to understanding both the mechanism of film formation and the behavior of the film in hostile (salt water, humidity) environments. Finally, the experimental data obtained will be used to develop a model for the growth of the observed structures.

A second adhesives research effort, planned to start in May 1979, will be directed by Dr. Chong S. P. Sung of MIT.

The objective of this work is to obtain a basic understanding of the role of silane type coupling agents on the adhesion promotion and wet-strength improvement of metal-polymer adhesive joints. Single crystals of aluminum oxide will be used as model surfaces on which the silanes will be adsorbed from aqueous or organic solutions. Since a single crystal of aluminum oxide does not absorb IR in the range of 3-7μ, the

IR spectra in this range only reflects the chemical changes on silanes and interaction between silanes and aluminum oxide. For thicker films of silanes, Fourier Transform IR transmission spectroscopy will be used. And for thin films of silanes, Fourier Transform IR internal reflection spectroscopy and ESCA will be used to study the structure of the silane films and interaction between silanes and aluminum oxide. When adhesive molecules are introduced, IR internal reflection spectroscopy will be utilized to determine if any chemical interaction between coupling agent and adhesive polymer molecule occurs.

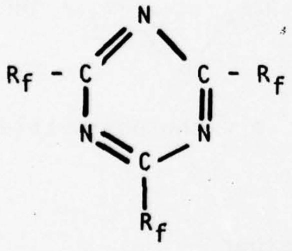
In order to correlate the structure of the silane film with the adhesive joint strength of the metal-polymer joint, peel tests (for ductile polymer) and lap shear tests (for rigid and thermoset polymer) will be performed and failure mode and locus will be analyzed. The durability of the joints to the wet environment will be tested and the attempts will be made to correlate the durability with the structure of the silane films and their changes during aging.

FLUIDS AND LUBRICANTS RESEARCH

DR. ANTHONY J. MATUSZKO

For many years thermal stability was perhaps the most important property for fluids and lubricants. Lubricants and hydraulic fluids which could withstand temperatures to 350°F were adequate to meet existing requirements of the Air Force. Petroleum oils and hydrocarbon ethers and esters fulfilled the needs quite adequately. As operational and environmental conditions became more severe, with the advent of hypersonic vehicles, requirements changed. Fluids and lubricants were not only expected to withstand higher temperatures but fluidity at lower temperatures became an important consideration. Exposure to extremes in pressure presented the need for liquids of low volatility. Other factors to be considered were oxidative stability, corrosiveness of decomposition products and so on.

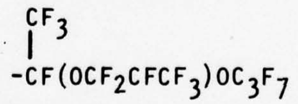
Through work done at the Air Force Materials Laboratory and elsewhere, perfluoroalkyl- and perfluoroalkylether - substituted s-triazines (I) have been shown to possess excellent high temperature properties and oxidative stability.



an s-triazine

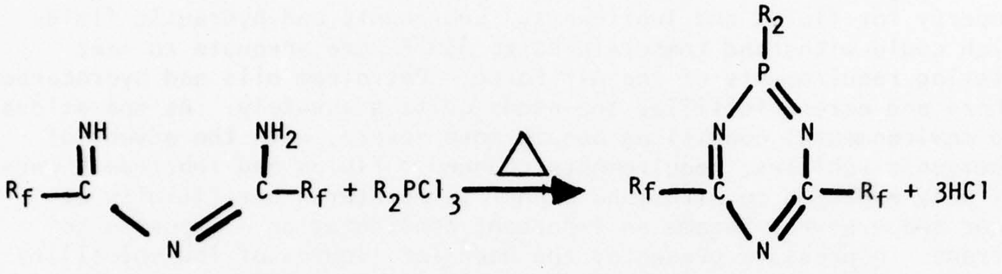
I

where $R_f = -OCH_2(CF_2)_6H$

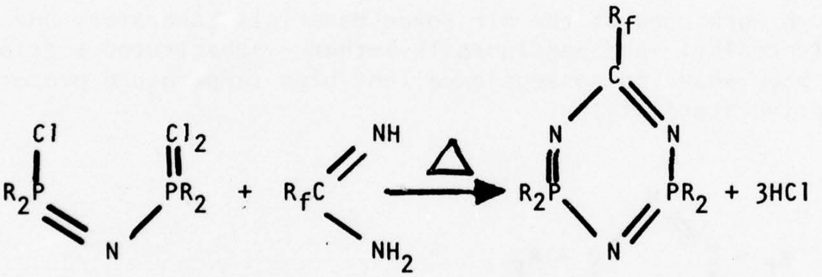
or  $-\overset{CF_3}{\overset{|}{C}}F(OCF_2CFCF_3)OC_3F_7$

or one of several other perfluorocarbon groups

It was also observed that certain phosphorus-containing additives increased the lubricity of fluids and some reduced corrosion caused by metals exposed at high temperatures to perfluorinated fluids. Based on these observations, Drs. Paciorek and Kratzer of Ultrasystems Inc. in Irvine, Calif., proposed that suitably substituted phospha-s-triazines could very well combine the desirable characteristics of the triazine ring system with the lubricating and corrosion inhibiting properties of the phosphorus component within the same compound. Under an AFOSR contract and using the following reaction schemes they successfully prepared the monophospha- and diphospha-s-triazines.



an imidoylamidine a trichlorophosphorane a monophospha-s-triazine

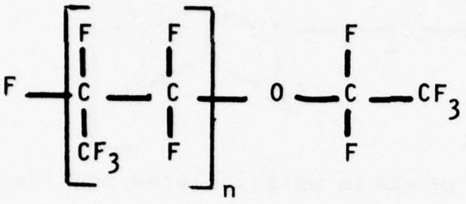


an imidodiphosphinic acid trichloride an amidine a diphospha-s-triazine

R_f = perfluoroalkyl
or perfluoroalkylether
R = C_6H_5

The perfluoroalkyl-substituted derivatives were low melting solids whereas the perfluoroalkylether-containing compounds were liquids. Degradative studies showed these compounds to be thermally and oxidatively stable in addition to exhibiting metal corrosion inhibiting action. These materials, unfortunately, had vapor pressures which were too high to be employed as high temperature fluids. The synthesis of higher molecular weight homologues is in process. It is expected that these new materials will have lower vapor pressures and will find wider applications under extreme operational conditions.

Another group of compounds which have received attention as high temperature fluids and lubricants are the perfluoroalkyl polyethers (II)



$$F-\left[\begin{matrix}F\\|\\C\\|\\CF_3\end{matrix}-\begin{matrix}F\\|\\C\\|\\F\end{matrix}\right]_n-O-\begin{matrix}F\\|\\C\\|\\F\end{matrix}-CF_3$$

a perfluoroalkyl polyether

II

Although these compounds have many desirable properties, methods for making them are limited and the compounds which have been made are generally quite expensive. Some of the problems encountered at high temperatures with presently available perfluoroalkyl polyethers are corrosiveness and metal catalyzed oxidative instability. Additives in most cases have overcome these problems.

AFOSR Chemistry has been looking at new methods of making fluorocarbon ethers under a grant with the University of Texas with Professor Richard Lagow. Professor Lagow has synthesized and isolated a series of perfluoro polyethers.

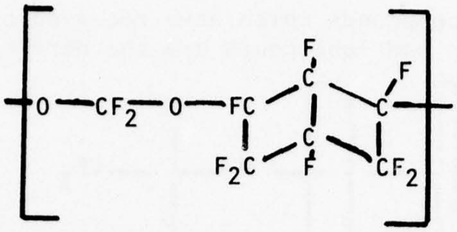
$$CF_3 - (O-CF_2-CF_2)_n - O - CF_3$$

$$CF_3 - (O-CF_2-CF_2)_m - O - CF_2 - CF_3$$

where n and m = 1-5

He is in the process of fully characterizing these polyethers and studying their physical properties.

New and unique fluorocarbon ether derivatives have been synthesized under a contract to Dr. Madeline Toy of SAI in Sunnyvale, California. Thermal and photopolymerization reactions of bis(fluoroxy)difluoromethane and "Dewar" hexafluorobenzene resulted in oligomers with molecular weights in the order of 2600 to 2800 which included the following groups in the oligomer chain.



Other lower molecular weight products were isolated and identified.

The chemistry learned from the studies of perfluoro polyethers and phospha-s-triazines will be useful in the synthesis of usable high temperature fluids and lubricants of the future.

AIR FORCE RESEARCH IN STRUCTURAL CHEMISTRY - AN OVERVIEW

DR. DONALD R. ULRICH

An overview of the Structural Chemistry task was last presented in the 21st Annual AFOSR Chemistry Program Review, FY 75 and 76. An updated report is presented here for FY 78 with an emphasis on research directions and results. The purpose is to provide the reader with a progress report of the total program, providing detail where important and significant results have been obtained.

The Structural Chemistry task consists of subtasks in polymers, glass, solid state chemistry and carbon-carbon materials. The objective of this task is to relate mechanical, thermal, physical, optical, electromagnetic and environmental properties to structure from the molecular to microstructional level in nonmetallic materials. Emphasis during the FY 1978 has been on: (1) the processing science of ordered polymers for molecular composites; (2) the process chemistry base for carbon-carbon composites; and (3) solid state chemistry for the design of new electromagnetic materials for microelectronic and electro-optic applications.

SOLID STATE CHEMISTRY

The thrust of the solid state chemistry task is directed toward the understanding of solid state phenomena and microstructures in nonmetallic electromagnetic materials. The subtask was expanded during FY 1977 and FY 1978 so that programs are now focusing on cooperative and dynamic phenomena in molecular solids, the defect chemistry of inorganic crystalline materials, and the synthesis, reactivity, and characterization of new molecules and complexes with unique electromagnetic properties. A long-term goal which this research supports is development of the nonmetallic materials chemistry base in support of microstructural sciences for electronic devices.

Professor Crosby's research at Washington State University is addressing the utilization of transition metal complexes and their charge transfer excited states in solids to guide the design of new electronic materials. Emphasis is shifting from synthesis and classical spectroscopy toward the measurement of temperature-dependent phenomena, in particular, the effect of intense external magnetic fields on substances possessing metal ions with nd^6, nd^{10}, and $4f^n$ configurations and ligands with extended Π structures. Examples include the series $[Ru(NH_3)_5L][ClO_4]_2$, where L represents pyridine and substituted pyridine, and sets of molecules of the type $[Ru(L\text{-}L)_3](BF_4)_2$, $[Ru(L\text{-}L\text{-}L)_2](BF_4)_2$, and $[Ru(L\text{-}L)_n(L^1\text{-}L^1)](BF_4)_2$ ($n=1, 2, 3$; L, L^1 = coordinating ligand).

In an effort complementary to Professor Crosby's research, a new grant was started with Professor Paras N. Prasad of the State University of New York at Buffalo to develop an understanding of both the topochemical and the energetic (dynamical) requirements for reactivity in the solid state. The method of investigation, time-resolved Raman spectroscopy using phonon spectra, has not been employed in the past for such study. By judicious choice of a crystalline matrix into which the reactive species can be incorporated, the proper orientation and energy dynamics of this molecule can be selected to control the course of a solid state reaction. This can lead to the synthesis of novel molecules and polymers of desirable electromagnetic properties.

Addressing the molecular crystal chemistry which is essential for predicting electromagnetic materials and transitions, Professor Bernstein at Colorado State University has been investigating the phase stability and solid state dynamics of molecular solids through the use of Raman scattering. In his work on the interaction between light and molecular crystals, the existence of polaritons in molecular solids was observed and verified for the first time during FY 1978. Polaritons have been observed in ionic solids, but never before in molecular crystals. Transverse electromagnetic modes which are propagating in a crystal and have a mixed photonlike and optical phononlike nature are referred to as polaritons. He has shown that the coupling of light with the solid to form polarization waves is a much weaker effect in molecular crystals than in ionic systems due to the short-range nature of the intermolecular forces in molecular solids. He has also shown that the accepted crystal structures of several molecular solids may be incorrect. An example is triazine. The observation of polariton coupling in Raman scattering has shown that the crystal does not have a center of inversion as previously believed. Polariton modes can potentially give more information about solid state phase dynamics than simple phonon modes. Phase transitions can be studied (by Raman scattering) over a much wider range of wave vector (reciprocal) space than previously shown.

The basic mechanisms behind the electro-optical phenomena in inorganic crystals such as lithium niobate are intimately connected with the defect chemistry of the material. A program was started with Professor Donald M. Smyth at Lehigh University for a detailed study of the defect chemistry of lithium niobate by means of high temperature, equilibrium conductivity measurements on high purity and doped single crystals as a function of temperature (600-1150°C), oxygen partial pressure, lithia activity, impurity type and concentration, and lithium-niobium stoichiometry. A thermodynamic characterization will be developed and the results compared with alternative, self-consistent defect models, which indicate that currently accepted models are not in accord with existing experimental observations.

GLASS CHEMISTRY

During FY 1978, the level of effort for glass research remained at the FY 1977 level. Research focused on the surface chemistry of glass, the interaction of glass with visible and infrared radiation, and the relation of structure to thermal and optical properties.

Professor Hench of the University of Florida is conducting a study of glass, glass-ceramic and silicon nitride (Si_3N_4) materials aimed at developing predictive relationships for the lifetime of materials under various combinations of chemical, mechanical, and thermal environments. The primary mechanism of corrosion in glass-ceramic composites has been identified as preferential grain boundary attack between the crystals and the glass matrix. A nondestructive infrared reflection spectroscopy (IRRS) method has been developed to analyze the volume fraction of crystallization and the chemical attack. An effect of volume fraction crystallization on the time decay of the Auger electron signal of the mobile ions in the glass-ceramics has also been discovered and the consequence on surface physics of poly-phase ceramics is being investigated. Dynamic fatigue measurements of Li_2O-SiO_2 glasses yield environment sensitive fatigue parameters that can be used for lifetime predictions when a given mechanical stress is applied in the chemical environment tested. Exploratory studies extending the glass-ceramic results have shown that infrared reflection spectroscopy can be used to characterize the glassy films that develop on certain Si_3N_4 materials exposed to high temperature oxidation.

Because of the need for very low expansion glasses and glass-ceramics which would minimize thermal shock on exposure to lasers, Professor Mackenzie at the University of California, Los Angeles, has been studying glasses based on Cu_2O-$A\ell_2O_3$-SiO_2. In the course of heat-treatment, a new family of glass ceramics was discovered which have negative, zero, and small positive expansions and high temperature stability to 1000°C. The additions of minor amounts of B_2O_3, ZnO, and Na_2O lower the melting temperatures of the glass, but do not effect the expansion of the glass-ceramics.

Professor Mackenzie has initiated research on the optical properties of fluoride glasses which transmit in the visible and are known to transmit at least to about 6μ in the infrared. Theoretical considerations, however, suggest that fluoride glasses should transmit to beyond 12μ. Since little is known about the infrared absorption of fluoride glasses, experiments were started with the aim of understanding what controls infrared absorption in these materials. A technique has been devised for the preparation of large, colorless, transparent samples based on ZrF_2. Preliminary transmission measurement results support the theoretical predictions.

CARBON-CARBON MATERIALS CHEMISTRY

The Office of Naval Research and AFOSR are jointly supporting a basic research program in carbon-carbon composite materials and structures. While the focus of the program is on rocket nozzle applications and environments, the research is establishing the science base which is essential for the reliable processing and performance of carbon materials for nosetips, heat shields, aircraft brakes and large space structures. The Structural Chemistry task in a jointly planned and executed effort with the Air Force Materials Laboratory is addressing the processing science of carbon-carbon composites.

This thrust is an example of Air Force basic research reacting quickly to meet a near-term Department of Defense requirement. It is planned as a five year effort and will be completed during FY 1981.

The objective of the process chemistry program is to understand the influence of process variations on microstructure formation and composite properties. That is, the precursor and process chemistry data base for carbon fibers and carbon-carbon composites which is essential to developing controlled microstructures and tailoring mechanical, thermal and physical properties will be established. Process chemistry is the key to controlling microstructure, which is the link between processing and response in a given environment, and microscopic structural defects, which limit strength in service.

Since the fiber/matrix interface is considered to be the major influence in the formation of the mesophase and subsequent development of defects and microstructures, two fundamental research programs were initiated in late FY 1977 with Professor Uhlmann at MIT and Professor Diefendorf at Rennselaer Polytechnic Institute to develop the process-structural-property relations of carbon fibers and the relation between structural features of the composite and the structure of the fibers.

Concurrent composite matrix research programs were initiated early in FY 1978. These, in particular, are closely coordinated with the AFML 6.2 (exploratory research) analytical modeling program for improved processing. Dr. Gebhardt at General Electric and Mr. Pope at Science Applications Inc. are providing fundamental data key to the analytical effort.

Professor Diefendorf at RPI is investigating the effects of processing on carbon fiber structure, longitudinal and transverse properties (modulus, thermal expansion coefficient, and strength), and flaws using quantitative optical measurements. Professor Uhlmann at MIT, addressing the stabilization and graphitization of acrylic fibers and microstructure of carbon-carbon composites, has determined the high-temperature mechanical properties of a number of acrylic fibers used as precursors in the manufacture of carbon fibers. Notable differences in behavior are seen between fibers containing a weak acid comonomer and those without such comonomers. The results suggest the development of cracks in the fibers during stabilization. They are suggested to result from differences in mechanical properties between oxidized and unoxidized material. These results, which have important implications for the development of improved continuous processing of acrylic fibers to carbon fibers, are presently being pursued and extended to structural development in carbon-carbon composites.

Dr. Gebhardt is studying the chemistry of formation of the graphite precursor (mesophase) during pressure pyrolysis of the carbon-carbon matrices with emphasis on the determination of viscosity, density, compressibility, and other fundamental properties of a model compound such as phenanthrene and typical commercial pitches. These are being studied as a function of processing temperatures, times, and pressures. Mr. Pope at Science Applications Inc. is studying the time-temperature-pressure relationships on the decomposition of coal-tar pitches used as matrices with consideration of relating chemical and kinetic phenomena to microstructure and the fluid dynamics of processing.

POLYMER CHEMISTRY

Polymer chemistry is the largest subtask in the Structural Chemistry task, since polymers are widely used as structural, containment and electromagnetic materials in aircraft, weapons and weapon delivery systems, and satellites. The polymer chemistry subtask consists of two initiatives. One is a corporate effort of AFOSR and the Air Force Materials Laboratory to develop the processing science of ordered polymers for self-reenforced or molecular composites. The other is the establishment of structural-property relationships in resins and adhesives. Research covers the range from materials for the future to those that are in operational usage.

ORDERED POLYMERS

The Air Force Office of Scientific Research and the Air Force Materials Laboratory are sponsoring extramural and inhouse research directed toward the synthesis, characterization and processing of nematically (liquid crystal) ordered rigid rod polymers with the potential of being used for very high strength, environmentally resistant self-reenforced composites. The objective is the attainment of mechanical properties for a structural material comparable with those currently obtained with fiber reenforced composites, but with significantly higher environmental resistance and without the use of a fiber reenforcement. Research has centered on the rigid rod, extended chain aromatic-heterocyclic polymers.

Of the aromatic-heterocyclic polymer systems being explored, the para-ordered polybenzoxazoles (PBO) polymers have been the most thoroughly studied. A phase of the FY 1978 effort has been the successful synthesis of PBO polymers containing a limited number of swivel segments by Dr. Robert Evers of AFML. Solutions of these swivel polymers exhibit more desirable processing characteristics such as higher molecular weight, improved solubility, and higher concentration while still displaying anisotropy. This approach is, in part, a result of a statistical thermodynamic treatment for mixtures of rodlike particles in terms of phase equilibria being carried on by Professor Flory of Stanford University under AFOSR sponsorship. Professor Flory's theory has been developed for rigid rod polymers containing swivel segments and predicts that solutions of these polymers, as exemplified by PBO swivel polymers, should also exhibit anisotropic behavior similar to completely rigid rod polymers. Preliminary characterization results on PBO swivel polymers indicate that anisotropic behavior in solution occurs as predicted by Dr. Flory's studies, that unusual polymer morphology is also present in cast films, and - also as predicted - processing is facilitated by higher solubility.

AFOSR principal investigators, along with Dr. Flory, include Dr. Berry of Carnegie-Mellon University, Professor Mark of the University of Cincinnati, and Dr. Wolfe of Stanford Research Institute. Dr. Berry is investigating the kinetics of polymerization of PBO. A new grant was initiated with Dr. James Mark of the University of Cincinnati to use standard semi-empirical potential energy functions to calculate energies of different conformations of relatively rigid chain molecules and interaction energies between such chains in the ordered polymer systems. The basic goals are molecular understanding of the unusually high strengths of materials such as the polybenzoxazoles and knowledge of how currently available structures could be modified to improve these strengths.

Looking to future ordered polymer systems, a new contractual effort was initiated with Dr. James Wolfe of SRI International for studies of step-growth propagation of high molecular weight rigid rod polymers, in particular, P-phenylene-2, 6-benzobisthiazole (PBT). The research is designed to contribute to the understanding of the difficulty of obtaining high molecular weight in aromatic polymers capable of forming liquid crystalline solutions.

STRUCTURE-PROPERTY RELATIONS IN POLYMERS

The second thrust in polymer chemistry focuses on establishing fundamental structure-property correlations in structural, containment, electromagnetic and environmentally resistant materials. Research during FY 1978 was brought to completion on contracts by Dr. Roger Morgan at the McDonnell Douglas Research Laboratory and Dr. Joseph Nanevicz at SRI, International.

The work of Dr. Nanevicz, described in the completed project summary, is an example of Air Force basic research systematically generating a fundamental understanding which is essential to the solution of a current operational problem. The interaction of a synchronous-orbit satellite with its environment activates electrification and electric discharge processes producing electromagnetic noise pulses and effluents which deteriorate satellite materials, surfaces and components. Dr. Nanevicz has systematically investigated the basic processes of satellite electrification and charge transport in polymers used on external surfaces of operational satellites under dynamic rather than steady state conditions. The research has revealed and identified new bulk storage and discharge mechanisms which have not been taken into account in current prediction codes and models for the effects of spacecraft charging.

Polymers used by the Air Force are exposed to extreme service environments in many applications. Dr. Morgan addressed the need to predict the durability of these materials over long periods without resorting to empiricism by establishing a detailed understanding of the structure-property relations of epoxies and polycarbonates and how such relations are modified by fabrication and environmental factors.

There is currently a high level of interest in this area within the non-defense as well as the defense sectors of industry and government. For this reason, the findings and conclusions of Dr. Morgan's research on epoxies are summarized in detail in the completed project summary of this review. In a cooperative effort with Dr. Morgan, who investigated the pertinent physical phenomena induced and modified by sorbed moisture in operational epoxy systems, Dr. Karasz at the University of Massachusetts studied the correlation between structure, properties and water sorption of model epoxy resin systems.

Probably the most significant overall result of Dr. Morgan's research is that it reveals that the importance of microstructures in controlling properties and durability in polymers has not been recognized, or understood. Professor Uhlmann at MIT has been conducting research to provide insight into the most important microstructural features of polymers, their dependence on processing variables, and their relations to mechanical and optical properties. High resolution electron microscope studies of amorphous polymers have been carried out on polyvinyl chloride, polyethylene terephthalate, polycarbonate, polymethyl methacrylate and polystyrene, using both bright field and dark field microscopy. The general absence of microstructural features of a size down to the resolution limit of the electron microscope is indicated. Only 'pepper and salt' features on a scale about 5 Angstroms are seen as characteristic of the structure. These features reflect simple interferences as the resolution limit is approached, and are seen for single crystals and oxide glasses as well as for the polymers. The present results, taken together with structural information from light scattering, small angle X-ray scattering and small angle neutron scattering, indicate that glassy polymers should be regarded as having random structures. The combined results are inconsistent with heterogeneous microstructures having regions of locally high order present in large volume fractions.

In another area of microstructural importance, Dr. Hay of the Celanese Research Company has continued his research to identify the principles underlying the processing mechanisms of high temperature polymeric alloys. Since many stable Air Force polymer systems are relatively intractable, the processibility by alloying with compatible polymers and monomers to yield combinations of polymers which are more readily fabricable and have high temperature properties similar to the major intractable components is being pursued. In complementary research Dr. Karasz at the University of Massachusetts has continued his research to determine the principles of polymer-polymer compatibility and how molecular structures and morphology govern polymeric interactions and their resultant physical and mechanical properties.

A new grant, which is intimately related to the aforementioned microstructure and durability studies, has been co-funded with the Surface Chemistry task (2303/A2). Dr. Jerome B. Lando and Professor Charles E. Rogers, Case Western Reserve University, will address controlled structural adhesive interphases.

Dr. Jonas of the University of Illinois continued his nuclear magnetic resonance studies of viscoelastic fluids and elastomers under extreme conditions of temperature and pressure. He has concluded that natural abundance Carbon-13 relaxation measurements appear very promising for studying molecular motions in viscoelastic liquids. Using di (2-ethylhexyl) phthalate (DEHP), the Carbon-13 T_1 (the spin-lattice relaxation times) behavior of individual carbon atoms could be described by using the standard expression for T_1 and calculating the approximate reorientation times from the Debye equation. A distribution of correlation times was not required to describe the Carbon-13 relaxation behavior in DHEP at viscosities up to 1 poise and above.

In collaboration with Dr. Jonas and the Air Force Materials Laboratory, Dr. Berry and Professor Markovitz of Carnegie-Mellon University are investigating the relation of structure to rheological properties in channel sealants, the Air Force integral fuel tank sealants of the future.

Their current research is focused on polymeric solutions and dispersions which are intended to serve as model systems for understanding the flow and transport properties of the sealants.

ATMOSPHERIC SCIENCE

MAJOR WILLIAM J. MCKECHNEY

In contrast to the AFOSR program in chemical sciences, the Air Force atmospheric sciences basic research program is largely in-house with the Air Force Geophysics Laboratory as the chief performer. AFOSR is the manager and does maintain a moderate extramural research program. This extramural program supports research in a wide range of disciplines under the umbrella of "Atmospheric Sciences". Several examples might show the wide variety of research support in understanding the physical processes occurring in the atmosphere between the earth's surface and approximately 400 kilometers altitude.

Support is provided for the work of Dr. Peter Hobbs at the University of Washington (Seattle) in investigating the internal structure and dynamics of extratropical cyclonic storms. These storms, the low pressure systems on a weather map, are a complex interaction of various scales. Understanding their internal structure in time and space is important for modeling, forecasting, and weather modification purposes. Dr. Hobbs has organized a yearly six week field measurement program consisting of instrumented aircraft, doppler and conventional radars, a dense rain gauge network, and balloon borne system to measure winds, temperatures, humidities, and rain and cloud droplet and ice crystal sizes and number densities.

The result has been an upgrading of the classical model of cyclones. The analysis of air motions, moisture fluxes and the organization and structure of clouds and precipitation has revealed a banded nature in the precipitation both in the warm and in the cold sectors, the critical role played by ice crystals in the precipitation processes, the role played by "generating cells" - high altitude clouds whose ice crystals falling into lower clouds act as seeding agents, and quantitative models of the precipitation and cloud particulates.

Dr. Vincent Wickwar's work at SRI reflects the Air Force's interest in the dynamics of the upper atmosphere. The interaction of the magnetosphere, ionosphere and thermosphere lead to a large deposition of energy and momentum in the auroral region. This deposition affects the structure of the local ionosphere and thermosphere and produces dynamic effects that lead to worldwide changes in the upper atmosphere. Dr. Wickwar, using data from the Chatanike Incoherent Scatter Radar, is able to deduce these energy depositions and the resultant neutral winds between 85 and 300 km. In the ionospheric F region (165-300 km), the only meridianal component can be acquired, whereas in the E region (85-150 km), the entire vector can be deduced.

To date the analyses have shown that, in aurorally quiet-times, the F-region meridional wind varies qualitatively as expected from solar heating, flow is to the north in the daytime and southward at night. There is a net southward flow, which increases with auroral activity. Considerable gravity wave activity, which appears as large oscillations, is evident in much of the data. Finally, the first comparison between this technique and winds deduced from doppler shifted air glow measurements was made. The two methods agreed well except for the apparent effects of gravity waves. Future analyses will focus on the E-region winds and the relationship between energy depositions and the resultant winds.

A third research effort is aimed at the dynamics of the intermediate altitude regime. Dr. Jeffrey Forbes of Boston College will be investigating the tidal structure of the mesosphere and lower thermosphere. Originally his AFOSR supported research focused on the development of a model of the thermospheric tidal structure based on the linearized tidal equations for a spherical, rotating, viscous atmosphere with anisotropic drag. The model was initialized using satellite and incoherent scatter radar temperature data and was then used to investigate the tidal structure as a function of position, time, and solar cycle. The fine detail of temperature and winds below 200 km is well represented. For example, the predominance of the semi-diurnal tide below 30° latitude in contrast to the predominance of the diurnal tides at mid-latitudes was correctly predicted.

Currently additional efforts are supported in atmospheric optics, atmospheric electricity, tidal theory, aeronomy and ionospheric physics.

CHEMISTRY ANNUAL BUDGET FOR PAST TEN YEARS

FY	Expenditures (thousands)
69	$3,338
70	3,169
71	3,205
72	3,210
73	2,512
74	3,080
75 *	3,213
76	3,620
77	4,364
78	4,884

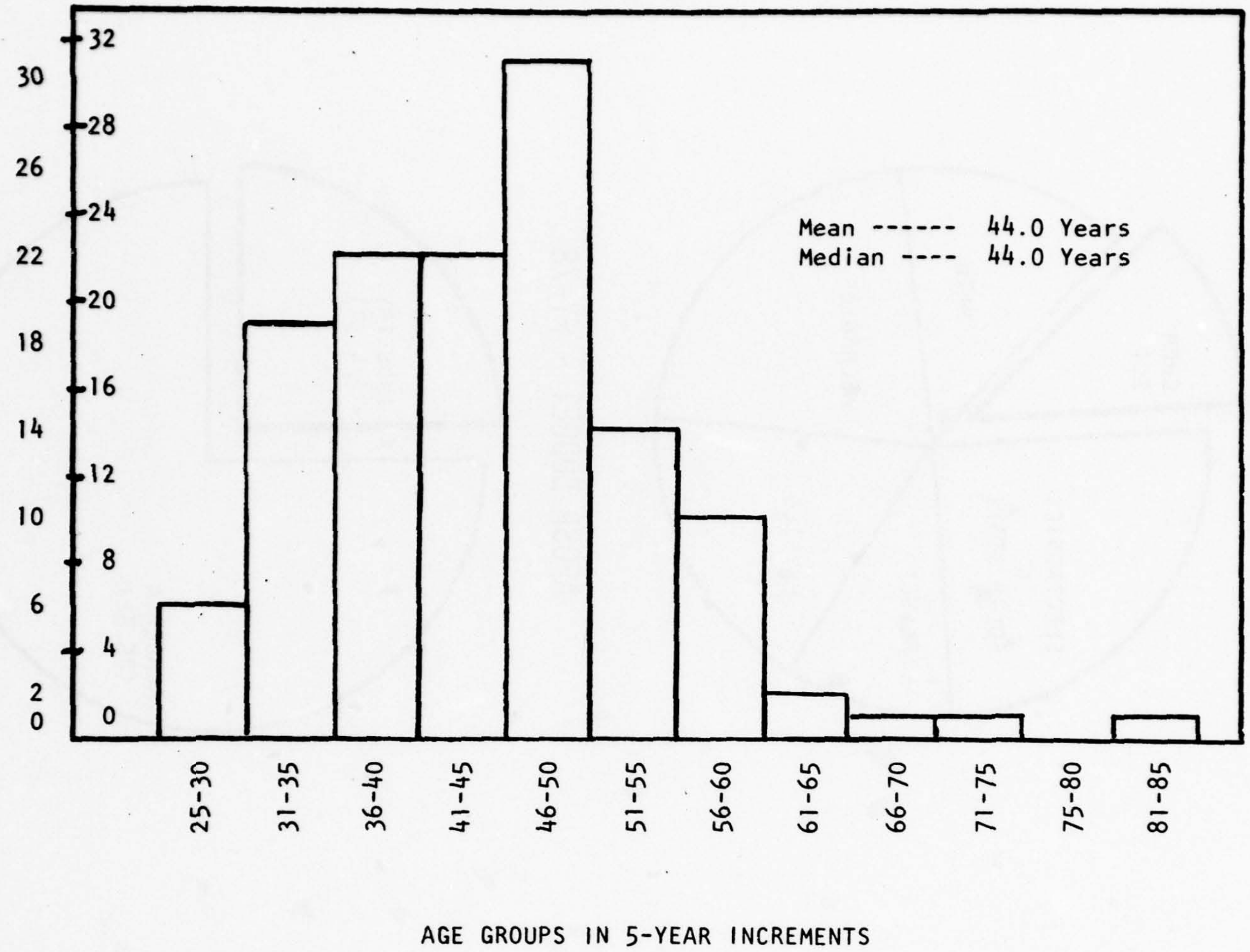
*FY75 total includes $570,449 from Project 9750 for Kinetics and Thermophysical Properties Research.

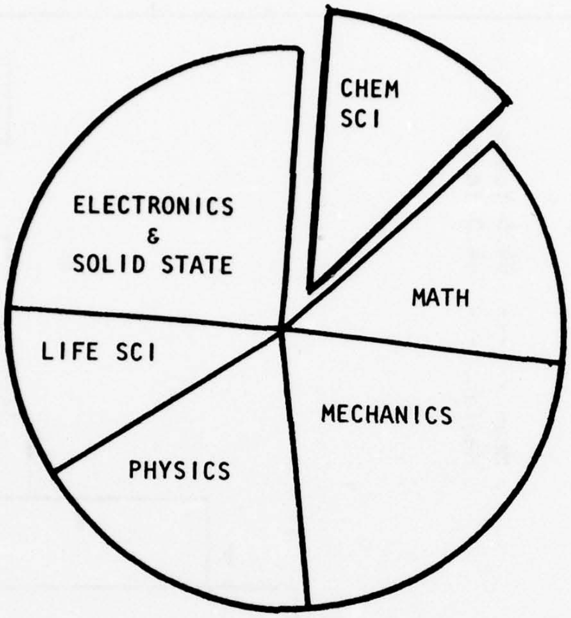
FY78 CHEMISTRY PROGRAM STATISTICS

Total number of proposals received	201
New work efforts initiated	30
Renewals	78
Proposals declined	72
Proposals withdrawn	10
Proposals transferred	2
Mini-Grants (one year funding)	2
Conferences and Symposia	7
Proposals pending disposition	7

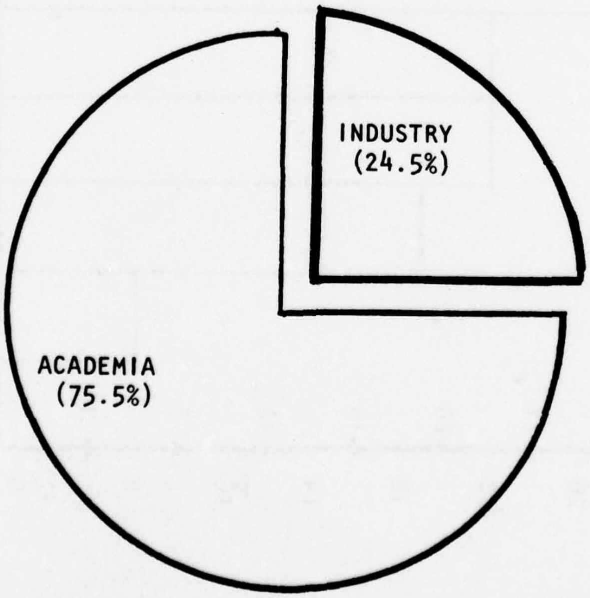
AGE DISTRIBUTION OF PRINCIPAL INVESTIGATORS

DIRECTORATE OF CHEMICAL SCIENCES





AFOSR BUDGET - FY-78



DISTRIBUTION OF SUPPORT TO ACADEMIA AND INDUSTRY
(DIRECTORATE OF CHEMICAL SCIENCES)

CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY 78 with funds provided in part or wholly by the Directorate of Chemical Sciences as a means of furthering areas of scientific research of particular interest to the Air Force.

ACS Symposium on the Mechanics of Fracture in Polymers

Dr. K. L. DeVries
Anaheim, California
13-16 March 1978

AFOSR/Air Force Geophysics Laboratory

Chemical Dynamics Contractors' Meeting
Hanscom Air Force Base, Massachusetts
26-27 October 1977

AFOSR/Air Force Materials Laboratory

Carbon-Carbon Composite Process Science
Contractor's Meeting
San Antonio, Texas
15-18 April 1978

Gordon Research Conference on Corrosion

Dr. Ellis D. Verink, Jr, Chairman
Colby-Sawyer College
New London, New Hampshire
10-14 July 1978

Gordon Research Conference on Electrochemistry

Dr. Royce W. Murray, Chairman
Miramir Hotel
Santa Barbara, California
23-27 January 1978

Gordon Research Conference on Organometallic Chemistry

Dr. Paul M. Treichel, Chairman
Procter Academy
Andover, New Hampshire
14-18 August 1978

Joint AFOSR/Air Force Rocket Propulsion Laboratory

Propulsion Research Meeting
Lancaster, California
3-7 April 1978

ACTIVE RESEARCH EFFORTS

AS OF 1 OCTOBER 1978

ALPHABETICAL BY PRINCIPAL INVESTIGATOR

Photoionization of Molecular Clusters (RAA) AFOSR-78-3638, 2303/B1	Ronald P. Andres Joseph M. Calo Department of Chemical Engineering Princeton University Princeton, New Jersey 08540
A Study of Transport Processes and Initiation of Corrosion Under Paint Films (RWH) F49620-76-C-0029, 2303/A2	T. R. Beck Electrochemical Technology Corp. 3933 Leary Way, N.W. Seattle, Washington 98107
Diagnostics and Chemical Applications of Multiphoton Absorption Processes (RAA) AFOSR-77-3279, 2303/B1	Sidney W. Benson Department of Chemistry University of Southern California Los Angeles, California 90007
Electrochemistry of Solutes in Chloroaluminate Systems (DWE) AFOSR-76-2978, 2303/A1	Elliot R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521
Molecular Crystal Chemistry (DRU) AFOSR-77-3317, 2303/A3	Elliot R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521
Property-Structure-Processing Relations in Polymeric Materials (DRU) AFOSR-77-3404, 2303/A3	Guy C. Berry Herschel Markovitz Department of Chemistry Carnegie-Mellon University Pittsburgh, Pennsylvania 15213
Reactions and Transfer of Excited Molecules (RAA) AFOSR-78-3643, 2303/B1	Philip R. Brooks Department of Chemistry Rice University Houston, Texas 77001

Solid Electrode Studies Related to Corrosion Prevention, Fuel Cells and Batteries (DWE) AFOSR-78-3621, 2303/A1	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, New York 14214
Program to Investigate Laser Induced Synthesis of Chemical Materials (AJM) F49620-78-C-0113, 2303/B2	P. M. Castle Westinghouse R&D Center Westinghouse Electric Corporation Pittsburgh, Pennsylvania 15222
Fast Ion Transport in Solids (DWE) AFOSR-77-3427, 2303/D1	Alan V. Chadwick John H. Strange Department of Chemistry University of Kent Canterbury, Kent, U.K.
Effects of Surface Morphology and Chemical Composition on the Durability of Adhesively Bonded Aluminum Structures (RWH) F49620-78-C-0097, 2303/A2	Jar-Mo Chen Martin-Marietta Laboratories 1450 South Rolling Road Baltimore, Maryland 21227
Kinetics Studies Involving Electronically-Excited Interhalogens and Halogens (RAA) AFOSR-75-2843, 2303/B1	M. A. A. Clyne Department of Chemistry Queen Mary College London E1 4NS, England
Chemical Kinetic Studies Involving NF Radicals (RAA) AFOSR-78-3507, 2303/B1	M. A. A. Clyne Department of Chemistry Queen Mary College London E1 4NS, England
Novel Chemical Laser Systems (RAA) AFOSR-77-3258, 2303/B1	Terrill A. Cool School of Applied & Engineering Physics Cornell University Ithaca, New York 14853
Synthesis and Spectroscopic Investigation of Inorganic Materials Possessing Unusual Electronic Properties (DRU) AFOSR-76-2932, 2303/A3	Glenn A. Crosby Department of Chemistry Washington State University Pullman, Washington 99163
Theoretical Studies of Metal Oxides (RAA) AFOSR 78-3677, 2303/B1	Alex Dalgarno Harvard College Observatory Cambridge, Massachusetts 02138

Double Layer Structure and Electrode Kinetics (DWE) AFOSR-76-3027, 2303/A1	Robert deLevie Department of Chemistry Georgetown University Washington, D.C. 20057
New Laser Dye Systems Based on Luminescent Transition Metal Complexes (AJM) AFOSR-78-3590, 2303/B2	James N. Demas Department of Chemistry University of Virginia Charlottesville, Virginia 22901
Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials (AJM) AFOSR-75-2749, 2303/B2	Michael J. S. Dewar Department of Chemistry University of Texas Austin, Texas 78712
Relation of Structure to Properties in Graphite Fibers (DRU) AFOSR-77-3436, 2303/A3	Russell J. Diefendorf Department of Materials Engineering Renesselaer Polytechnic Institute Troy, New York 12181
Investigation of Electron Attachment Processes in Polyatomic Molecules (RAA) F49620-77-C-0071, 2303/B1	Jerry T. Dowell IRT Corporation 7650 Convoy Court San Diego, California 92138
Evaluation of Chemical Research Relevant to Current and Projected U.S. Air Force Interests (DWE) F44620-75-C-0001, 2303/A1	Joseph E. Earley Department of Chemistry Georgetown University Washington, D.C. 20057
Picosecond Laser Studies of Excited State Proton Transfer (AJM) AFOSR-77-3407, 2303/B2	Kenneth B. Eisenthal Department of Chemistry Columbia University New York, New York 10027
Rates of Surface Reactions (RWH) AFOSR-77-3255, 2303/A2	Edward M. Eyring Department of Chemistry University of Utah Salt Lake City, Utah 84112
Time Resolved Spectroscopy of Reactive Chemical Systems (DWE) AFOSR-78-3617, 2303/A1	W. G. Fateley Robert M. Hammaker Department of Chemistry Kansas State University Manhattan, Kansas 66506

Molecular Beam Studies of Collisional Excitation and Energy Exchange in Polyatomic Studies (RAA) AFOSR-75-2863, 2303/B1	J. B. Fenn Department of Engineering Sciences Yale University New Haven, Connecticut 06520
One- and Two-Photon Optically Pumped Laser Devices: New Chemical Laser Diagnostics and Kinetic Probes (RAA) AFOSR-76-3056, 2303/B1	Robert W. Field Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
The Structure and Properties of Polymeric Materials (DRU) AFOSR-77-3293, 2303/A3	Paul J. Flory Department of Chemistry Stanford University Stanford, California 94305
Kinetic Spectroscopy of Metal Atom/Oxidizer Chemiluminescent Reactions for Laser Applications (RAA) F44620-76-C-0108, 2303/B1	Arthur Fontijn AeroChem Research Laboratories, Inc. Princeton, New Jersey 08540
Chemical and Physical Aspects of Mesophase Formation During Carbon Carbon Composite Processing (DRU) F49620-78-C-0006, 2303/A3	J. J. Gebhardt Re-entry and Environmental Systems Division General Electric Company Philadelphia, Pennsylvania 19101
Microscopic Theory of Electronic Transitions in Molecular Rate Processes (RAA) F49620-78-C-0005, 2303/B1	Thomas F. George Department of Chemistry University of Rochester Rochester, New York 14627
Multiphoton Dynamics: Energy Disposal During Decomposition of Molecules (RAA) F49620-78-C-0107, 2303/B1	David M. Golden John R. Barker Physical Sciences Division SRI International Menlo Park, California 94025
Selective Chemical Pumping of Electronic States (RAA) AFOSR-78-3515, 2303/B1	James L. Gole School of Chemistry Georgia Institute of Technology Atlanta, Georgia 30332
New Materials for Electrochemical Cells (DWE) AFOSR-77-3402, 2303/A1	John B. Goodenough Peter G. Dickens Inorganic Chemistry Laboratory Oxford University Oxford, OX1 3QR, England

Energy Transfer in Chemically Reacting Systems and in Surface Characterization (RAA) AFOSR-77-3138, 2303/B1	David O. Harris Department of Chemistry University of California Santa Barbara, California 93106
Processing Mechanisms, Structure, and Morphology of High-Temperature Polymeric Alloys (DRU) F49620-77-C-0046, 2303/A3	Ian L. Hay Physics Research Department Celanese Research Co. Summit, New Jersey 07901
Structure-Property-Environmental Relations in Glass and Glass-Ceramics (DRU) AFOSR-77-3210, 2303/A3	Larry L. Hench Department of Materials Science University of Florida Gainesville, Florida 32611
Energy Disposal in Electronically Excited Halogen Atoms and Molecular Oxygen (RAA) AFOSR-78-3513, 2303/B1	Paul L. Houston Department of Chemistry Cornell University Ithaca, New York 14853
NMR Study of Viscoelastic Fluids and Elastomers Under Extreme Conditions of Temperature and Pressure (DRU) AFOSR-77-3185, 2303/A3	Jiri Jonas Department of Chemistry University of Illinois Urbana, Illinois 61801
Effect of Structure on Physical Polymer Interactions and Properties (DRU) AFOSR-76-2983, 2303/A3	Frank E. Karasz Polymer Science & Engineering University of Massachusetts Amherst, Massachusetts 01002
Energy Partitioning and Transfer in H + HI System (RAA) AFOSR-78-3612, 2303/B1	J. V. V. Kasper Charles Knobler Department of Chemistry University of California Los Angeles, California 90024
Computer Modeling of Pulsed Chemical Lasers (RAA) AFOSR-75-2842, 2303/B1	Ronald L. Kerber Electrical & Mechanical Engineering Department Michigan State University East Lansing, Michigan 48824
Novel Organophosphorus and Organonitrogen Derivatives and their Use for the Synthesis of Unusual Transition Metal Complexes (AJM) AFOSR-75-2869, 2303/B2	R. Bruce King Department of Chemistry University of Georgia Athens, Georgia 30601

Post Doctoral Resident Research Associateship Program (RWH) F44620-76-C-0084, 2303/D8	R. W. Kinney Commission on National Resources National Research Council, NAS/NAE Washington, D.C. 20418
Spectroscopic Determination of Intermolecular Potentials of Gas Laser Components and of Major Atmospheric Constituents (RAA) AFOSR-77-3269, 2303/B1	William Klemperer Department of Chemistry Harvard University Cambridge, Massachusetts 02138
The Measurement of Vibrational Intensities for Infrared Active Exhaust Plume Species from Advanced Propellant Rocket Boosters (RAA) F49620-77-C-0075, 2303/B1	C. E. Kolb M. E. Gersh Aerodyne Research, Inc. Bedford, Massachusetts 01730
The Quantum Dynamics of Chemical Reactions (RAA) AFOSR-77-3394, 2303/B1	Aron Kuppermann Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, California 91125
Chemically Modified Electrodes and Oxygen Electrocatalysis (DWE) AFOSR-78-3672, 2303/A1	Theodore Kuwana Department of Chemistry The Ohio State University Columbus, Ohio 43212
Synthesis of Organofluorine Compounds by Direct Fluorination (AJM) AFOSR-78-3658	Richard J. Lagow Department of Chemistry University of Texas Austin, Texas 78712
Controlled Structural Adhesive Interphases (RWH) AFOSR-78-3692, 2303/A1	Jerome B. Lando Charles E. Rogers Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106
Analysis of Lubricant Films in Bearings Under Incipient Failure Conditions (RWH) AFOSR-78-3473, 2303/A2	James L. Lauer Department of Mechanical Engineering Rensselaer Polytechnic Institute Troy, New York 12181
Chemical Transfer Lasers (RAA) AFOSR-76-2959, 2303/B1	Paul H. Lee Department of Physics University of California Santa Barbara, California 93106

Infrared Chemiluminescence Studies of Ion-Molecule Reactions in a Flowing Afterglow (RAA) AFOSR-78-3565, 2303/B1	Stephen R. Leone G. Barney Ellison Veronica M. Bierbaum Department of Chemistry University of Colorado Boulder, Colorado 80309
Energy and Chemical Change (RAA) AFOSR-77-3135, 2303/B1	Raphael D. Levine James L. Kinsey Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Structure and Properties of Glasses (DRU) AFOSR-75-2764, 2303/A3	John D. Mackenzie Materials Department University of California Los Angeles, California 90024
Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants (RWH) F44620-76-C-0097, 2303/A2	L. R. Mahoney Fuels and Lubricants Department Ford Motor Co. Dearborn, Michigan 48121
Chemical Structure by Laser-Produced X-Rays (DWE) AFOSR-78-3575, 2303/A1	Philip J. Mallozzi Robert E. Schwerzel Battelle Memorial Institute 505 King Avenue Columbus, Ohio 43201
Low Temperature Fluorine Chemistry of Electronegative Elements (AJM) AFOSR-77-3165, 2303/B2	Gleb Mamantov Department of Chemistry University of Tennessee Knoxville, Tennessee 37916
Anisotropic and Electro-Optical Effects in Liquid Crystals (DWE) F49620-77-C-0017, 2303/A1	J. David Margerum Hughes Research Laboratories Hughes Aircraft Co. Malibu, California 90265
Intermolecular Flexibility of Rigid Polymers and Intermolecular Interactions in Ordered Systems (DRU) AFOSR-78-3683, 2303/A3	James E. Mark Department of Chemistry University of Cincinnati Cincinnati, Ohio 45221

Fabricable Polymers for Matrices and Adhesives Which Are Extremely Stable to Heat, Oxidation and Hydrolysis (AJM) AFOSR-77-3112, 2303/B2	Carl S. Marvel Department of Chemistry University of Arizona Tucson, Arizona 85721
Structure and Chemistry of Surfaces (RWH) F49620-77-C-0118, 2303/A2	Robert P. Merrill School of Chemical Engineering Cornell University Ithaca, New York 14853
Calculation of the Energetics and Collision Dynamics for Electronic Transitions (RAA) F49620-77-C-0064, 2303/B1	Harvey H. Michels United Technologies Research Center United Technologies Corporation East Hartford, Connecticut 06108
Energy Paths in Chemical Reactions (RAA) AFOSR-78-3535, 2303/B1	C. Bradley Moore Department of Chemistry University of California Berkeley, California 94720
Ion Photofragment Spectroscopy - Potential Surfaces of Molecular Ions (RAA) F44620-76-C-0095, 2303/B1	John T. Moseley James R. Peterson Physical Sciences Division SRI International Menlo Park, California 94025
Investigation of Electrochromic Diphthalocyanines (AJM) F49620-77-C-0074, 2303/B2	M. M. Nicholson Electronics Research Division Rockwell International Corp. Anaheim, California 92803
Viscosity of Chloroaluminate Melts, Part II (DWE) AFOSR-77-3198, 2303/A1	Harald A. Øye Institute of Inorganic Chemistry University of Trondheim Trondheim-NTH, Norway
Synthesis of Phosphatriazines for Potential High Temperature Fluids Applications (AJM) F44620-76-C-0065, 2303/B2	Kay L. Paciorek Chemical & Materials Research Ultrasystems, Inc Irvine, California 92664
High Resolution Vacuum Ultraviolet Spectroscopy of Small Molecules (RAA) F49620-77-C-0010, 2303/B1	W. H. Parkinson D. E. Freeman K. Yoshino Harvard College Observatory Cambridge, Massachusetts 02138

Cyclic Polyfluorosilicone Polymers and Copolymers (AJM) F4960-77-C-0012, 2303/B2	Ogden Pierce Contract Research & Development Lab Dow Corning Corporation Midland, Michigan 48640
Carbon-Carbon Composite Matrix Decomposition Reactions and Densification Response (DRU) F49620-78-C-0002, 2303/A3	J. P. Pope Material Sciences Division Science Applications, Inc. Santa Ana, California 92707
Raman Study of Solid State Reactions (DRU) 2303/A3	Paras N. Prasad Department of Chemistry State University of New York at Buffalo Buffalo, New York 14260
Studies in Non-Equilibrium Statistical Mechanics (RAA) AFOSR-78-3724, 2303/B1	Herschel Rabitz Stuart D. Augustin Department of Chemistry Princeton University Princeton, New Jersey 08540
Experimental and Theoretical Studies of Intramolecular and Intermolecular Dynamics (RAA) F49620-76-C-0017, 2303/B1	Stuart A. Rice Department of Chemistry University of Chicago Chicago, Illinois 60637
Experimental and Theoretical Work in Chemical Dynamics and Nucleation (RAA) AFOSR-77-3214, 2303/B1	John Ross Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Inorganic Reactants for Synthesis of Novel Fluorocarbon Derivatives (AJM) F49620-77-C-0038, 2303/B2	C. J. Schack Rocketdyne Division Rockwell International Canoga Park, California 91304
Mechanisms of Photochemical Degradation in Xanthene Laser Dyes (AJM) AFOSR-77-3313, 2303/B2	Robert E. Schwerzel Battelle Columbus Laboratories 505 King Avenue Columbus, Ohio 43201
Organosilicon Compounds and Organo silicon Polymer Intermediates (AJM) AFOSR-79-0007, 2303/B2	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139

New Solid Superionic Conductors Containing CU+, GA+, IN+ and TL+ (DWE) AFOSR-77-3227, 2303/A1	Duward F. Shriver Donald H. Whitmore Materials Research Center Northwestern University Evanston, Illinois 60201
Experimental Studies of the State-to-State Chemical Dynamics of Reactions Involving Air Triatomics (RAA) AFOSR-77-3348, 2303/B1	S. Siegel M. E. Whitson, Jr. William H. Steier Graduate Center for Engineering and Computer Sciences University of Southern California Los Angeles, California 90007
New Chemical Analysis Techniques (DWE) F44620-76-C-0031, 2303/A1	Robert E. Sievers Department of Chemistry University of Colorado Boulder, Colorado 80309
Basic Studies Relating to the Synthesis of Unsymmetrical Dimethyl Hydrazine and Monomethyl Hydrazine by Chloramination (AJM) AFOSR-76-2915, 2303/B2	Harry Sisler Department of Chemistry University of Florida Gainesville, Florida 32611
Reactive Atomic Species Generated at High Temperatures and Their Low Temperature Reactions to Form Novel Substances (AJM) AFOSR-78-3634, 2303/B2	Philip S. Skell Department of Chemistry Pennsylvania State University University Park, Pennsylvania 16802
Studies of Energy Transfer and Selective Chemical Reaction Using Tunable IR Radiation (RAA) AFOSR-77-3240, 2303/B1	Ian W. M. Smith Department of Physical Chemistry The University of Cambridge Cambridge, U.K. England
Defect Chemistry of Crystalline Inorganic Materials (DRU) AFOSR-78-3505, 2303/A3	Donald M. Smyth Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015
Effects of Oxygen and Water Vapor on the Compressive Strength of Boundary Films on Iron Crystals (RWH) AFOSR-76-3051, 2303/A2	David K. Snediker Structures and Mechanics Research Dept Battelle Memorial Institute Columbus, Ohio 43201

Evaporation and Dispersion of Hazardous Materials from Accidental Spills (AJM) AFOSR-78-3559, 2303/D9, ASEE Mini Grant	Charles Springer Department of Chemical Engineering University of Arkansas Fayetteville, Arkansas 72701
Lithium-Based Anodes for Solid State Batteries (DWE) AFOSR-77-3460, 2303/A1	B.C.H. Steele Department of Metallurgy and Materials Science Imperial College, University of London London, England
Spectroscopy and Chemistry of Molecules with High Vibrational Energy Content (RAA) AFOSR-78-3725, 2303/B1	Jeffrey I. Steinfeld Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Synthesis of New Inorganic and Organometallic Materials (AJM) AFOSR-76-3102, 2303/B2	F. G. A. Stone Department of Chemistry University of Bristol Bristol, BS8 ITS, England
Multicomponent Oxide Systems for Corrosion Protection (RWH) AFOSR-77-3334, 2303/A2	Gary W. Stupian William H. Steier Graduate Center for Engineering & Computer Sciences University of Southern California Los Angeles, California 90007
Collisional Excitation and Ionization (RAA) F44620-76-C-0007, 2303/B1	Thomas O. Tiernan Department of Chemistry Wright State University Dayton, Ohio 45431
New Perfluoropolymer-Forming Reactions (AJM) F44620-76-C-0027, 2303/B2	Madeline S. Toy Science Applications, Inc. Sunnyvale, California 94086
Gordon Research Conference on Organometallic Chemistry (AJM) AFOSR-78-3553, 2303/B2	P. M. Treichel Gordon Research Conferences Pastore Chemical Laboratory University of Rhode Island Kingston, Rhode Island 02881

Structural and Dynamic Studies of Materials Possessing High Energy Content (AJM) AFOSR-78-3502, 2303/B2	Nicholas J. Turro Department of Chemistry Columbia University New York, New York 10027
Microstructure of Amorphous and Semi-Crystalline Polymers (DRU) AFOSR-77-3226, 2303/A3	Donald R. Uhlmann Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Stabilization and Graphitization of Acrylic Fibers and Carbon Composite Matrices (DRU) AFOSR-77-3466, 2303/A3	Donald R. Uhlmann Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Development and Practical Application of the Theory of Materials (AJM) AFOSR-77-3145, 2303/B2	John R. Van Wazer Department of Chemistry Vanderbilt University Nashville, Tennessee 37235
Radiation and Laser Potential of Homo- and Hetero-Nuclear Rare Gas Diatomic Molecules (RAA) AFOSR-77-3137, 2303/B1	W. C. Walker Y. Tanaka Department of Physics University of California Santa Barbara, California 93106
Correlation of Electrode Kinetics with Molecular Structure (DWE) AFOSR-77-3408, 2303/A1	Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824
Organosilicon Chemistry (AJM) AFOSR-77-3123, 2303/B2	William P. Weber Department of Chemistry University of Southern California Los Angeles, California 90007
High Temperature Molecules and Molecular Energy Storage (RAA) AFOSR-76-2906, 2303/B1	William Weltner, Jr. Department of Chemistry University of Florida Gainesville, Florida 32611
Multiphoton Gas Phase Spectroscopy (DWE) AFOSR-77-3438, 2303/A1	John E. Wessel J. Manushian Graduate Center for Engineering and Computer Sciences University of Southern California Los Angeles, California 90007

Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials (AJM) AFOSR-78-3570, 2303/B2	Robert C. West Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Gas-Surface Dynamics, High Power Laser-Solid Interactions (RWH) AFOSR-77-3186, 2303/A2	Lennard Wharton Department of Chemistry University of Chicago Chicago, Illinois 60637
Kinetic Aspects of Gas Phase Metal Atom Oxidation Reactions (RAA) AFOSR-76-3039, 2303/B1	John Wiesenfeld Department of Chemistry Cornell University Ithaca, New York 14853
Interactive Study of the Mechanics and Structure of Materials (DRU) AFOSR-ISSA-77-0020, 2303/A3	Ben A. Wilcox Metallurgy and Materials Section National Science Foundation Washington, D.C. 20550
Analytical Gas Phase Spectrometry and Combustion Diagnostics (DWE) F44620-76-C-0005, 2303/A1	James D. Winefordner Department of Chemistry University of Florida Gainesville, Florida 32611
X-Ray Photoelectron Spectroscopic Studies of Electrode Surfaces (DWE) AFOSR-76-2974, 2303/A1	Nicholas Winograd Department of Chemistry Purdue University Lafayette, Indiana 47907
Kinetic Studies of Gas Phase Free Radicals (RAA) AFOSR-78-3693, 2303/B1	Curt Wittig Department of Electrical Engineering University of Southern California Los Angeles, California 90007
The State Identification of Reaction Products (RAA) AFOSR-77-3363, 2303/B1	Richard N. Zare Department of Chemistry Stanford University Stanford, California 94305

RESEARCH EFFORTS COMPLETED IN FY78

(Alphabetical by Principal Investigator)

Fundamental Solid Electrode Studies of Phenomena Related to Corrosion Prevention, Fuel Cells and Batteries	Stanley Bruckenstein Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214
Nucleophilic Substitution Reactions of Alkyl, Vinyl, and Aryl Trifluoromethanesulfonates	William D. Closson Department of Chemistry State University of New York at Albany Albany, New York 12222
Elastohydrodynamic Lubrication Studies	John N. Crisp Department of Mechanical Engineering University of Dayton Dayton, Ohio 45469
Chemical Reactions Producing Electronically Excited Metal Atoms	P. Davidovits Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167
Structural Studies of Monomeric Model Compounds and Related Ordered Polymer Systems: The Crystal and Molecular Structures of Two Model Compounds for Polybisbenzoxazoles and Polybisbenzthiazoles	Albert V. Fratini Department of Chemistry University of Dayton Dayton, Ohio 45469
Theoretical and Computational Studies of Electronic Transitions in Molecular Collisions	Thomas F. George Department of Chemistry The University of Rochester Rochester, New York 14627
The Absolute Measurement of Rate Constants for Some Key Reactions Involving Free Radicals	David M. Golden Thermochemistry and Chemical Kinetics Group SRI International (formerly Stanford Research Institute) Menlo Park, California 94025

Influence of Annealing on the Strengths of Secondary Relaxations in Glasses	Martin Goldstein Department of Chemistry Yeshiva University New York, New York 10033
Formation and Deactivation Processes in Electronic Transition, Chemically Pumped Lasers	J. L. Gole Department of Chemistry Georgia Institute of Technology Atlanta, Georgia 30332
	J. I. Steinfeld Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Solid State Materials Derived from Planar Metal Complexes	Leonard V. Interrante and John S. Kasper General Electric Corporate Research and Development P.O. 8 Schenectady, New York 12301
Phosphorus Chemiluminescence Feasibility Studies for an Ultraviolet and Visible Chemical Laser	Ahsan U. Khan and Brian Stevens Chemistry Department University of South Florida Tampa, FL 33620
Synthesis of Organofluorine Compounds by Direct Fluorination	Richard J. Lagow Department of Chemistry University of Texas at Austin Austin, Texas 78712
Chemical Transfer Lasers	Paul H. Lee Department of Physics University of California Santa Barbara, California 93106
Solid Propellant Additives from Pentaborane-9	Amos J. Leffler Department of Chemistry Villanova University Villanova, Pennsylvania 19085

An Investigation of Charge Transport Modes in Nickel Hydroxide Electrodes	Joseph T. Maloy Department of Chemistry West Virginia University Morgantown, WV 26505
The Relation Between the Chemical and Physical Structure and the Mechanical Response of Polymers	Roger J. Morgan McDonnell Douglas Research Laboratories McDonnell Douglas Corporation St. Louis, MO 63166
Chemical Physics of Charge Mechanisms in Nonmetallic Spacecraft Materials	Joseph E. Nanevicz Electromagnetic Sciences Laboratory SRI International Menlo Park, California 94025
Parameters Affecting the Preparation of 3-Fluorosalicylaldehyde Via the Reimer-Tiemann Reaction	Dr. Paul A. Pinke Corporate Research Center UOP Inc. Des Plaines, Illinois 60016
Organosilicon Compounds and Organosilicon Polymer Intermediates	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Molecular Energy Transfer by Collisional Processes Characteristic of Gas Lasers	Hyung Kyu Shin Department of Chemistry University of Nevada Reno, Nevada 89507
Molecular Energy Transfer Studies	Hyung Kyu Shin Department of Chemistry University of Nevada Reno, Nevada 89557
Reactive Atomic Species Generated at High Temperatures and Their Low Temperature Reactions to Form Novel Substances	Philip S. Skell Department of Chemistry Pennsylvania State University University Park, PA 16802
Morphology and Mechanical Behavior of Isomeric Graft Copolymers and Interpenetrating Polymer Networks	L. H. Sperling Materials Research Center Lehigh University Bethlehem, PA 18015

Structural and Dynamic Studies of Materials Possessing High Energy Content	Nicholas J. Turro Department of Chemistry Columbia University New York, New York 10027
Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials	Robert West Department of Chemistry University of Wisconsin-Madison Madison, Wisconsin 53706
Studies of Rotationally Cooled Molecules in Molecular Beams by Laser Spectroscopic Technique	Lennard Wharton The James Franck Institute and Department of Chemistry The University of Chicago 5801 South Ellis Ave. Chicago, Illinois 60637
Lifetimes and Quenching Rates for the $^3\Pi$ States of Interhalogen Molecules	John J. Wright Department of Physics University of New Hampshire Durham, New Hampshire 03824

COMPLETED PROJECT SUMMARIES

FY78

COMPLETED PROJECT SUMMARY

1. TITLE: Fundamental Solid Electrode Studies of Phenomena Related to Corrosion Prevention, Fuel Cells and Batteries

2. PRINCIPAL INVESTIGATOR: Professor Stanley Bruckenstein
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

3. INCLUSIVE DATES: 1 August 1973 - 15 May 1978

4. GRANT NUMBER: AFOSR 74-2572

5. COSTS AND FY SOURCES: \$49,134, FY74, \$53,000, FY75; \$56,259, FY76
\$79,294, FY7T

6. SENIOR RESEARCH PERSONNEL:

Dr. H. D. Durst
Dr. Natsuko Kanzaki
Dr. Yasushi Kanzaki
Dr. Haruo Mizota
Dr. Swathira Sundarajan
Dr. Koichi Tokuda

7. JUNIOR RESEARCH PERSONNEL:

Deung Chu
Daniel Erenhalt
Lutz Grambow
Paul Gifford
Joseph Jolson
John Kosek
Robert Mack
Leo Melnicki
Greg Martinchek
Matthew Michalski
Thomas Reidhammer
Mani Shabang
William G. Sherwood
James Symmanski
Joseph Wang
Gregory Weselak

8. PUBLICATIONS:

"The Interpretation of Isopotential Points at Ring-Disk Electrodes", D. F. Untereker and S. Bruckenstein, J. Electroanal. Chem., 57, 77 (1974).

"Voltammetry of Bismuth (III) at a Continuously Mercury-Coated Rotating Platinum Disk Electrode", M. Z. Hassan and S. Bruckenstein, Anal. Chem., 46, 1827 (1974).

"Electroadsorptive Removal of Impurities from Perchloric, Sulfuric and Phosphoric Acids, and Sodium Hydroxide", M. Z. Hassan and S. Bruckenstein, Anal. Chem., 46, 1962 (1974).

"Equivalent Circuit for the Uncompensated Resistance Occurring at Ring-Disk Electrodes", M. Shabrang and S. Bruckenstein, J. Electrochem. Soc., 121, 1439 (1974).

"Digital Function Generator for Electrochemical Applications", W. G. Sherwood, D. F. Untereker, and S. Bruckenstein, Anal. Chem. 47, 84 (1975).

"An Analog Function Generator for Voltammetric Applications", D. F. Untereker, W. G. Sherwood, T. M. Reidhammer, G. A. Martinchek, and S. Bruckenstein, Chem. Instr., 6(3), 259 (1975).

"Simultaneous Electrochemical - Electron Spin Resonance Measurements Using a Coaxial Microwave Cavity", R. D. Allendoerfer, G. A. Martinchek, and S. Bruckenstein, Anal. Chem. 47, 890 (1975).

"The Frequence Response of Limiting Currents to Sinusoidal Speed Modulation at a Rotating Disk Electrode", K. Tokuda, S. Bruckenstein, and B. Miller, J. Electrochem. Soc. 122, 1316 (1975).

"Calculation of Diffusion Coefficients from Rotating Disk Electrode Data", S. Bruckenstein, J. Electrochem. Soc., 122, 1215 (1975).

"The Primary Resistance of a Ring Electrode", M. Shabrang and S. Bruckenstein, J. Electroanal. Chem., 65, 155 (1975).

"Compensation of Ohmic Potential Interactions Occurring at Ring-Disk Electrodes", M. Shabrang and S. Bruckenstein, J. Electrochem. Soc., 122, 1305 (1975).

"Ring-Disc Electrodes. Part 17. Ring Response to Periodic Disc Electrode Forcing Functions", S. Bruckenstein, K. Tokuda, and W. J. Albery, J. Chem. Soc., Faraday Transactions 1, 73 (1977).

"Mass Spectrometer Investigation of the Electrochemical Behavior of Absorbed Carbon Monoxide in 0.2 M Sulfuric Acid at Platinum", L. Grambow and S. Bruckenstein, Electrochemica Acta, 22, 377 (1977).

"The Adsorption and Underpotential Deposition of Thallium on Gold in 0.5 M Potassium Chloride", V. A. Vicente and S. Bruckenstein, J. Electroanalytical Chem., 82, 187 (1977).

"Phase-Selective Fundamental and 2nd Harmonic AC Voltammetry at the Continuously Mercury Coated Rotating Disk Electrode", N. Kanzaki, Y. Kanzaki, and S. Bruckenstein, Anal. Chem., 49, 1789 (1977).

"A Study of the Corrision of Dental Amalgam Using the Ring Disk Electrode", L. Gal-Or, S. Bruckenstein, and J. M. Carter, J. Biomed. Mat. Res., 12, 1 (1978).

"Coulostatic Deposition of Metals at Underpotential. Part I, Potential Relaxation in Absence of Chemical Reactions", D. F. Untereker, W. G. Sherwood, and S. Bruckenstein, J. Electrochem. Soc., 125, 380 (1978).

"Coulastatic Deposition of Metals at Underpotential. Part II, The Effect of Heterogeneous, Chemical Reactions on the Potential Relaxation Process", W. G. Sherwood, D. F. Untereker, and S. Bruckenstein, J. Electrochem. Soc., 125, 384 (1978).

"The Isotherm for Underpotential Mercury Deposition on Gold", W. G. Sherwood and S. Bruckenstein, J. Electrochem. Soc., 125, 1098 (1978).

"Sinusodial Hydrodynamic Voltammetry. I. Theory of Electron Transfer Processes", K. Tokuda and S. Bruckenstein, J. Electrochem. Soc., in press.

"Sinusodial Hydrodynamic Voltammetry. II. Experimental Test of the Electron Transfer Theory", Y. Kanzaki and S. Bruckenstein, J. Electrochem. Soc., in press.

"Micromolar Voltammetric Analysis by Ring Shielding at a Rotating-Ring Disk Electrode", S. Bruckenstein and P. Gifford, Anal. Chem., in press.

"The Apparent Electron Transfer Number for Underpotential Deposits of Silver on Polycrystaline Gold", T. Reidhammer, S. Melnicki, and S. Bruckenstein, Z. Phys. Chem. in press.

"A Closed Form Expression for the Primary Resistance at a Ring Electrode", S. Bruckenstein and G. Martinchek, J. Electrochem. Soc., submitted.

"The Open Circuit Corrosion and Anodic Dissolution of Copper-Nickel Alloys in Chloride Media", H. Mizota, G. Martinchek, and S. Bruckenstein, In Preparation.

"Surface Adsorbates Formed on Platinum During Carbon Monoxide Adsorption", J. Jolson and S. Bruckenstein, In Preparation.

9. INVENTIONS:

Name of Inventor	Title of Invention	Patent Application Serial Number	Patent Issued On
Stanley Bruckenstein and William G. Sherwood	Electrochemical gas monitor	USP 4,057,478	8 November 1977

10. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The study of surface phenomena at solid electrodes related to electrochemical power sources and corrosion processes was the major goal of this research. In particular, three kinds of surface processes were investigated: (1) Underpotential metal deposition, (2) neutral species adsorption and (3) insoluble film formation. New electroanalytical and electrochemical techniques were developed specifically for the purpose of studying these surface processes. These techniques made it possible to prepare solutions with extremely low levels of poisoning-substances, to distinguish between surface and mass transport controlled processes, and to perform quantitative studies involving micromolar levels of electroactive species.

Underpotential deposition, UPD, of thallium, mercury and silver on gold have resulted in the determination of accurate adsorption isotherms and highly precise determination of the electrosorption valency, γ. γ-values for silver show a minimum near surface coverages of 0.5. No minimum has ever been discovered before. We believe that this minimum is caused by either a superlattice phenomena and/or a change in double layer structure. Mercury UPD studies established the existence of a spontaneous coulostatic process that can produce UPD for open circuited metal electrodes.

Carbon monoxide, selected as a model neutral species absorbate, was shown to exist in a number of adsorbed states on platinum. When adsorbed at very cathodic potentials, a portion of the adsorbate corresponds to a reduced CO species. CO adsorbed at less cathodic potentials can exist in two forms, the relative amounts of each form depending on the flux of incoming CO. All forms are quantitatively oxidized to CO_2 at anodic potentials. Periodic, or single pulse, oxidation currents can be observed at constant potential.

Model studies of a classic three component dental amalgam (Ag, Hg, Sn) demonstrate that only tin dissolves and that a protective silver chloride film forms. All the mercury remains bound as either a silver or tin solid amalgam. Studies on copper-nickel alloys (100% Cu to 0% Cu) in neutral chloride media showed that copper is selectively leached from a thin surface layer of the alloy and that the rate of corrosion is then determined by rate of dissolution of nickel from the top of this layer.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Nucleophilic Substitution Reactions of Alkyl, Vinyl, and Aryl Trifluoromethanesulfonates

2. PRINCIPAL INVESTIGATOR: Dr. William D. Closson
Department of Chemistry
SUNY at Albany
Albany, NY 12222

3. INCLUSIVE DATES: 1 February 1977 - 31 July 1978

4. GRANT NO: AFOSR-77-3241 (Mini Grant)

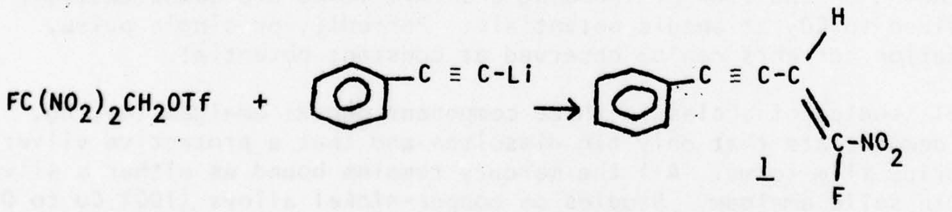
5. COSTS AND FY SOURCE: $8,264, FY77

6. PUBLICATIONS:

"Nucleophilic Substitution Reactions of Alkyl, Vinyl, and Aryl Trifluoromethanesulfonates", William D. Closson, Final Technical Report.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main objectives of this research dealt with the unusual reaction between lithium phenylacetylide and 2-fluoro-2,2-dinitroethyl trifluoromethanesulfonate (triflate or Tf), shown in equation 1, discovered by S. Shackelford at Seiler Research Laboratory. It was hoped to both determine the mechanism of this unusual transformation and also broaden its scope so as to extend it to triflate esters of other β-nitro alcohols and other lithium acetylide species. The reason this was felt to be important was that structures similar to 1, which would possess a conjugated enyne structure with attached fluoro and/or nitro groups but without the large, relatively inert phenyl group, would be promising materials for use as energetic binders, plasticizers, and crosslinking agents to replace nonenergetic materials currently used for these purposes. In addition,



(1)

certain other classes of reactions of triflate esters and triflyl derivatives were to be explored, partly for their possible bearing on the mechanism of the reaction in equation 1 and partly for their own intrinsic interest.

The reaction of carbanion type nucleophiles with nitro substituted alkyl trifluoromethanesulfonate (triflate) esters were shown to have very limited synthetic value. The usual result was the formation of mixtures of tarry materials.

Reaction of aryl triflates with various nucleophiles appeared to be limited to nucleophilic attack at sulfonyl sulfur and, for strongly basic, hindered, nucleophiles, generation of benzyne. Neither type of reaction offers significant synthetic utility.

Electron-transfer (ET) reactions of several classes of trifluoromethanesulfonyl derivatives were examined. For alkyl and aryl esters, the chemistry is very similar to that of the corresponding methanesulfonate esters. Trifluoromethanesulfonamides, however, display a behavior uniquely different from that of all other sulfonamides. They undergo reductive cleavage (to amine and triflite ion) much more easily than do methanesulfonamides, they cleave via a pre-equilibrium electron-transfer mechanism, and the substituent effect upon their rates of cleavage correlates extremely well with σ^n constants.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Elastohydrodynamic Lubrication Studies

2. PRINCIPAL INVESTIGATOR: Dr. John N. Crisp
Department of Mechanical Engineering
University of Dayton
Dayton, Ohio 45469

3. INCLUSIVE DATES: 1 January 1977 - 31 December 1977

4. GRANT NUMBER: AFOSR-77-3229 (Mini Grant)

5. COSTS AND FY SOURCE: $9,937, FY77

6. SENIOR RESEARCH PERSONNEL: Dr. John N. Crisp

7. JUNIOR RESEARCH PERSONNEL: H. E. Bandow

8. PUBLICATIONS:

"Pressure Distribution from Measured Film Thickness and Temperature Data for Elastohydrodynamic Point Conjunctions," J. N. Crisp and H. E. Bandow, UDSE-TR-78-01, Final Technical Report (Feb 1978).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this investigation was to develop a computer program to deduce the contact pressure distribution from simultaneously measured film thickness and temperature field data for EHD point contact conjunctions. Measured film thickness and the temperature field data of Nagaraj[1], was used to determine the pressure distribution for a specific case.

The geometry of elastohydrodynamically lubricated point contacts usually prohibits the direct measurement of the pressure distribution within such contacts but knowledge of the pressure distribution is needed to understand the behavior of the lubricant and the stress imposed on the bearing surfaces. Given the viscosity-temperature-pressure relationship for the lubricant, Reynolds' equation has been solved in finite measured film thickness and temperature distribution. The elasticity

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[1] Nagaraj, H. S., "Investigation of Some Temperature-Related Phenomena in Elastohydrodynamic Contacts Including Surface Roughness Effects," Ph.D. Thesis, Georgia Institute of Technology (Dec 1976).

relations for the bearing surfaces have also been formulated to yield the pressure distribution from the measured film thickness alone. The pressure distribution was obtained for representative contacts from measured data and it was found that great care must be taken to make measurements with sufficient accuracy.

AFOSR Program Manager: R. W. Haffner, LtCol, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Reactions Producing Electronically Excited Metal Atoms

2. PRINCIPAL INVESTIGATOR: Dr. P. Davidovits
Department of Chemistry
Boston College
Chestnut Hill, MA 02167

3. INCLUSIVE DATES: 1 March 1975 - 30 June 1978

4. GRANT NO: AFOSR-75-2822

5. COSTS AND FY SOURCES: $38,227, FY75; $43,665, FY76;
$29,314, FY77

6. SENIOR RESEARCH PERSONNEL:

Dr. P. Davidovits	Dr. E. J. Johnson
Dr. D. L. McFadden	Dr. A. T. Prengel

7. JUNIOR RESEARCH PERSONNEL:

Mr. U. C. Sridharan	Mr. T. DiGiuseppe
Mr. J. DeHaven	Ms. A. Brzychcy

8. PUBLICATIONS:

"Chemiluminescence from the Gas Phase Reaction of Atomic Boron with the Alkali Metal Fluorides", U. C. Sridharan, D. L. McFadden and P. Davidovits, J. Chem. Phys. 65, 5373 (1976).

"Production of Neutral Atoms by Pulsed Laser Heating", A. Prengel, J. DeHaven, E. J. Johnson and P. Davidovits, J. Appl. Phys., 48, 3551 (1977).

"Chemiluminescence from the Gas Phase Reactions of Atomic Carbon with PbO", U. C. Sridharan, T. G. DiGiuseppe, D. L. McFadden and P. Davidovits, Accepted for publication in Chem. Phys. Letters.

"Chemiluminescence Studies of Boron Atom Reactions with O_2, and N_2O, A. Brzychcy, J. DeHaven, A. T. Prengel and P. Davidovits, Accepted for publication Chem. Phys. Letters.

"Cross Sections for the Reaction of Boron Atoms with O_2, SO_2, N_2O and CO_2", U. C. Sridharan, T. G. DiGiuseppe, D. L. McFadden and P. Davidovits, Manuscript in preparation for submission to J. Chem. Phys.

"Beam Studies of the Reaction of Boron Atoms with the Alkali Metal Fluorides", J. DeHaven, A. Brzychcy and P. Davidovits, Manuscript in preparation for submission to J. Chem. Phys.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to study excited metal atoms produced in the reaction of boron and carbon with metal fluorides and oxides in an attempt to produce population inversions between electronic states.

Merged flow, diffusion and single collision experiments were performed to measure total reaction cross sections, chemiluminescence cross sections and population distributions in the electronically excited states of reaction products. The basic purpose of these studies was to gather a body of systematic data in order to understand the reaction mechanism and the production of electronically excited states for this important class of non-metal atom reactions. Total cross sections were measured for the reaction of carbon atoms with lead oxide (PbO). The cross section is 20Å^2. The total reaction cross sections of boron atoms with O_2 and SO_2 are respectively 1Å^2 and 0.8Å^2. The cross sections for the reaction of boron with N_2O and CO_2 is less than 0.08Å^2. The cross sections for the production of electronically excited states of reaction products were determined for the reactions of carbon atoms with PbO and boron atoms with O_2, CsF and RbF. These values are respectively 5Å^2, 0.05Å^2, 3Å^2 and 7Å^2. The population distribution in the electronically excited product states was determined for the reactions of carbon atoms with PbO, and boron atoms with CsF, RbF, KF, NaF, and O_2. Population inversion between electronically excited states was observed in several reactions.

AFOSR Program Manager: Capt Russell A. Armstrong

COMPLETED PROJECT SUMMARY

1. TITLE: Structural Studies of Monomeric Model Compounds and Related Ordered Polymer Systems: The Crystal and Molecular Structures of Two Model Compounds for Polybisbenzoxazoles and Polybisbenzthiazoles

2. PRINCIPAL INVESTIGATOR: Dr. Albert V. Fratini
Department of Chemistry
University of Dayton
Dayton, Ohio 45469

3. INCLUSIVE DATES: 15 April 1977 - 14 April 1978

4. GRANT NUMBER: AFOSR-77-3267

5. COSTS AND FY SOURCE: $9,703, FY77

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Structural Studies of Monomeric Model Compounds and Related Ordered Polymer Systems: The Crystal and Molecular Structures of 2,6-Diphenylbenzo [1,2-d:5,4-d′]-Bisoxazole and 2,6-Diphenylbenzo [1,2-d:4,5-d′] Bisthiazole," A. V. Fratini, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Ordered polymer systems are being investigated by AFOSR and the Air Force Materials Laboratory as molecular or self-reinforced composites. The preparation of high strength materials consisting of rod-like polymers, such as the aromatic polyamides, requires a high degree of orientation of the rods. On the other hand, the paraconfigured aromatic heterocyclic class of polymers, such as the rod-like polybenzoxazoles (PBO) and the polybenzthiazoles (PBT), are especially promising since precipitated films and fibers of these materials exhibit high tensile strengths and good thermal oxidative stabilities.

In order to achieve better understanding of precipitated film formation, film and fiber morphology, and microstructure in the polybenzoxazoles and polybenzthiazoles, a systematic study of the x-ray crystal structures of two monomeric model compounds for PBO and PBT were determined. These compounds embraced the different chemical environments for the repeat units of those PBO and PBT polymers which had already been synthesized.

The 2,6-Diphenylbenzo(1,2-d:5,4-d')-bisoxazole is orthorhombic, space group C_{mca}, with four molecules per unit cell of dimensions a =11.370(7), b = 5.940(3) and c =22.275 A. The molecules stack along b in two vertical columns of differing orientations and are inclined to b by an angle of 36°. The repeat distance along b is 5.94Å and the perpendicular distance between adjacent molecules in a particular stack is 3.4A. 2,6-Diphenylbenzo(1,2-d:4,5-d')-bisthiazole is monoclinic, space group $P2_1/c$, with two molecules per unit cell of dimensions a = 11,041(3), b = 6,633(2), c = 11,720(3) Å, and beta = 112.36(5)°. Molecules stack most efficiently along b with an inclination angle of 36.8°, similar to that observed for the benzobisoxazole. Adjacent molecules along c exhibit a crossing pattern with a dihedral angle of 73.6°. Detailed structure parameters were determined for the bisoxazole and bisthiazole moieties. The relationship between model compound structures and the gross packing features of polymer chains in PBO and PBT was also investigated.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Theoretical and Computational Studies of Electronic Transitions in Molecular Collisions

2. PRINCIPAL INVESTIGATOR: Thomas F. George
Department of Chemistry
The University of Rochester
Rochester, New York 14627

3. INCLUSIVE DATES: 15 May 1974 - 14 November 1977

4. CONTRACT NUMBER: F44620-74-C-0073

5. COSTS AND FY SOURCE: \$35,925, FY 74; \$48,766, FY 75; \$67,000, FY 76; \$35,000, FY 77

6. SENIOR RESEARCH PERSONNEL:

Dr. John C. Bellum
Dr. Paul L. DeVries
Dr. Stephen D. Druger
Dr. Richard L. Jaffe
Dr. Andrew Kormornicki
Dr. John R. Laing
Dr. Kai-Shue Lam
Dr. Hai-Woong Lee
Dr. Maurice S. Mahlab
Dr. Francis J. McLafferty
Dr. Jian-Min Yuan
Dr. I. Harold Zimmerman

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Semiclassical Treatment of Electronic Transitions in Molecular Collisions: Collinear $H^+ + D_2 \rightarrow HD^+ + D$," Y.-W. Lin, T. F. George and K. Morokuma, J. Chem. Phys. 60, 4311 (1974).

"Microscopic Reversibility and Complex-Valued Trajectories in a Semiclassical Theory of Molecular Collisions," Y. -W. Lin and T. F. George, J. Chem. Phys. 61, 1510 (1974).

"Quantum Resonance Effects in Electronic-to-Vibrational Energy Transfer in Molecular Collisions," I. H. Zimmerman and T. F. George, J. Chem. Phys. 61, 2468 (1974).

"Calculations of Potential Energy Surfaces in the Complex Plane. III. Branch-Point Structure and Rational Fractions," R. L. Jaffe, T. F. George and K. Morokuma, Mol. Phys. 28, 1489 (1974).

"Calculations of Potential Energy Surfaces in the Complex Plane. IV. *Ab Initio* Surfaces for H_3^+," R. L. Jaffe, K. Morokuma and T. F. George, *J. Chem. Phys.* *61*, 4717 (1974).

"Semiclassical Extension of Levinson's Theorem to a Particle Interacting with a Harmonic Oscillator," Y.-W. Lin and T. F. George, *J. Chem. Phys.* *61*, 5396 (1974).

"Semiclassical Treatment of Electronic Transitions in Molecular Collisions: Three-Dimensional $H^+ + D_2 \rightarrow HD^+ + D$," Y.-W. Lin, T. F. George and K. Morokuma, *Chem. Phys. Lett.* *30*, 49 (1975).

"Real and Complex Intersections between Potential Energy Surfaces of the Same Symmetry in Polyatomic Systems," T. F. George, K. Morokuma and Y.-W. Lin, *Chem. Phys. Lett.* *30*, 54 (1975).

"Complex-Valued Classical Trajectories for Tunneling and Well-Defined Paths," T. F. George, *J. Chem. Phys.* *62*, 750 (1975).

"Semiclassical Treatment of Charge Exchange at Low Energies: Collinear $H^+ + H_2$ Collisions," Y.-W. Lin, T. F. George and K. Morokuma, *J. Phys. B: At. Mol. Phys.* *8*, 265 (1975).

"Quantum Mechanical Study of Electronic Transitions in Collinear Atom-Diatom Collisions," I. H. Zimmerman and T. F. George, *Chem. Phys.* *7*, 323 (1975).

"Generalized Semiclassical Optical Model and Velocity-Dependent Potentials," T. F. George, I. H. Zimmerman and H. D. Franchino, *Mol. Phys.* *29*, 1717 (1975).

"The Vibronic Representation for Collinear Atom-Diatom Collisions: Two-State Semiclassical Model," J. R. Laing, T. F. George, I. H. Zimmerman and Y.-W. Lin, *J. Chem. Phys.* *63*, 842 (1975).

"Numerical Comparison between Electronically Adiabatic and Diabatic Representations for Collinear Atom-Diatom Collisions," I. H. Zimmerman and T. F. George, *J. Chem. Phys.* *63*, 2109 (1975).

"Multiple Potential Energy Surfaces in a Semiclassical Treatment of Molecular Collisions," F. J. McLafferty and T. F. George, *J. Chem. Phys.* *63*, 2609 (1975).

"*Ab Initio* and Semiempirical Study of Multiple Surfaces and their Analytic Continuation for Collinear $F(^2P_{3/2}, ^2P_{1/2}) + H_2 \rightarrow FH + H$," R. L. Jaffe, K. Morokuma and T. F. George, *J. Chem. Phys.* *63*, 3417 (1975).

"Theoretical Study of Isotope Effects in the Quenching of Electronically Excited Halogen Atoms by H_2, D_2 and HD," I. H. Zimmerman and T. F. George, *J. Chem. Soc. Faraday II* *71*, 2030 (1975).

"Symmetry Rules for Nonconcerted Reactions," H. Metiu, J. Ross and T. F. George, Chem. Phys. 11, 259 (1975).

"Calculations of Potential Energy Surfaces in the Complex Plane. V. The $^2\Sigma^+$ and $^2\Pi$ States of HF^+," R. L. Jaffe, A. D. Isaacson, J. R. Laing, K. Morokuma and T. F. George, Theoret. Chim. Acta (Berl.) 40, 189 (1975).

"On Nonadiabatic Transition State Theory," F. J. McLafferty and T. F. George, Chem. Phys. Lett. 37, 67 (1976).

"Analytic Structure of the Eigenvalue Problem as Used in Semiclassical Theory of Electronically Inelastic Collisions," P. Pechukas, T. F. George, K. Morokuma, F. J. McLafferty and J. R. Laing, J. Chem. Phys. 64, 1099 (1976).

"A Note on Semiclassical Bound States and Correspondence Principles," F. J. McLafferty and T. F. George, J. Chem. Phys. 64, 2778 (1976).

"Theory of Absorption and Emission of Radiation in Molecular Collisions: Semiclassical Model," J. M. Yuan, T. F. George and F. J. McLafferty, Chem. Phys. Lett. 40, 163 (1976).

"Decoupling Scheme for a Semiclassical Treatment of Electronic Transitions in Atom-Diatom Collisions: Real-Valued Trajectories and Local Analytic Continuation," A. Komornicki, T. F. George and K. Morokuma, J. Chem. Phys. 65, 48 (1976).

"Extending Menzel's Closed Form Approximation for the Error Function," I. H. Zimmerman, Amer. J. Phys. 44, 592 (1976).

"Electronic-to-Rotational Energy Transfer in Molecular Collisions," P. L. DeVries and T. F. George, Chem. Phys. Lett. 43, 391 (1976).

"How Much Do Multiple Electronic Surfaces Influence Chemical Reactivity? $F + H_2$: A Case Study," A. Komornicki, T. F. George and K. Morokuma, J. Chem. Phys. 65, 4312 (1976).

"A Semiclassical Magnus Approximation to Coupled Space-Time-Dependent Scattering Equations," J. R. Laing and K. F. Freed, Chem. Phys. 19, 91 (1977).

"Semiclassical Theory of Molecular Collisions in a Laser Field," J. M. Yuan, J. R. Laing and T. F. George, J. Chem. Phys. 66, 1107 (1977)

"Quantum Mechanical Study of Electronic Transitions in Coplanar Atom-Diatom Collisions: Quenching of Fluorine by H_2," P. L. DeVries and T. F. George, J. Chem. Phys. 66, 2421 (1977).

"Numerical Test of the Semiclassical Approximation for the Multicurve-Crossing Problem: Three-State Model for He^+ + Ne Collisions," J. R. Laing and T. F. George, Phys. Rev. A 16, 1082 (1977).

"Theory of Molecular Collisions in the Presence of a Laser Field," T. F. George, J. R. Laing, J. M. Yuan and I. H. Zimmerman (invited paper), Proc. Third Europ. Electro-Optics Conf., 1976, SPIE 99, 248 248 (1977).

"A New Concept in Laser-Induced Chemistry: The Electronic-Field Representation," T. F. George, I. H. Zimmerman, J. M. Yuan, J. R. Laing and P. L. DeVries, Acc. Chem. Res. 10, 449 (1977).

"Semiclassical Dynamics on Multiple Electronic Surfaces: Three-Dimensional Treatment of Reactive F + H_2," A. Komornicki, K. Morokuma and T. F. George, J. Chem. Phys. 67, 5012 (1977).

"Quantum Mechanical Theory of Collisional Ionization in the Presence of Intense Laser Radiation," J. C. Bellum and T. F. George, J. Chem. Phys. 68, January (1978).

"Semiclassical Approach to Collision-Induced Emission in the Presence of Intense Laser Radiation: An Aspect in the Study of Cooperative Chemical and Optical Pumping," K. S. Lam, I. H. Zimmerman, J. M. Yuan, J. R. Laing and T. F. George, Chem. Phys., in press.

"Computational Study of a Molecular Collision Process in the Presence of an Intense Laser Radiation Field: Enhanced Quenching of F by Xe in the 248 mm Light of the KrF Laser," P. L. DeVries, M. S. Mahlab and T. F. George, Phys. Rev. A 16, February (1978).

"Semiclassical Theory of Unimolecular Dissociation Induced by a Laser Field," J. M. Yuan and T. F. George, J. Chem. Phys. 68, April (1978).

"Theoretical and Computational Studies of Electronic Transitions in Molecular Collisions," T. F. George, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research program involved the development of formal theories and computational algorithms suitable to the microscopic description of electronic transitions in molecular collision systems. Such a description must allow for the dynamic coupling between two or more potential energy surfaces. The research is divided into two general parts, Field-Free Processes and Laser-Assisted Processes.

Field-Free Processes: Two general approaches were taken, a quantum mechanical approach and a semiclassical approach. The quantum mechanical approach involves the direct solution of the time-independent Schrödinger equation as accurately as possible for an assumed form of the potential interaction. The main type of process considered in this approach was the nonreactive collision

$$X(^2P_{1/2}) + H_2(v,j) \rightarrow X(^2P_{3/2}) + H_2(v',j') \qquad (1)$$

where X represents a halogen atom.

For the case where X is the fluorine atom, the probability of quenching from the excited $^2P_{1/2}$ spin-orbit state is found to be small (~0.1) for thermal collision energies but rises quickly to values greater than 0.5 for higher energies provided $\Delta v(H_2) = 0$. For chlorine atom the results are similar, although the rise in the quenching probability at higher energies is not as great as for fluorine. For bromine atom the quenching probability is low for a large range of collision energies if H_2 does not switch vibrational states. However, if H_2 makes a transition between adjacent vibrational states, there is a large quenching probability (greater than 0.5) beginning at the threshold for this transition, which reflects a resonance behavior in electronic-to-vibrational energy transfer, in accord with experimental results obtained elsewhere. The results for iodine collisions indicate a low quenching probability regardless of the vibrational transitions occurring in H_2, somewhat in disagreement with experimental results. Results for bromine collisions with hydrogen isotopes reveal that HD is a more efficient quencher than H_2, and H_2 is more efficient than D_2, in accord with a comparison of the energy defects.

The quantum mechanical studies of Reaction (1) were extended to include rotational degrees of freedom. Cross lengths (the two-dimensional analog of cross sections) were obtained from a coupled-channel calculation carried out in the diabatic representation. The results revealed a particularly strong cross length for quenching with para-H_2 (v=o) making a transition from its ground to its second excited rotational state. This reflects a resonance behavior in electronic-to-rotational energy transfer.

Semiclassical calculations were carried out for collinear Reaction (1) in parallel with the quantum calculations. Beginning with the case of fluorine collisions, both translation and vibration were assumed to behave classically. Results from these calculations are in very good agreement with those from the quantum calculations. For bromine collisions, owing to the resonance between electronic and vibrational degrees of freedom, vibration had to be treated quantum mechanically. Results were again in very good agreement with those from the quantum calculations.

The semiclassical approach was then applied to full three-dimensional representations of the chemical reaction

$$F(^2P_{1/2}) + H_2 \rightarrow HF(^1\Sigma^+) + H \qquad (2)$$

Results for the rate constants indicate that although $F(^2P_{3/2})$ is more reactive than $F(^2P_{1/2})$, the reaction from $F(^2P_{1/2})$ is significant even for thermal collision energies. Hence, a proper dynamical treatment of the F + H_2 reactive system should include the effects of the spin-orbit splitting in fluorine.

The H_3^+ system was considered within the semiclassical approach, and calculations were carried out for collinear charge-exchange by the process

$$H^+ + H_2 \rightarrow H_2^+ + H \qquad (3)$$

and rearrangement by the process

$$H^+ + D_2 \rightarrow HD^+ + D. \qquad (4)$$

Reaction (4) was treated for full three-dimensional as well as collinear collisions. Whereas translation is the dynamic motion mainly responsible for electronic transitions in Reactions (1) and (2), vibration is mainly responsible for electronic transitions in Reactions (3) and (4).

In order to test the validity of the semiclassical approach beyond the two-(electronic) state approximation, calculations were carried out for the process

$$He^+(1s) + Ne(2p^6) \rightarrow He^+(1s) + Ne(2p^5 3s, {}^2P_{3/2}) \qquad (5)$$

$$\rightarrow He^+(1s) + Ne(2p^5 3s, {}^2P_{1/2}). \qquad (6)$$

A parallel quantum coupled-channel calculation was carried out, and the cross sections from both calculations for Reactions (5) and (6) are in excellent agreement over a broad energy range.

Since the semiclassical approach involves the analytic continuation of potential energy surfaces (or curves) to complex intersection points, an investigation of surfaces in the complex plane was carried out within the framework of ab initio calculations. Calculations were carried out for the HF^+, H_3^+ and FH_2 systems in the regions of selected intersection points, and some estimations of accuracy were established.

Laser-Assisted Processes: The availability of intense laser radiation (power density > 10^6 watts/cm^2) has opened the door to a variety of new phenomena in the area of laser-assisted chemistry. For example, for high enough intensity a laser can actually interact with the dynamics in a collision system, with dramatic effects on the mechanism of reaction and energy transfer. This phenomenon can be viewed as 'cooperative chemical and optical pumping', and to achieve this the photon energy need not be in resonance with the level separations that characterize the individual asymptotic reactants or products. This observation motivated the theoretical study of molecular collision processes in the presence of intense laser radiation by both quantum mechanical and semiclassical approaches, with particular emphasis where the radiation field comes into resonance with the electronic degrees of freedom of the molecular system.

In the quantum mechanical approach, a set of coupled equations was derived which could then be solved for the scattering matrix (S-matrix). A special feature of these equations is the appearance of both field-free potential coupling and radiative coupling, so that special interference effects are anticipated when both types of coupling are of comparable strength.

Results were obtained for the process

$$\mathrm{Br}(^2P_{3/2}) + \mathrm{H}_2\ (v=0) + \hbar\omega \rightarrow \mathrm{Br}(^2P_{1/2}) + \mathrm{H}_2(v=0) \qquad (7)$$

restricted to collinear collisions. $\hbar\omega$ is the photon energy, chosen to be 1.001 times the spin-orbit splitting in bromine, which is too large to induce a spin-orbit transition without the cooperative effect of the colliding H_2. The probability for Reaction (7), at a collision energy of 0.163 eV, shows nonlinear behavior for intensities greater than 10^8 W/cm^2. In this nonlinear region the probability is more than an order of magnitude greater than the corresponding probability with the field turned off. The only portion of radiative coupling considered in this study was the magnetic dipole contribution from bromine. A more realistic calculation which includes electric dipole contributions would show even more dramatic effects due to the laser field.

A more realistic calculation was carried out for

$$\mathrm{F}(^2P_{1/2}) + \mathrm{Xe} + \hbar\omega \rightarrow \mathrm{F}(^2P_{3/2}) + \mathrm{Xe} + \hbar\omega \qquad (8)$$

for three-dimensional collisions, where $\hbar\omega$ corresponds to the 248 nm line of the KrF laser. It is important to realize that there is no net photon absorption in Reaction (8), and $\hbar\omega$ never comes into resonance with the two curves correlating to the asymptotic states of interest. At a collision energy of 0.05 eV, cross sections range from a factor of two (for intensity = 10 GW/cm^2) to over an order of magnitude (for intensity $\sim$ 100 GW/cm^2) greater than cross sections calculated for Reaction (8) with the field turned off. As the collision energy increases, the cross sections with the field turned on tend to approach those with the field turned off.

Turning to the semiclassical approach, where at least one nuclear degree of freedom is assumed to behave classically, expressions were derived for the S-matrix, whose evaluation involves the integration of classical trajectories propagating on electronic-field surfaces. Such surfaces include both the field-free potential interaction and the radiative coupling between the field and the molecular system. The semiclassical approach was applied to Reaction (7) for collinear collisions, yielding results in excellent agreement with those from the quantum mechanical calculations.

An important aspect in the overall study of laser-assisted processes is the representation of the laser field. Instead of the Fock representation it is possible to choose a coherent state, and this was explored for the case where all molecular degrees of freedom are treated quantum mechanically and the case where at least one nuclear degree of freedom is treated classically. It was found that the introduction of the rotating wave approximation was necessary to yield a tractable solution, and this solution was capable of describing only single-photon processes, not multiphoton processes. This problem is still under investigation.

Several other problems also under investigation include the explicit consideration of a laser linewidth, unimolecular decay induced by intense laser radiation and bound-continuum interactions. This last problem involves topics such as collision-induced ionization and spontaneous emission in intense laser radiation.

AFOSR Program Manager: Capt Russell A. Armstrong

COMPLETED PROJECT SUMMARY

1. TITLE: The Absolute Measurement of Rate Constants for Some Key Reactions Involving Free Radicals

2. PRINCIPAL INVESTIGATOR: Dr. David M. Golden
Thermochemistry and Chemical Kinetics Group
SRI International (formerly Stanford Research Institute)
Menlo Park, CA 94025

3. INCLUSIVE DATES: 1 January 1975 - 28 February 1978

4. CONTRACT NUMBER: F44620-76-C-0067

5. COSTS AND FY SOURCE: \$25,997, FY76; \$30,813, FY77; \$15,252, FY78

6. SENIOR RESEARCH PERSONNEL:

Dr. Sidney W. Benson	Dr. Gregory P. Smith
Dr. Miriam Lev-On	Dr. Stephen E. Stein
Dr. Friedhelm Zabel	Dr. Michel Rossi

7. JUNIOR RESEARCH PERSONNEL: Karan E. Lewis

8. PUBLICATIONS:

"Analysis of the Rates of Ion-Molecule Association Reactions. Proton-Bound Dimers of NH_3, CH_3NH_2, and $(CH_3)_2NH$", William N. Olmstead, Mirian Lev-On, David M. Golden, and John I. Brauman, J. Amer. Chem. Soc., 99, 992 (1977).

"Infrared Photodecomposition of Ethyl Vinyl Ether. A Chemical Probe of Multiphoton Dynamics", Robert N. Rosenfeld, John I. Brauman, John R. Barker, and David M. Golden, J. Amer. Chem. Soc., 99, 8063 (1977).

"The Heat of Formation of Acetonyl Radical: VLPP Studies of Acetonyl Bromide, Isopropenylmethylether, and Hexanedione-2,5 in a Search for Acetonyl Stabilization Energy", F. Zabel, S. W. Benson, and D. M. Golden, Int. J. Chem. Kinetics, 10, 295 (1978).

"Application of RRKM Theory to the Reactions $OH + NO_2 + N_2 \rightarrow HONO_2 + N_2$ (1) and $ClO + NO_2 + N_2 \rightarrow ClONO_2 + N_2$ (2); A Modified Gorin Model Transition State", G. P. Smith and D. M. Golden, Int. J. Chem. Kinetics, 10, 489 (1978).

"Pyrolysis and Oxidation of Aromatic Compounds", David M. Golden, to be published by AIAA as part of Symposium volume of Alternate Fuels, Columbia, MD, September 1977.

"A Modified Gorin Transition State in Bond Scission Reactions. An Application to Ethane Dissociation", G. P. Smith, M. Lev-On, and D. M. Golden, submitted for publication, J. Chem. Phys.

"The Equilibrium Constant and Rate Constant for Allyl Radical Recombination in the Gas Phase", M. Rossi, K. D. King, and D. M. Golden, submitted for publication to J. Amer. Chem. Soc.

"Absolute Rate Constants for Metathesis Reactions of Allyl and Benzyl Radicals with HI(DI). The Heat of Formation of Allyl and Benzyl Radicals", submitted for publication to J. Amer. Chem. Soc.

"Homogeneous Decomposition of Vinyl Ethers. The Heat of Formation of Ethanal-2-yl", M. Rossi and D. M. Golden, Int. J. Chem. Kinetics, submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In the course of this work, several distinct advances in areas of gas-phase chemical kinetics can be identified.

We have shown how the use of a modified Gorin model transition state can be used to embody the data from neutral radical-radical interactions to ion-molecule processes. The former use has simplified the interpolation and extrapolation of data of interest for pyrolyses and other combustion processes, as well as for processes of importance in the understanding of tropospheric and stratospheric pollution. The latter use helps to understand gas-phase ion-molecule kinetics, which is the baseline for understanding of solvation effects on ionic chemistry.

We have modified our VLPP (Very Low-Pressure Pyrolysis) technique so as to perform all analysis with molecular beam sampling phase-sensitive detection and have applied this to several important problems.

Specifically, we have determined the heat of formation of allyl radicals by both equilibrium and kinetic experiments. This radical serves as a prototype for stabilized systems. We have also measured the combination rate for allyl radicals and applied our previously mentioned model to this process.

We have measured rate constants for allyl and benzyl radicals reacting with HI and thus have begun to remove the uncertainty cost on iodination methods for measurement of bond dissociation energies.

We have made a study of the thermal dissociation of several vinyl ethers and studied the kinetics of the $\dot{}CH_2CHO\dot{}$ radical as a companion to our experiments in the new area of infrared photochemistry.

We have constructed an infrared CO_2 TEA-laser and used it in some preliminary work on the dissociation of ethylvinylether, which we have shown to decompose by two competing pathways. By introducing the concept of studying a molecule with two pathways, especially such diverse paths as exhibited by ethylvinylether, we have opened up a new way to obtain dynamic information from these types of processes.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Influence of Annealing on the Strengths of Secondary Relaxations in Glasses

2. PRINCIPAL INVESTIGATOR: Professor Martin Goldstein
Department of Chemistry
Yeshiva University
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3. INCLUSIVE DATES: 1 May 1973 - 31 October 1977

4. GRANT NUMBER: AFOSR 73-2540

5. COSTS AND FY SOURCE: $13,740, FY73; $30,096, FY75; $31,967, FY76

6. PUBLICATIONS:

"Validity of the Ehrenfest Equation for a System with More than One Ordering Parameter: Critique of a Paper by Di Marzio", M. Goldstein, J. Appl. Phys. 46 4153 (1975)

"Viscous liquids and the glass transition. V. Sources of the Excess Specific Heat of the Liquid", M. Goldstein, J. Chem. Phys. 64 4767 (1976)

"Statistical Thermodynamics of Configurational Properties", M. Goldstein, Annals N.Y. Acad. Sciences 279 68 (1976)

"Sources of the Configurational Specific Heat and Entropy of Liquids Near the Glass Transition", M. Goldstein, in Non-Crystalline Solids G. H. Frischat, Ed. Transtech Publications, Rockport, Mass. 1977

"Viscous Liquids and the Glass Transition. VIII Effect of Fictive Temperature on Dielectric Relaxation in the Glassy State", J. Haddad and M. Goldstein, J. Non-Crystalline Solids, in press

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to determine the quantitative relationships between glass structure, relaxation processes, and annealing treatments in the transition range of noncrystalline solids. It was intended that this research would contribute a better understanding of the glass transition phenomena and generate information for the control of the glass transition temperature and, thereby, polymer processing and the resultant engineering properties.

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In view of a critique by DiMarzio (J. Appl. Phys. 45, 4143 (1974)) of the standard thermodynamic treatment of the glass transition by Davies and Jones, a reexamination of that treatment was made, and its original conclusions reaffirmed. Examination of calorimetric data on quenched and annealed glasses and on the crystalline phase shows that a major part of the liquid "configurational" specific heat and entropy arise from non-configurational factors, specifically a dependence on structural state (fictive temperature) of (1) lattice vibrational frequencies (2) anharmonicity (3) the numbers of molecular groups capable of participating in secondary relaxational motions.

A study of the influence of annealing (as measured by the fictive temperature) on the strength of dielectric loss in glasses was studied on six molecular liquid glass-formers. A remarkable sensitivity of dielectric loss to fictive temperature was found (1-3 per cent per degree fictive). This sensitivity decreased as the temperature of measurement decreased. It was not possible to determine whether the changes in the β-relaxation region were greater than the changes in the background loss. The thermodynamic implications of these results for the glass transition were pointed out.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Formation and Deactivation Processes in Electronic Transition, Chemically Pumped Lasers

2. PRINCIPAL INVESTIGATORS:

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3. INCLUSIVE DATES: 1 September 1974 - 30 September 1978

4. GRANT NO: AFOSR 75-2578

5. COSTS AND FY SOURCE: $75,333, FY75; $78,000, FY76; $84,206, FY77; $26,500, FY78

6. SENIOR RESEARCH PERSONNEL:

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7. JUNIOR RESEARCH PERSONNEL:

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A. J. Kotlar
D. Liu
D. R. Niver
S. Oblath
D. Preuss
Lt. T. Quelly, USAF

8. PUBLICATIONS:

"Optical Model for Potential Surface Crossing", B. Garetz, L. L. Poulsen, and J. I. Steinfeld, Chem. Phys. 9, 385 (1975).

"Collision-Induced Electronic Deactivation of $N_2^*(B^3\Pi_g)$", B. Garetz, J. I. Steinfeld, and L. L. Poulsen, Chem. Phys. Letters 38, 365 (1976).

"Single Collision Selective Chemical Reaction of Group III Metals (Sc, Y, La) and Halogens (F_2, ClF, SF_6, and Cl)", C. Chalek, D. R. Preuss, and J. L. Gole, in Proceedings, 2nd Summer Colloquium on Electronic Transition Lasers, (J. I. Steinfeld, ed.), p. 50, MIT Press, Cambridge, Mass., 1976.

"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).

"Al + O_3 Chemiluminescence: Perturbations and Vibrational Population Anomalies in the $B^2\Sigma+$ State of AlO", D. M. Lindsay and J. L. Gole, J. Chem. Phys., 66, 3886 (1977).

"Characterization of the Ground and Excited States of Lanathanum Oxide through Bimolecular Oxidation of La Metal with O_2, NO_2, N_2O, and O_3", J. L. Gole and C. L. Chalke, J. Chem. Phys., 65, 4384 (1976).

"Reactions of Silanes with Halogens: Chemiluminescent Products in the UV-Visible Spectrum", C. P. Conner, G. W. Stewart, D. M. Lindsay, and J. L. Gole, J. Am. Chem. Soc. 99, 2540 (1977).

"Single Collision Chemiluminescence Studies of Scandium and Yttrium Oxidation with O_2, NO_2, N_2O, and O_3", C. L. Chalek and J. L. Gole, Chem. Phys., 19, 59 (1977).

"Bimolecular Single Collision Reaction of Ground and Metastable Excited States of Titanium with O_2, NO_2, and N_2O - Confirmation of D_0(TiO)", L. H. Dubois and J. L. Gole, J. Chem. Phys., 66, 779 (1977).

"Development of Visible Chemical Lasers from Reactions Yielding Visible Chemiluminescence", J. L. Gole, in Proceedings, 3rd Summer Colloquium on Electronic Transition Lasers (J. I. Steinfeld, S. Suchard, and L. E. Wilson, eds.) p. 136, M.I.T. Press, Cambridge, Mass. (1977).

"The Temperature Dependence of Chemiluminescene Reactions - Activation Energies for Excited State Formation", D. R. Preuss and J. L. Gole, in Proceedings, 3rd Summer Colloquium on Electronic Transition Lasers (J. I. Steinfeld, S. Suchard, and L. E. Wilson, eds.), p. 176, M.I.T. Press, Cambridge, Mass. (1977).

"High Temperature Chemistry: Modern Research and New Frontiers", J. L. Gole, Ann. Rev. Phys. Chem. 27, 525 (1976).

"Fluorescence and Double Resonance Studies of Energy Transfer", J. I. Steinfeld, in Proceedings, Conference on Energy Transfer Processes in Chemical Reactions, Konigstein, Sept. 1976; published in Berichte der Deutsche Bunsengesellschaft 81, 221 (1977).

"Semiclassical Study of Collision Induced Predissociation: Comparison of the Landu-Zener Model with the Method of Analytic Continuation", G. L. Bendazzoli, M. Ruimondi, B. A. Garetz, T. F. George, and K. Morokuma, Theoretica Chimica Acta, 44, 341 (1977).

"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).

"Activation and Deactivation Rates in High-Power Lasers", J. I. Steinfeld, Proceedings, Colloquium on High-Power Lasers and Applications (Munich, June 1977); Series in Optical Sciences No. 9 (K.-L. Kompa, and H. Walther, eds.), pp. 66-73, Springer-Verlag, Berlin, 1978.

"The Use of Temperature Dependent Reaction Rates to Correct Metal Halide (Oxide) Dissociation Energies as Determined from Chemiluminescence Reactions", D. R. Preuss and J. L. Gole, J. Chem. Phys. 66, 880 (1977).

"Microscopic and Macroscopic Analysis of Non-Linear Master Equations: Vibrational Relaxation of Polyatomic Molecules", M. Tabor, R. D. Levine, A. Ben-Shaul, and J. I. Steinfeld, Mol. Phys., in press.

"Near-Resonant Electronic Energy Transfer from NF($a^1\Delta$) to Bi", G. A. Capelle, D. G. Sutton, and J. I. Steinfeld, J. Chem. Phys., in press.

"Multiphoton CO_2 Laser Vibrational Heating of the Triplet State of Biacetyl", I. Burak, T. J. Quelly, and J. I. Steinfeld, J. Chem. Phys., in press.

"Analysis of Perturbations in the $A^2\Pi$- $X^2\Sigma$+ 'Red' System of CN", A. J. Kotlar, R. W. Field, and J. I. Steinfeld, to be published.

"Formation and Deactivation Processes in Electronic Transitions, Chemically Pumped Lasers", J. I. Steinfeld, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The present research program was concerned with measurement of the rates of formation of excess populations of electronically excited small molecules, particularly in chemiluminescent metal + oxidant reactions, and characterization of the deactivation processes which tend to relax these excited states. One of the motivations for these investigations was the possibility of finding a suitable candidate for a chemically-pumped, electronic transition (i.e., visible - wavelength) laser system. Although such a system was not developed in the course of this work, a great deal of information on the pertinent reaction and relaxation rates was obtained. Initially, this program was under the joint direction of Professors J. L. Gole and J. I. Steinfeld at M.I.T.; Professor Gole moved his part of the research to the Georgia Institute of Technology during the final year of the grant.

For convenience, we list here the principal findings arising from the overall research program.

1. Aluminum - Ozone Reaction. The reaction of aluminum with ozone produces the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ emission spectrum of AlO. Coupling between the $B^2\Sigma^+$ and $A^2\Pi$ levels of AlO is attributed to perturbations.

2. Lanthanum-Oxidant Reactions. Reactions of lanthanum with oxidants (O_2, NO_2, N_2O, O_3) results in chemiluminescent emission from the $A^2\Pi$, $B^2\Sigma^+$, $C^2\Pi$, and in the latter three instances the $D^2\Sigma^+$ states of LaO. The dissociation energy of LaO and a potential function for its $D^2\Sigma^+$ state have been deduced from the data. The electronic state distribution in the La + O_2 reaction was shown by Levine and Ben-Shaul to follow a simple zero-surprisal form.

3. Reactions of Silanes and Boranes with Oxidants. The reactive systems B_2H_6 + O_3, F_2; B_5H_9 + O_3, F_2; and Si_2H_6 + O_3, F_2 were studied. The B_2H_6 + O_3 and B_5H_9 + O_3 systems yield primarily BO_2* with some BO*. The B_2H_6 + F_2 and B_5H_9 + F_2 systems yield HBF* and BH*. The Si_2H_6 + O_3 system is believed to yield HSiO. The reaction of disilane (Si_2H_6) with F_2 is characterized by strong emission from the $A^2\Sigma^+$ - $X^2\Pi$ transition of SiF, the $A(^2B_1)$ - $X(^2A_1)$ transition of SiF_3, and the $A^2\Delta$ - $X^2\Pi$ transition of SiH. By contrast, the principal emission from monosilane - chlorine or disilane - chlorine reactions is the $^1A''$ - $^1A'$ transition of HSiCl. An attempt was made to run the B_5H_9 + F_2 reaction in a laser cavity, but stimulated emission was not observed.

4. Scandium and Yttrium Oxidation Reactions. The reactions of Sc and Y with O_2 are characterized by emission from the $A^2\Pi$ and the previously unobserved $A'^2\Delta$ states of ScO and YO. The reactions of Sc and Y with NO_2, N_2O and O_3 result in emission from the $A^2\Pi$ and $B^2\Sigma^+$ states of ScO and YO. Dissociation energies of ScO and YO[$D_0^0(YO) \geq 7.49$ eV] were deduced from the data.

5. Titanium-Oxidant Reactions. The reaction of Ti with O_2, NO_2, and N_2O results in chemiluminescent emission from the $B^3\Pi$ and $C^3\Delta$ states. From analysis of the temperature dependence, we conclude that Ti(^5F) excited atoms are the most likely precursors of the $C^3\Delta$ state.

6. Chemiluminescent Reactions of the Group IIIB Metals. The reactions of scandium, yttrium, and lanthanum with F_2, Cl_2, Br_2, SF_6, ClF, and IBr have been studied under "single collision" conditions using a beam-gas arrangement. The observed chemiluminescent spectra were primarily attributed to emission from the metal monohalides. Dihalide emission was also observed in the Sc-Br_2 and Sc-Cl systems. We found extremely selective production of monohalide excited electronic states in both the scandium and yttrium reactions. The lanthanum reactions are

characterized by relatively moderate selective excitation of monohalide excited states. The selective feature dominating the scandium and yttrium monohalide spectra has not been observed by previous researchers. On the basis of molecular orbital theory, energy conservation, and known spectra for scandium and yttrium fluoride, the selective emission feature is assigned to a $^3\Sigma^+ - {}^1\Sigma^+$ or $^3\Sigma^+ - {}^3\Delta$ band system. We have determined the molecularity with respect to oxidant for all reactions studied, monitoring chemiluminescent intensity versus oxidant pressure. All reactions producing metal monofluoride were found to be first order with respect to oxidant while reactions producing the monochloride or monobromide are found to be "faster than first order." This behavior was explained in terms of the kinetics of metastable excited states. The production of $ScCl_2$ and $ScBr_2$ also occurs via a "faster than first order" process. Based upon mechanistic considerations entailed in the kinetics of metastable excited states, the radiative lifetimes of the selectively populated excited states of ScCl, ScBr, and YCl are estimated to be on the order of 2×10^{-3} seconds. Analysis of the temperature dependence for six representative reactions indicates that selective excited state formation of the metal monohalides proceeds by a direct mechanism with negligible activation energy. From the short wavelength limits of the chemiluminescent spectra, lower bounds to the dissociation energies of the monohalides were determined. For some of the chemiluminescent reactions studies, we found evidence for "super-relaxation" on collision.

In the reactions of Group IIIB metals with F_2 and NO_2, cross sections for excited-state metal monohalide formation considerably exceed those for monoxide formation. The experimentally determined cross sections were compared with total reactive cross sections, calculated on the basis of mechanistic models used to describe the oxidation reactions of Group IIIB atoms. Based upon this comparison, the ratio of excited state to ground state formation (quantum yield) was determined to be not less than 0.1 for the monohalides.

7. Optical Model for Surface Crossing. Several approaches were investigated to the problem of calculating the rates of collision-induced relaxation between molecular electronic states. Following a classical trajectory (surface-hopping) study of $I_2{}^*\ B^3\Pi_{0u^+} \rightarrow {}^3\Pi_g$ (dissociative), the same system was analyzed using an equivalent optical potential model which yielded a great saving in computation time. This model was also applied to the $N_2{}^*\ B^3\Pi \rightarrow (A^3\Sigma,\ W^3\Delta)$ system, but difficulties were encounted with $\Omega \neq 0$ systems, such as CN $A^2\Pi$. The Landau-Zener calculation of the probabilities employed in the optical model was also compared with more recent semiclassical scattering theories.

8. Information-Theoretic Analysis of Deactivation Rates. The Information-Theoretic treatment of nonequilibrium processes, due to Levine and Bernstein, has proven to be remarkably useful for characterizing relaxation processes, and several aspects of applying these methods

were investigated in this program. A set of state-to-state rates for V-V relaxation in HF was calculated by the "Surprisal Synthesis" method (work performed at Air Force Weapons Laboratory, Kirtland AFB), and the nonlinear master equation governing V-V equilibration in HF was solved using exponential-gap rate constants, in collaboration with Professor R. D. Levine.

9. Spectroscopy and Deactivation of CN $A^2\Pi$. Laser action has been observed from the CN A state produced by photodissociation or electric-discharge pumping, and this system has also been suggested as a promising candidate for a chemically-pumped laser system. Since little is known about the quenching of this state, several investigations were undertaken. Some 39 bands of the "Berkeley" atlas of the CN $A^2\Pi$ - $X^2\Sigma$ transition, along with 16 bands measured at high resolution by R. Bacis of the University of Lyon, were reanalyzed with a least-squares technique, allowing for all ($A^2\Pi \sim X^2\Sigma$) and ($A^2\Pi \sim B^2\Sigma$) perturbations. This provided mixing coefficients for the perturbed levels in the A state. Attempts to carry out monochromatically excited fluorescence experiments on selected levels of the CN A state were, however, inconclusive.

10. Near-Resonant Electronic Energy Transfer. In collaboration with Dr. D. Sutton of the Aerospace Corporation, a measurement was carried out of the rate constant for the nearly resonant ($\Delta E = 16\ \text{cm}^{-1}$) energy transfer process,

$$NF(a^1\Delta) + Bi(^4S_{3/2}) \rightarrow NF(X^3\Sigma) + Bi(^2D_{3/2}).$$

The measured value, $1 \times 10^{-9}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}$ ($\sigma \approx 200$ Å), is one of the largest that has been observed for such a process. Since both optical transitions are highly forbidden, a simple dipole interaction model cannot account for this observation. A technically important example of such a process is the chemically pumped $O_2{*}(^1\Delta)$ - I atom transfer laser recently developed at AFWL.

11. Multiphoton CO_2 Laser Vibrational Heating of Metastable Electronic States. Biacetyl molecules, prepared in the triplet metastable state by intersystem crossing from the ^1A_u electronic state which in turn is excited by irradiation with the 457.9 nm line of a cw Ar^+ laser, were pumped by an intense CO_2 laser pulse which excites the system vibrationally. Changes in the luminescence characteristics of the electronically excited molecules induced by the infrared pulse were studied in various visible spectral regions. In the region characteristic of the biacetyl phosphorescence, a fast decay of the phosphorescence was observed. A burst of delayed fluorescence was observed in the fluorescence region of the biacetyl; this signal was characterized by a very fast rise time. Both the

fluorescence and phosphorescence signals exhibited the same decay time. Attenuation of the CO_2 laser beam resulted in an increase of the decay time and in a decrease of the amplitudes of the fluorescence signal.

The experimental results were explained in terms of mixed singlet-triplet vibronic wave functions, characterizing the triplet vibrational manifold, with vibrational energy exceeding the ^1A_u-^3A_u energy separation. A calculation of the decay times as a function of the absorbed CO_2 laser energy, which is based on a recent model for delayed fluorescence, gave good agreement with the experimental data. This is the first well-characterized example of reverse intersystem crossing resulting from multiple infrared photon excitation of vibrational modes, which are then converted into electronic excitation.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Solid State Materials Derived from Planar Metal Complexes

2. PRINCIPAL INVESTIGATORS: Dr. Leonard V. Interrante and
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P.O. 8
Schenectady, New York 12301

3. INCLUSIVE DATES: 1 July 1975 - 30 September 1978

4. CONTRACT NUMBER: F44620-76-C-0006

5. COSTS AND FY SOURCE: $40,000, FY76; $9,837, FY7T; $40,163, FY77;
$40,003, FY78

6. SENIOR RESEARCH PERSONNEL:

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Dr. I. S. Jacobs
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7. JUNIOR RESEARCH PERSONNEL:

S. H. Wee
P. A. Piacente

8. PUBLICATIONS:

"Spin-Peierls Transitions in Heisenberg Antiferromagnetic Linear Chain Systems", J. W. Bray, H. R. Hart, Jr., L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, S. H. Wee, and J. C. Bonner, AIP Conference Proceedings, 21st Conference on Magnetism and Magnetic Materials, No. 29, p. 504, 1976.

"Nuclear Relaxation Studies of the Spin-Peierls Transition", L. W. Smith, E. Ehrenfreund, A. T. Heeger, L. V. Interrante, J. W. Bray, H. R. Hart, Jr., and I. S. Jacobs, Solid State Communications, Vol. 19, p. 377, 1976.

"Tetrathiafulvalinum bis-cis-(1,2-perfluoromethylethylene-1, 2-dithiolato) Platinum", J. S. Kasper, L. V. Interrante, Acta Crystallographica, B32, 2914 (1976).

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"One-Dimensional Magnetic Variety in a Family of TTF-Bis-Dithiolene Metal Complex Compounds", I. S. Jacobs, H. R. Hart, Jr., L. V. Interrante, J. W. Bray, J. S. Kasper, G. D. Watkins, D. E. Prober, W. P. Wolf and J. C. Bonner, Physica 86-88B, 655 (1977).

"Studies of Intermolecular Interactions in Transition Metal Complexes. VI The Electrical Properties of Some Quasi-One Dimensional Mixed Valence Complexes at Ultra-High Pressures", L. V. Interrante and F. P. Bundy, Journal of Inorganic and Nuclear Chemistry, 39, 1333 (1977).

"(Tetrathiotetracene)$_{1.2}$ Nickel Bis(ethylene-1, 2-dithiolene). A New One Dimensional Organic Conductor", L. V. Interrante, J. W. Bray, H. R. Hart, Jr., J. S. Kasper, P. A. Piacente, and G. D. Watkins, Journal of the American Chemical Society, 99, 3523 (1977).

"Properties of Tetrathiotetracene Nickel Bis-(ethylene-1, 2-dithiolene)", J. W. Bray, H. R. Hart, Jr., L. V. Interrante, I. S. Jacobs, J. S. Kasper, and P. A. Piacente, Phys. Rev. 16B, 1359 (1977).

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"Molecular Design of Solid State Systems. Organic-Metal Complex Π-Donor-Acceptor Compounds", L. V. Interrante, J. W. Bray, H. R. Hart, Jr., J. S. Kasper, P. A. Piacente, and G. D. Watkins, Annals of the N.Y. Acad. of Sciences, 313, 407 (1978).

"Thermal and Magnetic Study of Exchange in the Quasi-1-D Molecular Compound, $TTF \cdot PtS_4C_4(CF_3)_4$", J. C. Bonner, T. S. Wei, H. R. Hart, Jr., L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, and H. W. J. Blöte, J. Appl. Phys., 49, 1321 (1978).

"The Spin-Peierls Transition and Other Aspects of the Magnetic Behavior of the Compounds, $TTF \cdot MS_4C_4(CF_3)_4$(M=Pt, Cu, Au)", L. V. Interrante, J. W. Bray, H. R. Hart, Jr., I. S. Jacobs, J. S. Kasper and P. A. Piacente, Proceedings of the International Conference on Quasi One-Dimensional Conductors, Lecture Notes in Physics (Springer-Verlag Publ), in press.

"Solid State Materials Derived from Planar Metal Complexes", L. V. Interrante and J. S. Kasper, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

There is a continuing need, both in the Air Force and in industry, for new electromagnetic devices which will permit accurate and reliable environmental monitoring, signal processing as well as certain process control functions. Such devices often require, in turn, new materials with electronic and magnetic properties which are highly sensitive to specific environmental stimuli and whose response can be predicted and controlled to within specified limits. Transition metal complexes, with their exceptionally high capacity for systematic molecular structure variations, coupled with their known ability to participate in strong intermolecular electronic and magnetic interactions in the solid state, are prime candidates for meeting these requirements. The main objectives of this research program were to explore this potential by preparing new organic-transition metal complex systems with scientifically interesting and, ultimately, technologically useful properties and, as a result of systematic synthesis and solid state property investigations, to develop guidelines that might be useful in the design of molecular systems of this type to achieve specific desired solid state property objectives.

The principal focus of the work has been on the preparation and study of π-donor-acceptor compounds derived from the interaction of the organic donors, tetrathiafulvalene and tetrathiotetracene, with bis(1,2-ethylenedithiolene) metal complexes as the π-acceptors. These new compounds have been studied using electronic conductivity, magnetic susceptibility, and various other types of solid state property measurement techniques. In addition, the crystal structures have been characterized using single crystal x-ray diffraction methods. The results have been used to obtain information regarding the electronic and magnetic interactions occurring in the solid state and to derive synthetically useful structure-property relationships.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Phosphorus Chemiluminescence Feasibility Studies for an Ultraviolet and Visible Chemical Laser

2. PRINCIPAL INVESTIGATORS:

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3. INCLUSIVE DATES: 1 August 1977 - 31 July 1978

4. GRANT NUMBER: AFOSR 77-3376

5. COSTS AND FY SOURCE: $77,000, FY77

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL:

M. Herbst
J. Rizk
G. Rizk

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Feasibility studies for the development of an electronic chemical laser from phosphorus chemiluminescence. Phosphorus chemiluminescence is very unusual in that the metal vapor reacts with oxygen under atmospheric conditions without any increase in temperature. A large number of electronic excited species have been identified as flame components, states of HPO, PO, and PO excimer. Some of these electronically excited states are at energy levels in the vacuum uv region. The aim of this project was to explore whether an inverted population of electronically excited species either, 1) exists among the intermediates of the phosphorus chemiluminescence reaction or, 2) can be generated by excitation of atomic and molecular species added to the flame. The project was divided into two sections:

i) Electronic excitation of Na, K and NaK by an oxygen-deficient white phosphorus chemiluminescence. Several apparatus were designed and constructed using university facilities to provide for the addition of a stream of Na and K and the intermetallic alloy NaK carried by an inert gas into a reaction vessel containing the phosphorus chemiluminescence. The table summarizes the experimental results:

OBSERVED λ_A	ASSUMED CHEMICAL SPECIES	TENTATIVE ASSIGNMENT	COMMENT
5765.3	NaK	$B^1\Pi \dashrightarrow X^1\Sigma$	Very strong, approx. 10^3 over P-chemiluminescence
5787.6	K	$(7s)^2S_{1/2} \dashrightarrow (4_p)^2P^\circ_{1/2}$	Identification of both chemical species and the transition is assumed positive
5806.0	K	$(7s)^2S_{1/2} \dashrightarrow (4_p)^2P^\circ_{3/2}$	
5920	Na	$(3P)\begin{matrix} {}^2P^\circ_{1/2} \\ {}^2P^\circ_{3/2} \end{matrix} \dashrightarrow (3s)^2S_{1/2}$	Positive assignment
7670	K	$(4_p)\begin{matrix} {}^2P^\circ_{1/2} \\ {}^2P^\circ_{3/2} \end{matrix} \dashrightarrow (4s)^2S_{1/2}$	Positive assignment

ii) An investigation of laser light amplification on traversing phosphorus chemiluminescent flames using light in the 280-500 nm region. The experimental set-up used the frequency doubled output of a Molectron DL 200 tunable dye laser, pumped by a UV 400 Nitrogen Laser, directed through a beam splitter. The main beam traverses one hundred phosphorus flames, and the intensities of the two beams are measured with two photomultipliers and a dual channel Boxcar Averager PAR 162 with

Sampled Integrator Model 163 and Gated Integrator Model 164 with Sampling Head Model S-5. The ratio was taken and the output was recorded on an XY plotter. An identical ratio of the outputs of the laser beam was recorded with no phosphorus flame. The intensities of the normalized laser beam with and without the phosphorus flame was compared. Under room temperature and atmospheric pressure, scattering from the interfaces of the flames was the dominant effect. We estimate a flux of 3×10^{10} photons per pulse at 290 nm through an intersection of 4×10^9 P_4 molecules, so that we are at the detectibility limit of the experiment. It appears with the present experimental set-up under certain conditions there is suggestion of amplification but because of the scattering at the interfaces no definite conclusion can be drawn. Initial attempts were also made to obtain laser induced fluorescence from components of a single phosphorus flame both at atmospheric and reduced pressure conditions.

iii) Conclusion. In the case of the light amplification studies the conclusion is to dispense with the multiple flame design and thereby eliminate light scattering at the interfaces. The obvious solution is to enclose the flame in a heat pipe oven where pressure, temperature, and the concentration of the reactants can be regulated. In the chemi-excitation experiments of Section i) the two emission lines at 5787 and 5806 A which we have tentatively assigned as excited state - excited state transitions of K are good candidates for lasing. The other emissions, the 5765 A emission tentatively assigned to NaK and the Na and K doublets have lasing potential depending on the mechanism of excitation. The phosphorus flame and the atomic and molecular composition of the NaK stream are extremely susceptible to pressure and temperature changes and, as in the light amplification studies, the obvious next step is to confine the system in a heat pipe oven where these variables can be strictly controlled. Considering the broader aspects, the project has achieved chemi-excitation of atomic and molecular species by interaction with phosphorus flame components. This interaction can be extremely efficient judging from the very strong intensity of the 5765 A NaK emission. Also there appears to be a preferential excitation of selected electronic transitions, depending on the experimental conditions of the system studied.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis of Organofluorine Compounds by Direct Fluorination

2. PRINCIPAL INVESTIGATOR: Dr. Richard J. Lagow
Department of Chemistry
University of Texas at Austin
Austin, TX 78712

3. INCLUSIVE DATES: 30 June 1976 - 30 June 1978

4. GRANT NUMBER: AFOSR 76-3031

5. COSTS AND FY SOURCE: $32,870, FY76; $37,000, FY77

6. SENIOR RESEARCH PERSONNEL:

Dr. J. L. Adcock	Dr. J. W. Thompson
Dr. Basil Catsikis	Dr. Linda Harmon
Dr. Shoji Inoue	Dr. Tom Blackburn

7. JUNIOR RESEARCH PERSONNEL:

N. J. Maraschin	R. A. Beh
L. A. Shimp	R. E. Aikman
E. K. S. Liu	J. Glanz
G. Robertson	D. Persico
G. Gerhardt	

8. PUBLICATIONS:

"The Synthesis of Perfluoroglyme and Perfluorodiglyme by Direct Fluorination", R. J. Lagow and J. L. Adcock, J. Org. Chem., 38, 3617 (1973).

"The Synthesis of Perfluoro 1,4-Dioxane, Perfluoro(ethyl acetate) and Perfluoropivolyl Fluoride by Direct Fluorination", R. J. Lagow and J. L. Adcock, J. Amer. Chem. Soc., 96, 7588 (1974).

"The Successful Direct Fluorination of Oxygen-Containing Hydrocarbons", R. J. Lagow, J. L. Adcock, and R. A. Beh, J. Org. Chem., 40, 3271 (1975).

"The Synthesis of Structurally Unusual Fluorocarbons by Direct Fluorination", R. J. Lagow, N. J. Marschin, B. D. Catsikis, L. H. Davis, and G. Jarvinen, J. Amer. Chem. Soc., 97, 513 (1975).

"The Synthesis of Novel Fluorine Containing Small Carboranes and Bis(difluoroboryl)Methane", R. J. Lagow and N. J. Maraschin, Inorganic Chemistry, 14, 1855 (1975).

"Nitrogen Compounds as High Yield Precursors to Branched Fluorocarbons by Direct Fluorination", R. J. Lagow, J. L. Adcock, B. D. Catsikis, and J. W. Thompson, J. Fluorine Chem., 7, 197 (1976).

"The Synthesis of Perfluoropoly(ethylene glycol) Ethers: CF_3-$(O-CF_2-CF_2)_n-O-R_f$ ($R_f = CF_3$, C_2F_5: n = 1-5), R. J. Lagow and G. Gerhardt, J. Chem. Soc. Chem. Comm., 259 (1976).

"Preservation of Metal Carbon Bonds and Metalloid Carbon Bonds During Direct Fluorination: A Surprise Even to Fluorine Chemists", R. J. Lagow and E. K. S. Liu, J. Amer. Chem. Soc., 98, 8270 (1976).

"The Direct Fluorination of Carbon Disulfide. A Practical Synthesis for Difluoromethylene Bis(sulfur trifluoride)", R. J. Lagow and L. Shimp, Inorg. Chem., 16, 2974 (1977).

"Preservation of Metal Carbon Bonds During Direct Fluorination; A Practical Synthetic Method. The Synthesis of Tetrakis(trifluoromethyl) germanium", R. J. Lagow and E. K. S. Liu, J. Chem. Soc., 450 (1977).

"Simultaneous Fluorination and Functionalization of Hydrocarbon Polymers", R. J. Lagow, J. Amer. Chem. Soc., 100, 1948 (1978).

"Fluorination of Dimethylmercury, Tetramethylsilane and Tetramethylgermanium. Synthesis and Characterization of Polyfluorotetramethylsilanes, Polyfluorotetramethylgermanes, Bis(trifluoromethyl)mercury and Tetrakis(trifluoromethyl)germanium", R. J. Lagow and E. K. S. Liu, J. Organometallic Chem., 145, 167 (1978).

"Trifluoromethylsulfur Trifluoride. An Improved Synthesis, New NMR Data and Stereochemistry", R. J. Lagow, R. W. Braun, A. H. Cowley, and M. C. Cushner, Inorg. Chem., 17, 1679 (1978).

"Direct Fluorination of Tetramethyltin. Synthesis of Trifluoromethyltin Compounds", R. J. Lagow and E. K. S. Liu, Inorg. Chem., 17, 618 (1978).

"Synthesis of Perfluoro-Adamantane Compounds by Direct Fluorination", R. J. Lagow, G. Robertson, and E. K. S. Liu, J. Org. Chem., (in press).

"The Synthesis of the Perfluoropoly(ethylene glycol) Ethers by Direct Fluorination", R. J. Lagow and G. Gerhardt, J. Org. Chem., (in press).

"The Synthesis of Bis(trifluoromethyl)sulfone and Bis(trifluoromethyl)-sulfate by Direct Fluorination", R. J. Lagow and L. A. Harmon, J. Chem. Soc., (in press).

"The Synthesis of Highly Branched Fluorine Compounds; Synthesis and Characterization of F-2,2,5,5-Tetramethylhexane", R. J. Lagow and E. K. S. Liu, J. Fluorine Chem., (in press).

"Synthesis of Organofluorine Compounds by Direct Fluorination", R. J. Lagow, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of the research was to study new fluorination techniques and their utilization in making fluorocarbon oligomers and polymers.

A number of speculative efforts which have been recently successful in this laboratory offer opportunities for new research efforts in the coming few years. One of the most surprising was the development of the ability to preserve metal-carbon bonds during direct fluorination. Initially, it was found that the low temperature fluorination of bistrimethylmercury gave low yields (7%) of bistrifluoromethylmercury:

$$Hg(CH_3)_2 + F_2/He \xrightarrow[5\ \text{days}]{-78°} Hg(CF_3)_2 + HgF_2 + CF_4 + CF_3H + CF_2H_2 + CFH_3$$

Subsequently the reaction of fluorine with tetramethylsilane produced a series of fluorinated silanes:

$$Si(CH_3)_4 + F_2/He \xrightarrow[7\ \text{days}]{-110°} Si(CH_3)_x(CH_2F)_y(CHF_2)_z,\ x + y + z = 4$$

It was quite encouraging that the overall yield of polyfluorotetramethylsilanes was 70-80% indicating that at least that percentage of carbon-silicon bonds survived the fluorination process.

The most exciting experiment so far in fluorination of organometallic compounds was the synthesis of tetrakistrifluoromethyl germane in 63% yield on a two gram scale from tetramethylgermane. Also under milder conditions it became clear that partially fluorinated tetramethylgermanes similar to the silane materials could be isolated under conditions different from those used to optimize the yield of $Ge(CF_3)_4$.

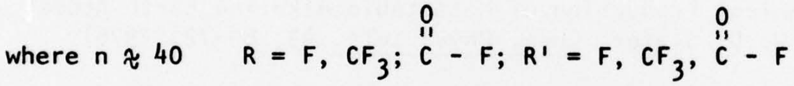
It was found that the oxidation of sulfur can be controlled such that fluorination to a four coordinate is possible. Carbon disulfide was reacted with fluorine at low temperatures to produce difluoromethylenebis(sulfur)trifluoride:

$$CS_2 \xrightarrow[-120^{\circ}C]{F_2/He} SF_3CF_2SF_3$$

More extreme conditions may be employed to prepare the compound $(SF_5)_2CF_2$ if the six coordinate product is desired. A number of previous studies of the oxidation of carbon disulfide using other fluorination techniques has been reported. However, the isolation of practical quantities of $SF_3CF_2SF_3$ has not been previously reported.

Recent work in this laboratory has also been focused toward the high temperature fluorination and cleavage of high molecular weight fluorinated polyethylene oxide to produce new discrete high boiling polyether materials. Controlled direct fluorination of polyethylene oxide results in the production of an oligomer which has a degree of polymerization of about 40 units and is composed of a mixture of nonfunctional, monofunctional, and difunctional polyethers of the perfluoroglyme structure:

$$RCF_2O(CF_2CF_2O)_nCF_2R'$$



$$\text{where } n \approx 40 \qquad R = F,\ CF_3;\ \overset{O}{\overset{\|}{C}} - F;\ R' = F,\ CF_3,\ \overset{O}{\overset{\|}{C}} - F$$

These materials have been partially separated, but their full characterization has taken a temporary back seat to the synthesis of slightly lower molecular weight perfluoro polyethers. By raising the fluorination temperature to 120°, to promote fragmentation, the synthesis of a series of perfluoro polyethers was reported. A range of products was characterized.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Transfer Lasers

2. PRINCIPAL INVESTIGATOR: Dr. Paul H. Lee
Department of Physics
University of California
Santa Barbara, CA 93106

3. INCLUSIVE DATES: 15 October 1975 - 14 October 1977

4. GRANT NUMBER: AFOSR 76-2959

5. COSTS AND FY SOURCE: $49,960, FY76; $7,046, FY7T; $52,000, FY77

6. SENIOR RESEARCH PERSONNEL:

Dr. W. D. Slafer
Dr. David J. Benard

7. PUBLICATIONS:

"Efficient Chemical Production of Metastable Alkaline Earth Atoms", D. J. Benard, W. D. Slafer, Chem. Phys. Lett. 43, 69-72 (1976).

"Chain Reaction Chemiluminescence of Alkaline Earth Catalyzed N_2O-CO Flames", D. J. Benard, W. D. Slafer, and J. Hecht, J. Chem. Phys. 66, 1012-1016 (1977).

"Mechanism of Chemiluminescent Chain Reaction in Mg Catalyzed N_2O-CO Flames", D. J. Benard and W. D. Slafer, J. Chem. Phys. 66, 1017-1020 (1977).

"Experimental Investigations and Gain Measurements of Alkaline Earth Catalyzed N_2O+CO Flames", D. J. Benard, W. D. Slafer, J. Hecht, and P. H. Lee, presented at Third Summer Colloquium on Electronic Transition Lasers, Snowmass Village, Colorado (7-10 September 1976). Published in Electronic Transition Lasers II, eds. L. E. Wilson, S. N. Suchard, J. I. Steinfeld, MIT Press, Cambridge, Mass., Chapters 11-7 (1977).

"Efficient Chemical Generation of Metastable Alkaline Earth Atoms", W. D. Slafer, D. J. Benard, and P. H. Lee, presented at Third Summer Colloquium on Electronic Transition Lasers, Snowmass Village, Colorado (7-10 September 1976). Published in Electronic Transition Lasers II, eds. L. E. Wilson, S. N. Suchard, J. I. Steinfeld, MIT Press, Cambridge, Mass., Chapter 11-8 (1977).

"Energy Transfer and Excimer Formation in a Flowing Afterglow of Mg Metastables", D. J. Benard, P. J. Love and W. D. Slafer, Chem. Phys. Lett., 48, 321-326 (1977). Presented at the IV Conference on Chemical and Molecular Lasers, St. Louis, Missouri, (April 1977).

"Modulated Transmission Spectroscopy of Gaseous Chemi-Excited Ca and Sr Monoxides", D. J. Benard, W. D. Slafer, P. J. Love and P. H. Lee, Appl. Optics 16, 2108-2115 (1977).

"A Mechanistic Study of Potential Chain Reaction Supported Metal Oxide Chemical Lasers", D. J. Benard, W. D. Slafer, presented at the Annual Electrochemical Society Fall Meeting, Atlanta, Georgia (October 9-14, 1977).

"Efficient Metal Hydride Arc Source", W. D. Slafer, D. J. Benard, submitted to Appl. Phys. Lett. (1978).

"Laser Induced Fluorescence Spectra of KMg", D. J. Benard, W. D. Slafer, submitted to Chem. Phys. Lett. (1978).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of the program were to obtain increased understanding of the metal - N_2O - CO flame reaction system by a study of parametric variations in reacting conditions using a laser gain technique and to optimize the optical performance of the flame system. The flames are generated in a fast flow low pressure apparatus by reacting Mg, Ca or Sr atoms with a premixed flow of N_2O and CO. The resultant chain reaction is characterized by a high density and efficient production of excited metal atoms. The reaction mechanisms are determined by spectroscopic and laser probing techniques. Separate measurements were made of the radiative lifetimes, reactive cross sections, branching ratios using pulsed dye laser techniques and a flowing afterflow apparatus.

During the period of this grant, metal oxidation flames such as Ba plus N_2O were intensively studied as laser candidates. It was determined that adding CO to a M plus N_2O flame, where M is Mg, Ca and Sr, had several interesting effects, including efficient production of M (triplet P) metastable species. The production of triplet species appeared to be essentially 100 percent efficient, but the metastables were subject to quenching and further reaction. Coproduction of CO_2 with M* was demonstrated using CO_2 laser induced fluorescence techniques. Results showed that the MO reservoir state is much more stable in the lighter MO species. The identity of the reservoir state remains unknown but may be polyatomic, such as $(MO)_2$. It was concluded that there are no useful inversions inherent in the M plus N_2O plus CO flames and that laser potential, if any, in such flame systems lies with their use as M* generators. A means of extracting the energy in M* by stimulated emission could occur by selective reaction of the M ground state, by energy transfer, or by excimer formation.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Solid Propellant Additives from Pentaborane-9

2. PRINCIPAL INVESTIGATOR: Dr. Amos J. Leffler
Department of Chemistry
Villanova University
Villanova, Pennsylvania 19085

3. INCLUSIVE DATES: 1 April 1977 to 30 June 1978

4. GRANT NUMBER: AFOSR 77-3301 (Mini Grant)

5. COSTS AND FY SOURCE: $9,969, FY 77

6. SENIOR RESEARCH PERSONNEL: Dr. Michael S. Spritzer

7. PUBLICATIONS:

"Solid Propellant Additives from Pentaborane-9," Amos J. Leffler and Michael S. Spritzer, Final Technical Report.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The aim of this research was to find suitable means of converting pentaborane-9 into air stable materials containing iron, chromium, or copper in high yield which would serve as solid propellant additives. The most convenient synthetic routes to new compounds from pentaborane are through metallation using alkyl lithium compounds or by bromination at room temperature. Both approaches were taken in this work.

The electrochemical behavior of pentaborane-9 and its reactivity with acetylenic halides were studied. Although pentaborane-9 is itself not electroactive it does react with other electrochemically generated species. It was found that methyl iodide, iodobenzene, chromium hexacarbonyl, dimanganese decacarbonyl, and iron pentacarbonyl generated electroactive species that reacted with pentaborane-9. The reaction of pentaboryllithium and propargyl chloride and with 1,4-dichlorobutyne-2 yielded mixtures of nidocarborane polymers and some higher boranes. The propargyl chloride reaction product reacted with anhydrous cobaltous chloride and cyclopentadienyllithium to give a mixture of cobaltaboranes and cobaltacarboranes which were not separable. An attempt was made to prepare phenylpentaborane but the product could not be isolated.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: An Investigation of Charge Transport Modes in Nickel Hydroxide Electrodes

2. PRINCIPAL INVESTIGATOR:

Dr. Joseph T. Maloy	Current Address:
Department of Chemistry	Department of Chemistry
West Virginia University	Seton Hall University
Morgantown, WV 26505	South Orange, NJ 07079

3. INCLUSIVE DATES: 15 May 1976 - 30 May 1978

4. GRANT NUMBER: AFOSR 76-2987

5. COSTS AND FY SOURCE: $9,996, FY76

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: Daher T. Wardy

8. PUBLICATIONS:

"Microelectrode Studies of Electrochemically Coprecipitated Cobalt Hydroxide in Nickel Hydroxide Electrodes", D. F. Pickett and J. T. Maloy, J. Electrochem. Soc., 125, 1026 (1978).

"Low Temperature Studies of the Effect of Cobalt Hydroxide Additives in Nickel Hydroxide Electrodes", D. T. Wardy and J. T. Maloy, to be submitted to J. Electrochem. Soc.

"Low Temperature Electrochemical Studies on Nickel-Cobalt Hydroxide Electrodes", D. T. Wardy, Ph. D. Dissertation, WVU, in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The role of electrochemically coprecipitated cobalt hydroxide in the electrochemical behavior of the nickel hydroxide electrode has been investigated at a nickel microelectrode in alkaline solution.

Nickel and cobalt hydroxide films were deposited onto the nickel electrode surface by the cathodic deposition process developed at AFAPL using boiling ethanol solution containing either $Ni(NO_3)_2$ or a mixture of $Ni(NO_3)_2$ and $Co(NO_3)_2$; the behavior of these film electrodes in 30% KOH solution was studied by cyclic voltammetry, chronoamperometry, and chronocoulometry.

In general, the presence of coprecipitated cobalt hydroxide in small quantities (ca. 10 mol %) appears to render the charge-discharge reaction more reversible (by usual cyclic voltammetry criteria). This allows the charging of the nickel hydroxide electrode to occur at less positive potentials, thereby minimizing concurrent oxygen evolution during the charging process.

The presence of large quantities of coprecipitated cobalt (ca. 50 mol %) appears to have an opposite effect. It appears that the oxygen overvoltage on film electrodes containing large quantities of cobalt is less than is observed on film electrodes containing little or no added cobalt. Thus, concurrent oxygen evolution during the charging process appears to be an even more serious problem when the concentration of coprecipitated cobalt exceeds the optimum 10-20 mol % range.

When the optimum range of coprecipitated cobalt is employed, charging takes place most efficiently in the vicinity of 0.2V vs. SCE. When no cobalt is added, the efficiency, as measured by the ratio of charge delivered to charge recovered, falls from a maximum of 90% to 60% and the potential of maximum efficiency shifts to 0.3V vs. SCE.

Low temperature cyclic voltammetry studies have been performed to confirm these observations. At reduced temperature, the oxygen overvoltage is increased because the rate of the electrode reaction is decreased. This allows the charging current to be distinguished from the current used to merely decompose the electrolyte.

The AFAPL cathodic deposition process was investigated by cyclic voltammetry studies at a nickel microelectrode and by scanning electron microscope studies on nickel plaque material containing potentiostatically deposited nickel and cobalt hydroxides. The cyclic voltammetry studies were useful in the characterization of the proper electrode conditions for the deposition of battery active hydroxides. The scanning electron microscope investigation was used to study the nickel-cobalt composition of the deposited hydroxides as a function of impregnation bath solution composition.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: The Relation Between the Chemical and Physical Structure and the Mechanical Response of Polymers

2. PRINCIPAL INVESTIGATOR: Dr. Roger J. Morgan
McDonnell Douglas Research Laboratories
McDonnell Douglas Corporation
St. Louis, MO 63166

3. INCLUSIVE DATES: 1 April 1976 to 30 June 1978

4. CONTRACT NUMBER: F44620-76-C-0075

5. COSTS AND FY SOURCE: $13,780, FY76; $13,780, FY7T; $50,337, FY77; $41,191, FY78

6. SENIOR RESEARCH PERSONNEL: James E. O'Neal

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS AND PRESENTATIONS:

"Relationship of Structure, Fracture Processes and Mechanical Response of Polymer Glasses", R. J. Morgan, presented at Gordon Research Conference on Deformation and Failure Mechanisms in Polymers and Composites, Santa Barbara, CA, January 1977.

"The Morphology and Failure Processes of Epoxies", R. J. Morgan, Educational Seminar presented for the Society of Plastic Engineers, held in conjunction with Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March 1977.

"The Network Structure and Microscopic Failure Processes of Epoxies", R. J. Morgan and J. E. O'Neal, presented at the American Physical Society Meeting, San Diego, CA, March 1977; Bull. Am. Phys. Soc. 22, 368 (1977).

"Microscopic Flow and Failure Processes in Polymer Glasses", R. J. Morgan and J. E. O'Neal, presented at Nonlinear Viscoelastic Behavior of Molten and Solid Polymers Symposium of the American Chemical Society Meeting, Chicago, 1977; Org. Plast. Coat. Preprints (ACS) 37, (No. 2), 480 (1977); also Polym. Sci. and Eng. (in press).

"The Microscopic Failure Processes and their Relation to the Structure of Amine-Cured Bisphenol-A-Diglycidyl Ether Epoxies", R. J. Morgan and J. E. O'Neal, J. Mater. Sci. 12, 1966 (1977).

"The Durability of Epoxies", R. J. Morgan and J. E. O'Neal, Polym. Plast. Tech. and Eng. 10(1), 49 (1978); also McDonnell Douglas Report MDC Q0631, August (1977).

"Epoxies as Composite Matrices", R. J. Morgan and J. E. O'Neal, presented at High-Performance Composites-Chemical Aspects Symposium of the American Chemical Society Meeting, Anaheim, 1978; Org. Plast. Coat. Preprints (ACS) 38, 485 (1978).

"The Structure, Modes of Deformation and Failure and Mechanical Properties of Diaminodiphenyl Sulfone Cured Tetraglycidyl 4,4'Diaminodiphenyl Methane Epoxy", R. J. Morgan, J. E. O'Neal, and D. B. Miller, J. Mater. Sci. (in press).

"The Modes of Deformation and Failure of Polycarbonate", R. J. Morgan and J. E. O'Neal, Polymer (submitted).

"The Effect of Thermal History and Strain-Rate on the Mechanical Properties of Diethylene Triamine-Cured Bisphenol-A-Diglycidyl Ether Epoxies", R. J. Morgan, J. Appl. Polym. Sci. (submitted).

"The Effect of Moisture on the Physical and Mechanical Integrity of Epoxies", R. J. Morgan, J. E. O'Neal, and D. L. Fanter, J. Mater. Sci. (to be submitted).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The aerospace industry utilizes polymers in numerous applications which include matrices for composite materials, adhesives, transparencies, sealants, and insulators for heat, sound and electricity. In many of these applications the polymeric materials are exposed to extreme service environments. The need to predict the durability of these materials requires a detailed understanding of their structure-property relations.

In this research program our studies were concentrated on crosslinked epoxies, high-impact strength polycarbonate and polybenzoxazole (an aromatic heterocyclic polymer). The overall objectives of this program were to study (1) the chemical structure and physical arrangement of the macromolecules in the bulk, (2) the modes of deformation and failure, (3) the structural parameters that control the modes of deformation and failure, (4) the effect of the modes of deformation and failure on the mechanical properties, and (5) how these structure-property relations are modified by fabrication procedures and the service environment.

Diethylene triamine cured bisphenol-A-diglycidyl ether (DGEBA-DETA) epoxies consist of intramolecularly crosslinked molecular domains interconnected by less highly crosslinked regions. These DGEBA-DETA epoxies are relatively ductile and deform and fail by a crazing process. Diaminodiphenyl sulfone cured tetraglycidyl 4,4'diaminodiphenyl methane (TGDDM-DDS) epoxies exhibit homogeneous crosslink densities. These epoxies are not highly crosslinked, despite the tetrafunctionality of the TGDDM molecule, because steric and diffusional restrictions inhibit the cure reactions. The TGDDM-DDS epoxies can microscopically deform by both crazing and shear banding.

The pertinent basic physical phenomena induced and/or modified by sorbed moisture that affect the durability of epoxies have been investigated. Sorbed moisture acts as a plasticizer and a swelling and solvent crazing agent to epoxies. The physical and mechanical integrity of the epoxies is deteriorated by certain thermal-moisture exposure combinations.

Factors controlling the toughness of polycarbonate were investigated. In tension the toughness of polycarbonate is controlled by the ease of shear-band deformation and the resultant strain-hardening characteristics of the cold-drawn material together with the characteristics of surface crazes which form prior to macroscopic necking. The effects of strain-rate and environmental exposure on the surface craze characteristics are reported.

Polybenzoxazole (PBO) is relatively ductile at room-temperature. The presence of sulfuric acid in PBO, which is eliminated only on decomposition of the polymer near 500°C, suggests that this acid is strongly associated with the rod-like macromolecules and may affect their aggregation characteristics.

10. EXTENDED ABSTRACT OF EPOXY DURABILITY RESEARCH:

Two epoxy systems were studied: (1) diethylene triamine-cured bisphenol-A-diglycidyl ether epoxy (DGEBA-DETA) and (2) diamino-diphenyl sulfone-cured tetraglycidyl 4, 4' diaminodiphenyl methane epoxy (TGDDM-DDS). DGEBA-DETA epoxies exhibit considerable microscopic flow during the failure processes and 15-20% extension to break 25°C below their gloss transition temperatures (T_g). Reversible thermal annealing cyclics, above and below T_g, produce reversible changes in the macroscopic yield stress of DGEBA-DETA epoxies, which are a result of free-volume changes. These epoxies, however, exhibited little swelling in organic solvents. The lack of swelling, the ductility, and the free-volume dependence of the mechanical properties of the DGEBA-DETA epoxies can be explained if these glasses possess a heterogeneous crosslink density distribution. It is suggested that these glasses consist of regions of high-crosslink density interconnected by free-volume-dependent, low-crosslinked or non-crosslinked material with the latter material controlling the flow properties. This morphological model is consistent with Morgan's bright-field transmission electron microscope observations. Films strained directly in the electron microscope revealed a network of interconnected 6-9 nm diameter particles. These particles remained intact and flowed past one another during the flow processes. It is suggested that these particules are molecular domains that are intra-molecularly crosslinked and form during the initial stages of polymerization.

The fracture topographies of the DGEBA-DETA epoxies can be interpreted in terms of a crazing failure process. The coarse initiation region of the fracture topography of these epoxies, which has a mica-like appearance, is at the center of a cavity and is surrounded by a smooth, mirror-like, slow crack-growth region. The mica-like structure results from void growth and coalescence through the center of a simultaneously growing, poorly developed craze, which consists of coarse fibrils. The diameters of the broken fibrils depend on the relative rates of craze and void propagation. The smooth, mirror-like region results from crack propagation either through the center or along the craze-matrix boundary interface of a thick-well-developed craze consisting of fine fibrils.

The TGDDM-DDS epoxies are not highly cross-linked systems, despite the tetrafunctionality of the TGDDM molecule, and exhibit 15-20% extension to break 25°C below their Tg's. Steric and diffusional restrictions inhibit the cure reactions for glasses prepared from $\gtrsim$ wt% DDS. (For all the epoxide groups to react with primary amines requires 54 wt% DDS.) For glasses with $\gtrsim$ 30 wt% DDS, unreacted DDS molecules act as plasticizers and lower the T_g. Aggregates of these unreacted molecules recrystallize in the epoxy glass and have been identified by electron diffraction and X-ray emission spectroscopy. The elimination of unreacted molecules during the later stages of the cure produces stress-raising microvoids in these glasses.

No evidence was found for heterogeneous crosslink-density distributions in TGDDM-DDS (15-35 wt% DDS) epoxies on straining films in the electron microscope. However, transmission electron microscopy reveals that the poor network produced for lower DDS concentrations (10-15 wt% DDS) breaks into $\sim$ 2.5 nm particles which are approximately the size of the TGDDM epoxide molecule.

TGDDM-DDS (12-35 wt% DDS) epoxies predominantly deform and fail in tension by a crazing process as indicated by fracture topography studies. These glasses also deform to a limited extent by shear banding as indicated by unique, regular, right-angle steps in the fracture topography initiation region. The shear-band mode of deformation becomes more predominant with increasing temperature and is the primary mode of deformation during the initial stages of fracture just below T_g. Fracture topographical features also indicate that mixed modes of deformation that involve both shear banding and crazing can occur in these epoxies. The shear-band mode of deformation enhances the high-temperature ductility of these TGDDM-DDS epoxies.

The pertinent basic physical phenomena induced and/or modified by sorbed moisture that affect the durability of the aforementioned epoxies were investigated. The conclusions are as follows: (1) epoxies are plasticized by sorbed moisture, and their T_g's are lowered to a greater extent than predicted from free-volume considerations; (2) moisture diffusion in epoxies can be adequately described by Fick's laws of diffusion with non-Fickian diffusion with accelerated moisture sorption occurring, however, in environments that cause microvoid or crack formation in the epoxies; (3) local swelling stresses generated by the sorption of moisture in epoxies cannot be predicted accurately without detailed knowledge of the epoxy network structure and the moisture distribution within the network; (4) sorbed moisture enhanced the craze cavitation and propagation processes in the epoxies by plasticization; and (5) combined thermal-moisture exposure can deteriorate the physical and mechanical integrity of epoxies. With reference to (4), the craze cavitation stress is more susceptible to sorbed moisture than T_g, particularly when microscopic regions of high-moisture concentration are present in the epoxy. Therefore, modification of T_g by sorbed moisture alone cannot be utilized as a sensitive guide to predict deterioration in the mechanical response and durability of epoxies. In discussing (5), for certain conditions, moisture clusters form in epoxies which on subsequent elimination produce stress-raising microvoids in the glass that reduce the tensile strength by $\sim$ 25%. Thermal spiking causes enhanced moisture sorption because of the breaking of crosslinks and further growth of fabrication-induced surface micro-cracks.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Physics of Charge Mechanisms in Nonmetallic Spacecraft Materials

2. PRINCIPAL INVESTIGATOR: Dr. Joseph E. Nanevicz
Electromagnetic Sciences Laboratory
SRI International
Menlo Park, California 94025

3. INCLUSIVE DATES: 15 May 1977 - 30 September 1978

4. CONTRACT NUMBER: F44620-77-C-0113

5. COSTS AND FY SOURCE: $16,875, FY77; $27,957, FY78

6. SENIOR RESEARCH PERSONNEL: Mr. Richard C. Adamo

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS: None at this time

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The interaction of a synchronous-orbit satellite with its environment activates electrification and electrical discharge processes producing electromagnetic noise pulses and effluents which deteriorate satellite materials, surfaces and components. The objective of this effort was to perform research to understand the mechanisms underlying spacecraft charging in polymeric dielectrics.

The charge deposition and transfer properties of polymer materials are determined by the characteristics of the materials themselves as well as by both past and present conditions to which the materials are exposed. Polymer materials on external surfaces of operational spacecraft are subjected to constantly changing charged particle and solar illumination environments. Temporal variations of internal and external electric fields and currents in exposed surface polymer materials can therefore be quite complex, particularly on a spinning spacecraft.

Several series of laboratory experiments were performed in which samples of typical spacecraft polymers (e.g., Kapton and Teflon) were exposed to monoenergetic electron beams with energies from 1 to 20 keV and beam-current densities from 1 to 10 nA/cm^2. At the same time, these samples were exposed to illumination from a solar simulator modulated at a rate of from 1 to 10 rpm to simulate conditions on a spinning spacecraft.

During these tests, both external electric-field and bulk sample current were monitored and recorded. The observed waveforms were complex and varied considerably in both amplitude and waveshape over the range of test conditions for each sample material. Of particular interest is the fact that under certain electron-beam conditions, particularly at lower beam energies, periodic repeatable current transients were observed during sample illumination at simulated vehicle spin rates of one to a few rpm. These transients did not occur at higher simulated spin rates or under conditions of steady illumination or darkness. This phenomenon may be responsible for the spin synchronism of electrical transients that has been observed by in-orbit instruments.

Additional parametric laboratory studies of these phenomena were made to obtain data for comparison with presently available theoretical and computer model predictions of expected material behavior under actual space conditions.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Parameters Affecting the Preparation of 3-Fluorosalicylaldehyde Via the Reimer-Tiemann Reaction

2. PRINCIPAL INVESTIGATOR: Dr. Paul A. Pinke
Corporate Research Center
UOP Inc.
Des Plaines, Illinois 60016

3. INCLUSIVE DATES: 1 May 1977 - 30 September 1977

4. CONTRACT NUMBER: F49620-77-C-0104

5. COSTS AND FY SOURCE: $28,993, FY77

6. SENIOR RESEARCH PERSONNEL: Mr. Michael D. Tufano

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to study the parameters affecting the Reimer-Tiemann reaction of ortho-fluorophenol (o-FP) whereby 3-fluorosalicylaldehyde (3-FSA) is made. An improvement in the yield of 3-FSA by the Reimer-Tiemann method would make it a more practical manufacturing procedure. Reducing the cost of 3-FSA manufacture would lower the cost of a cobalt chelate utilizing 3-FSA called fluomine, which is useful for concentrating oxygen from our atmosphere. A fluomine-based breathing system was being considered by the U.S. Air Force for use in aircraft. The use of the Reimer-Tiemann reaction for the manufacture of 3-fluorosalicylaldehyde (3-FSA) from ortho-fluorophenol (o-FP) was looked at in greater detail. Substantial improvements were made in both the yield of 3-FSA and in the recovery of unreacted o-FP. These improvements have resulted in a manufacturing cost estimate for 3-FSA of $51-66/lb. The other method developed by UOP, a four-step Claisen route, afforded a manufacturing cost estimate of $58/lb. These are both improvements over the current manufacturing cost of $81-400/lb.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Organosilicon Compounds and Organosilicon Polymer Intermediates

2. PRINCIPAL INVESTIGATOR: Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

3. INCLUSIVE DATES: 1 October 1975 - 30 September 1978

4. GRANT NUMBER: AFOSR-76-2917

5. COSTS AND FY SOURCE: $33,000, FY76; $36,768, FY7T; $38,400, FY78

6. SENIOR RESEARCH PERSONNEL:

Dr. T. F. O. Lim
Dr. W. Hölderich

7. JUNIOR RESEARCH PERSONNEL:

D. Dagani
C. K. Haas
C. P. Duncan
J. L. Lefferts
D. C. Annarelli
S. C. Vick
M. L. Shannon
P. Holl

8. PUBLICATIONS:

"Halomethyl-Metal Compounds. LXXVIII. Cyclohexyl- and β-Phenylethyl (trihalomethyl) Mercury Compounds as Dihalocarbene Precursors at Room Temperature", D. Seyferth, C. K. Haas and D. Dagani, J. Organometal. Chem., 104, 9 (1976).

"Halomethyl-Metal Compounds. LXXIX. The Generation of Isopropylidene Carbene by the Organomercury Route", D. Seyferth and D. Dagani, J. Organometal. Chem., 104, 145 (1976).

"Molecular Structure and Bonding of a Silacyclopropane, Dimethyl-dispiro[bicyclo[4.1.0]heptane -7,2'-silacyclopropane-3,7''-bicyclo [4.1.0]heptane", G. L. Delker, Y. Wang, G. D. Stucky, R. L. Lambert, Jr., C. K. Haas and D. Seyferth, J. Amer. Chem. Soc., 98, 1779 (1976)

"Evidence for the Generation of a Disilacyclopropane in Solution", D. Seyferth and D. P. Duncan, J. Organometal. Chem., 111, C21 (1976).

"1,1-3,3-Tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane and Its 1,3-Digerma- and 1,3-Distanna Analogs: Unexpected Products from the Reaction of Bis(trimethylsilyl) bromomethyllithium with Dimethyldihalo Derivatives of Silicon, Germanium and Tin", D. Seyferth and J. L. Lefferts, *J. Organometal. Chem.*, *116*, 257 (1976).

"Dimethylsilylene Transfer from Hexamethylsilirane to Olefins", D. Seyferth and D. C. Annarelli, *J. Organometal. Chem.*, *117*, C51 (1976)

"1,1-Dimethyl-3,3-bis(trimethylsilyl)-1-silirene, a Stable Silacyclopropene", D. Seyferth and D. C. Annarelli, *J. Amer. Chem. Soc.*, *98*, 6382 (1976).

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"The Preparation of a 1,2-Disilacyclobutane and a 1,2-Disilacyclobut-2-ene by Dimethylsilylene Insertion into the Silacyclopropane and Silacyclopropene Ring Systems. New Silacyclopropenes", D. Seyferth and S. C. Vick, *J. Organometal. Chem.*, *125*, C11 (1977).

"Two Atom Insertions into the Silacyclopropane and Silacyclopropene Rings: Mechanistic Considerations", D. Seyferth, S. C. Vick, M. L. Shannon, T. F. O. Lim, and D. P. Duncan, *J. Organometal. Chem.*, *135*, C37 (1977).

"The Reaction of *gem*-Dichloroallyllithium with Aldehydes, Ketones and Other Organic Substrates. An Example of Electronic Control of Regioselectivity in the Reactions of an Ambident Nucleophile", D. Seyferth, G. J. Murphy and B. Mauze, *J. Amer. Chem. Soc.*, *99*, 5317 (1977).

"The Reactions of *gem*-Dichloroallyllithium with Halides of Silicon, Germanium, Tin and Mercury, and with Triphenylborane. Equilibrium vs. Kinetic Control of Regioselectivity", D. Seyferth, G. J. Murphy and R. A. Woodruff, *J. Organometal. Chem.*, *141*, 71 (1977).

"Synthesis of 1,8-Bis(trimethylsilyl-) and 1,8-Bis(trimethylstannyl) naphthalene. The Relative Steric Effects of Carbon, Silicon and Tin in the 1,8-Bis(trimethylelement)naphthalenes", D. Seyferth and S. C. Vick, *J. Organometal. Chem.*, *141*, 173 (1977).

"Reactions of Bis(trimethylsilyl)bromomethyllithium and Tris (trimethylsilyl)methyllithium. The Synthesis of Alpha-Bromovinylsilanes", D. Seyferth, J. L. Lefferts, and R. L. Lambert, Jr., J. Organometal. Chem., 142, 39 (1977).

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"The Extraordinary Reactivity of the Ring Si-C Bonds in 1,1-Dimethyl-trans-2,3-bis(2'2'-dimethylcyclopropylidene)-1-Silacyclopropane", D. Seyferth, C. K. Haas, R. L. Lambert, Jr., and D. C. Annarelli, J. Organometal. Chem., 152, 131 (1978).

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"Hyper-reactive Organosilicon Compounds: Silacyclopropanes and Silacyclopropenes", D. Seyferth, R. L. Lambert, Jr., D. C. Annarelli, S. C. Vick, T. F. O. Lim, D. P. Duncan and M. L. Shannon, Science-Ciencia, 5, 144 (1978).

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A. Silacycopropanes and Filacyclopropenes

1) Development of the chemistry of the newly discovered (under AF-AFOSR-72-2204) hexamethylsilacyclopropane.

a) Its use as a source of dimethylsilylene under exceptionally mild conditions.

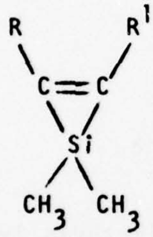
b) Insertions into its SiC_2 ring: diazomethane, dimethylsilylene, "two-atom" insertions of activated olefins, 1,3-dienes, terminal acetylenes, aldehydes and ketones, imines, dimethylsilanone, elemental sulfur.

c) fragmentation reactions with chlorophosphines

d) ring-opening reactions with primary and secondary phosphines and a mercaptan

e) its use in the generation of $R_3\overset{+}{P}-\overset{-}{Si}Me_2$

2) Preparation and first isolation and characterization of silacyclopropenes (1a-e)



	R	R^1
a	Me_3Si	Me_3Si
b	Me_3Si	Me_3C
c	Me_3Si	CH_3
d	Me_3C	CH_3
e	Me_2HSi	Me_2HSi

(Noteworthy is the unexpectedly high thermal stability and the high reactivity of these compounds.)

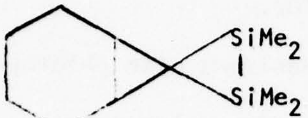
Development of the chemistry of silacyclopropene 1a:

a) ring-opening by alcohols and water

b) *insertion reactions into its SiC_2 ring:* dimethylsilylene, "two-atom" insertion reactions of activated olefins, 1-3-dienes, terminal acetylenes, aldehydes and ketones, dimethylsilanone.

c) Oxidation under very mild conditions by Me_2SO to give $Me_2Si{=}O$ as a trappable intermediate.

3) Preparation of the first disilacyclopropane, II



II

B. Halogenated Organometallics

(Completion of projects begun under AF-AFOSR-72-2204)

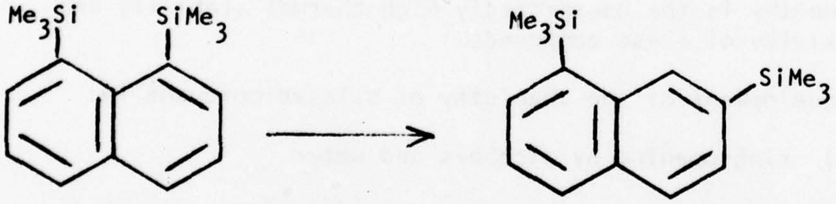
1) Reactions of gem-dichloroallyllithium with element halides.

2) Synthesis of α-bromovinysilanes

C. Miscellaneous

1) Attempted synthesis of 1,2-dilithioethylene (unsuccessful, but interesting chemistry).

2) Synthesis and isomerization of 1,8-bis(trimethylsilyl) naphthalene:



AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Molecular Energy Transfer by Collisional Processes
   Characteristic of Gas Lasers

2. PRINCIPAL INVESTIGATOR: Professor Hyung Kyu Shin
   Department of Chemistry
   University of Nevada
   Reno, Nevada 89507

3. INCLUSIVE DATES: 1 January 1972 - 31 December 1976

4. GRANT NUMBER: AFOSR 72-2231

5. COSTS: $56,530, FY72; $31,309, FY75; $8,856, FY76

6. SENIOR RESEARCH PERSONNEL: (Visiting Professors)

   Dr. Y. H. Kim
   Dr. J. Keizer

7. JUNIOR RESEARCH PERSONNEL:

   A. W. Young
   A. Takagi
   F. Bowers

8. PUBLICATIONS:

"Excitation of Molecular Vibration on Collision. Simultaneous Vibrational and Rotational Transitions in H_2 + Ar at High Collision Velocities", H. K. Shin, J. Phys. Chem., 76, 2006 (1972).

"Temperature Dependence of Vibrational Transition Probabilities for O_2, N_2, CO, and Cl_2 in the Region Below 300°K", H. K. Shin, J. Chem. Phys., 57, 3484 (1972).

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NOTE: This grant was completed in FY77; however, the summary was received too late to be included in the FY77 Chemistry Program Review.

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"Vibration-to-rotation Energy Transfer in H_2O, D_2O, and NH_3", H. K. Shin, J. Phys. Chem., 77, 346 (1973).

"Comparison of the WKB and Purely Classical Methods for Vibrational Transition Probabilities", H. K. Shin, Chem. Phys. Letters, 18, 359 (1973).

"Nonadjacent Vibrational Transitions in Molecular Collisions: Interface Between One- and Two-Quantum Excitation Processes", H. K. Shin, J. Phys. Chem., 77, 1394 (1973).

"Vibration-to-Rotation Energy Transfer in Hydrogen Fluoride: Effects of the Dipole-Dipole and Hydrogen Bond Interactions", H. K. Shin, J. Chem. Phys., 59, 879 (1973).

"Vibrational Transitions in Atom + Diatomic Systems: Use of the Lennard-Jones Potential", H. K. Shin, J. Phys. Chem., 77, 1666 (1973).

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"Vibrational Transitions in Anharmonic Oscillators", H. K. Shin, J. Phys. Chem., 77, 2657 (1973).

"Vibrational Deexcitation of HF(v=1) in HF + Ar: Importance of Rotational Transitions", H. K. Shin and A. W. Young, J. Chem. Phys., 60, 193 (1974).

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"Temperature Dependence of V → R, T Energy Transfer Probabilities in CO $(00^\circ 1)$ + HF/DF", H. K. Shin, J. Chem. Phys., 60, 2167 (1974).

"Temperature Dependence of the Probability of Vibration-Vibration-Rotation Energy Transfer in $HCl(v=2) + HCl(v=0) \rightleftarrows HCl(v=1) + HCl(v=1)$", H. K. Shin, J. Chem. Phys., 60, 2305 (1974).

"Simultaneous Vibrational and Rotational Transitions in HF + Ar", H. K. Shin, J. Korean Chem. Soc., 18, 12 (1974).

"A Collision Model for the Vibrational Relaxation of Hydrogen Fluoride at Low Temperatures", H. K. Shin, Chem. Phys. Letters, 26, 450 (1974).

"The Breakdown of Local Equilibrium in Coupled Relaxation Processes: Translational Non-Equilibrium During Vibrational Relaxation", J. Keizer, J. Chem. Phys., 61, 361 (1974).

"Interference Between Two Adjacent Collisions in Vibrational Relaxation", H. K. Shin and J. Keizer, Chem. Phys. Letters, 27, 611 (1974).

"Vibration-to-Vibration Energy Transfer in $N_2 + CO$ in the Temperature Region 100° - 3000°K", H. K. Shin, J. Chem. Phys., 61, 2474 (1974).

"Vibrational Deactivation of HF(v=1) in the H_2O + HF Dimer: $HF(v=1) + H_2O(000) \rightarrow HF(v=0) + H_2O(001) + \Delta E$", H. K. Shin, Chem. Phys. Letters, 32, 218 (1975).

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"Intermolecular Vibration-to-Vibration Energy Transfer in $HF/DF(v=1) + HF/DF(v=1) \rightarrow HF/DF(v=0) + HF/DF(v=2)$ through the formation of Dimers", H. K. Shin, IEEE J. Quantum Electron., QE-11, 679 (1975).

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"Vibrational Energy Transfer in H_2 + He", H. K. Shin, Chem. Phys. Letters, 37, 143 (1976).

"Energy Dependence of the Cross Section for $CH_3I + K \rightarrow CH_3 + KI$ near Threshold", H. K. Shin, Chem. Phys. Letters, 38, 253 (1976).

"Vibrational Energy Transfer in DF + DF", H. K. Shin, Proceedings Army Symp. on High Energy Lasers, Redstone Arsenal, Ala.

"Temperature Dependence of the Vibration-Vibration Deexcitation Rates of $HF(v=n) + HF(v=0) \rightarrow HF(v=n-1) + HF(v=1)$ for $n = 2 - 5$", H. K. Shin and Y. H. Kim, J. Chem. Phys., 64, 3634 (1976).

"Temperature Dependence of Intramolecular Vibrational Energy Transfer in CO_2: $CO_2(00^\circ 1) + Ne/CO_2 \rightarrow CO_2(nm^\ell 0) + Ne/CO_2$", H. K. Shin, Chem. Phys. Letters, 40, 316 (1976).

"Model of Hydrogen-Bond Interactions near the Equilibrium Configuration: Application to Vibrational Energy Transfer in $DF(v=n) + DF(v=0)$", H. K. Shin, J. Am. Chem. Soc., 98, 5765 (1976).

"Vibrational Relaxation of Hydrogen Fluorides: $HF(v=1) + F \rightarrow HF(v=0) + F$", H. K. Shin, Chem. Phys. Letters, 43, 4 (1976).

"F-Atom Deexcitation of $DF(v=1)$: Isotope Effect", H. K. Shin, Chem. Phys. Letters, 46, 260 (1977).

"Direct Non-Stepwise Multiple Quantum Excitations in Translation-Vibration Energy Transfer", Y. H. Kim and H. K. Shin, J. Korean Chem. Soc., 20, 97 (1976).

"Intramolecular Vibration-Vibration Energy Transfer in Carbon Dioxide", A. Takagi, M. S. Thesis, University of Nevada, 1972.

"Direct Multiple Quantum Transitions in Translation-Vibration Energy Transfer", Y. H. Kim, PhD Thesis, University of Nevada, 1972.

"Vibrational Deexcitation of $HF(v=1)$ in $HF + Ar$: Importance of Rotational Transitions", A. W. Young, PhD Thesis, University of Nevada, 1974.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The major objective of this project was to develop theoretical models for the calculation of transition probabilities in collisions of atoms and molecules. New methods were developed, and existing techniques were refined to provide both a quantitative and a qualitative interpretation of the mechanisms and dynamics of molecular collisions. Special emphasis was given to the problem of deriving explicit expressions for energy transfer probabilities, so their dependence on pertinent collision parameters could be readily determined. Whenever possible, the theoretical study was tested against experimental data, not only for demonstrating the utility of the theoretical formulation for the prediction and correlation of experimental results, but also for explaining the observations and using the discrepancies between theory and experiment

to further refine our understanding of energy transfer processes. The most important investigation carried out during the tenure of this grant dealt with the vibrational energy transfer processes in hydrogen fluoride molecules, which play major roles in chemical laser operation. In this investigation, we considered the self-relaxation of HF(1)/DF(1), near-resonant vibration-vibration energy transfer processes in HF(n) + HF(0) and DF(n) + DF(0), vibrational energy transfer in CO_2(00°1) + HF/DF, and F-atom deexcitation of HF/DF. In addition, the following aspects of molecular collisions were also investigated: vibration-rotation energy transfer in H_2O and NH_3, near-resonant vibration-vibration energy transfer in N_2 + CO, intramolecular vibration-rotation energy transfer in HF + Ar, simultaneous vibrational and rotational transitions in H_2 + Ar, semiclassical approach to vibrational energy transfer in H_2 + He, and translational energy dependence of the reaction cross sections of alkali-methyl iodide reactions.

The major activity under this grant was the study of the vibrational energy transfer in hydrogen fluoride molecules. One of the systems investigated was the self-relaxation of hydrogen fluoride over wide temperature ranges. Vibrational relaxation times of HF were calculated on the basis of the vibration-rotation energy transfer theory over the temperature range 300 - 4000°K. We have shown that the vibrational relaxation of hydrogen fluoride molecules can be rigorous explained in terms of the model of vibration-to-rotation energy transfer when the effects of dipole-dipole and hydrogen-bond interactions are included. Statistically the colliding molecules spend more time in those orientations for which the dipole-dipole and hydrogen-bond attractions are large, thus causing the molecules to exchange their energies efficiently. Below 1000°K, the relaxation time becomes very short showing a strong negative temperature dependence, which can be attributed to the contributions of such attractive forces. Over the entire temperature range, the agreement between calculation based on the vibration-rotation energy transfer theory and experimental data in both the magnitude and temperature dependence of vibrational relaxation time was found to be good.

At temperatures below 300°K, the contribution of hydrogen-bond attraction becomes important. Because of this contribution, the colliding molecules can form a nonrigid bond and undergo oscillatory motion about their equilibrium orientations. Such sticky collisions are shown to be primarily responsible for the removal of the vibrational energy of HF(1) and lead to a negative temperature dependence of energy transfer probability. The model has been extended to study near-resonant collisions HF(n) + HF(0) → HF(n-1) + HF(1) and DF(n) + DF(0) → DF(n-1) + DF(1) for n = 2 - 5 in the temperature range 200 - 2000°K. We have shown that the formation of a nonrigid hydrogen bond is important at lower temperatures, while the complete rotational motion is responsible for the removal of vibrational energy at higher temperatures. For the latter case, the vibration-rotation energy transfer mechanism was used. At a given temperature the sum of these two contributions determines the efficiency of near-resonant vibrational energy transfer processes. The rate coefficient k for HF(n) + HF(0) → HF(n-1) + HF(1), where n = 2 and 3, shows a strong negative temperature dependence at low temperatures where the nonrigid dimer mechanism is of primary importance; after reaching a minimum value it then increases with rising temperature. For n = 5, no such dependence is found. At higher temperatures the rotational motion of HF is primarily responsible for the removal of energy mismatch. Another interesting result found was at low temperatures the rate coefficient decreases with n, but increases at higher temperatures. These two different n-dependent regions are separated approximately at 300°K; at this temperature, k for n = 3 is shown to be the largest. In the neighborhood of room temperature, the dependence of k on n is very sensitive to a small change in temperature. The maximum k occurs at either n = 3 or 4, but near 400°K, k can even be an increasing function of n. For DF systems, however, k always increases with n over the temperature range 200 - 2000°K, although the increase is much smaller at lower temperatures. The hydrogen-bond interaction model has also been used in the study of HF(1) + $H_2O(000)$ → HF(0) + $H_2O(001)$ in the temperature range 300 - 500°K.

Another important study involving hydrogen fluorides carried out under the support was the F-atom deexcitation of HF(1)/DF(1). We have developed a rigorous semiclassical approach to determine deexcitation rate coefficients of these collisions with special emphasis on the temperature dependence of rate coefficients and isotope effect. Near room temperature, k of HF(1) + F → HF(0) + F is small but it rapidly increases with temperature. At temperatures above 1500°K, k is very large with the magnitude 10^{13} cm^3/mole-sec. We have found that DF(1) relaxes two to three times faster than HF(1) in the range 100° - 3000°K.

We also studied the energy transfer in CO_2 + HF/DF in the temperature range 300 - 2000°K. The calculation based on the vibration-rotation energy transfer theory shows the efficient deexcitation of $CO_2(00°1)$. The calculated values are in agreement with laser-excited fluorescence measurements around 350°K. From a comparison with experimental data it was predicted that the (final) deexcited states of CO_2 are (00°0) and (01^10), respectively, for the $CO_2(00°1)$ + HF and $CO_2(00°1)$ + DF collisions. The vibration-rotation theory was used to study the temperature dependence of the near-resonant process HCl(2) + HCl(0) → HCl(1) + HCl(1). Since the hydrogen-bond interaction is weak in these molecules, the dimer model was not considered for this process.

Extension of the energy transfer theory has been made to other polar molecules such as H_2O and NH_3 over wide temperature ranges. Calculations showed that deexcitation probabilities are large in these collisions, and furthermore, D_2O was shown to be less efficiently deexcited than H_2O in the self-deexcitation processes.

Another area of research was the development of an impulsive collision model to study the translational energy dependence of the reaction cross section of all the alkali-methyl iodide reactions, the reactions which have been extensively investigated by molecular-beam kineticists. For $CH_3I + K \rightarrow CH_3 + KI$ the model gave reaction cross sections in good agreement with experimental data in the pre- and post-maximum energy regions. In all reactions of the family, the cross section increases sharply with the translational energy showing an Arrhenius-like positive energy dependence for the energy just past threshold and then takes a maximum value. In the post-maximum region the cross section decreases slowly with the translational energy.

The impulsive collision model was extended to study the dependence of vibration-translation energy exchange in nonreactive collisions on the number of impacts. For the collinear collisions C-B + A, the total number of impacts that a single collision can have is $n = 90°/\phi$, where $\phi = \underline{\text{arc}} \tan [m_B(m_A+m_B+m_C)/m_A m_B]^{1/2}$; for nonintegral values of $90°/\phi$, n is the interger which just exceeds the noninteger value $90°/\phi$. The model was applied to H-F + F, F-H + F, Cl-H + Cl, Br-H + Br, I-H + Cl, and several other hypothetical systems with particular emphasis on the dependence of energy exchange on the number of impacts. Comparison with exact trajectory calculations at high collision energies showed a diminished inelasticity as the result of repeated impacts between A and B in a single collision.

A rigorous semiclassical approach was developed to study vibrational energy transfer in H_2 + He by use of the <u>a priori</u> interaction potential including all nonzero impact parameter collisions. The calculated values of the rate coefficient were found to be in excellent agreement with experimental data available in the temperature ranges 60° - 450°K and 1350° - 3000°K.

We also investigated the following problems in molecular collisions. The importance of rotational transitions in the vibrational deexcitation of HF(1) in HF + Ar collisions was studied by a semiclassical three-dimensional approach. The temperature dependence of intramolecular vibrational energy transfer in $CO_2(00°1) + Ne/CO_2 \rightarrow CO_2(nm^{\ell}0) + Ne/CO_2$ was investigated. An analytic approach was developed to study vibration-vibration energy transfer in near-resonant collisions; the model was applied to Cl + M, where M = N_2, NO, O_2, and D_2. The $0 \rightarrow 1$ vibrational transition probability of an anharmonic oscillator was formulated using the potential function which is a sum of quadratic and cubic terms in the vibrational coordinate. The problem of vibrationally and rotationally inelastic scattering processes in H_2 + Ar for nonzero impact parameter was investigated in the collision velocity range 10^6 - 10^7 cm/sec by use of the sudden approximation. The interference between one- and two-quantum excitation processes in $0 \rightarrow n$ vibrational transitions taking place in molecular collisions was investigated. A rigorous comparison of the WKB evaluation of the quantal approach to vibrational energy transfer with the purely classical theory was carried out. The temperature dependence of vibrational energy transfer for O_2, N_2, CO and Cl_2 at temperatures below 300°K was investigated. Interference effects in the collision of a molecule with two incident particles was investigated using the classical approach to vibrational energy transfer. Also investigated were translational nonequilibrium during vibrational relaxation and collision-induced light scattering.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Molecular Energy Transfer Studies

2. PRINCIPAL INVESTIGATOR: Professor H. K. Shin
Department of Chemistry
University of Nevada
Reno, Nevada 89557

3. INCLUSIVE DATES: 1 October 1976 - 31 July 1978

4. GRANT NUMBER: AFOSR 77-3163

5. COSTS AND FY SOURCE: $33,860, FY77

6. SENIOR RESEARCH PERSONNEL: Dr. P. L. Altick
Dr. Y. H. Kim

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"F-Atom Deexcitation of DF (v=1): Isotope Effect", H. K. Shin, Chem. Phys. Letters, 46, 260 (1977).

"Determination of Vibrational Energy Level Spacings of van der Waals Molecules from the Lennard-Jones Potential", H. K. Shin, Chem. Phys. Letters, 47, 225 (1977).

"Vibrational Relaxation of H_2O at High Temperatures", H. K. Shin, J. Phys. Chem., 81, 1122 (1977).

"Vibrational and Thermodynamic Properties of ArHX van der Waals Molecules", H. K. Shin, Chem. Phys. Letters, 49, 193 (1977).

"Vibrational Relaxation of DF at Low Temperatures", H. K. Shin, Chem. Phys. Letters, 50, 377 (1977).

"Collision-Induced Intramolecular Vibration-Vibration Energy Transfer in CO_2: $CO_2(00^\circ 1) + H_2/D_2$", H. K. Shin, Chem. Phys. Letters, 51, 186 (1977).

"Approximate Solution of Vibration-Vibration Energy Transfer Probabilities", H. K. Shin and P. L. Altick, Chem. Phys. Letters, 52, 580 (1977).

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"A Model Calculation of Vibration-Translation Energy Transfer", P. L. Altick and H. K. Shin, J. Chem. Phys., 68, 3973 (1978).

"Transfer of Vibrational Energy to Oscillatory, Restricted Rotational and Translational Motion in HCl + Cl", H. K. Shin, J. Chem. Phys., 68, 5265 (1978)

"Vibrational Relaxation of Water Molecules near Room Temperature", H. K. Shin, J. Chem. Phys., in press.

"Molecular Energy Transfer Studies", H. K. Shin, Final Technical Report.

In Preparation:

"Deexcitation of $D_2O(010)$ near Room Temperature", Y. H. Kim and H. K. Shin.

"Vibrational Relaxation of Diatomic Molecules in Condensed Monatomic Media", H. K. Shin.

"Vibrational Relaxation of van der Waals Molecules", H. K. Shin.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The major concern has been with vibrational energy transfer in molecular collisions involving hydrogen halides and water molecules at low temperatures. As the temperature of the collision system is lowered, the reduction of thermal energy leads to the appearance of a number of interesting phenomena that are obscured or nonexistent at higher temperatures. One such phenomenon, which is of particular importance to the study of molecular energy transfer is the manifestation of intermolecular attraction. When the colliding molecules approach each other at low temperatures, they spend more time in those orientations for which the attraction is strong. If attractive forces are sufficiently strong ($E_{attr} >> kT$), the colliding molecules can form a weakly bound complex. In collision systems involving vibrationally excited molecules, the formation of such a complex can lead to efficient relaxation through intracomplex energy transfer. Since the subunit molecules cannot undergo free translation and/or rotation, conventional vibration-translation and/or vibration-rotation energy transfer theories are no longer useful, and new theories will have to be formulated. During the support period, we have developed such a theoretical approach recognizing the formation of loosely bound complexes.

To understand the details of energy transfer processes in the complex, it is essential to determine energy levels of the newly-formed bond.

An analytical approach to determine the levels by use of the Lennard-Jones potential in the WKB method has been developed. Specific systems considered are rare gas molecules and argon-hydrogen halide complexes. The former molecules are chosen to establish the method since experimental data are available for them. We have determined spectroscopic constants and energy levels of the bond of all these molecules and complexes, and found that results are in good agreement with experimental data. We have also predicted values of such constants for complexes for which no experimental data are available.

Energy transfer probabilities of DF $(v=1)$ + DF$(v=0)$ → 2DF$(v=0)$ in the temperature range of 200 - 400°K have been calculated recognizing the presence of strong attractive forces and formation of a DF dimer. Probabilities are large and exhibit a sharp negative temperature dependence below 300°K, the result which can be attributed to the transfer of energy to the oscillatory motion of DF in the dimer. The model has also been used to study the vibrational relaxation of $H_2O(010)$. Large values of the ν_2-deexcitation probability found near room temperature are incompatible with earlier sound-absorption data, but are in agreement with recent results obtained with laser excited fluorescence techniques. At present experimental data on the ν_2-deexcitation of $D_2O(010)$ are not available, but the present model gives deexcitation probabilities which are somewhat smaller than that of H_2O over the temperature range of 200 - 400°K. Another system investigated based on the complex formation is HCl$(v=1)$ + Cl. The attractive energy between the colliding partners is significantly less than that of DF or H_2O, but the energy transfer can be explained in terms of the model.

The model described above works for low-temperature relaxation processes. As the temperature increases, the role of weakly bound complexes becomes less important and an entirely different model will have to be used. The change in energy transfer mechanism has been demonstrated for $H_2O(010)$ calculating deexcitation probabilities over 1000 - 4000°K by use of vibration-rotation energy transfer theory. Probabilities are found to be large and are comparable to that at temperatures near 300°K obtained with the model of complex formation. The comparison shows the appearance of a probability minimum near 600°K.

We have investigated intramolecular vibration-vibration energy transfer in $CO_2(00^\circ1)$ + H_2/D_2 to determine the most efficient energy transfer pathway. Over the temperature range of 100 - 2500°K, the intramolecular process $(00^\circ1 \rightarrow 10^\circ0)$ is found to be the dominant process in both collision systems. Another system investigated is the F-atom deexcitation of DF(v=1). Near room temperature, the deexcitation rate constant is small but increases rapidly with increasing temperature. It is also found that the system relaxes faster than HF + F over the temperature range of 100 - 3000°K.

An approximate solution of the time-dependent Schrödinger equation was developed for vibration-vibration energy transfer in a collinear collision of two diatomic molecules. This work has been undertaken to obtain the solution for an arbitrary form of interaction potential. Also undertaken is a full quantum mechanical treatment of vibration-translation energy transfer in an atom-diatom collinear collision employing a simple step potential for which the resulting coupled differential equations were solved exactly.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Reactive Atomic Species Generated at High Temperatures and Their Low Temperature Reactions to Form Novel Substances

2. PRINCIPAL INVESTIGATOR: Dr. Philip S. Skell
Department of Chemistry
Pennsylvania State University
University Park, PA 16802

3. INCLUSIVE DATES: 1 October 1974 - 31 May 1978

4. GRANT NUMBER: AFOSR 75-2748

5. COSTS AND FY SOURCE: $54,000, FY75; $68,097, FY76; $37,157, FY7T; $86,827, FY77

6. SENIOR RESEARCH PERSONNEL:

Dr. J. E. Dobson
Dr. S. P. Kolesnikov
Dr. J. C. Day

7. JUNIOR RESEARCH PERSONNEL:

Tuula Asunta
Loren Beard
Robert Remick
Joseph Slanga
Bruce Wilburn

8. PUBLICATIONS:

"Reactions of Tungsten and Molybdenum Atoms with 1,3-Butadiene. Tris(butadiene) tungsten and -molybdenum", P. S. Skell, E. M. VanDam, and M. P. Silvon, J. Amer. Chem. Soc., 96, 626 (1974).

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"Organometallic and Organic Syntheses Using Main Group Elemental Vapors", P. S. Skell and M. J. McGlinchey, Cryochemistry 4, 137-165 (1976).

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"Succinimidyl and Related Radicals", P. S. Skell and J. C. Day, Organic Free Radicals, ed. by William A. Pryor, (Washington, DC.: Amer. Chem. Soc., 1978).

"Excited State Succinimidyl in Radical Chain Reactions", P. S. Skell and J. C. Day, J. Amer. Chem. Soc., 100, 1950 (1978)

"Addition Reactions of Imidyl Radicals with Olefins and Arenes", P. S. Skell, J. C. Day, M. G. Katsaros, W. D. Kocher, A. E. Scott, J. Amer. Chem. Soc., 100, 1950 (1978).

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"Ground State and Excited State Chemistry of Succinimidyl Radical and Its Congeners", P. S. Skell, and J. C. Day, will appear Accts. Chem. Research.

"Reactive Atomic Species Generated at High Temperatures and Their Low Temperature Reactions to Form Novel Substances", P. S. Skell, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The major thrust of this program was in the direction of exploration of new methods for vaporizing and studying the reactions of the high boiling elements, for the main part the high boiling transition elements. Thermal vaporizations of tungsten, molybdenum, rhodium, ruthenium, titanium, zirconium, and thorium were successfully carried out. Each of these metals makes bis-arene sandwich compounds with benzene and substituted aromatic compounds, of varying stabilities. The less stable ones are useful in further organometallic syntheses employing these metals. For example, from titanium atoms in benzene or toluene one makes a bis-arene compound which reacts readily with cyclooctatetraene to make either the bis-cyclooctatetraene titanium or the tris-cyclooctatetraene bis-titanium. Bis-arene molybdenum and tungsten compounds were prepared with halogen, methoxyl, carbethoxyl, and dimethylamino substituents. Compounds of this type had not been available.

Electron transfer properties of metal atoms were examined in their interactions with water and acetone. This led to a new reactivity series, significantly different from the standard potentials for the metals. This is a natural consequence of the very substantial differences in heats of vaporization of the metals. This is interestingly illustrated by the finding that copper and zinc have the same potential as atoms, and that the well known difference in reactivity of the metals must then be due to the large difference in heats of vaporization rather than electronic effects. This atom potential series will be useful in examining all electron transfer reactions of metal atoms.

The reaction of magnesium atoms with CO_2 produces CO_2^- radicals which in the presence of olefins add to make succinic acids. Such a bis-carboxylation of the unsaturated linkage is a new type of reaction.

It has been demonstrated that an entirely new type of heterogeneous catalyst has been prepared, a supported catalyst with molecularly defined active sites. This is a highly significant finding of great generality. The catalyst prepared has single rhodium atoms as the active sites. The method of preparation is such that it is clear it can be extended to include all the other transition metals, and further it should be possible to make catalysts with active sites consisting of diatoms, either the same or different ones, or triatoms in any combination, etc. If this speculation proves to be correct, the field of heterogeneous catalysis will have available a great variety of new catalysts, and further, the mechanisms of heterogeneous reactions will become accessible because the concentration and composition of the active site will be known, thus making possible, through kinetic studies, the composition of the transition states in heterogeneous catalysis.

Succinimidyl radical chemistry was explored for the first time. It proved to be a highly unusual radical in a number of its properties. Further the system proved to be very intriguing because it was found that two different electronic states of succinimidyl could be produced in thermal chain reactions, depending on the energetics of certain steps. This notion may have broad significance in other radical systems.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Morphology and Mechanical Behavior of Isomeric Graft Copolymers and Interpenetrating Polymer Networks

2. PRINCIPAL INVESTIGATOR: Dr. L. H. Sperling
Materials Research Center
Lehigh University
Bethlehem, Pennsylvania 18015

3. INCLUSIVE DATES: 1 October 1975 - 30 September 1978

4. GRANT NUMBER: AFOSR 76-2945

5. COSTS AND FY SOURCE: $22,290, FY76; $26,975, FY7T; $30,975, FY77

6. RESEARCH PERSONNEL:

S. Yomoda	P. Scarito
B. Atlig	E. Corwin
N. Devia	J. Lipko

7. PUBLICATIONS:

"Isomeric Graft Copolymers and Interpenetrating Polymer Networks. Theory and Experiment", L. H. Sperling, K. B. Ferguson, J. A. Manson, E. M. Corwin, and D. L. Siegfried, Macromolecules, 9, 743 (1976).

"Viscoelastic Behavior of Partly Decrosslinked Polymer Networks. 1. Acrylic Acid Anhydride - Crosslinked Poly(ethyl acrylate)", S. Yomoda and L. H. Sperling, J. Appl. Polym. Sci., 21, 2609 (1977).

"Effect of Grafting on Phase Volume Fraction, Composition, and Mechanical Behavior: Epoxy/Poly(n-butyl acrylate) Simultaneous Interpenetrating Networks", P. R. Scarito and L. H. Sperling, accepted Polym. Eng. Sci.

"Application of Kanig's Staining Technique to the Study of Simultaneous Interpenetrating Network Morphology by Transmission Electron Microscopy", N. Devia, J. H. Lipko, and L. H. Sperling, submitted to Polymer Letters.

"A Proposed Generalized Nomenclature Scheme for Multipolymer and Multimonomer Systems", L. H. Sperling and E. M. Corwin, to appear in Advances in Chemistry Series, issue to be edited by S. L. Cooper.

"Morphology and Mechanical Behavior of Isomeric Graft Copolymers and Interpenetrating Polymer Networks", L. H. Sperling, Final Technical Report

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of the research were to synthesize several interpenetrating polymer networks (IPNs) and to develop correlations among synthetic detail, morphology and physical and mechanical behavior. The accomplishments included the following:

(1) Controlled Grafting of Simultaneous Interpenetrating Polymer Networks. This research, which elucidated the relationship between polymer 1/polymer 2 compatibility and deliberately introduced graft sites, were accepted for publication by Polymer Science and Engineering. From an engineering point of view, the controlled morphology produced using epoxy/acrylic combinations yielded very tough, novel plastics.

(2) Novel Staining Techniques for Saturated Two-Phased Polymers. Up till now, the only good staining technique for polyblends utilized an osmium tetroxide attack on polymer containing double bonds. The research under this contract showed how this method could be successfully extended to carboxyl or ester containing systems such as acrylics or methacrylics.

(3) Polymer Blend and Interpenetrating Polymer Network Nomenclature. A major stumbling block in the development of multicomponent polymer systems has been an inadequate nomenclature.

(4) The first experiments on decrosslinking of interpenetrating polymer networks were done.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Structural and Dynamic Studies of Materials Possessing High Energy Content

2. PRINCIPAL INVESTIGATOR: Dr. Nicholas J. Turro
Department of Chemistry
Columbia University
New York, New York 10027

3. INCLUSIVE DATES: 1 September 1973 - 31 October 1977

4. GRANT NO: AFOSR 74-2589

5. COSTS AND FY SOURCE: $73,905 FY 74; $75,825 FY 75; $76,178 FY 76; $88,460 FY 77

6. SENIOR RESEARCH PERSONNEL:

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Dr. D. Bauer
Dr. D. Brewer
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Dr. W. Cherry
Dr. W. Farneth
Dr. E. Georgeson
Dr. Y. Ito
Dr. I. Kochevar
Dr. P. Lechtken
Dr. K. Liu
Dr. M. Mirbach
Dr. Y. Noguchi
Dr. J. Pouliquen
Dr. V. Ramamurthy
Dr. C. Renner
Dr. T. Sasaki
Dr. G. Schuster
Dr. J. Shields
Dr. K. Shima
Dr. H. Steinmetzer
Dr. W. Waddell

7. JUNIOR RESEARCH PERSONNEL:

M. Blaustein
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A. Lyons
M. Mirbach
J. Orell
F. Pagano
N. Schore
P. Stone
F. Warren
M. Wolf
A. Yekta

8. PUBLICATIONS:

"Indirect Chemiluminescence Activated by 1,2-Dioxetanes", N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H. C. Steinmetzer and W. Adam. J. Amer. Chem. Soc., 96, 1627 (1974).

"Quantum Chain Processes. A Novel Procedure for Measurement of Quenching Parameters", N. J. Turro, N. E. Schore, H. C. Steinmetzer and A. Yekta. J. Amer. Chem. Soc., 96, 1936 (1974).

"Peroxyoxalate Chemiluminescence Chemiexcitation of High Energy Excited States on Acceptor Molecules", P. Lechtken and N. J. Turro. Molecular Photochemistry, 6, 95 (1974).

"Tetramethyl-1,2-Dioxetane", N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H. C. Steinmetzer and A. Yetka. Accounts Chem. Research, 7, 97 (1974).

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"Mechanism of the Interaction of n,π* Excited Alkanones with Electron-Rich Ethylenes", N. E. Schore and N. J. Turro. J. Amer. Chem. Soc., 97, 2482 (1975).

"Novel Fluorescent Probe for Micellar Systems. 1,3-Dialkylindoles", N. E. Schore and N. J. Turro. J. Amer. Chem. Soc., 97, 2488 (1975).

"Energy Storage and Release. Direct and Sensitized Photoreactions of Benzvalene", C. A. Renner, T. J. Katz, J. Pouliquen, N. J. Turro and W. H. Waddell. J. Amer. Chem. Soc., 97, 2568 (1975).

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"Chemiexcitation Mechanisms. The Role of Symmetry and Spin-Orbit Coupling in Diradicals", N. J. Turro and A. Devaquet. J. Amer. Chem. Soc., 97, 3859 (1975).

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The technology related to reconnaissance, information retrieval, communications, radiation detection and other areas require and will advance as our knowledge of excited molecules and their emission properties expands. Novel laser uses, novel laser design and advancement of the state of the art of photochemistry depends heavily on both technical, theoretical and experimental developments. The goal of this research was to provide a theoretical and experimental basis for the understanding of the properties of excited molecules and their emission characteristics. What was sought was the elucidation of the available mechanisms for thermal and photochemistry activation of selected high energy content materials which are chemiluminescent. Several novel chemiluminescent organic reactions were discovered and thoroughly investigated. A particular emphasis was directed toward the identification of chemiluminescent systems which might have the highest likelihood of providing a framework for the development of operating chemical lasers which emit in the visible spectral range. The thermal chemistry and photochemistry of dioxetanes and of valence isomers of benzene have been investigated. The chemistry of singlet oxygen was explored to develop simple and convenient means of producing this species. An important development has been the discovery that the catalytic thermal generation of singlet oxygen from ground state (triplet) oxygen may be feasible. The possibility of using singlet oxygen in developing chemical lasers was also explored. Finally, the mechanisms of electronic energy transfer and oxidation in polymers is being investigated with the goal of providing a fundamental understanding of these processes that will allow the systematic and rational development of strategies for stabilization of polymer systems.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials

2. PRINCIPAL INVESTIGATOR: Dr. Robert West
Department of Chemistry
University of Wisconsin-Madison
Madison, WI 53706

3. INCLUSIVE DATES: 1 February 1974 - 31 January 1978

4. GRANT NO: AFOSR-74-2644

5. COSTS AND FY SOURCE: $29,654, FY 74; $57,030, FY 75; $53,379, FY 76; $33,829, FY 7T; $67,261, FY 77

6. SENIOR RESEARCH PERSONNEL: (Postdoctoral Associates)

Dr. Michael Biernbaum
Dr. Jamshid Soulati
Dr. Wieslaw Wojnowski
Dr. Richard Oakley

7. JUNIOR RESEARCH PERSONNEL: (Graduate Students)

Catherine Hurt
Thomas Newman
David Stanislawski
Lawrence Brough
Cynthia Wadsworth
Witta Priester
Timothy Drahnak
A. C. Buchanan III
Lawrence David
Rodney Schreiner

8. PUBLICATIONS:

"New Anionic Rearrangements. XVIII. 1,2-Anionic Rearrangements from Sulfur to Carbon in Benzylthiotrimethylsilane and Benzylthiotrimethylgermane," A. Wright and R. West, J. Amer. Chem. Soc., 96, 3222 (1974).

"New Anionic Rearrangements. XIX. Stereochemistry of the Alkoxysilane to Silylcarbinol Anion Rearrangement," A. Wright and R. West, J. Amer. Chem. Soc., 96, 3227 (1974).

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"Polylithium Compounds. X. Preparation and Chemistry of Polylithiated 2, 4-hexadiyne," W. Priester and R. West, *J. Amer. Chem. Soc.*, *98*, 8426 (1976).

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"Cyclic Polysilanes. XI. Reactivity of 1, 2, 3, 4-Tetra-*tert*-Butyltetramethylcyclotetrasilane: Stereospecific Chlorodemethylation," M. Biernbaum and R. West, *J. Organometal. Chem.*, *131*, 189 (1977).

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"The Preparation of α,ω-Dibromopermethylpolysilanes and Characterization of These and Related Chloropermethylpolysilanes by Mass Spectrometry," C. H. Middlecamp, W. Wojnowski and R. West, *J. Organometal. Chem.*, *140*, 133 (1977).

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"Characterization of Organosilicon Infiltrated Porous Reaction Sintered Si_3N_4," K. S. Mazdiyasni, R. West and L. D. David, submitted to *J. Amer. Cer. Soc.*

"Nmr and Esr Observation of Hindered Rotation in *Sym*-tetra-*tert*-butyldisilane and the Corresponding Disilanyl Radical," D. A. Stanislawski, A. C. Buchanan III and R. West, submitted to *J. Amer. Chem. Soc.*

"Cyclic Polysilanes. XIII. Ring Closure Reactions of α,ω-Dichloropermethylpolysilanes; the Preparation of Heterocyclic Phenylphosphinopermethylsilanes $(PhP)_m SiMe_2)_n$," R. T. Oakley, D. A. Stanislawski and R. West, submitted to *J. Organometal. Chem.*

"Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials," R. West, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

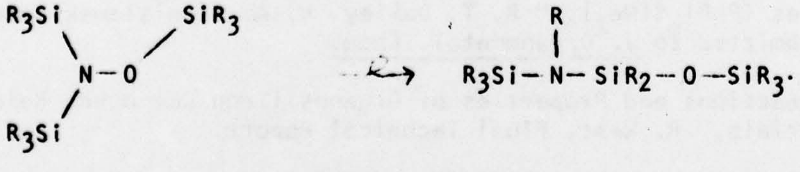
Research during this grant was concentrated on the chemistry of polysilanes, especially cyclic permethylpolysilanes and their derivatives.

The synthesis of permethylpolysilanes has been studied in detail; the reaction between dimethyldichlorosilane and sodium-potassium alloy leads mainly to polymer along with some $(Me_2Si)_5$, $(Me_2Si)_6$ and $(Me_2Si)_7$. Depolymerization of the polymer by an "unzipping" mechanism generates the six-ring $(Me_2Si)_6$. Admixture of phenylmethyldichlorosilane with dimethyldichlorosilane leads to a polymer which does not undergo depolymerization, and which may be useful as a source of strong silicon-carbide fiber by thermolysis.

In related syntheses, tert-butylmethyldichlorosilane was shown to condense with NaK to give three isomers of the four-membered ring (tert-BuMeSi)$_4$. These are air-stable and relatively inert unlike $(Me_2Si)_4$. A number of substituted five- and six-membered permethylcyclosilanes, RSi_5Me_9 and RSi_6Me_{11}, have been synthesized and their anion-radicals studied by electron spin resonance spectroscopy. Charge-transfer complexes between cyclic and linear permethylpolysilanes and pi-electron acceptors have been discovered and studied spectroscopically. Finally, a series of cyclic compounds containing phosphorus as well as silicon in the ring have been synthesized. Some of these compounds serve as ligands to transition metals, forming stable complexes.

In other work under the grant, polylithiation of hydrocarbons was investigated leading to the species C_3Li_4, $CH_3C_3Li_3$, $(CH_3)_2C_3Li_2$ and $CH_3C_5Li_3$. The use of these compounds in the synthesis of unusual hydrocarbons and organometallic compounds was explored. Finally, two kinds of rearrangement reactions of tris-organosilyl hydroxylamines were discovered and investigated: (1) reversible exchange of organosilyl groups between oxygen and nitrogen:

and (2) irreversible thermolysis to siloxysilazanes:



AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of Rotationally Cooled Molecules in Molecular Beams by Laser Spectroscopic Technique

2. PRINCIPAL INVESTIGATOR: Dr. Lennard Wharton
The James Franck Institute and
Department of Chemistry
The University of Chicago
5801 South Ellis Ave.
Chicago, Illinois 60637

3. INCLUSIVE DATES: 1 June 1975 - 31 October 1977

4. GRANT NUMBER: AFOSR 75-2853

5. COSTS AND FY SOURCE: $37,000, FY75; $40,000, FY76; $20,000, FY77

6. SENIOR RESEARCH PERSONNEL:

Dr. Dean W. Chandler, Visiting Professor (Williams College)
Dr. Richard E. Smalley
Dr. Daniel J. Auerbach

7. JUNIOR RESEARCH PERSONNEL:

Pamela S. H. Fitch
B. L. Ramakrishna
Hang Fung
M. S. Kim
Glenn Kubiak

8. PUBLICATIONS:

"Laser Spectroscopy of Supersonic Molecular Beams: Application to the NO_2 Spectrum", R. E. Smalley, B. L. Ramakrishna, D. H. Levy and L. Wharton, J. Chem. Phys. 61, 4363 (1974).

"The Fluorescence Excitation Spectrum of Rotationally Cooled NO_2", R. E. Smalley, D. H. Levy and L. Wharton, J. Chem. Phys. 63, 4977 (1975).

"Laser Spectroscopy with Supersonic Free Jets", R. E. Smalley, D. H. Levy, and L. Wharton, Laser Focus 11, 40 (1975).

"The Fluorescence Excitation Spectrum of the $HeNO_2$ van der Waals Complex", R. E. Smalley, D. H. Levy, and L. Wharton, J. Chem. Phys. 64, 3266 (1976).

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"Molecular Optical Spectroscopy with Supersonic Beams and Jets", R. E. Smally, D. H. Levy and L. Wharton, Accts. Chem. Res. 10, 139 (1977).

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"The Fluorescence Excitation Spectrum of s-Tetrazine Cooled in a Supersonic Free Jet" van der Waals Complexes and Isotopic Species", R. E. Smalley, D. H. Levy, and L. Wharton, submitted to J. Chem. Phys.

"Laser Spectroscopy in Supersonic Molecular Beams", R. E. Smalley, L. Wharton, J. A. Blazy, P. S. H. Fitch, M. S. Kim, and D. H. Levy, Laser Spectroscopy 18, 59 (1976).

"The Fluorescence Excitation Spectrum of the ArI_2 van der Waals Complex", G. Kubiak, P. S. H. Fitch, D. H. Levy, and L. Wharton, submitted to J. Chem. Phys.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of this research were four fold: extend the technique of spectroscopy in jets to species that require well controlled high temperature sources for their preparation; examine the dispensed fluorescence from species formed by photo-decomposition; demonstrate Raman scattering as a means to study vibrational spectra of high temperature on van der Waals molecules; examine the kinetics of formation of clusters and nucleation in supersonic jets.

The major accomplishments achieved in the performance of this research effort are as follows:

(1) The design, development and exploitation of first and second generation apparatus for studying the spectroscopy of ultra cold molecules by laser induced fluorescence. This technique was the first joining of supersonic jets and laser optical spectroscopy for the simplification of complex optical spectra, for the observation of new van der Waals molecules, and for the observation of photo-chemical processes.

(2) The fluorescence excitation spectrum of NO_2 was measured in the region 5708-6708 Å using a tuneable dye laser as an excitation source. The NO_2 was cooled to a rotational temperature of $\sim$ 3 K by expansion with argon as a carrier gas through a supersonic nozzle. This cooling drastically reduced the rotational structure and thereby permitted a clear separation and analysis of 140 vibronic bands found in this 1000 Å region of the spectrum.

(3) The HeI_2 van der Waals complex was prepared from a dilute mixture of iodine in helium at a pressure of 100 atm by supersonic expansion through a nozzle into a vacuum. Laser-induced fluorescence excitation spectra were recorded for the $\tilde{B} \leftarrow \tilde{X}$ transition of HeI_2 as well as corresponding spectra for the He_2I_2 and I_2 molecules in the expanding gas.

(4) The spectrum of the $HeNo_2$ molecule was identified as a weak broad feature $\sim$ 1.5 cm^{-1} to the high frequency side of the R (0) line of the NO_2 vibronic origin. The $\sim$0.8 cm^{-1} width is due to lifetime broadening, $\sim 10^{-11}$ seconds, and must be due to the dissociation of the complex.

(5) The vibrational energy distribution in the photodissociation products of HeI_2 has been shown to obey the propensity rule $\Delta v = -1$ by observation of fluorescence of the daughter I_2.

(6) The van der Waals molecule NaAr has been prepared in a supersonic expansion of sodium vapor plus a few percent argon in a helium carrier gas. The fluorescence excitation spectrum of the $X^2\Sigma+ \rightarrow A^2\Pi$ optical transition has been analyzed and the vibrational and rotational spectroscopic constants have been derived from this analysis.

(7) The fluorescence excitation spectrum of the $^1B_{3u}$ ($\nu' = 0$) $\leftarrow$ $^1\mathrm{Ag}$ ($\nu'' = 0$) transition in s-tetrazine has been observed and measured. The sample was cooled to a rotational temperature of <1K by expansion in a supersonic free jet. In this way the rotational structure arising from asymmetry split low J lines could be observed.

(8) The vibrational relaxation of I_2 by H_2 has been studied in a supersonic free jet. It was observed that the addition of 5% H_2 to the helium carrier gas greatly reduces the concentration of $X^1\Sigma_g^+(\nu'' = 1)I_2$ in the jet as compared to the concentration in a pure helium carrier. From this observation we have determined that the average vibrational relaxation cross sections of H_2 is 7.1 times as large as that of helium.

(9) The 0-0 band of the B ← X visible spectrum of iodine has been observed in spite of its very small Franck-Condon factor. The expected satellite band of the van der Waals molecule HeI_2 was not observed, and a mechanism is suggested to account for the absence of the van der Waals spectrum.

(10) The rotational structure of the fluorescence excitation spectrum of the B ($\nu' = 10$) $\leftarrow$ X ($\nu'' = 0$) transition of the van der Waals molecule HeI_2 has been measured and analyzed.

(11) Van der Waals complexes between s-tetrazine and a number of light gases have been observed and characterized by laser spectroscopic studies of a free supersonic expansion of s-tetrazine in a helium carrier gas. The observed complexes are of the form X-s tetrazine and X_2-s-tetrazine where X = He, H_2, and Ar. The spectra are consistent with the X species in both types of complexes being bound on or near the out-of-plane C_{2v} axis on the top and/or bottom of the s-tetrazine ring.

(12) The van der Waals molecule ArI_2 has been produced in a supersonic expansion of I_2 in mixed argon-helium carrier gas, and its fluorescence excitation spectrum has been observed. Spectra of the complex are only observed when the iodine stretching vibration is excited to $v' \geq 12$ in the excited $\tilde{B}$ electronic state. Above this value the intensity of the van der Waals spectrum is observed to be an oscillatory function of the iodine vibrational quantum number.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Lifetimes and Quenching Rates for the $^3\Pi$ States of Interhalogen Molecules

2. PRINCIPAL INVESTIGATOR:

Dr. John J. Wright
Department of Physics
University of New Hampshire
Durham, NH 03824

3. INCLUSIVE DATES: 1 Jul 1977 - 30 June 1978

4. GRANT NUMBER: AFOSR-77-3232 (ASEE Mini Grant)

5. COSTS AND FY SOURCE: $10,000, FY 78

6. SENIOR RESEARCH PERSONNEL: Dr. L. C. Balling

7. JUNIOR RESEARCH PERSONNEL: M. D. Havey

8. PUBLICATIONS:

"Lifetimes of IBR($B^3\Pi_0{}^+$) by Laser-Excited Time-Resolved Fluorescence," J. J. Wright and M. D. Havey, J. Chem. Phys., **68**, 864 (1978).

"Lifetime Measurements of $A^3\Pi_1$ Vibrational Levels of ICl," M. D. Havey and J. J. Wright, J. Chem. Phys., **68**, 4754 (1978).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The interhalogens are attractive candidates for chemically pumped electronic transition lasers. First, most of these molecules could be produced in an electronically excited state by a chemical reaction. Second, because the $^3\Pi$ state potential wells are displaced from the ground $X^1\Sigma$ potential wells, the Franck-Condon factors favor a partial inversion between low-lying vibrational state levels of the $^3\Pi$ state and high-lying vibrational levels of the ground state. Third, the spin-forbidden nature of the transition means that the decay rate may be less than the chemical reaction rate. This is necessary if the system is to store energy during the chemical reaction until a large enough inversion is attained to produce a net gain. For the same reason, quenching rates must be less than the chemical reaction rate.

This work was undertaken to investigate the lifetimes of the metastable $^3\Pi$ states of some of the interhalogens. The interhalogens IBr and ICl

were chosen for initial investigation because they are stable. However, they exist in equilibrium with I_2 and either Br_2 or Cl_2 and the absorption and fluorescence spectra of I_2 and Br_2 overlap those of IBr and ICl. Considerable effort went into devising a scheme of fractional distillation at liquid nitrogen temperatures to reduce the I_2 and Br_2 fluorescence to an acceptable level. Unfortunately, the scheme did not lend itself to measurements of quenching rates and so only qualitative information can be presented. For both Icl ($A^3\Pi_1$) and IBr($B^3\Pi_0$) the self-quenching rate was very large and suggested that fluorescence was quenched by nearly every collision. The measured lifetime of the $B^3\Pi_0$ state of IBr is so short ($\sim .5\mu$ sec) that it is doubtful it could exceed a reaction time unless the densities were very high but then collisional deactivation would dominate. The lifetime was independent of vibrational level. In the $A^3\Pi_1$ state of ICl, on the otherhand, the lifetime varied with vibrational level between 130 and 325 μsec. There was a strong suggestion of a perturbation between v' = 9 and v' = 10. These lifetime values are consistent with the requirements for a chemically pumped laser but the large quenching rates do not favor such a system.

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