

AD-A056 765

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH BOLLING AFB D C  
ANNUAL AFOSR CHEMISTRY PROGRAM REVIEW (22ND) FY77.(U)  
MAR 78 R W HAFFNER

F/G 5/1

UNCLASSIFIED

AFOSR-TR-78-0001

NL

1 of 2  
AD  
A056765



AFOSR-TR-78-0001

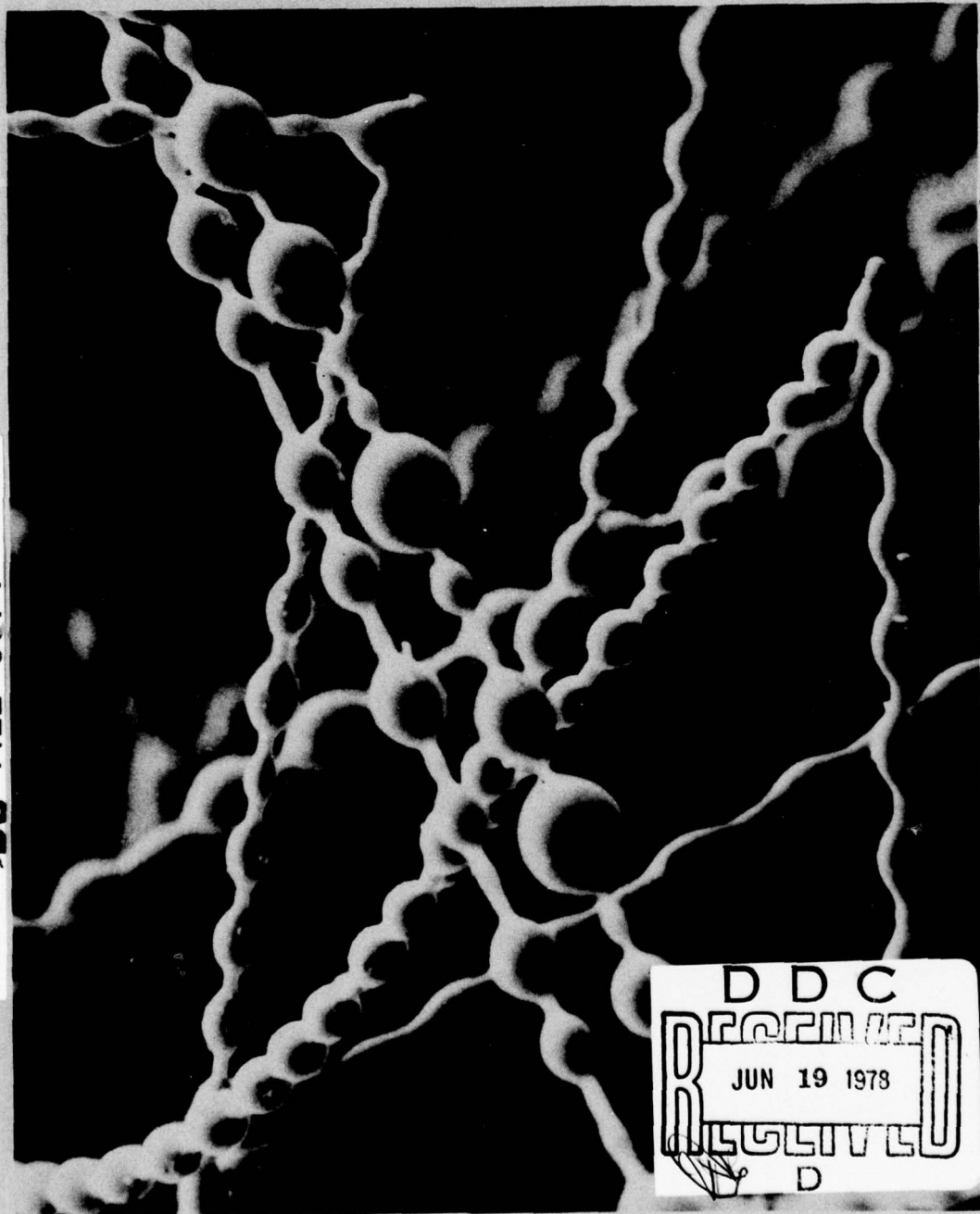
FOR FURTHER TRAN

# 22nd AFOSR Chemistry Program Review FY 77

②  
B.S.

AD A 056765

AD No. \_\_\_\_\_  
DDC FILE COPY



DDC  
RECEIVED  
JUN 19 1978  
D

*Air Force Office of Scientific Research  
Air Force Systems Command • USAF*

Approved for public release;  
distribution unlimited.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)  
NOTICE OF TRANSMITTAL TO DDC  
This technical report has been reviewed and is  
approved for public release IAW AFR 190-12 (7b).  
Distribution is unlimited.  
A. D. BLOSE  
Technical Information Officer

COVER

2

When polymeric polysilane formed by Professor Robert West of the University of Wisconsin (AFOSR 74-2644), from a mixture of  $\text{Me}_2\text{SiCl}_2$  and  $\text{PhMeSiCl}_2$  was thermally decomposed by K. S. Mazdidasni of the Air Force Materials Laboratory, very large and transparent greenish black whiskers of  $\beta\text{-SiC}$  were synthesized. The whisker morphology shown in the picture (scanning electron micrograph) is thought to be associated with the phase separation of mixed polymer into lower and higher molecular weight species having different glass transition temperatures during the thermal decomposition step. For example, when the higher molecular weight polymer is rigidized into a fibery structure, the lower molecular weight polymer is undergoing a glass transition temperature which consequently results in the development of droplets on the rigid fiber substrate and the formation of "rosary bead" whisker morphology of  $\beta\text{-SiC}$ . The newly developed polysilanes may be used either directly as fillers to improve thermomechanical properties of porous silicon-base non-oxide ceramics or as binders for sintering of structural ceramics for use in limited life turbine engines, rocket nozzles, and radomes. For a more detailed account of this work see story on page 15. (Cover photo compliments of K. S. Mazdidasni, Metals and Ceramics Division, AFML.)

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)

NOTICE OF TRANSMITTAL TO DDC

This technical report has been reviewed and is approved for public release IAW AFR 190-12 (7b). Distribution is unlimited.

A. D. Blose

Technical Information Officer

Additional copies of this document can be obtained from:

National Technical Information Service  
Department of Commerce  
5285 Port Royal Road  
Springfield, Virginia 22161

ACQUIRED BY	
DTIC	WDA Center <input checked="" type="checkbox"/>
DDC	DDP Center <input type="checkbox"/>
UNCLASSIFIED	<input type="checkbox"/>
AUTHORITY	
BY	
DISTRIBUTION/AVAILABILITY CODE	
SIC. AVAIL. and/or SPECIAL	
A	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>AFOSR-TR-78-0001</b> ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) <b>2ND ANNUAL AFOSR CHEMISTRY PROGRAM REVIEW, FY77</b>		5. TYPE OF REPORT & PERIOD COVERED Scientific Special
6. AUTHOR(s) <b>Richard W. Haffner</b> Editor (2nd)		7. PERFORMING ORG. REPORT NUMBER
8. PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Office of Scientific Research, AFSC Directorate of Chemical Sciences Bolling AFB, Washington, DC 20332		9. CONTRACT OR GRANT NUMBER(s) In-House
9. CONTROLLING OFFICE NAME AND ADDRESS <b>11 Mar 78</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <b>16</b> 2303 61102F
10. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) <b>12 113p.</b>		11. REPRODUCTION DATE March 1978
11. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		12. NUMBER OF PAGES
12. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) <b>14 AFOSR-TR-78-0001</b>		13. SECURITY CLASS. (of this report) UNCLASSIFIED
13. SUPPLEMENTARY NOTES		14. DECLASSIFICATION/DOWNGRADING SCHEDULE
14. KEY WORDS (Continue on reverse side if necessary and identify by block number) AF Research Program      Advanced Materials Chemistry      European Chemistry U.S. Air Force      Chemical Techniques Air Force Office of Scientific Research      Surface Chemistry Chemical Sciences		
15. ABSTRACT (Continue on reverse side if necessary and identify by block number) 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 three principle sections presents various technical aspects. It contains articles on Air Force research in Surface Chemistry, Chemical Techniques, and Materials Chemistry plus reports submitted by the European Office of Aerospace Research and the Frank J. Seiler Research Laboratory. The second section contains program statistics. The third section lists research efforts completed in FY77.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ii

012550

JB

22ND AFOSR

CHEMISTRY PROGRAM REVIEW

FY77

RICHARD W. HAFFNER, EDITOR

DENTON W. ELLIOTT, MANAGING EDITOR

MARCH 1978

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)

DIRECTORATE OF CHEMICAL SCIENCES

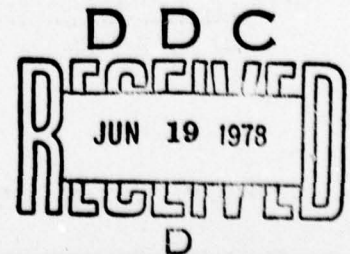
BUILDING 410

BOLLING AIR FORCE BASE

WASHINGTON, D. C. 20332

Approved for public release; distribution unlimited.

iii



## TABLE OF CONTENTS

Acknowledgements	v
Mission	vi
Technical Staff	vii
Chemistry Research Evaluation Panel, FY77	viii
Letter From The Director	ix
A Status Report from Abroad Lt Col David W. Seegmiller	1
Progress in Molten Chloroaluminate Electrochemistry Lt Col Ben A. Loving and Lt Col Lowell A. King	4
Chemical Techniques Denton W. Elliott	12
Silicon Carbide from Organopolysilanes Dr. Anthony J. Matuszko	15
AFOSR Corrosion Related Research Lt Col Richard W. Haffner	17
Duration of Support of Principal Investigators	21
Chemistry Annual Budget	22
FY77 Chemistry Program Statistics	22
Conferences and Symposia	23
Active Research Efforts as of 1 October 1977	24
Research Efforts Completed in FY77	37
Completed Project Summaries FY77	40

## ACKNOWLEDGEMENTS

This review is due to the combined efforts of the technical and secretarial staff of the Directorate of Chemical Sciences. Multiple thanks go to Mrs. Iris Worley, Ms. Debbie King, and Mrs. Barbara Murphy for their efforts in typing various parts of this report. The Editor wishes to express special appreciation to Ms. Anne Pahia for the many hours devoted to typing the final copy, preparing the article headings, and the preparation of the book into its final form for printing.

## 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 understanding of the science of chemistry, to stimulate the recognition of new chemical concepts, and to provide for early exploitation of their military implications.

The Directorate obtains and maintains for the Air Force a diversified program of chemical research through support of scientists in promising original endeavors of their own choosing. 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 aids the Air Force in its maintenance of technological superiority.

## TECHNICAL STAFF

Dr. Donald L. Ball  
Director

Mr. Denton W. Elliott  
Staff Scientist  
Chemical Techniques

Dr. Donald L. Ulrich  
Program Manager  
Chemical Structures

Lt Col John T. Viola  
Program Manager  
Molecular Dynamics

Dr. Frank J. Wodarczyk  
Program Manager  
Molecular Dynamics

Dr. Anthony J. Matuszko  
Program Manager  
Chemical Reactivity and  
Synthesis

Lt Col Richard W. Haffner  
Program Manager  
Surface Chemistry

Dr. Robert A. Osteryoung  
Program Manager  
Molecular Dynamics

## SECRETARIAL STAFF

Ms. Anne Pahla  
Secretary to the Director

Mrs. Iris Worley  
Proposal Clerk

## CHEMISTRY RESEARCH EVALUATION PANEL FY77

Chairman - Prof Howard Reiss, Department of Chemistry  
The University of California at Los Angeles  
Los Angeles, California 90024

Prof Harry R. Allcock  
Department of Chemistry  
The Pennsylvania State University  
University Park, Pennsylvania 16802

Prof Allen J. Bard  
Department of Chemistry  
The University of Texas at Austin  
Austin, Texas 78712

Prof Dwaine O. Cowan  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, Maryland 21218

Prof Gert Ehrlich  
Coordinated Science Laboratory  
College of Engineering  
University of Illinois at Urbana-  
Champaign  
Urbana, Illinois 61801

Mary L. Good  
Boyd Professor of Chemistry  
The University of New Orleans  
New Orleans, Louisiana 70122

Prof Frederick Kaufman  
Department of Chemistry  
The University of Pittsburgh  
Pittsburgh, Pennsylvania 15260

Prof Mark S. Wrighton  
Department of Chemistry  
The Massachusetts Institute of  
Technology  
Cambridge, Massachusetts 02139

Prof Yuan T. Lee  
Materials and Molecular Research Div  
Lawrence Berkeley Laboratory  
The University of California at Berkeley  
Berkeley, California 94720

Dr. William A. Lester, Jr.  
San Jose Research Laboratory  
IBM Corporation  
San Jose, California 95193

John L. Margrave  
Dean of Advanced Studies and Research  
Rice University  
Houston, Texas 77001

Arthur E. Martell  
Distinguished Professor and Head  
Department of Chemistry  
Texas A and M University  
College Station, Texas 77843

Prof Guy E. Rindone  
Chairman, Ceramic Science Section  
Department of Material Sciences  
The Pennsylvania State University  
University Park, Pennsylvania 16802

Dr. Field H. Winslow  
Head, Organic Chemistry Research and  
Development Department  
Bell Laboratories  
Murray Hill, New Jersey 07974

### SPECIAL CONSULTANT:

Prof Joseph E. Earley  
Department of Chemistry  
Georgetown University  
Washington, D. C. 20007

DEPARTMENT OF THE AIR FORCE  
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)  
BOLLING AIR FORCE BASE, DC 20332



TO: MEMBERS OF CHEMISTRY RESEARCH EVALUATION PANEL  
AND OTHER FRIENDS OF AFOSR

As has been our tradition since the first "Program Review" in 1955, this letter is addressed to a special group of people who assist us in judgments as to the scientific merit of formal research proposals under our review. Naturally, our final selections for support are based on larger, more complex considerations in addition to scientific quality -- of which known and foreseeable relevance to Air Force technology is most important. We have the help of many other special friends in the technology laboratories of the Air Force Systems Command in assessing this essential factor. We work with them more closely, today, than ever before due to the role of the AFOSR Director, Dr. William Lehmann, as the "single manager" for Air Force Research. AFOSR, thus, manages in-house as well as extramural programs in some twelve AFSC laboratories. In chemistry, for example, in-house research is underway at the Air Force Materials Laboratory and Aero Propulsion Laboratory at Wright-Patterson AFB, Ohio, the Weapons Laboratory at Kirtland AFB, New Mexico, the Geophysics Laboratory at Hanscom AFB, Massachusetts, the Rocket Propulsion Laboratory at Edwards AFB, California, and the Frank J. Seiler Research Laboratory which is co-located at the Air Force Academy in Colorado.

On a more local scene, from the AFOSR Washington office, two of the Directorate Program Managers have been away for special, advanced military education -- Lieutenant Colonel John T. Viola at the Defense Systems Management College and Dr. Donald Ulrich at the Air War College. In their temporary absence we have been privileged to have the services of Professor Robert Osteryoung from Colorado State University and Dr. Frank Wodarczyk from the Rome Air Development Center, Detachment for Electronic Technology at Hanscom AFB, Massachusetts.

Best regards,

*Donald L. Ball*

DONALD L. BALL  
Director, Chemical Sciences

## A STATUS REPORT FROM ABROAD

### CHEMISTRY IN EUROPE AND ISRAEL

(Lieutenant Colonel David W. Seegmiller wrote the following article to express his impressions of European Chemical research after spending a year with the European Office of Aerospace Research and Development.)

In general, European Chemistry is highly developed, progressive and very competitive in quality with that found in the States. Instrumentation at most universities is comparable with that in US schools; institutions such as Cambridge and Oxford probably possess laboratory facilities and staff equal to any in the world. Research interests are similar to those found in the States; however, it is probably fair to say that Europeans and Israelis tend to concentrate their effort much more narrowly. For example, each major university in Israel boasts a very strong Physical Chemistry department, but the research in any given department is very restricted in scope and overlaps little with that of other Israeli universities. Israeli materials research seems concentrated at the Technion. Molecular dynamics programs are particularly strong at the Hebrew University, and Tel Aviv University boasts a very competent electrochemistry group.

In terms of costs, research in Scandinavia is probably more expensive than in the States, Central Europe is probably similar to the States, and costs in Italy, Spain and the United Kingdom are decidedly lower. Israel is also very competitive cost-wise, although somewhat more expensive than the UK. In terms of research accomplished per dollar spent, Chemistry related research in the UK may be one of the world's best bargains. The following paragraphs outline a few chemically related topics that have come to the attention of the author. The listing is not exhaustive in any way.

Polymer Science. Numerous international polymer related symposia and conferences are well attended and very international in character. Some are highly specific in nature, such as the EUCHEM "Conference on the Study of Macro-Molecules by n.m.r." and the "Seminar on Ultra-High Modulus Polymers" which the author attended. Very strong groups in the area of high modulus materials are headed by Professor I. Ward at the University of Leeds, UK, Professor A. Ciferri at the University of Genoa, Italy. Little contact has been made with the industrial polymer community, but company representatives are in attendance and highly visible at all meetings.

Tribology. In the opinion of the author, tribology may be better developed in the UK than anywhere else in the world. Britain is the land where this interdisciplinary science was born and developed. The work "tribology", taken

from the Greek "tribos", which means "rubbing", is the "science and technology of interacting surfaces in relative motion and of the practices relating thereto". In addition to numerous large university programs, the UK boasts of three Tribology Centers: (1) the National Centre of Tribology (NCT), Warrington, Lancashire, which is staffed by twenty professional members and is totally self-supporting through industrially-funded programs; (2) the Leeds Tribology Centre at the University of Leeds; and (3) the Swansea Tribology Centre at the University College of Swansea. Other significant centers include the Admiralty Materials Laboratory, the National Engineering Laboratory (NEL), the "Lube Lab" at Imperial College, and the Tribology Branch in the Department of Mechanical Engineering, Cranfield Institute of Technology. Large programs are also conducted by industrial firms such as Rolls Royce and Shell Research Ltd. The "UK Mechanical Health Monitoring Group" meets quarterly. The group offers the following services to any interested party: (1) holds periodic informal meetings of persons and organizations involved in the development and use of techniques, (2) maintains a register of persons and organizations involved in the development of techniques, (3) maintains a register of organizations involved in the manufacture of devices, (4) maintains a register of users and interested parties, (5) organizes periodic seminars and infirm courses for organizations using techniques and devices, (6) provides an advisory and consultancy service. As an example of the type of topics considered at the quarterly meetings, the following papers which were presented at the November 1976 seminar are listed: Introduction to Contaminant Analysis; SOAP developments; Oil System Particulate Monitoring in Gas Turbines; X-ray Diffraction Analysis - Sterioscan X-ray Analysis; Ferrography Applied to Contaminant Analysis in Relation to Deterioration; Contaminant Analysis to Very Small PPM; and Thin Layer Activation - An Application of Energetic Ion Beams to the Measurement of Wear and Corrosion.

**Batteries.** Very good state-of-the-art research is being performed in Europe and Israel on the improvement of current battery systems and the development of new, principally high energy batteries. SAFT (France) is undoubtedly one of the world's foremost battery manufacturers and supportive research is of the highest caliber. If their new PVA separator material is as good as preliminary tests imply, battery manufacturing throughout the world will be affected. CNRS (France) work on molten salt systems may prove significant if their, as yet experimental, method for increasing chlorine storage on graphite by incorporation into lamellar compounds proves successful. Related work at CNRS involves the absorption of large amounts of hydrogen by lanthanum/nickel alloys. Claim is made that various alloys can be discharged at about 1 volt vs. SCE and display a storage capacity in excess of 320 mAh/g of alloy. Some Ti materials can apparently be made to absorb as much as 5 atoms of hydrogen for each molecule of alloy. TADIRAN, a large Israeli electronics firm, whose products include Li/SOCl<sub>2</sub> high energy batteries, sponsors the work of Professor Peled of Tel Aviv University who has had considerable success with experimental electrodes composed of Li or Mg-Ca. The TADIRAN lithium cell consists of a metallic lithium anode, a carbon cathode and a thionyl chloride based electrolyte. The cell container is made of nickel-plated steel and either high energy or high power

cells are available. The high power cell contains a spirally wound Li anode and heating and shorting problems have not been completely solved. In the UK, Chloride Technical Limited is very actively engaged in the development of high energy density batteries designed for vehicle propulsion. They claim sodium sulphur battery single cell capacities of about 550 Wh. The firm is a development company and formidable technical problems have already been overcome in bringing the development of the sodium sulphur battery to its present states. There appears to be a great deal of interest and a significant number of proposals have been received from workers in the UK involved in the development or improvement of solid state electrolytes. Strong groups exist at the University of Kent, Oxford University and at the University of Aberdeen.

Molecular Dynamics. This is a broad, catch-all title that includes at least the following topics: intermolecular forces; atom-atom, atom-molecule, and atom-solid surface interactions; the dynamics of molecular collision; chemical reactions and energy transfer; chemical lasers; energy transfer; relaxation phenomena and the statistical theory of chemical reactions. Internationally recognized experts in this field with whom contact has been made include: Professor E. W. Schlag (Munich), Professors I. Smith and D. Hussain (Cambridge), Professor R. D. Levine and Dr. Ben-Shaul (Hebrew University), Professor Joshua Jortner (Tel Aviv University), Dr. K. Bray (Southampton University). The work being performed by the aforementioned individuals is probably as good and progressive as any in the world.

Energetic Materials. Contact was established with the European explosives community by attendance at a conference sponsored by and at the Institut für Treibund Explosivstoffe" (Analytical Methods for Propellants and Explosives). The facility in the opinion of many of the conference delegates (including Americans) may be one of the world's better-equipped explosives laboratories. Instrumentation of every conceivable type is employed for the synthesis and study of energetic compounds and materials. It is strongly recommended that if anyone from the Air Force's explosives community has cause to visit Europe, arrangements should be made to visit this facility. The institute hosts an explosives meeting annually in June. The 1978 meeting topic is, "Modern Techniques and the Production of Rocket and Gun Propellants and Explosives - Stressing Safety".

PROGRESS IN MOLTEN CHLOROALUMINATE ELECTROCHEMISTRY

Lt Colonel Ben A. Loving

and

Lt Colonel Lowell A. King

Directorate of Chemical Sciences  
F. J. Seiler Research Laboratory (AFSC)  
U. S. Air Force Academy, Colorado

When the F. J. Seiler Research Laboratory was established fifteen years ago investigation of the chemistry of molten aluminum chloride salt mixtures as potential battery electrolytes was selected as a long term program of high potential. The original proposal cites as justification the requirement for high power to weight ratio batteries as the principal limiting factor in development of practical electrically powered vehicles. By extension, a variety of rechargeable high energy density or high power density battery applications in aircraft and other military hardware became evident. The low cost and favorable chemical and physical properties of aluminum chloride-containing battery electrolytes stand in sharp contrast to all alternate high energy content electrochemical power sources thus far employed or proposed for use.

The first decade of study was at a low level of effort, yet there were major advances in understanding this new electrolyte, which led to recent major successes. Realization of a chloroaluminate based secondary battery still stands as the ultimate goal, however we are pleased to report on achievement of an intermediate one: Invention and subsequent development of a family of thermally activated primary batteries.

During the past year development feasibility of a thermal battery with a lithium chloroaluminate electrolyte, a lithium-aluminum alloy anode, and a molybdenum pentachloride cathode was demonstrated by an Air Force contractor. This battery has become known among technologists as the ALLiMo Battery. This contract was a direct follow on to the fundamental studies carried out at FJSRL, in which these battery components were identified as the most promising for engineering evaluation. Along the way some very enjoyable and challenging science was encountered by a long list of Air Force Officer scientists - best enumerated by the attached list of publications. Reflection back onto the milestones leading to the first new thermal battery system to emerge from science in almost thirty years displays an interesting sequence.

Workers at three non-government laboratories in the late '60's independently attempted to construct a working battery utilizing a chloroaluminate electrolyte. Their developmental attempts were premature and unsuccessful. Failure was probably due to the absence of adequate details of the structure and physical properties of the electrolyte. On battery discharge the electrolyte composition shifted in such a way to result in formation of solids and poor conductivity.

The structure of  $\text{AlCl}_3$ -NaCl liquid mixtures was first addressed by the FJSRL group as the most fundamental unknown. Although experimentation to more definitively establish these fundamental relationships continues, a major milestone was realized as early as the 1967-68 time frame. Complete formulation of the physical and chemical model that emanated from these earlier experimental findings coalesced in 1970 and was published in the 1972 "benchmark paper" by Fannin, King, and Seegmiller entitled "Chloroaluminates Equilibria in  $\text{AlCl}_3$ -NaCl Melts". In that paper a model involving the numerous components present in this complex mixture was advanced. It was the first suggested model by any investigators, and has stood essentially unchanged since that time.

By 1972 numerous potential electrochemical couples (anodes and cathodes) for both primary and secondary batteries had been identified. The extensive work of Dr. Robert Osteryoung and his group at Colorado State University under support from the AFOSR Directorate of Chemical Sciences provided insight into melt electrochemical behavior as well. This permitted selection of general classes of compounds which offered the highest potential.

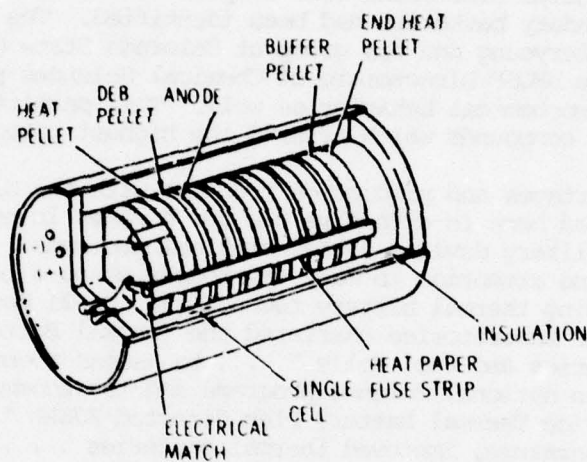
In 1974 materials shortages and production problems with the LiCl/KCl thermal batteries which had been in extensive use for decades in hundreds of weapon systems and military devices caused critical problems. These difficulties brought command attention to many previously obscure technical deficiencies in existing thermal battery technology. On 21 November 1975, the Joint Deputies for Laboratories chartered the Thermal Battery Subpanel of the JTCG for Batteries and Fuel Cells ". . . to assess thermal battery technology . . . impact on national defense programs and to recommend actions." The resulting Triservice Thermal Battery Plan directed FJSRL ". . . to develop new, low temperature, improved thermal batteries . . . for application in munition fuses, expendable ECM devices and other weaponry."

In response two program modifications were made. Fundamental anode and cathode electrochemical studies were initiated as companion to ongoing work on physical and electrolyte properties. Secondly, selection of optimum electrolyte composition and electrochemical couples was necessary. The fundamental science underlying these decisions had been accumulated. A screening effort in which laboratory pelletized electrochemical thermal cells were fabricated and tested was rapidly set into motion. This expanded program filled in many information holes which gave rise to rapid and successive publication of numerous scientific papers and patent disclosures. It established the springboard from which the AF Aeropropulsion Laboratory initiated its successful development feasibility demonstration in 1977 of a thermal battery manifesting an order of magnitude improvement over those in current state of the art technology.

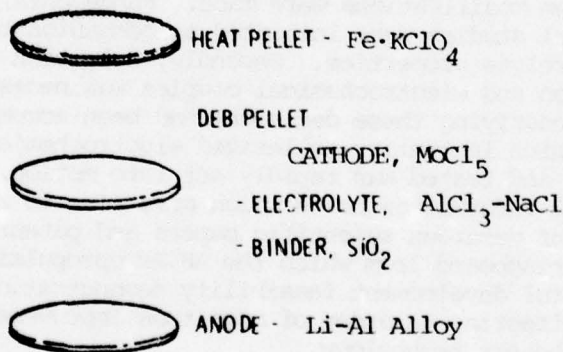
The basic science of this battery was presented at the 1977 Gordon Conference on Molten Salts and Metals.

These improvements were called for in the AFSC Research Planning Guide R.O. 5.3.1, which states ". . . new material with the intent of providing low cost, reliable thermal batteries and ease of meeting OSHA and manufacturing requirements." R.O. 6.6.12, on Low Cost/Light Weight Batteries states,

"At least a threefold improvement in battery specific power and specific volume is required", for expendable jammers. The new FJSRL/AFAPL Chloroaluminate Thermal Battery has been demonstrated to meet and exceed these requirements. It displays significantly higher energy density, a lower operating temperature of 175°C vs 500°C, and longer operational life of minutes or even hours as opposed to seconds. Further, this new battery is expected to be lower in cost and lighter weight while constructed of materials that are readily available and non-toxic. These latter are considerations which had proved to be a major recent problem in meeting systems production requirements. Construction and performance characteristics are shown in Figure 1 and Table 1 respectively.



THERMAL BATTERY CONSTRUCTION



CELL COMPONENTS

Figure 1

Table 1. Single Cell and Battery Performance

	LiAl/NaAlCl <sub>4</sub> /MoCl <sub>5</sub>			LiCl/KCl Battery <sup>c</sup> State of the Art
	Single Cell <sup>a</sup> Achieved	Battery <sup>b</sup> Achieved    Projected		
Operating temp., °C	175	200	200	500
Operating life, min	60	15	45	1
No. of Cells	1	11	11	9
Voltage, V	2.7	28	28	28
Current, A	0.9	0.8	2	1.9
Current <sub>2</sub> Density, mA/cm <sup>2</sup>	35.5	43	350	50
Energy Density, Wh/lb	N/A	15	42	1.0

<sup>a</sup>Ref. Nos. 16 and 21.

<sup>b</sup>Ref. No. 19.

<sup>c</sup>F. Tepper, "A Survey of Thermal Battery Designs and Their Performance Characteristics", in 9th Intersociety Energy Conversion Engineering Conference Proceedings, 1974, p. 671.

Our thermal battery related program continues in support of the AFAPL development efforts. Full development is currently proceeding under contract at the Eureka Co., Eagle-Picher Co., and KDI SCORE. Hughes Missile Systems Group is considering one of the batteries for flight evaluation in a new system this year. The transition of some fresh ideas and fundamental research in this laboratory into an active Air Force development effort stands as a conspicuous reminder of how the Air Force research and development program is designed to work.

In 1977 a new class of aluminum chloride containing electrolytes were identified for use in room temperature molten salt batteries. These electrolytes contain any one of several organic chloride salts which form with aluminum chloride very low melting analogs of the electrolytes described earlier in this paper. There is a dearth of information on the properties and behavior of such melts.

Present studies at FJSRL include studies on the thermal batteries indicated above, but are mostly directed at the investigation of electrode materials and electrolytes and the electrochemical behavior of both for use in new rechargeable batteries. Perhaps the flavor of the work can best be seen

from the most recent entries on the bibliography. In-house studies are complemented by the continued efforts of Osteryoung's group at Colorado State University and by a program begun in 1977 with Professor Harald Øye and his group at Norwegian Institute of Technology in Trondheim, also supported by AFOSR.

#### PUBLICATIONS

1. "High Energy Density Electrochemical Cells," L. A. King, A. D. Brown, Jr. and F. H. Frayer, Proc. of the Third OAR Research Applications Conf., 1, J-1, March 1968.
2. "Electrochemical Behavior of a Molten Aluminum Chloride Sodium Chloride Electrolyte," L. A. King and D. W. Seegmiller, Proc. of the Fourth OAR Research Applications Conf., 1, J-1, March 1969.
3. "Preparation of Crystals of Aluminum Chloride," D. W. Seegmiller, G. W. Rhodes and L. A. King, Inorg. Nucl. Chem. Lett., 6, 885 (1970).
4. "Liquid and Vapor Densities of Aluminum Chloride," L. A. King and D. W. Seegmiller, J. Chem. Eng. Data, 16, 23 (1971).
5. "The Structure of Aluminum Chloride-Sodium Chloride Melts," A. A. Fannin, Jr., L. A. King and D. W. Seegmiller, F. J. Seiler Research Laboratory Technical Report SRL-TR-71-0018, October 1971.
6. "A Lightweight High Energy Battery," A. A. Fannin, Jr., L. A. King and D. W. Seegmiller, Proc. of the Air Force Systems Command 1971 Science and Engineering Symp., October 1971; also available as F. J. Seiler Research Laboratory Technical Report SRL-TR-71-0019, October 1971.
7. "Aluminum High Energy Density Concentration Cells," L. A. King, D. W. Seegmiller and A. A. Fannin, Jr., Air Force Res. Rev., 3, 8 May - December 1971.
8. "Aluminum-Chlorine Battery," G. D. Brabson, A. A. Fannin, Jr., L. A. King and D. W. Seegmiller, F. J. Seiler Research Laboratory Technical Report SRL-TR-72-0013, May 1972.
9. "Chloroaluminate Equilibria in  $AlCl_3$ -NaCl Melts," A. A. Fannin, Jr., L. A. King and D. W. Seegmiller, J. Electrochem. Soc., 19, 801 (1972).
10. "Liquid and Vapor Densities of Aluminum Chloride. II. Extension to the Critical Temperature," D. W. Seegmiller, A. A. Fannin, Jr., D. S. Olson and L. A. King, J. Chem. Eng. Data, 17, 295 (1972).
11. "Liquid and Vapor Densities of Aluminum Bromide," D. S. Olson, F. C. Kibler, Jr., D. W. Seegmiller, A. A. Fannin, Jr. and L. A. King, J. Chem. Eng. Data, 19, 27 (1974).
12. "Densities of Liquid Aluminum Chloride-Sodium Chloride Mixtures I. Single Liquid-Phase Region," A. A. Fannin, Jr., F. C. Kibler, L. A. King and D. W. Seegmiller, J. Chem. Eng. Data, 19, 266 (1974).

13. "Exploratory Aluminum - Chlorine Thermally Activated Battery: Single Cell Experiments," G. D. Brabson, J. K. Erbacher, L. A. King, and D. W. Seegmiller, F. J. Seiler Research Laboratory Technical Report SRL-TR-76-0002, January 1976.
14. "High Energy Density Pelletized Aluminum Chloride Thermal Batteries," C. L. Hussey, J. K. Erbacher, and L. A. King, F. J. Seiler Research Laboratory Technical Report SRL-TR-76-0003, January 1976.
15. "The Discharge Behavior of a  $\text{LiAl}/\text{NaAlCl}_4/\text{CuCl}_2$  Pelletized Thermal Cell," J. K. Erbacher, C. L. Hussey, and L. A. King, F. J. Seiler Research Laboratory Technical Report FJSRL TR-77-0001, February 1977.
16. "Experimental Optimization and Characterization of a  $\text{LiAl}/\text{NaAlCl}_4/\text{MoCl}_5$  Pelletized Thermal Cell," J. C. Nardi, J. K. Erbacher, C. L. Hussey, and L. A. King, F. J. Seiler Research Laboratory Technical Report FJSRL TR-77-0002, February 1977.
17. "The Aluminum Chloride Thermal Battery Program," J. K. Erbacher and J. C. Nardi, Proc. of the 4th Biennial Air Force Electrochemistry Conf., USAF Academy, CO, 27-28 April 1977; also available as F. J. Seiler Research Laboratory Technical Report SRL-TR-77-0013, August 1977.
18. "High Energy Density Pelletized Aluminum Chloride Thermal Batteries: Part II. Cathode Screening," J. C. Nardi, J. K. Erbacher, and C. L. Hussey, F. J. Seiler Research Laboratory Technical Report FJSRL-TR-77-0004, April 1977.
19. "High Energy Density Pelletized Aluminum Chlorine Thermal Batteries," D. M. Ryan and L. C. Bricker, Air Force Aero Propulsion Laboratory Technical Report AFAPL TR-77-12, April 1977.
20. "Electrolytic Etching of Aluminum from an  $\text{Al}-\text{Al}_3\text{Ni}$  Two-Phase Matrix in Aluminum Chloride Containing Molten Salts," C. L. Hussey, J. C. Nardi, L. A. King, and J. K. Erbacher, J. Electrochem. Soc., 124, 1451 (1977).
21. "Evaluation and Optimization of Pelletized  $\text{LiAl}/\text{NaAlCl}_4/\text{MoCl}_5$  Electrochemical Cells," J. C. Nardi, J. K. Erbacher, C. L. Hussey, and L. A. King, Extended Abstracts Intern. Sym. on Molten Electrolytes and High Temperature Batteries, The Electrochemistry Group of the Chemical Society, Brighton, England, 22-23 September 1977; J. Power Sources, in press.
22. "The  $\text{Al}/\text{NaAlCl}_4/\text{MoCl}_5$  Thermal Battery," R. A. Marsh, D. M. Ryan, and J. C. Nardi, Extended Abstracts Intern. Sym. on Molten Electrolytes and High Temperature Batteries, The Electrochemistry Group of the Chemical Society, Brighton, England, 22-23 September 1977; J. Power Sources, in press.
23. "New Low Temperature, High Energy Density Battery Systems," J. K. Erbacher, C. L. Hussey, and J. C. Nardi, Proc. of the 1977 Air Force Systems Command Science and Engineering Sym., Wright-Patterson AFB, OH, 27-28 October 1977.

24. "Vapor Pressure of Aluminum Chloride Systems. 1. Vapor Pressure and Triple Point of Pure Aluminum Chloride," J. T. Viola, D. W. Seegmiller, A. A. Fannin, Jr., and L. A. King, J. Chem. Eng. Data, 22, 367 (1977).
25. "Vapor Pressure of Aluminum Chloride Systems. 2. Pressure of Unsaturated Aluminum Chloride Gas," J. T. Viola, A. A. Fannin, Jr., L. A. King, and D. W. Seegmiller, J. Chem. Eng. Data, in press.
26. "Vapor Pressure of Aluminum Chloride Systems. 3. Vapor Pressure of Aluminum Chloride-Sodium Chloride Melts," J. T. Viola, L. A. King, A. A. Fannin, Jr., and D. W. Seegmiller, J. Chem. Eng. Data, in press.
27. "An Electrochemical Study of Chromium in Molten NaCl-AlCl<sub>3</sub>," C. L. Hussey, L. A. King, and J. K. Erbacher, J. Electrochem. Soc., in press.
28. "Novel Radical Cation Formation in Ambient Temperature Molten Salts," C. P. Keszthelyi, C. L. Hussey, L. P. Davis, and J. L. Pflug, submitted to J. Am. Chem. Soc.
29. "The Electrochemistry of Copper in an Ambient Temperature Molten Salt: 1-Methylpyridinium Chloride-Aluminum Chloride," C. L. Hussey, L. A. King, and R. A. Carpio, submitted to J. Electrochem. Soc.
30. "Density, Electrical Conductivity, and Viscosity of Several n-Alkylpyridinium Halides and Their Mixtures with Aluminum Chloride," R. A. Carpio, L. A. King, C. L. Hussey, R. E. Lindstrom, and J. C. Nardi, submitted to J. Electrochem. Soc.
31. "Densities of AlCl<sub>3</sub>-Rich Molten AlCl<sub>3</sub>-LiCl Systems," R. A. Carpio, L. A. King, and A. A. Fannin, Jr., submitted to J. Chem. Eng. Data.
32. "Conductivities of AlCl<sub>3</sub>-Rich Molten AlCl<sub>3</sub>-LiCl Mixtures," R. A. Carpio, L. A. King, F. C. Kibler, Jr., and A. A. Fannin, Jr., submitted to J. Electrochem. Soc.
33. "Conductivity Cell for Studying Air Sensitive Liquids," R. A. Carpio, F. C. Kibler, Jr., L. A. King, and D. W. Seegmiller, submitted to J. Electrochem. Soc.

#### PATENTS

34. "Electrochemical Cell with Aluminum Electrodes and Different Electrolyte Concentrations in Two Compartments," L. A. King and D. W. Seegmiller, U. S. Patent No. 3,671,322; June, 1972.
35. "Two Compartmented Electrochemical Cell Having Aluminum Anode Bud (sic) Powdered Carbon Suspended in the Cathode Compartment," G. D. Brabson, Jr., L. A. King, D. W. Seegmiller, and A. A. Fannin, Jr., U. S. Patent No. 3,770,503; November 1973.
36. "Electrochemical Cell with Aluminum Electrodes and Different Electrolyte Concentration in Two Compartments," D. W. Seegmiller and L. A. King, U. S. Patent No. 3,787,242; January 1974.

37. "Aluminum-Chlorine Thermal Battery," L. A. King, G. D. Brabson, J. K. Erbacher, D. W. Seegmiller, A. A. Fannin, and J. T. Viola, U. S. Patent Applied For, 1977.
38. "Molybdenum Chloride-Tetrachloroaluminate Thermal Battery", J. C. Nardi, C. L. Hussey, J. K. Erbacher, L. A. King, and A. A. Fannin, Jr., U.S. Patent Applied For, 1977.
39. "Electrolytic Separation Procedure for Removing Aluminum From a Solid Two Phase Mixture of Aluminum and Trialuminum Nickelide," C. L. Hussey, J. C. Nardi, L. A. King, and J. K. Erbacher, U. S. Patent Applied For, 1977.
40. "AlCl<sub>3</sub>/1-Alkyl Pyridinium Chloride Room Temperature Electrolytes", J. C. Nardi, C. L. Hussey, and L. A. King, U. S. Patent Applied For, 1977.
41. "Copper(II) Chloride-Tetrachloroaluminate Thermal Battery," J. K. Erbacher, C. L. Hussey, and L. A. King, Air Force Invention Disclosure Submitted, January 1978.

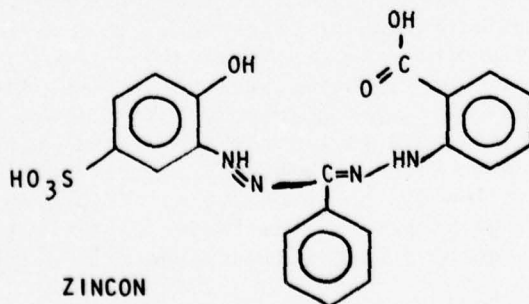
## CHEMICAL TECHNIQUES

DENTON W. ELLIOTT

Continuous monitoring of all functional systems is essential if the Air Force is to successfully carry out its world-wide missions in reconnaissance, surveillance, communications, navigation and weapons delivery. The need exists for detecting and identifying defects in power systems, impurities in cabin environments, and hazards encountered in the atmosphere as well as on the ground. New and improved analytical instrumentation and techniques to assist in solving these and related problems is a must. It is because of these ever-present requirements that the Chemical Techniques program is focused on the general topics of (1) Detection and (2) Electrochemistry. Examples of sponsored research in each of these technical areas follow:

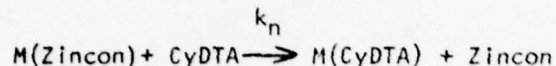
At Purdue University the Chemistry Directorate has supported the research of Professor Dale W. Margerum on simultaneous kinetic analysis (SKA). Simultaneous kinetic analysis is a method of determining multiple components which obtains its specificity from differences in the reaction rates of individual components, as an alternative to physical separation or equilibrium measurements. The use of differentiating reaction rates for the analysis of multi-component mixtures is not new to Professor Margerum's group as they have been exploring this area for a number of years. They have emphasized the importance of using the entire response signal (i.e., absorbance vs. time) as opposed to graphical methods based on the signal after all but the slowest components have reacted, or initial rate methods for only the fastest component, or two-point methods. The availability of minicomputers makes it possible to acquire hundreds of experimental points along the entire response signal with good precision in the measurement of the signal magnitude and time for each point, even for fast reactions. They have also devised and used a method which permits on-line computer processing of data from a stopped-flow spectrophotometer followed by a linear least squares fit of the regression equation, also done on-line. This regression analysis has been applied to mixtures of metal ions and to the analysis of mixtures of aminopolycarboxylic acids. They have now improved the technique to acquire, to calculate, and to test data sets for simultaneous kinetic analysis.

The method developed is a new kinetic analysis system using the reagent zincon for the simultaneous determination of trace levels of  $Zn^{++}$ ,  $Cd^{++}$ ,  $Hg^{++}$ , and other metal ions.



(In 1954, Rush and Yoe described a calorimetric method for the determination of zinc and copper using the reagent 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene, which they call zincon.)

Zincon will form blue complexes with  $\text{Cu}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Cd}^{++}$ , AND  $\text{Pb}^{++}$ . The ligand exchange reaction of these metals from zincon to CyDTA (trans-1, 2-diaminocyclohexane-N,N,N,N-tetraacetate ion) were investigated by Margerum and his research group and found that only  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ , and  $\text{Hg}^{++}$  undergo rapid reaction.



The reaction rates are first order in M (Zincon) concentration and independent of the CyDTA concentration. Thus, a method is devised to simultaneously determine the concentrations of these three ions in solutions containing other metal ions by kinetic analysis. The reaction is followed at 620nm by watching the disappearance of the metal-Zincon complexes which all have different molar absorptivities. -"G. M. Riddar and D. W. Margerum, Analytical Chemistry, Vol 49, pp 2090, November 77."

In the electrochemistry programs of the Air Force, there is much concern as to the research being performed relative to fuel cell and battery development. Of particular interest is the thermal battery which is being developed for use in missiles, munitions, proximity fuzes, and satellites.

Thermal batteries are generally solid-state batteries using an inorganic salt electrolyte, with pyrotechnic materials within each cell. These batteries have no self-discharge mechanisms because the solid electrolyte is inert until melted. Once melted, the electrolyte reacts instantaneously with the electrode materials and maintains a specific conductivity until it solidifies again when the heat source is spent. Thermal batteries usually have an activation time of several milliseconds and a discharge service life of from several seconds to minutes. They can withstand severe shock, acceleration, and radioactive environments.

The Frank J. Seiler Research Laboratory, at the Air Force Academy, developed a thermal battery which utilized a mixture of chloroaluminates as the solid electrolyte. In support of this work, the Directorate of Chemical Sciences, AFOSR, sponsored basic chemical research in chloroaluminate systems at Colorado State University under the direction of Professor Robert A. Osteryoung. Electrochemical investigations in these molten salt systems have been predominantly carried out, up to the present time, using stationary electrode techniques such as chronopotentiometry, chronoamperometry, cyclic voltametry, pulse polarography and coulometry. Another technique that has been finding application in solution electrochemistry is the rotating ring-disc electrode. This technique was first exploited in this country by another AFOSR investigator - Prof Stanley Bruckenstein, University of Buffalo, SUNY. However, the highly sensitive standard rotating ring-disc was not suitable for these molten salt systems. The difficulty was in the fabrication of these particular electrodes, since the problem of solution leakage, often encountered at ambient temperatures in aqueous solution, is intensified by elevation of the temperature. This problem precludes the use of Teflon in the design because of the large coefficient of expansion. Professor Osteryoung and his group successfully solved this difficulty by

fabricating a glassy carbon rotating ring-disc electrode, sealed in Pyrex glass, suitable for work in a variety of molten salts. Although the use of the electrode was designed for chloroaluminate melts at 175°C, it may be satisfactorily employed in a LiCl/KCl eutectic at 450°C with slight modifications.

Details of the fabrication of this electrochemical instrumentation and experimental results obtained may be found in Analytical Chemistry, Vol 48, No 8, pp 1266-1268, July 1976.

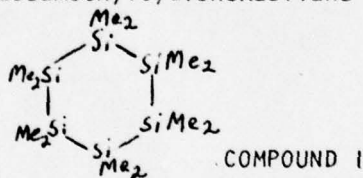
## SILICON CARBIDE FROM ORGANOPOLYSILANES

DR. ANTHONY J. MATUSZKO

Over the past twenty years, the Directorate of Chemical Sciences of AFOSR has supported a considerable amount of basic research in organosilicon chemistry. This work has resulted in the synthesis of a large variety of organosilicon compounds possessing a broad range of chemical and physical properties. As technologists began to realize the broad range of these properties, many uses were found for the compounds. One of the earlier applications of organosilicon was in the manufacture of silicone polymers which may be resins (cross-linked structures with high molecular weights), fluids (linear structures with blocking groups at the ends), or elastomers (linear structures of very high molecular weight with occasional cross-links). Of recent interest has been the reported conversion of organopolysilanes to silicon carbide fibers by Yajima and coworkers.<sup>1</sup> With encouragement from AFOSR, a cooperative effort with the purpose of looking at alternate methods of making silicon carbide from organosilanes was initiated between Professor Robert West of the University of Wisconsin and K. S. Mazdiyasi, Metals and Ceramics Division of the Air Force Materials Laboratory. The picture on the cover of this Annual Review represents a scanning electron micrograph of silicon carbide whiskers prepared by Mazdiyasi when a sample of polysilane provided by West was heated to 1400°C.

The Air Force is interested in silicon carbide for reinforced ceramics used in turbine engine blades, rocket nozzles and radomes, and potentially as high strength fibers for metal matrix composites. Prior to the discovery that organopolysilanes could be converted to silicon carbide, a common method used for making this material involved a sintering procedure which was expensive and generally yielded a porous product.

During his research into organosilicon compounds over the past few years, Prof West at Wisconsin did an extensive study of the properties of various cyclic organopolysilanes, particularly dodecamethylcyclohexasilane (I), a compound which had first been reported in 1948.<sup>2</sup>



Some of the results of this work were described in the FY72 and 73 AFOSR Chemistry Program Review.

In 1976, Yajima and coworkers<sup>1</sup> reported that melt spinning of permethylpolysilane or "polycarbosilane", (Me<sub>2</sub>Si)<sub>n</sub>, followed by heat treatment to between 800-1300°C resulted in the formation of continuous β-SiC fibers with high tensile strength. Their method for preparation of permethylpolysilane requires the preparation of pure Compound I which is thermally polymerized at 400°C and then solution fractionated to give useful polymer.

A recent discovery in Professor West's laboratory indicates that addition of small amounts (7-20 mole %) of PhMeSiCl<sub>2</sub> in the condensation polymerization of Me<sub>2</sub>SiCl<sub>2</sub>



This work together with the results of pyrolyzing a mixture of porous  $\text{Si}_3\text{N}_4$  with West's polysilane resin was presented at a national meeting of the American Ceramic Society in September 1977, and has been submitted as a publication to the Journal of the American Ceramic Society.<sup>4</sup>

Much of the work being done is still exploratory. However, the results obtained in the next few months through the University of Wisconsin/AFOSR-AFML coordinated effort should give a clearer indication as to the utility of the silicon carbide materials produced. In the meantime, ongoing AFOSR supported organosilicon research with West at Wisconsin, together with related research at MIT (Prof Dietmar Seyferth) and University of Southern California (Prof William Weber) will hopefully yield basic information leading to improved processes and materials.

#### REFERENCES

1. "Synthesis of Continuous SiC Fibers with High Tensile Strength", S. Yajima, K. Okamura, J. Hayashi, and M. Omari, J. Amer. Ceram. Soc. 59, 7-8, 324 (1976).
2. "Polydimethylsilane", C. Burkhard, J. Amer. Chem. Soc., 71, 963 (1948).
3. "Invention of Phenylmethylpolysilane Polymer Convertible to Silicon Carbide", Patent application pending.
4. "Characterization of Organosilicon Infiltrated Porous Reaction Sintered  $\text{Si}_3\text{N}_4$ ", K. Mazdhyasni and R. West, presented at meeting of American Ceramic Society, Sep 25-28, 1977, in Hyannis, Massachusetts and submitted to J. Amer. Ceram. Soc.

## AFOSR CORROSION RELATED RESEARCH

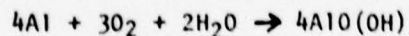
R. W. HAFFNER, Lt Col, USAF

The Air Force corrosion research program is aimed at reducing the structural damage to Air Force equipment due to corrosion thereby conserving resources and improving mission capability. Specifically, the AFOSR surface chemistry program focuses on three facets of the problem: direct chemical attack, electrochemical phenomena, and surface protection. Within these broad areas, individual theoretical and experimental studies are being conducted on chemical kinetics of corrosion reactions, adsorption-desorption on metallic surfaces, models for mass transport of water and various ionic species in protective coating films, multi-component oxide systems and other advanced concepts for surface protection; e.g., ion-implantation. Throughout the program emphasis is placed on using the most modern surface analytical techniques and instrumentation available for collection and evaluation of data.

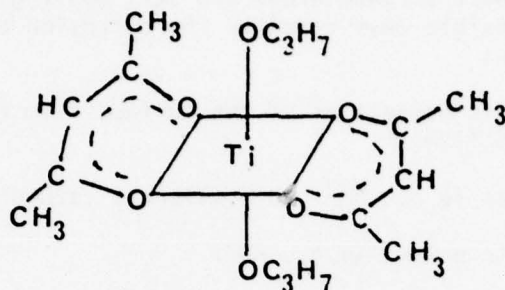
More detail about ongoing corrosion research programs follows:

Dr. Robert Merrill at Cornell University, as a part of his studies of catalytic surfaces, is devoting special attention to the composition and morphology of oxide layers which develop on aluminum and titanium. The objective is to determine what effects the presence of impurities in the oxide layer, physical defects, and the degree of epitaxy have on the way these surfaces interact with the local environment. Merrill intends first to examine the structure and kinetics of the growth of oxide layers on selected faces of single crystals of aluminum and titanium. Growth conditions will be controlled in such a way that the kinetics and structure of the layers can be well characterized. Next rapid growth rates (controlled by temperature), simultaneous incorporation of water during growth, electrically assisted growth, and electrolytic growth will be studied. Also, the effects of ion bombardment and mechanical flexure on the structure and integrity of the oxide layers will be examined.

Aerospace Corporation, in conjunction with the University of Southern California, is pursuing a program to develop and characterize new multicomponent oxide coatings for aluminum alloys. The chromate chemical conversion coatings which represent current state-of-the-art have already been examined by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (ESCA), and ion-microprobe for mass analysis (IMMA). This first phase of the research was necessary to determine the mechanism by which the chromate coating is formed and how it affords corrosion protection in a salt-spray chamber. The chromate coating solution found to give the best protection is made from a formula consisting of  $\text{CrO}_3$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$  and  $\text{NaF}$ . Auger depth profiles of samples after various residence times in the salt-spray chamber give an insight into the corrosion mechanism. At first the coatings are thinned to about 100Å. The Cr and Al are leached from the surface. The dissolved ions are replaced by Al from the bulk. The F in the coating apparently aids this dissolution process since the F concentration decreases. Finally, Cl ion breaks through to the Al surface and corrosion occurs. The corrosion product consists of hydrated aluminum oxide, presumably formed by the reaction:

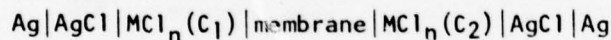


Subsequent work will investigate organotitanium coatings on aluminum. Organic titanates were chosen as model systems for the application of oxide coatings on aluminum because: (1) they are commercially available from duPont (trade name "Tyzor"), (2)  $TiO_2$  films have been well characterized, and (3) the hydrolysis of the organic titanates to give  $TiO_2$  is well understood. The chelate Tyzor AA has the structure shown below:



Niobium and tantalum alkoxides will also be studied to determine if these metals form multioxide coatings with aluminum.<sup>1</sup>

Another AFOSR research project is studying transport processes and initiation of corrosion under paint films. The principal investigator is Dr. Theodore R. Beck at Electrochemical Technology Corporation. Dr. Beck is pursuing two main objectives. The experimental part will measure the performance of painted test panels exposed to NaCl solutions and the electrochemical transport properties of free films. Paint films of the type used on aircraft structures are being tested. Open-circuit potentials and measurements of resistance and capacitance have been made as a function of time of exposure of painted panels to salt solutions. Also, transference numbers of various ions through free polyurethane films were measured. The measurements were made in a concentration cell.



A second objective of Dr. Beck's research is to develop a more quantitative understanding of how paint films protect. To do this, a general electrochemical transport model has been formulated for transport of various ionic and molecular species in paint films. Initially, a simple system consisting of painted zinc in an acidified NaCl solution was chosen. Beck has reduced the problem to a set of five independent equations which are functions of twenty-one transport parameters (diffusion coefficients, etc.). Solutions have been obtained by numerical methods using the boundary conditions of equilibrium at the paint-solution interface and all fluxes linked by the stoichiometry of the reactions at the paint-metal interface. Using the model as a guide, experiments are underway which will yield values of the necessary parameters and thereby quantitatively describe corrosion in these systems.<sup>2</sup>

For the future we are considering new ideas to control corrosion. One idea presently being evaluated is ion implantation. Ion implementation is a process by which the surface properties of a solid can be modified by bombarding it with

appropriate atoms in the form of a beam of ionized particles. Initial studies indicate that properties such as hardness, friction, oxidation and corrosion can be modified in this way without change to the bulk properties of the target material. Ion implantation will modify the properties of a metal surface to a depth of perhaps  $1000\text{\AA}$ . Although this is a very thin layer, the technique may be useful where the surface film implanted in the substrate metal is very abrasion resistant, or where paint films or other coatings can be used to protect the implanted area, or where abraded areas are self-healing. Researchers have proposed at least six possible ways to alter the corrosion characteristics of a metal by ion implantation:

- Change the electronic properties of the surface film to retard mass transfer across the film.<sup>3</sup>
- Introduce a catalyst (e.g.,  $\text{Pb}^3$ ) to accelerate cathodic reaction.
- Introduce a cathodic poison (e.g.,  $\text{Pb}^4$ ).
- Induce the formation of a passive surface film by introducing elements such as  $\text{Cr}^5$  or  $\text{Ta}^6$ .
- Extend the passive range of potentials by introducing elements such as  $\text{Mo}^7$  or N.

Effort is presently underway to investigate one or more of these approaches.

#### References:

1. G. W. Stupian, H. A. Katzman, G. M. Malouf, "Multicomponent Oxide Systems for Corrosion Protection." Interim Progress Report prepared by Aerospace Corporation for AFOSR, January 1978.
2. T. R. Beck, "A Study of Transport Processes and Initiation of Corrosion Under Paint Films." A progress report submitted to AFOSR, February 1978.
3. W. A. Grant, "Surface Chemistry of Ion-Implanted Solids," Inst. Phys. Conf. Ser. No. 28, Chapter 4, p. 127 (1976).
4. V. Ashworth, W. A. Grant, R.P.M. Procter, and E. J. Wright, unpublished work, quoted in Reference 7.
5. V. Ashworth, D. Baxter, W. A. Grant, and R.P.M. Procter, "The Effect of Ion Implantation on the Corrosion Behavior of Pure Iron--II. Chromium Ion Implantation." *Corrosion Science*, Vol. 16, p. 775 (1976).
6. V. Ashworth, D. Baxter, W. A. Grant, and R.P.M. Procter, "The Effect of Ion Implantation on the Corrosion Behavior of Pure Iron--III. Tantalum Ion Implantation," submitted for publication in *Corrosion Science* (1977).
7. A. H. Al-Saffar, V. Ashworth, W. A. Grant, and R.P.M. Procter, "The Effect of Ion Implantation on the Corrosion Behaviour of Aluminium." Presented at Sixth European Congress on Corrosion, London, England, September 1977.

### DURATION OF SUPPORT OF PRINCIPAL INVESTIGATORS

The duration of 'continuous' support of Principal Investigators was compiled for all Chemistry work units in effect as of 30 September 1977. The total includes all regular research efforts managed directly by the Chemical Sciences Directorate; it does not include symposia and 'mini-grants.' Continuous support is defined to include principal investigators whose support was not interrupted by an interval exceeding six months. The indicated median duration is slightly over two years. The overall data reveals a concerted effort to include new investigators while maintaining only older ones of the highest quality. In fact, the list is a bit heavy in new investigators because of the sharp funding increase after FY76 including the special circumstances of extending FY76 for three 'transition' months to establish a new Federal fiscal year beginning 1 October 1976.

<u>Duration of Support</u>	<u>Number of "PIs"</u>	<u>Duration of Support</u>	<u>Number of "PIs"</u>
0-1 years	32	10-11 years	1
1-2 "	19	11-12 "	0
2-3 "	11	12-13 "	2
3-4 "	6	13-14 "	6
4-5 "	4	14-15 "	1
5-6 "	8	15-16 "	1
6-7 "	3	16-17 "	3
7-8 "	1	17-18 "	0
8-9 "	1	18-19 "	0
9-10 "	4	19-20 "	1
		20-21 "	0
		21-22 "	1

TOTAL: 105

CHEMISTRY ANNUAL BUDGET FOR PAST TEN YEARS

<u>FY</u>	<u>Expenditures (thousands)</u>
68	\$3,329
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

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

---

FY77 CHEMISTRY PROGRAM STATISTICS

Total number of proposals received	210
New work efforts initiated	38
Renewals	64
Proposals declined	77
Proposals withdrawn	7
Proposals transferred	2
Mini-Grants (one year funding)	4
Conferences and Symposia	8
Proposals pending disposition	10

## CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY77 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.

### AFOSR/AFML Corrosion Workshop II

Dr. Ellis D. Verink, Jr.  
University of Florida  
Gainesville, Florida  
13-15 September 1977

### Gordon Conference on Electrochemistry

Dr. Herbert P. Silverman  
Miramar Hotel  
Santa Barbara, California  
17-21 January 1977

### Gordon Conference on Inorganic Chemistry

Dr. D. W. Margerum  
New Hampton School  
New Hampton, New Hampshire  
1-5 August 1977

### Gordon Conference on Molecular Energy Transfer

Dr. George W. Flynn  
Brewster Academy  
Wolfeboro, New Hampshire  
11-15 July 1977

### Interactive Study of the Mechanics and Structure of Materials

Mr. B. A. Wilcox  
National Science Foundation  
Summer 1978

### Third International Summer Institute in Surface Science

Dr. Rolf Vanselow  
University of Wisconsin-Milwaukee Campus  
Milwaukee, Wisconsin  
22-26 August 1977

### Workshop on Ordered Polymers

Dr. R. L. Van Deusen  
Dayton, Ohio  
4-5 May 1977

## ACTIVE RESEARCH EFFORTS

AS OF 1 OCTOBER 1977

### ALPHABETICAL BY PRINCIPAL INVESTIGATOR

Reactions and Electrochemical Kinetics  
of Newly Generated Metal Surfaces (RWH)  
F49620-76-C-0029, 2303/A2

T. R. Beck  
Electrochemical Technology Corp.  
3933 Leary Way, N.W.  
Seattle, Washington 98125

Theoretical and Experimental Analysis  
of Alkaline Zinc Batteries (DWE)  
F44620-76-C-0098, 2303/A1

Douglas N. Bennion and John Newman  
Department of Chemical Engineering  
University of California  
Los Angeles, California 90024

Diagnostics and Chemical Applications  
of Multiphoton Absorption Processes (JTV)  
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  
Department of Chemistry  
Carnegie-Mellon University  
Pittsburgh, Pennsylvania 15213

Energy Transfer in Chemically Reacting  
Systems and in Surface Characterization (JTV)  
AFOSR-77-3138, 2303/B1

Herbert P. Broida  
Department of Physics  
University of California  
Santa Barbara, California 93106

Inelastic and Reactive Collisions of  
Translationally Excited Molecules (JTV)  
AFOSR-74-2692, 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-74-2572, 2303/A1

Stanley Bruckenstein  
Department of Chemistry  
State University of New York  
Buffalo, New York 14214

Energy Transfer and Chemical Reactions  
Important in Molecular Lasers (JTV)  
AFOSR-75-2856, 2303/B1

Fast Ion Transport in Solids (DWE)  
AFOSR-77-3427, 2303/D1

Nucleophilic Substitution Reactions of  
Alkyl, Vinyl, and Aryl  
Trifluoromethanesulfonates (AJM)  
AFOSR-77-3241, 2303/D9, ASEE Mini Grant

Kinetics Studies Involving  
Electronically-Excited Interhalogens  
and Halogens (JTV)  
AFOSR-75-2843, 2303/B1

Chemical Kinetic Studies Involving NF  
Radicals (RAO)  
AFOSR-78-3507, 2303/B1

Novel Chemical Laser Systems (JTV)  
AFOSR-73-2550, 2303/B1

Elastohydrodynamic Lubrication Studies (RWH)  
AFOSR-77-3229, 2303/D9, ASEE Mini Grant

Synthesis and Spectroscopic Investigation  
of Inorganic Materials Possessing  
Unusual Electronic Properties (DRU)  
AFOSR-76-2932, 2303/A3

Chemical Reactions that Produce  
Electronically Excited Metal Atoms (JTV)  
AFOSR-75-2822, 2303/B1

Double Layer Structure and Electrode  
Kinetics (DWE)  
AFOSR-76-3027, 2303/A1

George Burns  
Department of Chemistry  
University of Toronto  
Toronto, Canada M5S 1A1

Alan V. Chadwick and John H. Strange  
Department of Chemistry  
University of Kent  
Canterbury, Kent, U.K.

William D. Closson  
Department of Chemistry  
State University of New York  
Albany, New York 12222

M. A. A. Clyne  
Department of Chemistry  
Queen Mary College  
London E1 4NS, England

M. A. A. Clyne  
Department of Chemistry  
Queen Mary College  
London E1 4NS, England

Terrill A. Cool  
School of Applied & Engineering Physics  
Cornell University  
Ithaca, New York 14853

John N. Crisp  
Department of Mechanical Engineering  
University of Dayton  
Dayton, Ohio 45469

Glenn A. Crosby  
Department of Chemistry  
Washington State University  
Pullman, Washington 99163

Paul Davidovits  
Department of Chemistry  
Boston College  
Chestnut Hill, Massachusetts 02167

Robert deLevie  
Department of Chemistry  
Georgetown University  
Washington, D.C. 20057

The Mechanics of Fracture in Polymers,  
ACS Symposium (DRU)  
AFOSR-78-3517, 2303/A3

Development of Practical MO Techniques  
for Prediction of the Properties and  
Behavior of Materials (AJM)  
AFOSR-75-2749, 2303/B2

Relation of Structure to Properties in  
Graphite Fibers (DRU)  
AFOSR-77-3436, 2303/A3

Investigation of Electron Attachment  
Processes in Polyatomic Molecules (JTV)  
F49620-77-C-0071, 2303/B1

Evaluation of Chemical Research Relevant  
to Current and Projected U. S. Air Force  
Interests (DWE)  
F44620-75-C-0001, 2303/A1

Picosecond Laser Studies of Excited State  
Proton Transfer (AJM)  
AFOSR-77-3407, 2303/B2

Rates of Rapid Chemical Reactions (RWH)  
AFOSR-77-3255, 2303/A2

One- and Two-Photon Optically Pumped  
Laser Devices: New Chemical Laser  
Diagnostics and Kinetic Probes (JTV)  
AFOSR-76-3056, 2303/B1

The Structure and Properties of Polymeric  
Materials (DRU)  
AFOSR-77-3293, 2303/A3

Gordon Research Conference on Molecular  
Energy Transfer (JTV)  
AFOSR-77-3371, 2303/B1

K. L. DeVries  
College of Engineering  
University of Utah  
Salt Lake City, Utah 84112

Michael J. S. Dewar  
Department of Chemistry  
University of Texas  
Austin, Texas 78712

Russell J. Diefendorf  
Department of Materials Engineering  
Rensselaer Polytechnic Institute  
Troy, New York 12181

Jerry T. Dowell  
IRT Corporation  
7650 Convoy Court  
San Diego, California 92138

Joseph E. Earley  
Department of Chemistry  
Georgetown University  
Washington, D.C. 20057

Kenneth B. Eisenthal  
Department of Chemistry  
Columbia University  
New York, New York 10027

Edward M. Eyring  
Department of Chemistry  
University of Utah  
Salt Lake City, Utah 84112

Robert W. Field  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Paul J. Flory  
Department of Chemistry  
Stanford University  
Stanford, California 94305

George Flynn  
University of Rhode Island  
Kingston, Rhode Island 02881

Kinetic Spectroscopy of Metal Atom/  
Oxidizer Chemiluminescent Reactions  
for Laser Applications (JTV)  
F44620-76-C-0108, 2303/B1

Structural Studies of Monomeric Model  
Compounds and Related Ordered Polymer  
Systems (DRU)  
AFOSR-77-3267, 2303/D9, ASEE Mini Grant

Chemical and Physical Aspects of  
Mesophase Formation During Carbon-  
Carbon Composite Processing (DRU)  
F49620-78-C-0006, 2303/A3

Theoretical and Computational Studies of  
Electronic Transitions in Molecular  
Collisions (JTV)  
F44620-74-C-0073, 2303/B1

Microscopic Theory of Electronic  
Transitions in Molecular Rate  
Processes (JTV)  
F49620-78-C-0005, 2303/B1

Absolute Rate Constants for Combustion  
Reactions Involving Free Radicals (JTV)  
F44620-75-C-0067, 2303/B1

Influence of Annealing on the Strengths  
of Secondary Relaxations in Glasses (DRU)  
AFOSR-73-2540, 2303/A3

Selective Chemical Pumping of Electronic  
States (RAO)  
AFOSR-78-3515, 2303/B1

New Materials for Electrochemical  
Cells (DWE)  
AFOSR-77-3402, 2303/A1

Processing Mechanisms, Structure, and  
Morphology of High-Temperature  
Polymeric Alloys (DRU)  
F49620-77-C-0046, 2303/A3

Arthur Fontijn  
AeroChem Research Laboratories, Inc.  
Princeton, New Jersey 08540

Albert V. Fratini  
Department of Chemistry  
University of Dayton  
Dayton, Ohio 45469

J. J. Gebhardt  
Re-entry and Environmental Systems  
Division  
General Electric Company  
Philadelphia, Pennsylvania 19101

Thomas F. George  
Department of Chemistry  
University of Rochester  
Rochester, New York 14627

Thomas F. George  
Department of Chemistry  
University of Rochester  
Rochester, New York 14627

D. M. Golden  
Stanford Research Institute  
Menlo Park, California 94025

Martin Goldstein  
Belfer Graduate School of Science  
Yeshiva University  
New York, New York 10033

James L. Gole  
School of Chemistry  
Georgia Institute of Technology  
Atlanta, Georgia 30332

John B. Goodenough and Peter G. Dickens  
Inorganic Chemistry Laboratory  
Oxford University  
Oxford, OX1 3QR, England

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

Energy Disposal in Electronically  
Excited Halogen Atoms and Molecular  
Oxygen (RAO)  
AFOSR-78-3513, 2303/B1

Solid State Materials Derived from  
Planar Metal Complexes (AJM)  
F44620-76-C-0006, 2303/B2

NMR Study of Viscoelastic Fluids and  
Elastomers Under Extreme Conditions  
of Temperature and Pressure (DRU)  
AFOSR-77-3185, 2303/A3

Effect of Structure on Physical Polymer  
Interactions and Properties (DRU)  
AFOSR-76-2983, 2303/A3

Phosphorus Chemiluminescence Feasibility  
Studies for an Ultraviolet and Visible  
Chemical Laser (JTV)  
AFOSR-77-3376, 2303/B1

Novel Organophosphorus and Organo-  
nitrogen Derivatives and their Use for  
the Synthesis of Unusual Transition  
Metal Complexes (AJM)  
AFOSR-75-2869, 2303/B2

Post Doctoral Resident Research  
Associateship Program (RWH)  
F44620-76-C-0084, 2303/D8

Spectroscopic Determination of Inter-  
molecular Potentials of Gas Laser  
Components and of Major Atmospheric  
Constituents (JTV)  
AFOSR-77-3269, 2303/B1

The Measurement of Vibrational  
Intensities for Infrared Active  
Exhaust Plume Species from  
Advanced Propellant Rocket Boosters (JTV)  
F49620-77-C-0075, 2303/B1

Larry L. Hench  
Department of Materials Science  
University of Florida  
Gainesville, Florida 32611

Paul L. Houston  
Department of Chemistry  
Cornell University  
Ithaca, New York 14853

Leonard V. Interrante and John S. Kasper  
General Electric Co.  
Research & Development Center  
Schenectady, New York 12301

Jiri Jonas  
Department of Chemistry  
University of Illinois  
Urbana, Illinois 61801

Frank E. Karasz  
Polymer Science & Engineering  
University of Massachusetts  
Amherst, Massachusetts 01002

Ahsan U. Khan and Brian Stevens  
Department of Chemistry  
University of South Florida  
Tampa, Florida 33620

R. Bruce King  
Department of Chemistry  
University of Georgia  
Athens, Georgia 30601

R. W. Kinney  
Commission on National Resources  
National Research Council, NAS/NAE  
Washington, D.C. 20418

William Klemperer  
Department of Chemistry  
Harvard University  
Cambridge, Massachusetts 02138

C. E. Kolb and M. E. Gersh  
Aerodyne Research, Inc.  
Bedford, Massachusetts 01730

The Quantum Dynamics of Chemical  
Reactions (JTV)  
AFOSR-77-3394, 2303/B1

Synthesis of Organofluorine Compounds  
by Direct Fluorination (AJM)  
AFOSR-76-3031, 2303/B2

Analysis of Lubricant Films in  
Bearings Under Incipient Failure  
Conditions (RWH)  
AFOSR-78-3473, 2303/A2

Chemical Transfer Lasers (JTV)  
AFOSR-76-2959, 2303/B1

Solid Propellant Additives from  
Pentaborane-9 (AJM)  
AFOSR-77-3301, 2303/D9

Energy and Chemical Change (JTV)  
AFOSR-77-3135, 2303/B1

Structure and Properties of Glasses (DRU)  
AFOSR-75-2764, 2303/A3

Time-Temperature Studies of High  
Temperature Deterioration Phenomena in  
Lubricant Systems: Synthetic Ester  
Lubricants (RWH)  
F44620-76-C-0097, 2303/A2

Charge Transport Modes in Nickel  
Hydroxide Electrodes (DWE)  
AFOSR-76-2987, 2303/A1

Low Temperature Fluorine Chemistry of  
Electronegative Elements (AJM)  
AFOSR-77-3165, 2303/B2

Aron Kuppermann  
Division of Chemistry and  
Chemical Engineering  
California Institute of Technology  
Pasadena, California 91109

Richard J. Lagow  
Department of Chemistry  
University of Texas  
Austin, Texas 78712

James L. Lauer  
Department of Mechanical  
Engineering  
Rensselaer Polytechnic Institute  
Troy, New York 12181

Paul H. Lee  
Department of Physics  
University of California  
Santa Barbara, California 93106

Amos J. Leffler  
Department of Chemistry  
Villanova University  
Villanova, Pennsylvania 19085

Raphael D. Levine and John M. Deutch  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

John D. Mackenzie  
Materials Department  
University of California  
Los Angeles, California 90024

L. R. Mahoney  
Fuels and Lubricants Department  
Ford Motor Co.  
Dearborn, Michigan 48121

Joseph T. Maloy  
Department of Chemistry  
University of West Virginia  
Morgantown, West Virginia 26506

Gleb Mamantov  
Department of Chemistry  
University of Tennessee  
Knoxville, Tennessee 37916

1977 Gordon Conference on Inorganic  
Chemistry (AJM)  
AFOSR-77-3370, 2303/A1

Anisotropic and Electro-Optical  
Effects in Liquid Crystals (DWE)  
F49620-77-C-0017, 2303/A1

Fabricable Polymers for Matrices and  
Adhesives Which Are Extremely Stable  
to Heat, Oxidation and Hydrolysis (AJM)  
AFOSR-77-3112, 2303/B2

Experimental Studies of the State-to-  
State Chemical Dynamics of Reactions  
Involving Air Triatomics (JTV)  
AFOSR-77-3348, 2303/B1

Kinetics and Mechanisms of Reactions  
in the Sisler UDMH Process (AJM)  
AFOSR-MIPR-77-0002, 2303/B2

Structure and Chemistry of Surfaces (RWH)  
F49620-77-C-0118, 2303/A2

Calculation of the Energetics and  
Collision Dynamics for Electronic  
Transitions (JTV)  
F49620-77-C-0064, 2303/B1

Energy Paths in Chemical Reactions (JTV)  
AFOSR-78-3535, 2303/B1

The Relation Between the Chemical and  
Physical Structure and the Mechanical  
Response of Polymers (DRU)  
F44620-76-C-0075, 2303/A3

Ion Photofragment Spectroscopy -  
Potential Surfaces of Molecular  
Ions (JTV)  
F44620-76-C-0095, 2303/B1

Dale W. Margerum  
Department of Chemistry  
University of Rhode Island  
Kingston, Rhode Island 02881

J. David Margerum  
Hughes Research Laboratories  
Hughes Aircraft Co.  
Malibu, California 90265

Carl S. Marvel  
Department of Chemistry  
University of Arizona  
Tucson, Arizona 85721

Robert J. McNeal and William H. Steier  
Graduate Center for Engineering  
and Computer Sciences  
University of Southern California  
Los Angeles, California 90007

William McQuiston  
Propellant Sciences Department  
Naval Surface Weapons Center  
Silver Spring, Maryland 20910

Robert P. Merrill  
School of Chemical Engineering  
Cornell University  
Ithaca, New York 14853

Harvey H. Michels  
United Technologies Research Center  
United Technologies Corporation  
East Hartford, Connecticut 06108

C. Bradley Moore  
Department of Chemistry  
University of California  
Berkeley, California 94720

Robert P. Morgan  
McDonnell Douglas Research Labs  
McDonnell Douglas Corp.  
St. Louis, Missouri 63166

John T. Moseley and James R. Peterson  
Physical Sciences Division  
Stanford Research Institute  
Menlo Park, California 94025

Gordon Research Conference on  
Electrochemistry (DWE)  
AFOSR-78-3472, 2303/A1

Chemical Physics of Charge Mechanisms  
in Nonmetallic Spacecraft Materials (DRU)  
F49620-77-C-0113, 2303/A3

Investigation of Electrochromic  
Diphthalocyanines (AJM)  
F49620-77-C-0074, 2303/B2

Viscosity of Chloroaluminate Melts (DWE)  
AFOSR-77-3198, 2303/A1

Synthesis of Phosphatriazines for  
Potential High Temperature Fluids  
Applications (AJM)  
F44620-76-C-0065, 2303/B2

High Resolution Vacuum Ultraviolet  
Spectroscopy of Small Molecules (JTV)  
F49620-77-C-0010, 2303/B1

Cyclic Polyfluorosilicone Polymers and  
Copolymers (AJM)  
F49620-77-C-0012, 2303/B2

Carbon-Carbon Composite Matrix  
Decomposition Reactions and  
Densification Response (DRU)  
F49620-78-C-0002, 2303/A3

Experimental and Theoretical Studies  
of Intramolecular and Intermolecular  
Dynamics (JTV)  
F49620-76-C-0017, 2303/B1

Experimental and Theoretical Work in  
Chemical Dynamics and Nucleation (JTV)  
AFOSR-77-3214, 2303/B1

Royce W. Murray  
Department of Chemistry  
University of Rhode Island  
Kingston, Rhode Island 02881

Joseph E. Nanevicz  
Electromagnetic Sciences Laboratory  
Stanford Research Institute  
Menlo Park, California 94025

M. M. Nicholson  
Electronics Research Division  
Rockwell International Corp.  
Anaheim, California 92803

Harald A. Øye  
Institute of Inorganic Chemistry  
University of Trondheim  
Trondheim-NTH, Norway

Kay L. Paciorek  
Chemical & Materials Research  
Ultrasystems, Inc.  
Irvine, California 92664

W. H. Parkinson, D. E. Freeman and  
K. Yoshino  
Harvard College Observatory  
Cambridge, Massachusetts 02138

Ogden Pierce  
Contract Research & Development Lab  
Dow Corning Corporation  
Midland, Michigan 48640

J. P. Pope  
Material Sciences Division  
Science Applications, Inc.  
Santa Ana, California 92707

Stuart A. Rice  
Department of Chemistry  
University of Chicago  
Chicago, Illinois 60637

John Ross  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Molecular Beam Studies of Ionization  
Processes (JTV)  
AFOSR-75-2770, 2303/B1

Erhard W. Rothe  
Department of Chemical Engineering  
Wayne State University  
Detroit, Michigan 48202

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  
Organosilicon Polymer Intermediates (AJM)  
AFOSR-76-2917, 2303/B2

Dietmar Seyferth  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Molecular Energy Transfer Studies (JTV)  
AFOSR-77-3163, 2303/B1

Hyung Kyu Shin  
Department of Chemistry  
University of Nevada  
Reno, Nevada 89507

New Solid Superionic Conductors  
Containing  $\text{Cu}^+$ ,  $\text{Ga}^+$ ,  $\text{In}^+$  and  $\text{Tl}^+$  (DWE)  
AFOSR-77-3227, 2303/A1

Duward F. Shriver and Donald H. Whitmore  
Materials Research Center  
Northwestern University  
Evanston, Illinois 60201

New Chemical Analysis Techniques (DWE)  
F44620-76-C-0031, 2303/A1

Robert E. Sievers  
Department of Chemistry  
University of Colorado  
Boulder, Colorado 80309

Gordon Research Conference on  
Electrochemistry (DWE)  
AFOSR-77-3201, 2303/A1

Herbert P. Silverman  
Department of Chemistry  
University of Rhode Island  
Kingston, Rhode Island 02881

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-75-2748, 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 (JTV)  
AFOSR-77-3240, 2303/B1

Defect Chemistry of Crystalline  
Inorganic Materials (DRU)  
AFOSR-78-3505, 2303/A3

Effects of Oxygen and Water Vapor on the  
Compressive Strength of Boundary Films  
on Iron Crystals (RWH)  
AFOSR-76-3051, 2303/A2

Morphology and Mechanical Behavior of  
Isomeric Graft Polymers and  
Interpenetrating Polymer Networks (AJM)  
AFOSR-76-2945, 2303/B2

Lithium Based Anodes for Solid State  
Batteries (RAO)  
AFOSR-77-3460, 2303/A1

Formation and Deactivation Processes in  
Electronic Transition, Chemically  
Pumped Lasers (JTV)  
AFOSR-75-2758, 2303/B1

Synthesis of New Inorganic and  
Organometallic Materials (AJM)  
AFOSR-76-3102, 2303/B2

Multicomponent Oxide Systems for  
Corrosion Protection (RWH)  
AFOSR-77-3334, 2303/A2

Molecular Beam Studies of Collisional  
Excitation and Energy Exchange in  
Polyatomic Studies (JTV)  
AFOSR-75-2863, 2303/B1

Collisional Excitation and  
Ionization (JTV)  
F44620-76-C-0007, 2303/B1

Ian W. M. Smith  
Department of Physical Chemistry  
The University of Cambridge  
Cambridge, U.K. England

Donald M. Smyth  
Materials Research Center  
Lehigh University  
Bethlehem, Pennsylvania 18015

David K. Snediker  
Department of Tribomechanics  
Battelle Memorial Institute  
Columbus, Ohio 43201

L. H. Sperling  
Department of Chemical Engineering  
Lehigh University  
Bethlehem, Pennsylvania 18015

B. C. G. Steele  
Department of Metallurgy and Materials  
Science  
Imperial College, University of London  
London, England

Jeffrey I. Steinfeld  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

F.G.A. Stone  
Department of Chemistry  
University of Bristol  
Bristol, BS8 ITS, England

Gary W. Stupian and William H. Steier  
Graduate Center for Engineering &  
Computer Sciences  
University of Southern California  
Los Angeles, California 90007

R. B. Subbarao and J. B. Fenn  
Department of Engineering Sciences  
Yale University  
New Haven, Connecticut 06520

Thomas O. Tiernan  
Department of Chemistry  
Wright State University  
Dayton, Ohio 45431

New Perfluoropolymer-Forming  
Reactions (AJM)  
F44620-76-C-0027, 2303/B2

Structural and Dynamic Studies of  
Materials Possessing High Energy  
Content (AJM)  
AFOSR-74-2589, 2303/B2

Microstructure of Amorphous and  
Semi-Crystalline Polymers (DRU)  
AFOSR-77-3226, 2303/A3

Stabilization and Graphitization of  
Acrylic Fibers and Carbon Composite  
Matrices (DRU)  
AFOSR-77-3466, 2303/A3

The Third International Summer  
Institute in Surface Science  
(ISISS 1977) (RWH)  
AFOSR-MIPR-77-0037, 2303/A2

Development and Practical  
Application of the Theory of  
Materials (AJM)  
AFOSR-77-3145, 2303/B2

Inhibitors for Corrosion Fatigue of  
High Strength Alloys (RWH)  
AFOSR-PD-77-0011, 2303/A2

Radiation and Laser Potential of  
Homo- and Hetero-Nuclear Rare Gas  
Diatomic Molecules (JTV)  
AFOSR-77-3137, 2303/B1

Correlation of Electrode Kinetics  
With Molecular Structure (DWE)  
AFOSR-77-3408, 2303/A1

Organosilicon Chemistry (AJM)  
AFOSR-77-3123, 2303/B2

Madeline S. Toy  
Science Applications, Inc.  
Sunnyvale, California 94086

Nicholas J. Turro  
Department of Chemistry  
Columbia University  
New York, New York 10027

Donald R. Uhlmann  
Department of Materials Science  
and Engineering  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Donald R. Uhlmann  
Department of Materials Science  
and Engineering  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Dr. Ralf Vanselow  
Department of Chemistry  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin 53201

John R. Van Wazer  
Department of Chemistry  
Vanderbilt University  
Nashville, Tennessee 37203

Ellis Verink, Jr.  
Department of Materials Sciences  
and Engineering  
University of Florida  
Gainesville, Florida 32611

W. C. Walker and Y. Tanaka  
Department of Physics  
University of California  
Santa Barbara, California 93106

Michael J. Weaver  
Department of Chemistry  
Michigan State University  
East Lansing, Michigan 48824

William P. Weber  
Department of Chemistry  
University of Southern California  
Los Angeles, California 90007

High Temperature Molecules and  
Molecular Energy Storage (RAO)  
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 and J. Munushian  
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-74-2644, 2303/B2

Robert C. West  
Department of Chemistry  
University of Wisconsin  
Madison, Wisconsin 53706

Studies of Rotationally Cooled Molecules  
in Molecular Beams by Laser Spectroscopic  
Technique (JTV)  
AFOSR-75-2853, 2303/B1

Lennard Wharton  
Department of Chemistry  
University of Chicago  
Chicago, Illinois 60637

Gas-Surface Dynamics, High Power  
Laser-Solid Interactions (RWH)  
AFOSR-77-3186, 2303/A3

Lennard Wharton  
Department of Chemistry  
University of Chicago  
Chicago, Illinois 60637

Chemical Kinetics of Metal Atom  
Reactions in the Gas Phase (JTV)  
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

Lifetimes and Quenching Rates for the  
Triplet PI States of Interhalogen  
Molecules (JTV)  
AFOSR-77-3232, 2303/B1, ASEE Mini Grant

John Wright  
Department of Physics  
University of New Hampshire  
Durham, New Hampshire 03824

The State Identification of Reaction  
Products (JTV)  
AFOSR-77-3363, 2303/B1

Richard N. Zare  
Department of Chemistry  
Stanford University  
Stanford, California 94305

## RESEARCH EFFORTS COMPLETED IN FY77

(Alphabetical by Principal Investigator)

Chemical Laser Studies of Chemical Reaction Dynamics	Michael J. Berry Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Inelastic and Reactive Scattering of Translationally Excited Molecules	Philip R. Brooks Department of Chemistry Rice University Houston, Texas 77001
Electrochemistry of Hydrazine-Hydrazine Azide Mixtures	Charles T. Brown United Technologies Research Center East Hartford, Connecticut 06108
Novel Chemical Laser Systems	Terrill A. Cool School of Applied and Engineering Physics Cornell University Ithaca, New York 14853
Rates of Rapid Chemical Reactions	Edward M. Eyring Department of Chemistry University of Utah Salt Lake City, Utah 84112
Synthesis and Polymerization of Fluorobicyclobutanes to Chemically, Dimensionally, and Thermally Stable Polymers	Henry K. Hall, Jr. Department of Chemistry University of Arizona Tucson, Arizona
Proposed Program for the Determination of DF and HF Rotational Relaxation Rates	J. J. Hinchey United Technologies Research Center East Hartford, Connecticut 06108
Mechanisms of Singlet Oxygen Generation by Chemical Reaction	James K. Hurst Oregon Graduate Center 19600 N.W. Walker Road Beaverton, Oregon 97005
Theories of Energy Disposal in Chemical Reactions	Aron Kuppermann Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, California 91125
Infrared Spectra of Fluid Film Under Conditions of Incipient Bearing Failure	Dr. James L. Lauer Suntech, Inc. P. O. Box 1135 Marcus Hook, Pennsylvania 19061

- Energy and Chemical Change  
R. D. Levine and R. B. Bernstein  
Chemistry Department  
The University of Texas at Austin  
Austin, Texas 78712
- Studies of Laser Induced Photochemical Kinetics  
Ross A. McFarlane  
School of Electrical Engineering  
Cornell University  
Ithaca, New York 14853
- Fundamental Studies of the Structure and Chemistry of Catalytic Surfaces  
Robert P. Merrill  
Department of Chemical Engineering  
University of California  
Berkeley, California 94720
- Calculation of Potential Energy Curves for Metal Oxides and Halides  
H. Harvey Michels  
United Technologies Research Center  
Silver Lane  
East Hartford, Connecticut 06108
- Chemical Lasers and Laser-Induced Kinetic Processes  
George C. Pimentel  
Department of Chemistry  
University of California, Berkeley  
Berkeley, California 94720
- Poly(fluoroorganophosphozenes)  
K. A. Reynard and A. H. Gerber  
Chemistry Department  
Horizons, Incorporated  
Cleveland, Ohio 44122
- Molecular Behavior Studies of Glassy Polymers Under Stress  
William O. Statton  
Department of Materials Science and Engineering  
The University of Utah  
Salt Lake City, Utah 84112
- Third Summer Colloquium on Electronic Transition Lasers  
Jeffrey I. Steinfeld  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139
- Transition Metal Compounds with Potential Electronic and Radiation Resistant Properties  
F. Gordon A. Stone  
Department of Inorganic Chemistry  
The University  
Bristol BS8 ITS, England
- Applied Quantum Chemistry of Nonmetallic Materials  
John R. Van Wazer  
Department of Chemistry  
Vanderbilt University  
Nashville, Tennessee 37235
- Unsaturated Organosilicon Heterocycles  
William P. Weber  
Department of Chemistry  
University of Southern California  
Los Angeles, California 90007

Energies and Conformations of Molecules

Kenneth B. Wiberg  
Department of Chemistry  
Yale University  
New Haven, Connecticut 06520

State Identification of Reaction Products

Richard N. Zare  
Department of Chemistry  
Columbia University  
New York, New York 10027

COMPLETED PROJECT SUMMARIES

FY77

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Laser Studies of Chemical Reaction Dynamics
2. PRINCIPAL INVESTIGATOR: Dr. Michael J. Berry  
Department of Chemistry  
University of Wisconsin  
Madison, Wisconsin 53706
3. INCLUSIVE DATES: 1 September 1972 to 31 August 1976
4. GRANT NUMBER: AFOSR-73-2423
5. COSTS AND FY SOURCE: \$40,953 FY 73; \$38,574 FY 74; \$55,671 FY 75;  
\$100,131 FY 76
6. SENIOR RESEARCH PERSONNEL: Dr. Robert G. Bray  
Dr. Oded Kafri  
Professor J. Thomas Knudtson
7. JUNIOR RESEARCH PERSONNEL: Sherwin T. Amimoto  
Steven N. Bittenson  
Bret D. Cannon  
Julianne C. Elward  
Robert J. Gill  
Wolfgang Henke  
Daniel E. Klimek  
Stephen K. Liu  
Kammalathinna V. Reddy  
William A. Tricumi, Jr.  
Gary A. West
8. PUBLICATIONS:  

"The F + H<sub>2</sub>, D<sub>2</sub>, HD Reactions: Chemical Laser Determination of the Product Vibrational State Populations and the F + HD Intramolecular Kinetic Isotope Effect," M. J. Berry, J. Chem. Phys., 59, 6229 (1973).

"Hot-Atom Initiated Chemical Laser Study of the H\* + SF<sub>6</sub> Reaction," M. J. Berry, Chem. Phys. Letters, 22, 507 (1973).

"Golden Rule Calculation of Reaction Product Vibronic State Distributions," M. J. Berry, Chem. Phys. Letters, 27, 73 (1974).

"The Chloroethylene Photochemical Lasers: Vibrational Energy Content of the HCl Molecular Elimination Products," M. J. Berry, J. Chem. Phys., 61, 3114 (1974).

"CN Photodissociation and Predissociation Chemical Lasers: Molecular Electronic and Vibrational Laser Emissions," G. A. West and M. J. Berry, J. Chem. Phys., 61, 4700 (1974).

"Analysis of Electronically Nonadiabatic Chemical Reactions: An Information Theoretic Approach," U. Dinur, R. Kosloff, R. D. Levine, and M. J. Berry, Chem. Phys. Letters, 34, 199 (1975).

"Laser Studies of Gas-Phase Chemical Reaction Dynamics," M. J. Berry, Ann. Rev. Phys. Chem., 26, 259 (1975).

"Chemical Laser Studies of Energy Partitioning into Chemical Reaction Products," M. J. Berry in R. D. Levine and J. Jortner (editors), Molecular Energy Transfer (Wiley, New York, 1976).

"A Polyatomic Chemical Laser: Vibrationally Excited Hydrogen Cyanide Produced by the  $CN + N_2$  Bimolecular Reaction," G. A. West and M. J. Berry, Opt. Comm., 18, 128 (1976).

"A New Empirical Potential Hypersurface for Bimolecular Reactions," O. Kafri and M. J. Berry, Faraday Div. Chem. Soc., 62, XXX (1976).

"An Intracavity Dye Laser Technique for Spectroscopic and Kinetic Measurements of Transients," R. G. Bray, W. Henke, S. K. Liu, K. V. Reddy, and M. J. Berry in J. I. Steinfeld (editor), Electronic Transition Lasers, Vol 2 (MIT Press, Cambridge, MA, 1977).

"Measurement of Highly Forbidden Optical Transitions by Intracavity cw Dye Laser Spectroscopy," R. G. Bray, W. Henke, S. K. Liu, K. V. Reddy and M. J. Berry, Chem. Phys. Letters, 47, 213 (1977).

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Chemical laser techniques have been used to analyze energy partitioning and chemical reaction dynamics in elementary bimolecular, unimolecular, and photochemical reaction systems. Several new chemical laser systems were discovered. A general method for the quantitative determination of product vibrational state distributions was developed and applied to many chemical laser systems. Important rate processes such as specific energy partitioning leading to population inversions plus energy redistribution steps that modify nascent population inversions were determined for operating chemical lasers.

A summary of accomplishments includes:

Extension of Chemical Laser Methodology: A simple grating-tuned cavity technique was devised that permitted the measurement of relative gains of lasing transitions; this information in turn allowed the determination of complete and accurate product vibronic state distributions and of other rate processes such as kinetic isotope effects.

Quantitative Determination of Energy Partitioning: Using the grating-tuned cavity technique, numerous chemical laser systems were analyzed to determine features of reaction energy partitioning. Notable accomplishments include:

1) complete analysis of HF and DF product vibronic state distributions generated by the  $F + H_2$ ,  $D_2$ , and HD elementary bimolecular reactions, complete analysis of HCl photochemical reaction product vibronic state distributions resulting from photolysis of  $CH_2 = CHCl$  and other chloroethylenes.

Synchrotron Radiation Experiments: A fully automated absorption and fluorescence spectroscopy apparatus was constructed using an intense continuum radiation source (the electron storage ring of the University of Wisconsin Synchrotron Radiation Facility), computer controlled one-meter normal incidence and Seya-Namioka monochromators, photon counting detection, and on-line data acquisition and processing using a PDP-12 computer. The apparatus can photoelectrically record VUV (and XUV) spectra of gas phase compounds at  $\lambda \geq 200 \text{ \AA}$  with high (digital) accuracy at resolution better than  $0.3 \text{ \AA}$ , store spectra in digital form, and output hard copies. Accurate absorption coefficients can be obtained.

The apparatus was used to measure UV and VUV spectra of interesting photochemical reactants such as chloroethylenes and cyanides and to obtain energy partitioning information for the products of photodissociation and predissociation reactions (e.g., electronically excited cyanide radical production). Fluorescence measurements aided in screening potential molecular electronic chemical laser systems.

Development of Sub-Microsecond Flash Photolysis Equipment: A linear array of flashlamps was constructed that produces a fast ( $100 - 200$  nanosecond risetime, depending on lamp construction), broadband ( $\lambda \geq 1500 \text{ \AA}$ ), high-intensity (500 - 600 J stored electrical energy is discharged through the array) photolysis source in a configuration suitable for chemical laser generation. Many known chemical laser systems ( $I^*$ ,  $CN^*$ , HF, etc.) have been operated readily in this device; several candidate electronic lasers failed to produce real lasers with this equipment.

Theoretical Approaches Toward Reaction Dynamics: Accomplishments include: 1) invention of an intuitively satisfying dynamical model that predicts product vibronic state distributions in many reaction and relaxation rate processes such as bimolecular reactions and photochemical reactions, 2) application of information theoretic methods to the analysis of reaction energy partitioning and to the prediction of electronic branching ratios, 3) computation of ab initio potential energy hypersurfaces for HFCO and for the  $CN + H_2$  bimolecular reaction system, and 4) invention of an empirical potential energy hypersurface for bimolecular reaction systems.

Dye Laser Spectroscopy: Considerable success was achieved in obtaining spectra of highly-forbidden optical transitions by dye laser quenching and by photoacoustic detection techniques. Dye laser methodology has been extended to transient measurements, culminating in the first observation of the cyanide radical  $B^2\Sigma \leftrightarrow A^2\Pi$  system in absorption. Applications to identification of optical gain in potential electronic chemical laser systems have been made, but candidates scrutinized ( $O^*(^1S)$ ,  $SnO^*$ ) have not exhibited gain.

Discovery of New Chemical Laser Systems: Over forty new chemical lasers were discovered based upon bimolecular, unimolecular, and photochemical reactions. The most notable systems are: 1) a "hot-atom" chemical laser, 2) cyanide radical molecular electronic chemical lasers, and 3) the HCN polyatomic chemical laser.

AFOSR Program Manager: John T. Viola, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Inelastic and Reactive Scattering of Translationally Excited Molecules

2. PRINCIPAL INVESTIGATOR: Dr. Philip R. Brooks  
Department of Chemistry  
Rice University  
Houston, Texas 77001

3. INCLUSIVE DATES: 1 April 1974 - 30 September 1977

4. GRANT NUMBER: AFOSR 74-2692

5. COSTS AND FY SOURCE: \$36,195, FY74; \$26,796, FY75; \$41,233, FY76;  
\$21,414, FY77.

6. SENIOR RESEARCH PERSONNEL:

Dr. T. L. Budzynski  
Dr. F. R. Grabiner

Dr. M. W. Geis  
Dr. H. Dispert

7. JUNIOR RESEARCH PERSONNEL:

J. G. Pruett  
S. L. Anderson  
J. Fite

J. R. Hardee  
R. Pendley  
K. Chang

8. PUBLICATIONS:

"Translational Excitation of the Molecular Beam Reaction  $K + HCl \rightarrow KCl + H$ ",  
J. Pruett, F. Grabiner and P. Brooks, J. Chem. Phys., 63, 1173 (1975).

"Total Cross Section Measurements of the Reaction  $K + HCl \rightarrow KCl + H$  as a  
Function of Translational Energy (2-20 kcal/mole)", M. Geis, H. Dispert,  
T. Budzynski and P. Brooks, ACS Symp. Ser., 56, 103 (1977)

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Chemical reaction rates are increased at high temperatures. While this has been known for over a hundred years (and exploited even longer) it is not yet known precisely why an increase in temperature should increase the reaction rate. For endothermic reactions increasing the temperature (or energy) clearly increases the fraction of species which can react, but no such explanation is possible for exothermic reactions. The temperature dependence of almost all reactions can be interpreted as evidence that some extra or "activation" energy must be supplied before the reagents can react, and this is frequently interpreted in terms of some "mountain pass" on a multidimensional potential energy surface.

This work has been undertaken to investigate the nature of this activation energy and to see how it can best be supplied to a potentially reactive system. Our plan was to isolate molecules in molecular beams where we could cleanly

study the reactivity of molecules which had been prepared in a variety of ways. Our interest focused on systems where energy could be supplied either as internal (vibrational) energy or as energy of translation. The reaction  $K + HCl \rightarrow KCl + H$  was chosen as a prototype because the reaction appeared to have a small energy of activation and because the HCl molecule could be excited with a chemical laser.

Most of our time and effort has gone into the design, testing and development of the apparatus. Our specific results have so far been restricted to the  $K + HCl$  reaction. We have shown that one quantum of HCl vibration is incredibly effective in stimulating reaction (100X increase), that a comparable amount of translational energy is less effective (10X increase) and that further increase in translational energy actually decreases the reaction probability. (One quantum of HCl vibrational energy (8 kcal/mole) corresponds to the average thermal energy at  $\sim 3500^\circ K$ , which is sufficiently hot that everyday experience is no longer applicable. Thus a decrease in cross section does not necessarily contradict everything known about reaction rates at lower temperatures.) The change in cross section with translational energy has been interpreted in terms of the variation in the microscopic state-to-state rate constant. We find this rate constant decays exponentially with speed and are able to predict (semi-quantitatively) the fall off of the reaction cross section at high energies. The state-to-state rate constant will allow extrapolation of rate data over large temperature ranges and will allow quantitative comparison with other systems.

AFOSR Program Manager: Dr. Robert A. Osteryoung

#### COMPLETED PROJECT SUMMARY

1. TITLE: Electrochemistry of Hydrazine-Hydrazine Azide Mixtures
2. PRINCIPAL INVESTIGATOR: Dr. Charles T. Brown  
United Technologies Research Center  
East Hartford, Connecticut 06108
3. INCLUSIVE DATES: 1 March 1972 - 30 June 1976
4. CONTRACT NUMBER: F44620-72-C-0049
5. COSTS AND FY SOURCE: \$38,579, FY72; \$19,960, FY73; \$32,392, FY74;  
\$41,501, FY75; \$42,978, FY76.
6. SENIOR RESEARCH PERSONNEL: None
7. JUNIOR RESEARCH PERSONNEL: Patrica DeFelice
8. PUBLICATIONS:

"The Preparation of Purified Hydrazine", by C. T. Brown, submitted to The Journal of Chemical and Engineering Data.

"The Cathodic Process in Anhydrous Hydrazine", by C. T. Brown, to be submitted to The Journal of the Electrochemical Society.

"Electrical Conductivity Studies of Hydrazine-Water, Hydrazine-Aniline and Hydrazine-Carbon Dioxide Mixtures", by C. T. Brown, to be submitted to The Journal of the Electrochemical Society.

"Electrochemistry of Hydrazine-Hydrazine Azide Mixtures", by C. T. Brown, Final Technical Report.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of the investigations was the identification of systems having high cell potentials, similar to those obtained in other non-aqueous media, but with solvent properties that permit high solubilities of the reacting species as well as low viscosity and high electrical conductivity. These investigations were initially directed toward determining the nature of the electrochemical process in anhydrous hydrazine and to studying the kinetics of the azide ion on this media.

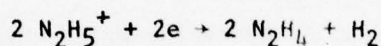
The experimental program was designed to examine hydrazine and hydrazine-derivatives as solvents for various electrolytes. In principle such solvent/solute mixtures could permit a wide range of electrochemical reactions which cannot be achieved in aqueous solutions. Hydrazine azide as an electrochemically active solute was selected because of the high theoretical oxidation potential for the azide ion. The kinetics of more conventional metal-metal ion couples were also investigated.

The effect of impurities on the electrochemical properties of hydrazine was investigated using as-received and specially purified samples. A purification procedure was developed which consisted of drying over  $\text{CaH}_2$  followed by a vacuum distillation. This procedure resulted in hydrazine with 0.05 percent water and less than 10 ppm  $\text{CO}_2$ .

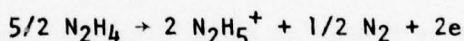
Conductivity measurements were used to characterize the effects of water, carbon dioxide and aniline (the three major impurities in hydrazine) on the electrochemical properties of hydrazine. Aniline had no effect on conductivity. The conductivity as a function of water content was found to obey the Onsager relationship for water concentrations up to 1.0 percent provided the hydrolysis reaction with hydrazine was taken into account. Above 1.0 percent water ionic association is evident and the effect of water on the ionic nature of hydrazine is minimized. Thus elaborate purification procedures are not necessary in order to use hydrazine as a solvent.

The effect of carbon dioxide on the conductivity of hydrazine was complex. It appears that both carbazic acid and ammonium carbonate are formed. It has been found that exposure of hydrazine to air must be minimized in order to maintain a carbon dioxide concentration on the order of 10 ppm. Proper control of the impurity levels resulted in hydrazine samples that could be used in electrode polarization studies without encountering interfering reactions.

Electrode polarization studies on platinum in hydrazine indicated a total potential range of about 1.2 volts without hydrazine decomposition. The cathodic reaction is diffusion controlled and proceeds according to:



The anodic reaction is activation controlled and proceeds according to:



Polarization experiments using hydrazine azide as a solute merely increased the conductivity of the system, there was no evidence of azide ion discharge. These experiments were repeated using monoethylhydrazine as a solvent. The cathodic process was the same as in hydrazine. In the absence of a supporting electrolyte it was possible to obtain a total potential range of + 3 volts. In the presence of solutes (including hydrazine azide) the cathodic overpotential was the same as in hydrazine, but there was no evidence of nitrogen evolution at overpotentials as high as + 4 volts (i.e., no azide in activity).

Studies of a variety of metal-metal ion couples in hydrazine indicated that aluminum and magnesium have high overpotentials for solvent decomposition and low overpotentials for the metal-metal salt couple. The aluminum electrode does not appear to be reversible, but the magnesium-magnesium chloride system indicates high reversibility at low overpotentials.

The results suggest that a research program should be conducted in which selected metal-metal ion and metal-insoluble metal salt couples would be investigated as a function of solvent composition and solute concentration in terms of high open-circuit potentials and low overpotentials. The solvent studies have been

brought to the point where the solvent-electrode interactions are well understood, and the specific electrode processes can be studied without problems associated with the solvent.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Novel Chemical Laser Systems
2. PRINCIPAL INVESTIGATOR: Professor Terrill A. Cool  
School of Applied and Engineering Physics  
Cornell University  
Ithaca, New York 14853
3. INCLUSIVE DATES: 15 June 1973 - 31 March 1977
4. GRANT NUMBER: AFOSR 73-2550
5. COSTS AND FY SOURCE: \$50,000, FY73; \$50,000, FY74; \$80,000, FY75;  
\$50,000, FY76
6. SENIOR RESEARCH PERSONNEL: Dr. M. S. Chou  
Dr. R. J. Pirkle  
Dr. J. S. Whittier
7. JUNIOR RESEARCH PERSONNEL:  

H. C. Brayman	A. C. Erlandson
D. R. Fischell	N. R. Friedman
D. R. Harris	K. K. Hui
R. A. Lucht	J. A. McGarvey, Jr.
D. I. Rosen	
8. PUBLICATIONS:  
"Vibrational Deactivation of O<sub>3</sub> Molecules in Gas Mixtures: II", D. I. Rosen and T. A. Cool, J. Chem. Phys. 62, 466 (1975).  
"Intermode Energy Transfer in Vibrationally Excited O<sub>3</sub>", K. K. Hui, D. I. Rosen, and T. A. Cool, Chem. Phys. Lett. 32, 141 (1975).  
"Vibrational Relaxation in HF and DF Mixtures", R. S. Lucht and T. A. Cool, J. Chem. Phys. 60, 2554 (1974).  
"Temperature Dependence of Vibrational Relaxation in the HF, DF, HF-CO<sub>2</sub> and DF-CO<sub>2</sub> Systems", R. A. Lucht and T. A. Cool, J. Chem. Phys. 60, 1026 (1974)  
"Temperature Dependence of Vibrational Relaxation in the HF-DF, HF-CO<sub>2</sub>, and DF-CO<sub>2</sub> Systems: II", R. Lucht and T. Cool, J. Chem. 63, 3962 (1975).  
"Overtone Emission Spectroscopy of HF and DF: Vibrational Matrix Elements and Dipole Moment Function", R. Sileo and T. Cool, J. Chem. Phys. 65, 117 (1976).  
"Laser Operation by Dissociation of Metal Complexes: New Transitions in As, Bi, Ga, Ge, Hg, In, Pb, Sb, and Tl", M. Chou and T. Cool, J. Appl. Phys. 47, 1055 (1976).

"Laser Operation by Dissociation of Metal Complexes (II): New Transitions in Cd, Fe, Ni, Se, Sn, Te, V, and Zn", J. Appl. Phys. 48, 1551 (1977).

"Transfer Chemical Lasers", Handbook of Chemical Lasers, T. Cool, John Wiley and Sons, Inc., p. 431.

"Vibrational Energy Transfer for H<sub>2</sub>-D<sub>2</sub> and H<sub>2</sub>-HCl Mixtures from 220-450°K", R. Pirkle and T. Cool, Chem. Phys. Lett. 42, 58 (1976).

"Double Quantum Vibrational Energy Transfer in the O<sub>3</sub>-CO and O<sub>3</sub>-OCS Systems", J. Chem. Phys. 65, 3536 (1976).

"Vibrational Energy Transfer in HF-HCN, DF, HCN, and H<sub>2</sub>-HCN Mixtures from 240-450°K", J. McGarvey, N. Friedman, and T. Cool, J. Chem. Phys. 66, 3189 (1977).

"Initiation with an Electron Beam of Chemical Reactions of Interest for Visible Wavelength Lasers", J. Whittier and T. Cool, Proceedings of the Second Summer Colloquium on Electronic Transition Lasers, Woods Hole, Mass., September, 1975.

"New Metal Atom Transitions in As, Bi, Cu, Ge, Hg, In, Pb, Sb, and Tl", M. Chou and T. Cool, Proceedings of the Second Summer Colloquium on Electronic Transition Lasers, Woods Hole, Mass., September 1975.

"Spontaneous Emission from ScF in a Supersonic Mixing Flame", D. Fischell and T. Cool, Proceedings of the Third Summer Colloquium on Electronic Transition Lasers, Snowmass, Colorado, September 1976.

"Chemical Lasers", T. Cool, to be published as Chapter 5 in Dynamics and Energetics of Elementary Reactions, I.W.W. Smith, Editor, Plenum Publishing Company.

"Experiments Concerning the Laser Enhanced Reaction Between Vibrationally Excited O<sub>3</sub> and NO", K. Hui and T. Cool, to be published, J. Chem. Phys.

"Novel Chemical Laser Systems", T. Cool, Final Technical Report.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of this research was the identification of suitable reaction systems for the development of chemical lasers capable of operation on molecular electronic transitions at wavelengths below 2 microns.

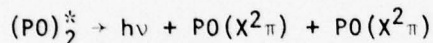
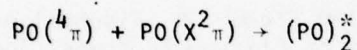
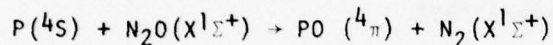
Candidate reactions of several metal atoms with various oxidizers were systematically studied. Chemiluminescent spectra were recorded for these reactions and measurements of fluorescence rates were performed for molecular bonds and atomic emissions of interest.

A major problem was the production of large concentrations of metal atoms ( $> 10^{13} \text{ cm}^{-3}$ ) on a short time scale ( $10^{-7}$  to  $10^{-6}$  seconds). Methods of shock-induced thermal dissociation and dissociation by electrical discharges and electron beams were employed for this purpose.

Nearly all of the systems investigated had low fluorescence rates for product metal oxide or metal halide molecules (two significant exceptions were the Sn/N<sub>2</sub>O and PH<sub>3</sub>/N<sub>2</sub>O systems. Laser action was observed, however, for over 40 new wavelengths from 17 metal atoms formed from the dissociation of metal halides, hydrides, alkyls, and carbonyls. These wavelengths were in the near infrared from 1.152 to 14.54 μ, and were identified with transitions in the atoms: As, Bi, Cd, Fe, Ga, Ge, Hg, In, Ni, Pb, Sb, Se, Sn, Te, Tl, V, and Zn.

Of continuing interest is the formation of electronically excited yttrium chloride via the reaction  $Y + Cl_2 \rightarrow YCl^* + Cl$ . Chemiluminescent spectra from YCl\* were recorded in a shock-tube-driven supersonic mixing-flame. These data show the existence of strong emission near 4000 Å and weaker bands at longer wavelengths believed to arise from triplet states of chemically formed YCl. This reaction system is of interest because of a high photon yield, a high degree of specificity in energy disposal among product states, and the possible existence of laser transitions of appropriate radiative lifetimes (10<sup>-3</sup>-10<sup>-5</sup> seconds) for chemical laser operation.

Another system of potential importance was identified. Chemical reactions initiated by electrical discharges in PH<sub>3</sub>/N<sub>2</sub>O mixtures lead to strong visible chemiluminescence by the steps:



The chemiluminescence is continuous from about 3200 Å to beyond 2μ with a broad maximum near 7500 Å. This emission is believed to arise from the (PO)<sub>2</sub><sup>\*</sup> excimer and may lead to a chemically pumped laser capable of broad band tuning throughout the visible spectral region.

AFOSR Program Manager - John T. Viola, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Rates of Rapid Chemical Reactions
2. PRINCIPAL INVESTIGATOR: Dr. Edward M. Eyring  
Department of Chemistry  
University of Utah  
Salt Lake City, Utah 84112
3. INCLUSIVE DATES: 1 December 1972 - 31 January 1977
4. GRANT NO: AFOSR 73-2444
5. SENIOR (POSTDOCTORAL) RESEARCH PERSONNEL:  

Dr. Max Auzanneau	Dr. Neil Purdie
Dr. Arthur L. Cummings	Dr. Licesio J. Rodriguez
Dr. Michael M. Farrow	Dr. Ronald P. Rohrbach
Dr. Johnathan E.C. Hutchins	Dr. F. Arce Vazquez
Dr. J. Thomas Knudtson	Dr. Robert D. White

6. JUNIOR RESEARCH PERSONNEL:

Dr. R. Bartholomew	Mr. P. Kiester	Mr. S. Olsen
Miss K. Evans	Dr. D. Lentz	Mrs. J. Siddoway
Mr. R. Greenwood	Dr. G. Liesegang	Mrs. M. Steggall
Mr. L. P. Holmes	Mr. G. Marshall	Miss K. Stephenson
Miss P. Hunt	Miss P. Michela	Mr. L. Wojcik
Mr. R. Jonas		

7. PUBLICATIONS:

"Kinetics of Octylphenyl Polyoxyethylene Alcohol Micelle Dissociation by a Stopped-Flow Technique", J. Lang, J. Auburn, and E. Eyring, J. Colloid Interface Sci., 41, 484 (1972).

"Molecular Associations in Non-Aqueous Solvents I. Thermodynamics of Dye-Dye Interactions in  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$ ", R. Graham, G. Henderson, E. Eyring, and E. Wooley, J. Chem. Eng. Data, 18, 277 (1973).

"Relaxation of Laser Induced Transient Plasmas in Liquids", Z. Schelly, J. Lang, and E. Eyring, Monatshefte fuer Chemi. 104, 1672 (1973).

"Solvent Isotope Effects for Sulphonphthalein Indicator Dinanion- $\text{H}^+$  Recombination Kinetics", D. Lentz, J. Hutchins, and E. Eyring, J. Phys. Chem., 78, 1021 (1974).

"Pulsed Spectrophotometric Chemical Relaxation Measurements", S. Olsen, L. Holmes, and E. Eyring, Rev. Sci. Instrum. 45, 859 (1974).

"Dissociation Field Effect Kinetic Study of Aqueous Samarium (III) Complexation by Murexide", M. Farrow, N. Purdie, and E. Eyring, Inorg. Chem. 13, 2024, (1974).

"Molecular Associations in Nonaqueous Solvents II. Temperature Effects on Thermodynamics of Dye-Dye Interaction in  $\text{C}_6\text{H}_6$ ", R. Graham, G. Henderson, E. Eyring, and E. Wooley, J. Chem. Eng. Data, 19, 297 (1974).

"Laser-Induced Chemical Reactions", J. Knudtson and E. Eyring, Ann. Rev. Phys. Chem. 25, 255 (1974).

"Photophysical Effects of Stereoisomers in Thiocarbocyanine Dyes", J. Knudtson and E. Eyring, J. Phys. Chem. 78, 2355, (1974).

"The Effects of Phlortin on Red Cell Nonelectrolyte Permeability", J. Owen, M. Steggall, and E. Eyring, J. Membrane Biol., 19, 79 (1974).

"The Kinetics of Complexation of Thallium (I) Triiodide in Aqueous Solution", M. Farrow, N. Purdie, and E. Eyring, J. Amer. Chem. Soc., 97, 1968 (1975).

"Kinetic Studies of Metal Ion Complexation and Dye Dimerization by Laser Ultrasound and Laser T-Jump", M. Farrow, N. Purdie, A. Cummings, W. Herrmann, Jr., and E. Eyring in Chemical and Biological Applications of Relaxation Spectrometry, E. Wyn-Jones, ed., D. Reidel Publishing Co., Dordrecht Holland, 1975, pp. 69-83.

"The Electric Field Jump Relaxation Method", E. Eyring, op. cit., pp. 85-90.

"Electric Field Jump Study of the Helix-Coil Transition of Aqueous Poly- $\alpha$ -L-Glutamic Acid", A. Cummings and E. Eyring, op. cit. 505-508.

"The Kinetics of Complexation of Silver(I) with Thiosulfate Ion in Aqueous Solution", M. Farrow, N. Purdie, and E. Eyring, Inorg. Chem., 14, 1584 (1975).

"A Reevaluation of the Ultrasonic Absorption Spectra of Aqueous Samarium (III) Sulfate Solution", M. Farrow, N. Purdie, and E. Eyring, J. Phys. Chem. 79, 1995 (1975).

"Helix Coil Transition Kinetics in Aqueous Poly ( $\alpha$ ,L-Glutamic Acid)", A. Cummings and E. Eyring, Biopolymers, 14, 2107 (1975).

"Ultrasonic Absorption Kinetic Studies of the Complexation of Aqueous Potassium and Cesium Ions by 18-Crown-6", G. Liesegang, M. Farrow, N. Purdie, and E. Eyring, J. Amer. Chem. Soc., 98, 6905, (1976).

"Automatic Ultrasonic Absorption Spectrometer", M. Farrow, S. Olsen, N. Purdie, and E. Eyring, Rev. Sci. Instrum. 47, 657 (1976).

#### 8. ABSTRACT OF ACCOMPLISHMENTS AND OBJECTIVES:

A nanosecond time scale laser flash photolytic study of the kinetic behavior of carbocyanine dyes in low temperature glasses was completed and published. So also was an ultrasonic absorption kinetic investigation of the complexation of aqueous silver (I) ion by thiosulfate ion. This latter work led into a large number of ultrasonic kinetic studies of metal ion complexation in solution by a variety of anionic and neutral ligands. In the case of crown ether ligands, such as 18-crown-6 and 15-crown-5, observed rates were surprisingly far below diffusion control and were influenced instead by cation desolvation kinetics and conformational changes in the uncomplexed ligand.

A minicomputerization of the laser Debye-Sears ultrasonic absorption technique played an especially important role in these successful complexation kinetic experiments. This very productive minicomputerization led us to automate a spectrophotometric electric field jump relaxation method experiment, a task completed just after the expiration of the grant.

A thorough study of the thermal degradation of a polyperfluoroalkyl ether in the presence of iron and titanium metal coupons was carried out by a variety of experimental techniques. Results obtained, particularly by thermogravimetric and gas chromatographic mass spectral analytical methods, indicated a free radical mechanism consistent with the conclusions of earlier workers.

The elucidation of the rate and mechanism of formation of titanium fluorides on the surface of titanium metal coupons bathed in hot polyperfluoroalkyl ether lubricant was set as a goal late in the four year grant period. An adaptation of photoacoustic spectroscopy (PAS) incorporating a piezoelectric transducer instead of a microphone was selected for this task. The feasibility of making optical absorbance measurements of an opaque surface at high chopping frequencies (up to  $\sim 250$  KHZ) of the incident light has been demonstrated. The use of this technique in measuring short fluorescence lifetimes in opaque materials has also been demonstrated by PAS signal phase angle measurements in ND:laser glass as well as in solid  $\text{Nd}_2\text{O}_3$ .

AFOSR Program Manager: Richard W. Haffner, Lt Col, USAF

### COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis and Polymerization of Fluorobicyclobutanes to Chemically, Dimensionally, and Thermally Stable Polymers
2. PRINCIPAL INVESTIGATOR: Professor Henry K. Hall, Jr.  
Department of Chemistry  
University of Arizona  
Tucson, Arizona
3. INCLUSIVE DATES: 1 October 1972 - 31 July 1977
4. GRANT NUMBER: AFOSR 73-2426
5. COSTS AND FY SOURCES: \$14,958, FY73; \$15,000, FY74; \$15,000, FY75;  
\$15,000, FY76.

6. SENIOR RESEARCH PERSONNEL:

Dr. Y. Okamoto  
Dr. A. M. Buyle

Dr. I. J. Westerman  
Dr. S. Morehead

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Synthesis and Copolymerization of 3,3-Difluorocyclobutene-1-Carbonitrile", H. Hall, Jr., and Y. Okamoto, J. Polymer Sci., Polymer Chem. Ed., 12, 1443 (1974)

"Synthesis and Polymerizations of Methyl 3,3-Difluorocyclobutene-1-carboxylate and Methyl 3,3,4,4-Tetrafluorocyclobutene-1-carboxylate", H. Hall, Jr., Y. Okamoto, A. Padias, A. Deutschman, Jr., submitted to J. Polymer Science.

"Cyclopropane Formation From a 3-Halo-1,4-dipole", H. Hall, Jr., A. Padias, A. Deutschman, Jr., and I. J. Westerman, submitted to Tetrahedron Letters.

"Synthesis and Polymerization of Fluorobicyclobutanes to Chemically, Dimensionally, and Thermally Stable Polymers", H. Hall, Jr., Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of the research was to synthesize and polymerize a variety of fluorinated bicyclobutanes in hopes of obtaining novel new materials possessing high thermal stability, low adhesion, and low creep properties.

Di- and tetrafluorocyclobutene esters and nitriles were synthesized via  $\pi^2 + \pi^2$  cycloaddition reactions. In general, they did not homopolymerize but copolymerized readily with electron-rich vinyl monomers and with bicyclobutane monomers. The copolymers were fairly thermally stable.

A variety of routes to fluorinated bicyclobutanes, cyclopropenes, and epoxides was explored without success.

A novel cyclopropane synthesis was found in the cycloaddition of bromoketene acetal to acrylonitrile or methyl  $\alpha$ -cyanoacrylate.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Proposed Program for the Determination of DF and HF Rotational Relaxation Rates
2. PRINCIPAL INVESTIGATOR: Dr. J. J. Hinchey  
United Technologies Research Center  
East Hartford, Connecticut 06108
3. INCLUSIVE DATES: 1 May 1976 to 30 June 1977
4. CONTRACT NUMBER: F44620-76-C-0112
5. COSTS AND FY SOURCE: \$16,000 FY76; \$24,000 FY77; \$55,302 FY78
6. SENIOR RESEARCH PERSONNEL: R. H. Hobbs
7. JUNIOR RESEARCH PERSONNEL: None
8. PUBLICATIONS: None at this time
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

IR double resonance measurements of population transfer between rotational levels of HF by both collisional energy exchange and rotational lasing were made. A pulsed laser operating in a single V(1-0) vibrational transition was used to pump population in an HF gas sample to a specific rotational J level in the V=1 vibrational level. A CW probe laser was used to monitor the rate of loss of population from the pumped rotational level or the rate of arrival of population into one of the other rotational levels. Populations pumped to a specific rotational level were followed out of the pumped level, to the level above and to the level below. Lasing between rotational levels strongly affected rates of loss from the pumped level and transfer to the lower levels. A measurement of gain and laser intensity were made and incorporated into a kinetic rate model to assess contributions to the total transfer rates. The collisional contributions are compared to linewidth data. Information was also obtained on population transfer rates for velocity cross relaxation and for vibration-rotation transfer.

AFOSR Program Manager: John T. Viola, Lt Col, USAF

### COMPLETED PROJECT SUMMARY

1. TITLE: Mechanisms of Singlet Oxygen Generation by Chemical Reaction
2. PRINCIPAL INVESTIGATOR: James K. Hurst
3. INCLUSIVE DATES: 1 June 1975 - 31 May 1977
4. GRANT NUMBER: AFOSR 75-2821
5. COSTS AND FY SOURCE: \$30,500, FY75; \$31,020, FY76.
6. SENIOR RESEARCH PERSONNEL: D. Halko, A. Held
7. JUNIOR RESEARCH PERSONNEL: None.
8. PUBLICATIONS:

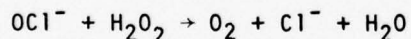
"Singlet Oxygen Generation by the Hypochlorite-Hydrogen Peroxide Reaction", A. Held, D. Halko and J. Hurst, J. Amer. Chem. Soc., submitted.

"Implications of Chlorine Oxidation Reactions Towards Myeloperoxidase-Mediated Phagocytosis", A. Held and J. Hurst, Biochem. Biophys. Research Comm., submitted.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Experiments were designed to elucidate reaction mechanisms for the hydrogen peroxide oxidation by hypochlorite ion, emphasis being placed on the identification of pathways for singlet oxygen formation and deactivation. Reaction rates were followed by stopped-flow spectrophotometry of hypochlorite consumed and oxygen-electrode analysis of oxygen produced.

In the pH range of 5-12 the reaction proceeds in accordance with the stoichiometry:



with a mixed second order rate law. Chemical trapping experiments using 2,5-dimethylfuran (DMFu) showed that singlet oxygen production is nearly quantitative in aqueous solutions with decreasing yields as well as slower reaction rates being exhibited in less polar solvents. The quenching of singlet oxygen by water is apparently independent of pH or salt effects, as inferred from the relative constancy of the quenching ratio ( $\beta$ ) of water to dimethylfuran. Optimization of gaseous singlet oxygen yields, therefore, depends only on minimizing solvent deactivation. Production of gaseous singlet oxygen was shown to be practicable by cryogenic pumping of oxygen from the reaction products under conditions of rapid mixing.

Kinetic studies in weakly acid solution (pH3-5) indicate the presence of an alternate reaction path requiring the presence of chloride ion as a catalyst. Reaction stoichiometries are unaltered, but rate is highly sensitive to surface conditions and buffering substances, as well as showing strong autoinhibition.

The observed rate law (pH 3-5) for the initial rate of reaction is:  $dO_2/dt = k(HOCl)(Cl^-)(H^+)$ . No singlet oxygen dimol emission was observed for this pathway; chemical trapping experiments were unsuccessful, presumably because the chlorine intermediate defined by the rate law reacted preferentially with DMFu.

In acid solutions the reaction of molecular chlorine with quenching agents is faster than with hydrogen peroxide, precluding the determination of singlet oxygen by competitive quenching methods. Singlet oxygen dimol emission was not observable, even under conditions maximizing rates of hydrogen peroxide oxidation.

AFOSR Program Manager: John T. Viola, Lt Col, USAF

### COMPLETED PROJECT SUMMARY

1. TITLE: Theories of Energy Disposal in Chemical Reactions
2. PRINCIPAL INVESTIGATOR: Professor Aron Kuppermann  
Division of Chemistry and Chemical Engineering  
California Institute of Technology  
Pasadena, California 91125
3. INCLUSIVE DATES: 1 June 1973 - 30 June 1977
4. GRANT NUMBER: AFOSR 73-2539
5. COSTS AND FY SOURCE: \$50,003, FY73; \$49,995, FY74; \$53,900, FY75;  
\$88,510, FY76.
6. SENIOR RESEARCH PERSONNEL: Dr. Rung T. Ling  
Dr. Gregory A. Parker  
Dr. Henry H. Suzukawa, Jr.

7. JUNIOR RESEARCH PERSONNEL:

Joel M. Bowman  
John P. Dwyer  
Alexander S. Gerwer

George C. Schatz  
Jack A. Kaye

8. PUBLICATIONS:

"Coplanar and Collinear Quantum Mechanical Reactive Scattering: The Importance of Virtual Vibrational Channels in the  $H + H_2$  Exchange Reaction", Aron Kuppermann, G. Schatz, and M. Baer, J. Chem. Phys. **61**, 4362 (1974)

"Quantum Mechanical Reactive Scattering: An Accurate Three-Dimensional Calculation", A. Kuppermann, and G. Schatz, J. Chem. Phys. **62**, 2502 (1975).

"A Useful Mapping of Triatomic Potential Energy Surfaces", A. Kuppermann, Chem Phys. Lett. **32**, 374 (1975).

"Exact Quantum, Quasiclassical, and Semiclassical Reaction Probabilities for the Collinear  $F + H_2 \rightarrow FH + H$  Reaction", G. Schatz, J. Bowman, and A. Kuppermann, J. Chem. Phys. **63**, 674 (1975)

"A Semi-Numerical Approach to the Construction and Fitting of Triatomic Potential Energy Surfaces", J. Bowman and A. Kuppermann, Chem. Phys. Lett. **34**, 523 (1975).

"Progress in the Quantum Dynamics of Reactive Molecular Collisions", A. Kuppermann. In the Physics of Electronic and Atomic Collisions (Invited Lectures, Review Papers, and Progress Report of the IXth International Conference on the Physics of Electronic and Atomic Collisions, Seattle, WA, 24-30 Jul 75), edited by J. S. Risley and R. Geballe (Univ of Washington Press, Seattle, 1976), pp 259-274.

"An Exact Quantum Study of Vibrational Deactivation by Reactive and Nonreactive Collisions in the Collinear Isotopic H + FH Systems", G. Schatz and A. Kuppermann, in the Proceedings of the Symposium on High Energy Transfer Lasers, Redstone Arsenal, Alabama, 3-4 Nov 75 (U.S. Army Missile Command, Redstone Arsenal, Aug 76), Special Report RH-7T-1, pp. 132-142.

"Dynamical Resonances in Collinear, Coplanar, and Three-Dimensional Quantum Mechanical Reactive Scattering", G. Schatz and A. Kuppermann, Phys. Rev. Lett. **35**, 1266 (1975).

"Quantum Mechanical Reactive Scattering for Planar Atom Plus Diatom Systems. I. Theory", A. Kuppermann, G. Schatz, and M. Baer, J. Chem. Phys. **65**, 4596 (1976).

"Quantum Mechanical Reactive Scattering for Planar Atom Plus Diatom Systems. II. Accurate Cross Sections for H + H<sub>2</sub>", G. Schatz and A. Kuppermann, J. Chem. Phys. **65**, 4624 (1976).

"Quantum Mechanical Reactive Scattering for Three-Dimensional Atom Plus Diatom Systems. I. Theory.", G. Schatz and A. Kuppermann, J. Chem. Phys. **65**, 4642 (1976).

"Quantum Mechanical Reactive Scattering for Three-Dimensional Atom Plus Diatom Systems. II. Accurate Cross Sections for H + H<sub>2</sub>", G. Schatz and A. Kuppermann, J. Chem. Phys. **65**, 4668 (1976).

"Large Quantum Effects in a Model Electronically Nonadiabatic Reaction: Ba + N<sub>2</sub>O → BaO\* + N<sub>2</sub>", J. Bowman, S. Leasure, and A. Kuppermann, Chem. Phys. Lett. **43**, 374 (1976).

"Validity of the Adiabatic Approximation for Vibrational Energy Transfer in Collisions Between Diatomic Molecules", J. Dwyer and A. Kuppermann, Chem. Phys. Lett. **44**, 499 (1976).

"Angular Momentum Decoupling Approximations in the Quantum Dynamics of Reactive Systems", A. Kuppermann, G. Schatz, and J. Dwyer, Chem. Phys. Lett. **45**, 71 (1977).

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this project was to perform accurate and approximate quantum dynamical calculations on elementary chemical reactions of importance for the fundamental aspects of chemical dynamics and for advanced technologies of interest to the United States Air Force, such as high energy chemical lasers, plume technology, and the chemical effects of high energy radiation. These included calculations of three-atom exchange reactions, breakup collisions, three-body recombinations, vibrational quenching by reaction, resonances, and electronic branching ratios. The aim of these calculations was to develop an understanding of these processes and to develop benchmark data against which approximate methods could be tested.

The main accomplishments achieved during the four years of this grant were:

1. An extensive series of accurate quantum dynamical calculations on the collinear F + H<sub>2</sub> → FH + H, F + D<sub>2</sub> → FD + D, F + HD → FH + D, and F + DH → FD + H

reactions. They showed the importance of quantum effects in this laser-pumping reaction and clarified the flow of energy into vibrationally excited states of products.

2. A quantum study of the effect of barrier height on the vibrational deactivation of FH by the collinear  $H + FH(v) \rightarrow HF(v' < v) + H$  reaction. These studies showed that the probability of this process becomes low at barrier heights significantly below the vibrational energy of the reagent.

3. A quantum dynamical calculation of the electronic branching ratio for a collinear model of the reaction  $Ba + N_2O \rightarrow BaO + N_2$ ,  $BaO^* + N_2$ . This calculation indicated the factors affecting the production of electronically excited states and the importance of quantum effects for such processes.

4. Development of the first accurate method of performing calculations of quantum mechanical reaction cross sections for coplanar and three-dimensional atom-diatom reactions and its application to the  $H + H_2$  system. They gave a quantitative assessment of the extent of tunneling in this reaction and predicted the existence of polarization selection rules. These are accurate benchmark calculations which permit reliable testing of approximate methods.

5. Development of a quantum mechanical method for studying breakup collisions using hyperspherical coordinates.

6. A study of collinear, coplanar, and three-dimensional dynamical Feshbach resonances in chemical reactions. These studies led to the first prediction that dynamical resonances exist in the real three-dimensional world and that their measurement could give important new information on potential energy surfaces.

AFOSR Program Manager: John T. Viola, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Infrared Spectra of Fluid Film Under Conditions of Incipient Bearing Failure

2. PRINCIPAL INVESTIGATOR:

Dr. James L. Lauer  
Suntech, Inc.  
P. O. Box 1135  
Marcus Hook, Pennsylvania 19061

CURRENT ADDRESS:  
Dept of Mechanical Engineering  
Rensselaer Polytechnic Inst.  
Troy, NY 12181

3. INCLUSIVE DATES: 30 September 1976 - 30 September 1977

4. CONTRACT NUMBER: F49620-76-C-0042

5. COSTS AND FY SOURCE: \$57,406 (Govt) + \$3,021 (Sun Oil Co) FY7T and FY77

6. SENIOR RESEARCH PERSONNEL:

Dr. James L. Lauer

Mr. Melvin Peterkin

7. JUNIOR RESEARCH TECHNICIAN: None.

8. PUBLICATIONS:

"Infrared Emission Spectra of Lubricants in Operating Bearings", presented at the 10th Middle Atlantic Regional ACS Meeting at the Marriott Hotel, Philadelphia, on 26 February 1976.

"Infrared Emission Spectra from Lubricant Films in Operating Bearings by Fourier Methods". Paper No. 333. Presented at the 27th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, 1-5 March 1976.

"High Pressure Infrared Interferometry," Chapter 5 in "Fourier Transform IR: Application to Chemical Systems" (J. R. Ferraro and L. J. Basile, editors). Academic Press, NY, pp 169-213, to be published in January 1978.

"Traction and Lubricant Film Temperature as Related to the Glass Transition Temperature and Solidification." Preprint No 77-AM-1A-3. Presented at the 32nd Annual Meeting in Montreal, Quebec, Canada, 9-12 May 1977.

"Glass Transition Pressures of Fluids from the Bandwidths and Frequencies of the Fluorescence Spectrum of Ruby." Paper No 261. Presented at 3rd Annual FACSS Meeting (Federation of Analytical Chemistry and Spectroscopy Societies), Philadelphia Civic Center, 15-19 November 1976.

"Glass Transition and Fluid Pressure Determinations from the Fluorescence Spectrum of Ruby." Canadian J. of Spectroscopy 21, 153-158 (Sep, Oct 1976).

"Differential Infrared Fourier Emission Microspectrometer for Lubrication Studies. Paper No M.B.3. Presented at the 1977 International Conference on Fourier Transform Infrared Spectroscopy, University of South Carolina, Columbia, S.C., 20-24 June 1977.

"Infrared Fourier Transform Emission Microspectrometer", Paper No 17. Presented at the 28th Pittsburgh Conference, Cleveland Convention Center, 28 February-4 March 1977.

"Polarized Infrared Emission Spectrophotometry with a Micro-Interferometer", American Laboratory, Vol. 9, 29-40 (November 1977).

"Polarized Infrared Emission Spectra from Operating Bearings", Paper No 592, Invited for presentation in the Coblenz Symposium at the 29th Pittsburgh Conference, Session on Application of Fourier Transform Infrared Spectroscopy, Little Theater, Cleveland Convention Center, 2 March 1978.

9. INVENTIONS:

<u>Name of Inventor</u>	<u>Title of Invention</u>	<u>Patent Application Ser. No.</u>	<u>Status</u>
J. L. Lauer/ M. A. Peterkin	Extremely High Pressure Measuring Device	S-75-G-121	Closed out, patentability questionable
"	Viscosity Measuring System	Ser 791,089	Filed on 27Feb76
"	System for Spectroscopic Analysis of a Chemical Stream	USP 3,997,786	Patent issued on 14Dec76
"	Emission Spectroscopic System having Compensation for Background Radiation	USP 4,009,962	Patent issued on 1Mar77

10. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Under conditions of high stress moving parts of machinery, such as bearings or gears, are prevented from self-destruction by the interposition of extremely thin films of lubricants. Since failure is unlikely to occur without warning, examination of the lubricant in operating bearings approaching failure appeared to be a procedure promising to provide clues on reasons for failure and thus to provide a basis for improved lubrication. The method of analysis chosen was infrared emission Fourier spectrophotometry, a relatively new procedure which is particularly well adapted to thin film analysis and which -- in contrast to absorption spectrophotometry -- requires only one window transparent to infrared radiation. The fluid film heated by internal friction during bearing operation takes the place of the source for the spectrophotometer.

This phase of the work was (1) to demonstrate that infrared emission spectrophotometry can be applied to bearing contact situations, (2) to provide background in the form of calibration spectra applicable to such situations, and (3) to show the potential of the method in specific instances relevant to the failure problem. Very substantial obstacles had to be overcome: (1) very weak radiant power passed through the window and most of it originating from the solid boundary surfaces rather than from the lubricant film; (2) different fluid and solid surface temperatures; (3) ignorance regarding expected lubricant spectral changes with pressure, temperature, shear rate, and fluid/glass transition. Accordingly much of the effort involved the development of appropriate hardware and background information.

Bearing failure is most likely to occur when the solid surfaces bounding the lubricant are elastically deformed under so-called elastohydrodynamic (EHD) lubrication. Curved surfaces are then flattened over the "Hertzian" contact region. Furthermore, sliding is more severe than rolling, hence a loaded bearing ball rotating, i.e., sliding, on a plate was adapted as a model to represent a bearing nearing failure. By making the plate a diamond window, some heat generated in the contact can be transmitted as radiation for spectroscopic analysis. Since diamond is transparent throughout most of the infrared spectrum, the examination of spectral changes even in the "fingerprint" infrared region (10-15  $\mu\text{m}$ ) and in the lattice region ( $>15 \mu\text{m}$ ) is feasible. For calibration of the spectral information of the ball-on-plate apparatus a high-pressure diamond anvil cell was used as a "simulated contact". Its sample volume could be subjected to most of the conditions likely to prevail in a sliding EHD Hertzian contact (thickness  $\sim 2 \mu\text{m}$ , open area  $0.25 \text{ mm}^2$ , pressures 0-75 kbar, temperatures 0-200°C) except for shear. As typical fluids, an ester, polyphenyl ether (5P4E), a standard petroleum lubricant, and a so-called "traction" fluid were used. A Fourier infrared interferometer was adapted for all the spectroscopic work.

In the initial stages of the program, absorption spectra were obtained with the diamond cell under various temperatures and pressures. From the splitting of the  $725\text{-}735 \text{ cm}^{-1}$  CH rocking frequency band it was possible to infer crystallization at certain pressures and temperatures for the ester and the petroleum fluid. Entrance optics were built to convert the Fourier infrared interferometer into an emission micro-interferometer and it was possible to show the equivalence between absorption and emission spectra at the same temperature and pressure. This achievement constitutes a major breakthrough; for while infrared emission spectra of thin layers of organic material on metal substrates have been obtained by previous investigators, spectra from contained volumes as small as Hertzian contacts and at average temperatures as low as 30-50°C very nearly represent the limit of today's instrumental capability.

A model ball-on-plate apparatus was then built for the same interferometer and entrance optics. The window was located at the bottom of a cup containing the test fluid. A loaded bearing ball rotated about a horizontal axis while sliding over the window provided the bearing contact. The apparatus was located above the interferometer entrance optics. Precise alignment of the contact region on the optic axis and in the focal plane of the entrance optics was essential and was achieved. Indeed it was possible to obtain "dynamic" infrared spectra from the fluids under various conditions prevailing in the Hertzian area.

The analysis of the spectra gave some surprising results. It was possible to deduce both ball surface and fluid film temperatures from the spectra. When temperature differences were plotted against shear rate, the data for all the fluids fell on practically the same curve, which showed a peak corresponding to an intermediate shear rate. The traction fluid reached the highest temperature difference under equal conditions. However, the polyphenyl ether would reach the highest absolute temperature at high shear rates -- just prior to bearing failure. At the same time its spectrum would change, indicating decomposition. Another observation was an intensity change with shear rate of one band, which could be related to polarization of the emitted radiation. The mechanism for it might well be stream birefringence, although other explanations have not yet been excluded. For example, glassification and strain

polarization (photoelastic effect) could be a mechanism which, moreover, is in agreement with recent theories by other investigators. The extent of this polarization could, conversely, be used as a measure of lubricant stress prior to failure.

Some of the spectra obtained in a diamond anvil cell for calibration purposes showed very significant changes with pressure. Absorption bands would shift and disappear possibly indicating molecular changes or, perhaps, changes in the distribution of isomers.

A separate but related achievement was the design and construction of apparatus to determine pressure and state of material in the diamond anvil cell from the peak frequency and width of the fluorescence band of ruby crystals contained within the sample. In contrast to earlier opinion considering traction as caused by glassy particles in the contact zone, the traction fluid tested needed higher pressures to be converted into the glassy state than the other fluids and must therefore function by a different mechanism.

Work has started toward a reliable determination of the state of the fluid (liquid or glassy) from the dynamic infrared spectra.

AFOSR Program Manager: R. W. Haffner, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Energy and Chemical Change
2. PRINCIPAL INVESTIGATOR: R. D. Levine and R. B. Bernstein  
Chemistry Department  
The University of Texas at Austin  
Austin, Texas 78712
3. INCLUSIVE DATES: 1 June 1974 - 31 October 1976
4. GRANT NUMBER: AFOSR-74-2725
5. COSTS AND FY SOURCE: \$33,578 FY74, \$40,828 FY75
6. RESEARCH PERSONNEL: R. Kosloff  
A. Ben-Shaul  
B. R. Johnson  
M. B. Faist  
M. Tamir  
O. Kafri  
P. Kahana  
I. Procaccia  
Sung Ho Suck

### 7. PUBLICATIONS:

"The Well Reasoned Choice: An Information-Theoretic Approach to Branching Ratios in Molecular Rate Processes", R. D. Levine and R. Kosloff, Chem. Phys. Lett. **28**, 300 (1974).

"Branching Ratios in Reactive Molecular Collisions", R. D. Levine and R. B. Bernstein, Chem. Phys. Lett **29**, 1 (1974).

"The Relation Between Collinear and 3-D Dynamical Calculations of Reactive Molecular Collisions", R. B. Bernstein and R. D. Levine, Chem. Phys. Lett. **29**, 314 (1974).

"Information-Theoretic Analysis of the Kinetic Intramolecular Isotope Effect for the F + HD Reaction", R. B. Bernstein and R. D. Levine, J. Chem. Phys. **61**, 4926 (1974).

"Prior-Expectation Distribution Functions for Energy Disposal and Energy Consumption in Reactive Molecular Collisions", A. Ben-Shaul, R. D. Levine and R. B. Bernstein, J. Chem. Phys. **61**, 4937 (1974).

"Energy Disposal and Energy Consumption in Elementary Chemical Reactions: The Information-Theoretic Approach", R. D. Levine and R. B. Bernstein, Acc. Chem. Res. **7**, 393 (1974).

"Ionization in Alkali-Halogen Atom Collisions: Comparison of the Landau-Zener Stueckelberg Approximation with JWKB Calculations", M. B. Faist, B. R. Johnson, and R. D. Levine. Chem. Phys. Lett. **32**, 1 (1975).

"Elastic and Electronic Excitation Collisions of  $\text{Br}(^2P_{3/2}) + \text{I}(^2P_{3/2})$ : Role of Potential Curve Crossing", Proc. IX ICPEAC, Univ of Washington Press, Seattle (1975), p. 226. M.B. Faist, R.B. Bernstein and R. D. Levine.

"Information-Theoretic Analysis of Reactive/Non-Reactive Branching Ratios for Triatomic Collision Complexes:  $K + C_2F$ " R. D. Levine, R. D. Bernstein and M. Tamir, Proc. IX ICPEAC, University of Washington Press, Seattle (1975), p. 333.

"Note on the Polanyi-Woodall Equation for Rotational Relaxation", R. B. Bernstein J. Chem. Phys. 62, 4570 (1975).

"Branching Ratios in Reactive Collisions: Theory vs. Experiment", R. B. Bernstein Int. J. Quant. Chem. S9, 385 (1975).

"The Formation of Electronically Excited Products in Chemical Reactions", R. D. Levine, in Electronic Transition Lasers, ed J. I. Steinfeld, (MIT Press, 1976) p. 251.

"Role of Energy in Reactive Molecular Scattering: An Information-Theoretic Approach", R. B. Bernstein and R. D. Levine, Adv. At. Mol. Phys. 11, 215 (1975).

"Chemical Lasers: A Thermodynamic Analysis of a System in Disequilibrium", A. Ben-Shaul, O. Kafri and R. D. Levine, Chem. Phys. 10, 367 (1975).

"Surprise! Analysis and Probability Matrices for Rotational Energy Transfer", R. D. Levine, R. B. Bernstein, P. Kahana, I. Procaccia and E. T. Upchurch, J. Chem. Phys. 64, 796 (1976).

"Cross Sections for Rotational Energy Transfer: An Information-Theoretic Synthesis", I. Procaccia and R. D. Levine, J. Chem. Phys. 64, 808 (1976).

"Collisional Ionization and Elastic Scattering in Alkali-Halogen Atom Collisions", M. B. Faist and R. D. Levine, J. Chem. Phys. 64, 2953 (1976).

"Computational Study of Elastic and Electronically Inelastic Scattering of Br by Ground State I Atoms: Role of Potential Curve Crossing", M. B. Faist and R. B. Bernstein, J. Chem. Phys. 64, 2971 (1976).

"Thermodynamic Functions for State Selected Chemical Reactions", R. D. Levine, Chem. Phys. Lett. 39, 205 (1976).

"Thermodynamic Approach to Collision Processes", in Modern Theoretical Chemistry Dynamics of Molecular Collisions, R. D. Levine and R. B. Bernstein, ed. W. H. Miller (Plenum, New York, 1976), Vol II, p. 323.

"Angular Entropy: The Information Content of Molecular Scattering Angular Distributions", M. B. Faist, R. D. Levine and R. B. Bernstein, J. Chem. Phys. 66, 0000 (1977).

Prepared for Publication:

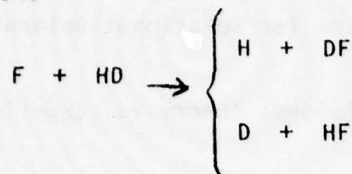
Sung Ho Suck, "Theory of Atom-Diatom Reactive Scattering Based on Distorted Wave Born Approximation".

Thesis:

"Atomic Collision Processes: Role of Curve Crossing", M. B. Faist, Ph.D. Thesis, The Ohio State University, Columbus, Ohio (1975).

## 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

a. Branching Ratios: The information theoretic approach to branching ratios has been applied to a number of different processes. In particular the predicted branching behavior for the



reaction has been experimentally verified by the Toronto group. The main practical conclusion of this work is that for direct, exoergic reactions with low activation barriers, even in the absence of any other knowledge, the 'prior branching ratio, which is very easy (slide rule) to estimate, already provides a useful guide.

b. Electronic Excitation in Collisions: The information theoretic approach to such processes has been reviewed. In addition, exact quantal close coupling computations were carried out for atom-atom collisions. Comparisons were carried out with more approximate (e.g., Landau-Zener) treatments leading to practical conclusions regarding the coupling constants for such processes.

c. Rotational Energy Transfer: The information theoretic analysis and synthesis of cross sections for rotational energy transfer in atom-diatom collision was studied in considerable detail. It was found possible to simulate an entire matrix of state-to-state cross sections by two constants. One of the two is just a scale factor for the absolute magnitude of the cross sections. The relative magnitude are governed (to the first approximation) by a single parameter. It was found possible to provide ready estimates for this parameter which measures the importance of the energy 'mismatch' in the collision.

d. Theoretical Developments: The concept of the 'prior' distribution was clarified. An approximation scheme for converting collinear computations (easy to carry out but not readily comparable to experiment) to 3-dimensional results has been developed. It has since been used by several groups. The concept of 'angular entropy' was examined and interpreted.

e. Macroscopic Systems: Applications of thermodynamic-like methods to macroscopic systems in disequilibrium have been considered. Here the ideas examined by microdisequilibrium have been found useful for macrodisequilibrium as well. The chemical lasers in particular) were examined.

f. Reviews: Several invited reviews, both topical and general, have been published. These illustrate the diverse applications of the information theoretic methodology and present the fundamental assumptions from somewhat difference points of view.

AFOSR Program Manager: Lt Col J. T. Viola

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of Laser Induced Photochemical Kinetics
2. PRINCIPAL INVESTIGATOR: Dr. Ross A. McFarlane  
School of Electrical Engineering  
Cornell University  
Ithaca, New York 14853
3. INCLUSIVE DATES: 1 September 1974 - 31 August 1977
4. GRANT NUMBER: AFOSR 75-2781
5. COSTS and FY SOURCE: \$39,000, FY75; \$40,000, FY76; \$43,360, FY77T.
6. SENIOR RESEARCH PERSONNEL: Dr. D. H. Burde - FY77  
Dr. C. C. Davis
7. JUNIOR RESEARCH PERSONNEL: D. H. Burde - FY75, 76
8. PUBLICATIONS:

"Studies of the Deactivation of Electronically Excited Iodine Atoms,"  
D. H. Burde, R. A. McFarlane, and J. R. Wiesenfeld, presented at the Fourth  
Conference on Chemical and Molecular Lasers, Oct 21-23, 1974, St. Louis, MO.

"Quantum Efficiencies for the Production of Electronically Excited Iodine  
Atoms  $1(5p^5 2p_{1/2})$  following Laser Photolysis of  $I_2$  Near  $5000\text{\AA}$ ", D. H. Burde,  
R. McFarlane, J. Wiesenfeld, Phys. Rev. A10, 1917 (1974).

"Collisional Quenching of Excited Iodine Atoms  $1(5p^5 2p_{1/2})$  by  $I_2$ ", D. Burde,  
R. McFarlane, and J. Wiesenfeld, Chem. Phys. Lett. 32, 296 (1975).

"Collisional Quenching of Excited Iodine Atoms", D. Burde, C. C. Davis, and  
R. McFarlane, presented at the Second Summer Colloquium on Electronic Transi-  
tion Lasers, Sep 17-19, 1975, Woods Hole, Massachusetts.

"Collisional Quenching of Excited Iodine Atoms  $1(5p^5 2p_{1/2})$  by Selected  
Molecules", D. Burde and R. McFarlane, J. Chem. Phys. 64, 1850 (1976).

"Observation of Collisional Release and Complex Photodecomposition Kinetics of  
Molecular Iodine", D. Burde and R. McFarlane, presented at the Third Summer  
Colloquium on Electronic Transition Lasers, Sep 7-10, 1976, Snowmass Village,  
Colorado

"Production of Electronically Excited Iodine Atoms  $1(5p^5 2p_{1/2})$  by Collisional  
Release in Molecular  $I_2$ ", D. Burde and R. McFarlane, Chem. Phys. 16, 295  
(1976).

"Lineshape Effects in Atomic Absorption Spectroscopy", C. C. Davis and  
R. McFarlane, J.Q.S.R.T. 18, 151 (1977).

"Temperature Dependence of the Collisional Deactivation of Excited Iodine Atoms  $I(5p^5\ ^2P_{1/2})^*$ ", D. Burde and R. McFarlane, submitted to J. Chem. Phys.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A new experimental technique has been developed to study gas phase kinetics on a timescale more than two orders of magnitude faster than previously possible. The kinetics of the collisional production and deactivation of electronically excited iodine atoms,  $I^*(^2P_{1/2})$ , were studied by selectively photolyzing molecular  $I_2$  with a short pulse (10 nsec) tunable dye laser. The excited atom population as a function of time following each laser pulse was detected by photoelectrically monitoring the absorption of atomic iodine resonance radiation at 206.2 nm. In this way, kinetic processes on a tens-of-nanosecond timescale were observable.

The primary goal of the project was to obtain the collisional quenching rates of  $I^*(^2P_{1/2})$  by several collision partners of interest in pulsed and CW iodine laser systems. The nonradiative decay by collisional quenching is an important loss mechanism in these lasers and accurate quenching rates are required for computer modelling and efficient laser design. A systematic study of the quenching rate of  $I^*$  as a function of added gas pressure was undertaken. By using a relatively low energy photolysis pulse and employing signal averaging to improve signal-to-noise ratios, many problems which complicated earlier high-energy flash photolysis studies were eliminated. High precision pressure measurement equipment and computer analysis of the digitized waveforms permitted accurate determination of the second order quenching rate constants at 295°K for deactivation of  $I^*$  by  $I_2$ ,  $O_2$ ,  $H_2O$ ,  $D_2O$ ,  $H_2O_2$ ,  $CO_2$ ,  $N_2$ ,  $H_2$ ,  $HD$ , and  $D_2$ . Very significant differences in quenching efficiency were observed in isotopically substituted species and a very high quenching efficiency was found for  $I_2$  and also for  $O_2$ , for which a near resonance  $E \rightarrow E$  energy transfer occurs with  $I^*$ . To further probe the physical processes causing the quenching, the temperature dependence of the quenching rates for  $I_2$ ,  $O_2$ ,  $H_2$ ,  $HD$ , and  $D_2$  were determined. Results of the temperature dependence studies supported the importance of resonant  $E \rightarrow V$  energy transfer for deactivation by  $H_2$ ,  $HD$ , and  $D_2$ . The quenching rate was found to increase with temperature for both  $I_2$  and  $O_2$ , with small activation energies for each.

The second major area of work involved the study of the collisional production of excited atoms ( $I^*$ ) from bound electronically excited states of  $I_2$ . Significant production of  $I^*$  was found for excitation as much as 4.5kT below the dissociation limit of the  $I_2(B)$  state. Using the high speed photolysis system, the concentration of  $I^*$  was seen to continue to rise for several hundred nanoseconds after the laser pulse. By studying the detailed behavior of the rising portion of the signal as a function of pressure, the collisional production of  $I^*$  atoms from bound states of  $I_2$  was confirmed and a kinetic model for this "collisional release" process was developed. In addition, evidence of two photon absorption to a higher lying bound electronic state was uncovered and collisional decomposition from this state was also measured.

The high speed photolysis system developed in the course of this work is extremely versatile and attractive for a variety of gas phase kinetic studies. It provides selective excitation and selective observation as well as excellent sensitivity and speed.

AFOSR Program Manager - John T. Viola, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Fundamental Studies of the Structure and Chemistry of Catalytic Surfaces

2. PRINCIPAL INVESTIGATOR:

Dr. Robert P. Merrill  
Dept of Chemical Engineering  
University of California  
Berkeley, California

Current Address:  
School of Chemical Engineering  
Cornell University  
Ithaca, New York 14853

3. INCLUSIVE DATES: 1 August 1975 to 30 June 1977

4. GRANT NO: AFOSR 76-2926

5. COSTS AND FY SOURCE: \$63,815, FY76; \$21,961, FY77; \$47,809, FY77.

6. SENIOR RESEARCH PERSONNEL:

Dr. D. Dion  
Dr. R. Ducros

Dr. J. J. Ehrhardt

7. JUNIOR RESEARCH PERSONNEL:

A. J. Baumgartner  
M. Komiyama  
D. R. Monroe  
H. H. Sawin

Gar B. Hoflund  
R. I. Masel  
R. J. Purtell  
R. E. White

8. PUBLICATIONS:

"Quantum Scattering from a Sinusoidal Hard-Wall: Atomic Diffraction from Solid Surfaces", R. Masel, R. Merrill and W. Miller, Physical Review, 12 (12), 5545 (1975).

"Crystal Field Surface Orbital-Bond Energy Bond Order (CFSO-BEBO) Calculations for Surface Reactions: I. The Reactions  $\text{CO} + \text{O}_2$ ,  $\text{NO} + \text{CO}$ , and  $\text{H}_2 + \text{O}_2$  on a Platinum (111) Surface", W. Weinberg and R. Merrill, J. Catalysis, 40, 268 (1975).

"Scattering of Argon and Neon from W(112)", R. White, J. Ehrhardt and R. Merrill, J. Chem. Phys., 64 (1), 1 (1976)

"A Semiclassical Model for Atomic Scattering from Solid Surfaces: He and Ne Scattering from W(112)", R. Masel, R. Merrill, and W. Miller, J. Chem Phys., 64 (1), 45 (1976).

"Helium Diffraction from Tungsten (112)", A. Stoll, J. Ehrhardt and R. Merrill, J. Chem Phys., 64 (1), 34 (1976).

"Semiclassical Theories and Quantum Hardwall Calculation of Atom Surface Scattering", R. Masel, R. Merrill and W. Miller, J. Vac. Sci. & Tech., 13 (1), 355 (1976).

"The Interaction of Oxygen with Pt(110)", R. Ducros and R. Merrill, Surface Science, 55, 227 (1976).

"Atomic Scattering from a Sinusoidal Hard Wall: Comparison of Approximate Methods with Exact Quantum Results", R. Masel, R. Merrill and W. Miller, J. Chem. Phys., 65 (7), 2690 (1976).

"A Molecular View of Diffusion and Reaction in Porous Catalysts", R. Merrill, J. Catalysis, 50, 104 (1977).

"Reply to Harold H. Kung", W. Weinberg and R. Merrill, J. Catalysis, 50, 384 (1977).

"Broad-Frequency Chopper with Adjustable Duty Cycle", H. Sawin, D. Wilkinson, W. Chan, S. Smiriga and R. Merrill, J. Vac. Sci. Technol., 14 (5), 1205 (1977).

"The Structure and Chemistry of Oxygen Adsorbed on Pt(111) and its Reactions with Reducing Gases", D. Monroe, PhD Thesis, 1977.

"Concentration Profiles in the Impregnation of Porous Catalysts: Nickel on Alumina", M. Komiyama, M.S. Thesis, 1977

"Scattering Characteristics and Catalytic Activity of Single Crystal Surfaces", R. Masel, PhD Thesis, 1977.

"Sulfur Poisoning of Hydrocarbon Oxidation by Palladium", A. Baumgartner, M.S. Thesis, 1977.

"A Theoretical and Experimental Investigation of the Chemisorption Bond", G. B. Hoflund, PhD, 1977.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The structure and chemistry of solid surfaces in reactive environments has been studied using LEED, Auger spectroscopy, temperature programmed decomposition and atomic scattering techniques which have become almost routine to modern surface science research. Considerable effort during this two year period has been directed toward the development of the use of X-ray and ultraviolet photoelectron spectroscopy which possesses the potential of establishing the electronic structure of adsorbed species. This has included the joint development (with Prof Thor Rhodin at Cornell Univ) of facilities for carrying out angle resolved photoemission at the National Laboratory for Synchrotron Radiation at Stoughton, Wisconsin, and one brief period on-line at Stoughton. Also, during this period the principal investigator has moved his laboratory from Berkeley, California to Ithaca, New York, in order to assume his new duties at Cornell University.

The research has continued to emphasize oxidation catalysis and corrosive oxidation on noble metals, the theory of elastic scattering of atoms from surfaces, molecular orbital representations of chemisorption, H<sub>2</sub> adsorption/desorption kinetics on Pt, the development of new research facilities, and equipment modifications required to complete studies of corrosive inhibition on Al and Ti and hydrazine decomposition on iridium.

In addition to adding capabilities for doing X-ray, ultraviolet, and angle resolved photoemission, fabrication and testing of a UHV to atmospheric catalytic reactor, and final construction of the time-of-flight (TOF) scattering system has been completed. The nozzle beam has been tested satisfactorily with argon and helium and mounted on the scattering chamber. Helium beams up to Mach 8 have been routinely obtained with *in situ* measurement of the TOF distribution. Spatial resolution of this beam is  $0.4^\circ$  as measured from the crystal. Both a liquid nitrogen cooled nozzle and a quartz nozzle for use with  $N_2H_4$  have been successfully tested. Facilities for the introduction and control of  $N_2H_4$  in the beam system are completed. Specular He scattering from a Pt(111) crystal has been observed, demonstrating the operability of the integrated scattering system. The goniometer for manipulating the mass spectrometer has been completed. It can be operated by direct computer control and has  $0.02^\circ$  resolution out of plane and  $0.135^\circ$  resolution in plane. Manipulating the quadrupole mass spectrometer within the vacuum system causes changes in the capacitance of the R. F. cables and it has been necessary to develop an electro-mechanical servo-system to provide dynamic balancing of these R. F. circuits.

Pulse counting detection of the mass spec has been implemented and a digital interface for the Nova computer has been designed, fabricated, but not yet debugged. Computer graphics have also been integrated into the data acquisition system.

The UHV catalytic reactor can measure reaction kinetics from  $10^{-10}$  torr up to atmospheric pressure while monitoring the work function of the surface. Very precise uptake, isothermal desorption, and temperature programmed desorption (TPD) can also be made. The system was tested initially with  $H_2$  adsorption/desorption on Pt(111). Considerable discrepancy exists between the TPD of  $H_2$  observed in other laboratories and that previously observed by Merrill. The source of this discrepancy seems to be the existence of bulk up-take of  $H_2$ , a phenomenon easily revealed by using variable uptake times and comparing both isothermal desorption and TPD.

A differentially pumped helium lamp for ultraviolet photospectroscopy has been constructed and successfully tested. Design of facilities (to be purchased from non-AFOSR funds) for angle-resolved photoemission at the storage ring (Stoughton) was initiated. Considerable time was spent fabricating two new crystal holders for the hydrazine work on Iridium. Because  $N_2H_4$  decomposes at room temperatures, these crystal holders must be cooled to LN<sub>2</sub> temperature in a matter of minutes. Commercially available systems take up to 30 minutes during which considerable background contamination of the iridium surface would occur. A mass spectrometer has been fabricated out of spare parts available in the laboratory. It will be used on the d.c. molecular beam system to permit mass analysis of hydrazine decomposition products during TPD.

Single crystals of Ir, Al, and Ti have been obtained, oriented, and samples prepared. Mechanical polishing techniques which produce a planar surface with minimum strain were far from trivial for Ir and Al.

Theoretical studies completed the development of an exact quantum formulation of atoms from hardwall potentials and the comparison of semi-classical theory with other approximate methods. The final semi-classical calculations for He and Ne on W(112) were presented and the CFSO-BEBO model was applied to surface catalytic reactions of CO, O<sub>2</sub>, NO, CO, H<sub>2</sub>, and O<sub>2</sub> on Pt (111).

The work on  $O_2$  adsorption on Pt(110) has been published and a comprehensive study of  $O_2$  adsorption, corrosive oxidation and their reactions with  $H_2$  and CO have been completed. As with the (110) surface, chemisorbed oxygen reacts with gaseous  $H_2$  and/or CO with unity reaction probabilities and cross sections much larger than the expected cross sections for adsorbed O atoms. Reaction probabilities for the reduction of corrosively oxidized Pt are much lower (one to three orders of magnitude) and highly temperature dependent. Diffusion into the bulk is strongly implicated as a dominant process during corrosive oxidation. Some preliminary work has also been directed toward understanding noble metal oxidation on commercially prepared catalysts and on techniques for controlling the distribution of metallic crystallites in such preparations.

AFOSR Program Manager: R. W. Haffner, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Calculation of Potential Energy Curves for Metal Oxides and Halides
2. PRINCIPAL INVESTIGATOR: Dr. H. Harvey Michels  
United Technologies Research Center  
Silver Lane  
East Hartford, Connecticut 06108
3. INCLUSIVE DATES: 1 June 1973 to 31 March 1977
4. CONTRACT NUMBER: F44620-73-C-0077
5. COSTS AND FY SOURCE: \$30,000 FY 73; \$18,738 FY 74; \$44,311 FY 75;  
\$61,025 FY 76; \$17,000 FY 77; \$35,031 FY 77
6. SENIOR RESEARCH PERSONNEL: R. H. Hobbs
7. JUNIOR RESEARCH PERSONNEL: J. B. Addison
8. PUBLICATIONS:

"Configuration Interaction Studies of the  $\text{HeH}^+$  Molecular Ion. III Singlet  $\Pi$  and Delta States," T. A. Green, H. H. Michels and J. C. Browne, Journal of Chemical Physics, 64, 3951 (1976).

"The Electronic Structure of  $\text{ArF}$  and  $\text{Ar}_2\text{F}$ ," H. H. Michels and R. H. Hobbs, to be published in Chemical Physics Letters, 1977.

"The Electronic Structure of Excimer Molecular Lasers," H. H. Michels and R. H. Hobbs, to be published in The International Journal of Quantum Chemistry, 1977.

"Electronic Structure and Radiative Lifetimes for  $\text{BO}$ ," H. H. Michels, R. Harris and J. Lillis, Electronic Transition Lasers, edited by Jeffrey I. Steinfield, MIT Press, 278 (1976).

"Electronic Structure of Excited States of Selected Atmospheric Systems," H. H. Michels, The Excited State in Chemical Physics, edited by J. Wm. McGowan, 1977.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Calculation of the electronic structure and radiative transition probabilities for certain diatomic molecules which are candidates for visible/UV laser systems were carried out. The objectives of this work were to uncover systems having a low-lying excited state with a reasonably long (greater than 10 microsec) radiative lifetime and situated energetically such that an inversion of population with respect to the dominant transitions to the ground state was possible. Systems studied included the group IIA metal oxides ( $\text{BeO}$ - $\text{BaO}$ ),

group IVA metal oxides (CO-PbO), NF, SiF, AlF and electron sequence:  $N_2^+$ , CN, CO and BeF. The latter systems have a common chemistry of their electronically excited states, including a common  $A^2\Pi \rightarrow X^2\Sigma^+$  Meinel transition, a  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$  first negative transition and a possible metastable  $4\Sigma^+ \rightarrow X^2\Sigma^+$  transition. Among these molecules BaO, BO, NF, SnO, SiF and AlF were studied in detail. Their value as laser candidates was analyzed.

AFOSR Program Manager: Dr. Robert A. Osteryoung

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Lasers and Laser-Induced Kinetic Processes
2. PRINCIPAL INVESTIGATOR: Dr. George C. Pimentel  
Department of Chemistry  
University of California, Berkeley  
Berkeley, California 94720
3. INCLUSIVE DATES: 1 October 1974 - 30 September 1977
4. GRANT NUMBER: AFOSR 74-2616
5. COSTS AND FY SOURCE:
6. SENIOR RESEARCH PERSONNEL: None.
7. JUNIOR RESEARCH PERSONNEL:

T. Schafer  
E. Cuellar  
O. Krogh  
J. Reilly  
E. Sirkin

Y. Lee  
G. Richmond  
D. Stone  
D. Martin

8. PUBLICATIONS:

"Rotational Chemical Lasers from Hydrogen Fluoride Elimination", E. Cuellar, J. Parker, and G. Pimentel, *J. Chem. Phys.* 61, 422 (1974).

"Temperature Dependence of the HF Vibrational Energy Distribution in the Insertion-Elimination Reactions between NH and Fluoromethanes", P. Poole and G. Pimentel, *J. Chem. Phys.* 63, 1950 (1975)

"Chemical Lasers", G. Pimentel, Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research XIX. Photon Chemistry, Oct, 1975.

"Photoelimination of HF by Hexafluoroacetylacetone: A Tandem Laser Study", G. Pimentel, F. Tablas, J. Hartmann, and E. Whittle, *Intl. J. Chem. Kinetics* VIII 877 (1976).

"What is a Chemical Laser? An Introduction", by G. Pimentel and K. Kompa, Chapter I in "Handbook of Chemical Lasers" edited by R.W.F. Gross and J. Bott, J. Wiley & Sons, Inc. (1976)

"Intracavity Dye Laser Spectroscopy as a Gain Probing Technique", J. Reilly and G. Pimentel, *Appl. Optics* 15, 2372 (1976)

"Vibrational Populations in the F+H<sub>2</sub> Chemical Lasers: V→V and V→R,T Energy Transfer Corrections", O. Krogh, D. Stone, and G. Pimentel, *J. Chem. Phys.* 66, 368 (1976).

"CF<sub>x</sub>-H<sub>2</sub> Chemical Lasers: Vibration-Rotation Emission by HF from States with High Rotational Excitation", O. Krogh and G. Pimentel, *J. Chem. Phys.* 67, 2993 (1977).

"Intracavity Dye Laser Spectroscopy Studies of the Ba + N<sub>2</sub>O, Ca + N<sub>2</sub>O + CO, and Sr + N<sub>2</sub>O + CO Reactions", E. Eckstrom, J. Barker, J. Hawley, and J. Reilly, Applied Optics, 16, 2102 (1977).

"HCO Radical Kinetics: Conjunction of Laser Photolysis and Intracavity Dye Laser Spectroscopy", J. Clark, C. Moore and J. Reilly, accepted for publication, J. Chem. Phys. (1977).

"Infrared Fluorescence", G. Pimentel, Chapter 4 in "Vibrational Spectroscopy - Modern Trends", edit. A. J. Barnes and W. Orville-Thomas, Elsevier, NY (1977).

"Thermoluminescence of S<sub>2</sub> in Cryogenic Samples", Y. Lee and G. Pimentel (in preparation).

"Thermoluminescence of SO in Cryogenic Samples", Y. Lee and G. Pimentel (in preparation).

"ClF<sub>x</sub>-H<sub>2</sub> Chemical Lasers: Vibration-Rotation Emission by HCl", O. Krogh and G. Pimentel (in preparation).

"HF Rotational Laser Emission by the ClF-H<sub>2</sub> Chemical Laser", E. Cuellar and G. Pimentel (in preparation).

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

During the grant period, the "Tandem Laser" and "Zero Gain" methods (developed in these laboratories) were exploited to study the primitive vibrational populations obtained in selected chemical reactions

The photolysis of hydrazoic acid, HN<sub>3</sub>, in the presence of fluorinated methanes and argon produces hydrofluoric acid, HF, through imine (NH, probably a <sup>1</sup>Δ) insertion-elimination reactions, but chemical laser emission has not been observed. Nevertheless, by the tandem laser, zero-gain temperature method, the HF vibrational population ratios have been measured as a function of temperature (225-400°K) for CF<sub>4</sub>, CF<sub>3</sub>H, CF<sub>2</sub>H<sub>2</sub>, and CFH<sub>3</sub>. Part of the HF is evidently produced by NH(a <sup>1</sup>Δ) insertion into the C-H bond with subsequent HF elimination. However, there is an unexpected, competing reaction that involves the C-F bonds, either NH insertion-elimination or hot H atom abstraction to form HF.

Driver chemical laser investigation of the effect of hexafluoroacetyl acetone (HFAA) photolysis proved beyond question that the photolysis produces HF in a primary reaction. This study confirms a rather unusual photochemical reaction. The HFAA exists in the enol form and, presumably, the carbonyl group provides the chromophore. Presumably, in the electronically excited state, the hydrogen bond that stabilizes the enol form is broken, permitting internal rotation into a conformation in which the OH and the opposite CF<sub>3</sub> group come into proximity. Elimination of HF and ring closure occurs. Thus this work reveals new type of HF photoelimination reaction that does not require vacuum ultraviolet wavelengths.

All of the ClF<sub>x</sub>-H<sub>2</sub> systems (x=1,3,5) emit both HCl and HF vibration-rotation laser emission. Chain reactions cause these chlorinefluorides to be among the highest gain chemically pumped HF and HCl lasers. Of special interest has been the emission observed from relatively high rotational quantum numbers.

HF vibration-rotation laser emission has been observed up to  $P_1(20)$ ,  $P_2(16)$ , and  $P_3(7)$  for the  $\text{ClF}_5\text{-H}_2$  system. The  $\text{ClF}_5\text{-H}_2$  system emits in HF transitions  $P_1(15)$ ,  $P_2(16)$ , and  $P_3(8)$ . Late threshold times and extended durations point to an energy transfer mechanism that involves rapid  $V\rightarrow R$  deactivation with large  $\Delta J$  coupled with  $V\rightarrow V$  pumping in  $\text{HF}^{\dagger}\text{-HF}^{\dagger}$  collisions to give a cumulative increase in rotational energy. Thus vibrational excitation will tend to "pool" in high  $J$  states for which rotational equilibration is a slow process. Such energy transfer processes and pooling could be a significant factor in the efficiency and spectral composition of chemical laser emission in all HF chemical lasers.

The focus of other attention has been on two rotational laser systems which emit HF rotational laser emission in the  $10$  to  $20\mu$  spectral region. With rather large pressures,  $80$ - $100$  torr of rather concentrated mixtures,  $\text{ClF}_5\text{:H}_2\text{:Ar} = 1\text{:}1\text{:}10$ , laser emission is seen in the spectral region  $985$ - $810\text{ cm}^{-1}$  with extremely long durations, up to  $70\ \mu\text{sec}$ . This corresponds to HF rotational transitions  $J=22\rightarrow 21$  and  $J=24\rightarrow 23$ . The available energy in the  $\text{F} + \text{H}_2$  reaction is insufficient to populate the  $v=0$ ,  $J=22$  state. The photoelimination from 1, 1-difluoroethylene has resulted in HF pure rotational transitions in the range  $J=25\rightarrow 24$  up to  $J=30\rightarrow 29$ . These would be, to our knowledge, the highest  $J$  transitions observed from chemical pumping of HF. The photoelimination laser has a plethora of energy since relatively little is lodged in HF vibration. Nevertheless, the manner in which this much energy ( $40$ - $50$  kcal/mole) becomes concentrated in the rotational degree of freedom is a matter of great interest. Since relatively few collisions are available for energy transfer processes, primitive distributions may be involved.

Two methods were attempted to induce pyrolysis of tetramethyl dioxetane on a time scale sufficiently short to permit a substantial population inversion and electronic transition lasing. In the first method, the dioxetane was mixed with a hydrogen-chlorine mixture and the  $\text{H}_2\text{-Cl}_2$  explosion was initiated through flash photolysis. This experiment was not promising. Severe decomposition occurred, suggesting that the chain carriers in the explosion were reacting with the parent dioxetane. The second approach was based upon shock tube heating. Experiments verified that dioxetane pyrolysis and light emission were taking place. It is plain that the dioxetanes offer a significant opportunity for producing a chemically pumped electronic laser.

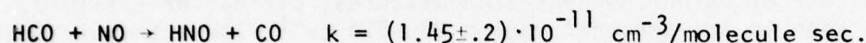
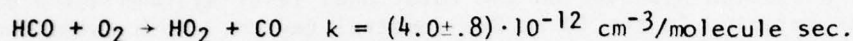
A number of chemical systems were investigated using intracavity dye laser spectroscopy (IDLS) either as a gain probe or in absorption. For the popular electronic laser candidate,  $\text{Ba}(\text{g}) + \text{N}_2\text{O}(\text{g}) \rightarrow \text{BaO}^* + \text{N}_2$ , gain on certain barium atomic transitions was detected but only absorption in the  $\text{BaO}$  transitions. In the corresponding reaction with  $\text{Sn}$  atoms, no positive gain was detected. Evidently, there is more  $\text{SnO}$  in the ground state than in either excited state, despite obvious chemiluminescence. A successful attempt was made to observe upper state electronic absorption from an electronic state of  $\text{Sr}$  atoms populated by the photon flux in the dye laser cavity. The experiment demonstrates the possible applicability of IDLS to excited state spectroscopy in which the dye not only produces the excited state but also reveals its absorption spectrum to still higher levels.

The extremely high sensitivity of the IDLS technique was demonstrated by detection of HF in absorption in the third harmonic,  $v=0\rightarrow 4$ , using a  $70\text{ cm}$  long intracavity cell containing  $10$  torr of HF. Individual rotational components were cleanly detected. Then, to search for laser-induced chemistry,  $22$  torr of HF and  $183$  torr of  $\text{D}_2$  were exposed to  $10^4$  dye laser flashes. Unfortunately,

the D<sub>2</sub> contained 4.4% HD impurity. After exposure, the HD found was larger, 4.7%, but by an amount within experimental uncertainty.

Samples of 2 to 10 torr of C<sub>2</sub>H<sub>4</sub> with and without a few percent O<sub>2</sub> impurity were flash photolyzed. In the presence of the O<sub>2</sub> impurity, absorption band heads at 6138 and 6144 Å were detected. The band heads correspond to known absorptions of HCO produced in chemical reactions of C<sub>2</sub>H<sub>4</sub><sup>\*</sup>, O<sub>2</sub><sup>\*</sup>, and/or O atoms.

In the photolysis of formaldehyde, not only was HCO detected, but the rate constants of two important HCO reactions were measured:



A variety of additional quantities were estimated, including the effect of photolysis wavelength on branching ratio, the rate of deactivation of vibrationally excited HCO, etc.

When free radicals react in a cryogenic matrix (e.g., solid argon) electronically excited products have a significant opportunity to decompose radiatively because of apparently inefficient deactivation processes under these experimental conditions.

The Herzberg bands of O<sub>2</sub> are observed when solid N<sub>2</sub>/Ar = 1/100 mixtures are photolyzed for an hour at 8°K and then warmed to 10-14°K. The photolysis of OCS in solid Ar, Kr, Xe, and SF<sub>6</sub> has also been studied. In every case, warming a few degrees induces thermoluminescence readily attributed to diffusion and reaction of ground state sulfur atoms. The highest frequency progression closely resembles the equivalent of the O<sub>2</sub> Schumann-Runge bands. In addition, there are two additional, distinct progressions at longer wavelengths, neither detected before by any spectroscopic technique. A variety of data indicate that the longer wavelength progression can be assigned to the S<sub>2</sub> A'→X transition. A variety of arguments lead to a rather definite assignment of the other, weaker progression to the S<sub>2</sub> c→a transition.

The observation of electronic transitions never before detected for a molecule as well known as S<sub>2</sub> suggests that this thermoluminescence technique will be of particular interest. We already have detected cryogenic thermoluminescence from SO<sub>2</sub>, SO, and two or three other reaction products whose identity is not yet positive. We believe that this novel technique will be an aid in our understanding of chemical pumping of electronic degrees of freedom.

AOFSR Program Manager: Dr. Francis J. Wodarczyk

### COMPLETED PROJECT SUMMARY

1. TITLE: Poly(fluoroorganophosphazenes)
2. PRINCIPAL INVESTIGATORS: Dr. K. A. Reynard and Dr. A. H. Gerber  
Chemistry Department  
Horizons Incorporated  
Cleveland, Ohio 44122
3. INCLUSIVE DATES: 1 May 1976 - 30 April 1977
4. CONTRACT NUMBER: F44620-76-C-0101
5. COSTS AND FY SOURCE: \$7,003, FY76; \$10,033, FY77; \$23,187, FY78.
6. RESEARCH PERSONNEL: Dr. K. A. Reynard and Dr. A. H. Gerber
7. PUBLICATIONS:

"Poly(fluoroorganophosphazenes)", A. Gerber, Final Technical Report.

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Novel cyclic and polymeric acetylenicphosphazenes of approximate structure  $[(C_6H_5C\equiv C)_2PN]_x$  were prepared by the reaction of alkali phenylacetylide salts and dichlorophosphazenes,  $[Cl_2PN]_x$ . The poly(acetylenicphosphazenes) are readily brominated and are potential intermediates to a variety of novel polyphosphazenes, such as poly(fluoroorganophosphazenes) and poly(ethylenicphosphazenes).

Preparation of cyclic or linear perfluoroalkoxyphosphazenes was unsuccessful. Alkali perfluoroalkoxides were prepared in situ, via alkali fluorides and perfluorocarbonyl compounds, and reacted with dihalophosphazenes,  $(Cl_2PN)_3$ ,  $(F_2PN)_3$ , and  $[Cl_2PN]_n$  polymer.

Chlorination of trifluoroethoxyphosphazenes as a route to cyclic or linear perfluoroethoxyphosphazenes was unsuccessful.

Preparation of perfluoroalkylphosphazenes via organometallic reagents and cyclic or linear dichlorophosphazenes was unsuccessful. The organometallic reagents were selected from  $R_fMgBr$ ,  $R_fMgI$ ,  $R_fCu$ , and  $R_fZnI$ , where  $R_f = n-C_3F_7$ .

A cyclic perfluoroaryloxyphosphazene  $[(C_6F_5O)_2PN]_3$ , was prepared but failed to polymerize at elevated temperature. Directed preparation of linear  $[(C_6F_5O)_2PN]_n$  polymer by substitution of  $[Cl_2PN]_n$  polymer afforded an impure intractable product.

AFOSR Program Manager: Dr. Anthony J. Matuszko

#### COMPLETED PROJECT SUMMARY

1. TITLE: Molecular Behavior Studies of Glassy Polymers Under Stress
2. PRINCIPAL INVESTIGATOR: Dr. William O. Statton  
Department of Materials Science and Engineering  
The University of Utah  
Salt Lake City, Utah 84112
3. INCLUSIVE DATES: 1 May 1975 - 31 October 1976.
4. GRANT NUMBER: AFOSR 75-2827
5. COSTS AND FY SOURCE: \$37,476, FY75.
6. SENIOR RESEARCH PERSONNEL: Dr. S. K. Sikka.
7. JUNIOR RESEARCH PERSONNEL: None.
8. PUBLICATIONS: None.
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall performance of Air Force systems has often been restricted by the limitation of materials used in their construction. Future systems with even higher performance requirements will demand improved materials whose properties can be readily defined and whose structural behavior can be accurately predicted. Several of these materials are amorphous, glassy polymers which are exceptionally important and useful materials having Air Force application. They have the limitation, however, of developing crazes and cracks under stress, leading to failure.

Molecular behavior of two commercially important glassy polymers, polystyrene and polycarbonate, has been studied under tensile stress, cyclic fatigue and in crazing conditions. These polymers are different in their chemical structure and mechanical properties. The primary technique employed in this study is a new Dynamic Infrared Spectroscopy using both the conventional Perkin Elmer Spectrophotometer, as well as the latest computer-equipped Fourier Transform spectrometer. This dynamic technique has been supplemented by standard characterizations, viz., X-ray scattering, dynamic mechanical measurements, tensile testing, density measurements and optical and scanning electron microscopies. Also, X-ray scattering under stress was used for the first time for these glassy polymers.

The study of polystyrene revealed that bulky phenyl side groups on the polymer backbone dictate its mechanical behavior by partially interlocking the chains. Therefore, any external stress is transmitted only to individual portions of the chains, causing distortions of phenyl side groups and breakage of certain phenyl interlockings. These interphenyl interferences have been found to depend upon the processing conditions, particularly the orientation conditions. It has been shown that the initial molecular state of the polymer is irreversibly affected by any small external stress, even before yielding. Cyclic fatigue of TRICITE (biaxially oriented) films causes better packing of polymer chains even though serious molecular level damage occurs in the process. In unoriented films, bulky phenyl side grouped highly restrict the chain mobility, preventing molecular chains to stress-relieve by plastic deformation. This causes chains to stress-relieve by creating crazes on the surface.

Applied stress to unoriented and uniaxially oriented polycarbonate (bisphenol A) was shown to distribute evenly over a large number of polymer chains. Cyclically fatigued polycarbonate films showed a shift of  $\alpha$  and  $\beta$  relaxation peaks toward lower temperatures, indicating an increase in free volume caused by molecular chain scission. Fatigue-crazing and solvent-crazing of polycarbonate have been found to occur via different molecular behavior. Fatigue-crazed material, though similar in surface appearance to solvent-crazed material, is actually damaged extensively throughout at the molecular level, whereas solvent-crazed materials is affected mostly at the surface.

Thus, the present study has shown the viability of the new dynamic infrared technique to studying behavior in glassy polymers under varying tensile stress, fatigue and crazing conditions. An understanding of this molecular behavior is vital to explain and improve end use properties.

AFOSR Program Manager: Dr. Donald R. Ulrich

AD-A056 765

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH BOLLING AFB D C  
ANNUAL AFOSR CHEMISTRY PROGRAM REVIEW (22ND) FY77 (U)  
MAR 78 R W HAFFNER

F/G 5/1

UNCLASSIFIED

AFOSR-TR-78-0001

NL

2 of 2  
AD  
A056765



END  
DATE  
FILMED  
9-78  
DDC

### COMPLETED PROJECT SUMMARY

1. TITLE: Third Summer Colloquium on Electronic Transition Lasers
2. PRINCIPAL INVESTIGATOR: Dr. Jeffrey I. Steinfeld  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139
3. INCLUSIVE DATES: 1 June 1975 - 31 May 1977
4. GRANT NUMBER: AFOSR 75-2826
5. COSTS AND FY SOURCE: \$5,182, FY75; \$5,253, FY76.
6. SENIOR RESEARCH PERSONNEL: None
7. JUNIOR RESEARCH PERSONNEL: None
8. PUBLICATIONS:

"Electronic Transition Lasers II Proceedings of the Third Summer Colloquium", edited by L. Wilson, S. Suchard, and J. Steinfeld; published by M.I.T. Press (June, 1977).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

There is a continuing Air Force need for new laser systems operating at higher efficiencies and shorter wavelengths. To facilitate exchange of information on potentially significant developments in this area, it was felt desirable to conduct a workshop on electronic transition lasers. At such a workshop, researchers in the field would present the results of their research, conduct an open interchange of ideas, and evaluate and assess progress in this area.

At the colloquium/workshop held in September 1975, in Woods Hole, Massachusetts, a number of new laser systems were described. Since it was evident that a considerable amount of development remained to be done on these systems, the colloquium participants decided to convene once again in a year's time. Thus, the Third Summer Colloquium was held in Snowmass, Colorado, in September, 1976. There were 160 registered participants. Approximately 56 papers were presented in seven technical sessions.

The colloquium was extensively reported by Laser Focus magazine in its January 1977, issue. Complete proceedings have been published by the M.I.T. Press.

AFOSR Program Manager: John T. Viola, Lt Col, USAF

### COMPLETED PROJECT SUMMARY

1. TITLE: Transition Metal Compounds with Potential Electronic and Radiation Resistant Properties
2. PRINCIPAL INVESTIGATOR: Professor F. Gordon A. Stone  
Department of Inorganic Chemistry  
The University  
Bristol BS8 ITS, England
3. INCLUSIVE DATES: 1 August 1971 - 31 July 1976
4. GRANT NUMBER: AFOSR 71-2090
5. COSTS AND FY SOURCE: \$24,984, FY71; \$9,870, FY74; \$9,870, FY75; \$9,900, FY76.
6. SENIOR RESEARCH PERSONNEL: Dr. M. I. Bruce  
Dr. M. Green  
Dr. S. A. R. Knox
7. JUNIOR RESEARCH PERSONNEL:

G. K. Barker	J. L. Davidson	P. K. Maples
R. L. Bennett	C. H. Game	R. P. Phillips
D. H. Bowen	R. C. F. Gardner	G. Shaw
Miss J. Browning	R. D. George	B. Sosinsky
W. E. Carroll	B. L. Goodall	J. L. Spencer
J. Clemens	J.A.K. Howard	B. F. Taylor
C. H. Davies	A. C. Laguna	B. J. Thomson
		A. J. Welch

### 8. PUBLICATIONS:

"Chemistry of the Metal Carbonyls. Part LXIII. New Cluster Carbonyl Compounds Containing Platinum and Iron", M. Bruce, G. Shaw and F. Stone, J. Chem. Soc. 1082 (1972)

"Chemistry of the Metal Carbonyls. Part LXIV. New Cluster Carbonyl Compounds Containing Platinum and either Ruthenium or Osmium", M. Bruce, G. Shaw and F. Stone, J. Chem. Soc., 1781 (1972)

"Chemistry of the Metal Carbonyls. Part LXV. Reactions Between Dodecacarbonyl Triruthenium and Tertiary Phosphines or Arsines", M. Bruce, G. Shaw and F. Stone, J. Chem. Soc., 2094 (1972)

"Metallation and Related Reactions with  $\pi$ -Cyclopentadienyl-ruthenium Complexes", M. Bruce, R. Gardner and F. Stone, J. Org. Chem., 40, C39, (1972)

"Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXIV. Chloronitrosylbis(triphenyl-, methylphenyl- and dimethylphenyl-phosphine) ruthenium and Nitrosyl(triphenylphosphine)iridium", J. Clemens, M. Green and F. Stone, J. Chem. Soc., 375, (1973).

- "Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXV. Phosphine-, Phosphite- and Cyclo-octa-1,5-diene Platinum Complexes", J. Browning, H. Empsall, M. Green and F. Stone, J. Chem. Soc., 381, (1973)
- "Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXVI. 1,1,1-Tris(diphenylphosphinomethyl)- and 1,1,1-Tris(diphenylarsinomethyl)-ethane", P. Maples, M. Green and F. Stone, J. Chem. Soc., 388 (1973)
- "Metallocarboranes: New Syntheses", J. Spencer, M. Green and F. Stone, Chem. Comm., 1178 (1972)
- "Chemistry of the Metal Carbonyls. Part LXVI. Complexes Derived from a Carbon-ylosmium Anion", R. George, S. Knox and F. Stone, J. Chem. Soc., 972, (1973)
- "Triaryl Phosphite Derivatives of Dodecacarbonyltriruthenium", M. Bruce, G. Shaw and F. Stone, J. Chem. Soc., 1667 (1973)
- "Lewis Acid Promoted Vinyl-rearrangement and Halogen-exchange of Platinum-fluoroolefin Complexes", P. Maples, M. Green and F. Stone, J. Chem. Soc., 2069, (1973)
- "Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXVIII. Nickelocene and Tricarbonyl( $\pi$ -allylic)cobalt Complexes with Bis(trifluoromethyl)diazomethane", J. Clemens, M. Green and F. Stone, J. Chem. Soc., 93, (1974).
- "Cyclometallation Reactions. Reactions of Benzo[h]quinoline", M. Bruce, B. Goodall and F. Stone, J. Org. Chem., 60, 343 (1973)
- "Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXIX. Zero-valent Nickel and Platinum Complexes with Hexafluorobut-2-yne and Hexakis(trifluoromethyl)benzene", J. Browning, M. Green, J. Spencer, and F. Stone, J. Chem. Soc., 97, (1974)
- "Reaction of Amines with Nickel, Palladium and Platinum Complexes Containing Isocyanide and Fluorocarbon Ligands", C. Davies, C. Game, M. Green and F. Stone, J. Chem. Soc., 357, (1974)
- "Formation of Tetrahydropentalenyl Complexes from Organo-silicon and-germanium (carbonyl)ruthenium Compounds", S. Knox, R. Phillips and F. Stone, J. Chem. Soc. 658, (1974)
- "Tin(IV) Halide Promoted Vinyl Rearrangement of Hexafluorobuta-1,3-diene-platinum Complexes", P. Maples, M. Green and F. Stone, and J. Spencer, J. Chem. Soc., 1194 (1974).
- "The Synthesis and Crystal Structure of a Carbadibora-allyl Nickel Complex", M. Green, J. Howard, J. Spencer and F. Stone, J.C.S. Chem. Comm., 153 (1974)
- "Formation of closo- and nido-Metallocarboranes from closo-C<sub>2</sub>B<sub>9</sub> and -C<sub>2</sub>B<sub>7</sub> Carboranes; Molecular Structures of closo-1,1-(Me<sub>2</sub>PhP)<sub>2</sub>-2,4-Me<sub>2</sub>-1,2,4-PtC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> and nido-10,10-(Et<sub>3</sub>P)<sub>2</sub>-2,8-Me<sub>2</sub>-10,2,8-PtC<sub>2</sub>B<sub>7</sub>H<sub>7</sub>", M. Green, J. Spencer, F. Stone and A. Welch. J.C.S. Chem. Comm., 571 (1974)

"Synthesis of a Boron Analogue of Co-ordinated Cyclobutadiene; Molecular Structures of closo- and nido- $L_2PtC_2B_6H_6R_2$  [ $L = PMe_3$  or  $PEt_3$ ;  $R = H$  or  $Me$ ]", M. Green, J. Spencer, F. Stone and A. Welch, J.C.S. Chem Comm. 794, (1974).

"2-(Phenylazo)phenyl Complexes of Iridium(III)", M. Bruce, B. Goodall, F. Stone, and B. Thomson, Austral. J. Chem., 27, 2135 (1974).

"Reactions of Fluorinated Ketones with Ferrocenes", M. Bruce, F. Stone and B. Thomson, J. Organometal Chem., 77, 77 (1974).

"Metallaborane Chemistry. Oxidative-insertion Reactions of 11-atom Carborane and Metallacarborane Species with Zerovalent Nickel, Palladium and Platinum Complexes", M. Green, J. Spencer, F. Stone and A. Welch, J. Chem. Soc., 179 (1975).

"Reactions of Hexafluoroacetone, Hexafluoropropene, and Tetrafluoroethylene with Bis(cyclo-octa-1,5-diene)platinum; Molecular Structure of  $[Pt_2\{(CF_3)_2CO\}\{1,5-C_8H_{12}\}_2]$ ", M. Green, J. Howard, A. Laguna, M. Murray, J. Spencer and F. Stone, J.C.S. Chem. Comm., 451, (1975).

"Metallaborane Chemistry. Oxidative-insertion Reactions of 11-atom Monocarbon Carborane Species with Zerovalent Nickel, Palladium and Platinum Complexes; the Molecular and Crystal Structure of  $1,1-(Bu^tNC)_2-2-NMe_3-1,2-PdCB_{10}H_{10}$ ", W. Carroll, M. Green, F. Stone and A. Welch, J. Chem. Soc., 2263, (1975).

"Metallaborane Chemistry. Reactions of Zerovalent Nickel and Platinum Complexes with arachno-5,9- $C_2B_7$  Carboranes; Crystal and Molecular Structure of a carbadibora-allyl Nickel Complex", M. Green, J. Howard, J. Spencer and F. Stone, J. Chem. Soc., 2274, (1975).

"Synthesis of nido- and closo-Diplatinacarborane Complexes by Direct Insertion; Crystal and Molecular Structures of closo- $2,3-[(Et_3P)_2]-1,2,3,6-CPt_2CB_5H_7$ , nido- $1,4,8-[(Me_3P)_2Pt]-8,8-[(Me_3P)_2]-7,8,10-CPtCB_8H_{10}$  and nido- $8,8-[(Me_3P)_2]-7,8,10-CPtCB_8H_{10}$ ", G. Barker, M. Green, J. Spencer, F. Stone, B. Taylor, and A. Welch, J.C.S. Chem. Comm., 804, (1975).

"Formation of Tetra- and Trinuclear Cluster Complexes from Tetra-carbonylnickel and Hexafluorobut-2-yne; The Molecular Structures of  $[Ni_4(CO)_4(CF_3C_2CF_3)_3]$  and  $[Ni_3(CO)_3(CF_3C_2CF_3)(C_8H_8)]$ ", J. Davidson, M. Green, F. Stone and A. Welch, J. Amer. Chem. Soc., 97, 7490, (1975)

"Cyclometallation Reactions. Some Reactions of Cyclopentadienyl Ruthenium Phosphine Complexes", M. Bruce, R. Gardner and F. Stone, J. Chem. Soc., 81, (1976)

"Formation of 16-Electron Alkyne Complexes by Reaction of Halo(tricarbonyl) ( $\eta^5$ -cyclopentadienyl)-molybdenum and -tungsten Complexes with Alkynes; Crystal and Molecular Structure of  $[WCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$ ", J. Davidson, M. Green, F. Stone, and A. Welch, J. Chem. Soc., 738, (1976)

"Insertion Reactions of Hexafluorobut-2-yne, Tetrafluoroethylene and Hexafluoroacetone with  $\eta^5$ -Cyclopentadienyl-Iron, -Ruthenium, -Palladium and -Molybdenum Complexes: Molecular and Crystal Structures of  $[\text{Fe}_2(\text{CO})(\text{C}_4(\text{CF}_3)_4\text{CO})(\eta^5\text{-C}_5\text{H}_5)_2]$  and  $[\text{Fe}(\text{COCF}_2\text{C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)]$ ", J. Davidson, M. Green, F. Stone and A. Welch, J. Chem. Soc., 1976, in press.

"Syntheses Involving Coordinatively Unsaturated Cyclopentadienyl-molybdenum and -tungsten Complexes: Molecular and Crystal Structure of  $[\text{Mo}(\text{C}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{C}_5\text{H}_5)(\text{CF}_3\text{C}_2\text{CF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ", J. Davidson, M. Green, F. Stone and A. Welch, J. Chem. Soc., in press.

"Cyclopentadienylruthenium Phosphine Complexes. Some Complexes Derived from 1-Alkynes: Molecular and Crystal Structure of the Cumulene Derivative  $[\text{Ru}(\text{C}(\text{CF}_3)_2\text{C}(\text{H})\text{C}(\text{CF}_3)_2\text{C}:\text{C}:\text{CH}(\text{CF}_3))(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ", M. Bruce, R. Gardner, J. Howard, F. Stone, M. Welling and P. Woodward, J. Chem. Soc., in press

"Transition Metal Compounds with Potential Electronic and Radiation Resistant Properties", F. Stone, Final Technical Report.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Advances have been made in two main areas of organometallic chemistry: (a) Polynuclear metal complexes, and (b) Chemical activation of small molecules by metal complex formation.

New metal cage structures containing nickel, palladium or platinum atoms have been prepared by polyhedral expansion of carboranes with zero-valent complexes of these metals. Entirely new structural types have been identified for the first time including a diplatinum complex in which one metal atom is located within the cage of boron and carbon atoms while the second is external to the cage but joined to it by a Pt-Pt and a Pt-B bond. In another area of metal cluster chemistry several polynuclear carbonyl compounds of ruthenium and platinum have been characterized, as have two novel nickel complexes  $[\text{Ni}_4(\text{CO})_4(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)_3]$  and  $[\text{Ni}_3(\text{CO})_3(\mu_3\text{-C}_8\text{H}_8)(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)]$ . In the latter, a planar C<sub>8</sub> ring bridges a nickel triangle, whereas in the former structure three acetylene ligands bridge faces of a Ni<sub>4</sub> tetrahedron.

Several new cyclometallation reactions have been identified, particularly involving the group  $[\text{Ru}(\text{Ph}_3\text{P})(\eta^5\text{-C}_5\text{H}_5)]$  and azobenzene derivatives. Numerous fluorocarbon metal complexes have been prepared by oxidative-addition reactions of d<sup>8</sup> and d<sup>10</sup> metal compounds. The activation of carbon-fluorine bonds towards substitution by chlorine or bromine has been demonstrated for fluoro-olefin metal complexes. Novel insertion products have been obtained by reacting hexafluoro-but-2-yne, tetrafluoroethylene and hexafluoroacetone with cyclopentadienyl-iron, -ruthenium, -palladium and -molybdenum complexes. A detailed study has been made of the chemical reactivity of the 16-electron complexes  $[\text{MCl}(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$  (M = Mo, W).

The research is described in detail in the 33 journal articles listed above.

AFOSR Program Manager: Dr. Anthony J. Matuszko

### COMPLETED PROJECT SUMMARY

1. TITLE: Applied Quantum Chemistry of Nonmetallic Materials
2. PRINCIPAL INVESTIGATOR: Professor John R. Van Wazer  
Department of Chemistry  
Vanderbilt University  
Nashville, Tennessee 37235
3. INCLUSIVE DATES: 1 February 1972 - 31 October 1976
4. GRANT NUMBER: AFOSR 72-2265
5. COSTS AND FY SOURCE: \$44,934, FY72; \$26,369, FY73; \$40,475, FY74;  
\$40,474, FY75; \$24,959, FY76.
6. SENIOR RESEARCH PERSONNEL:  

Dr. Ilyas Absar	Dr. Raymond Gangi
Dr. Patrick Coffey	Dr. James Howell
Dr. James Eberhardt	Dr. Roman Osman
Dr. Carl Ewig	

#### 7. PUBLICATIONS:

"An Ab Initio LCAO-MO-SCF Study of the Electronic Structure of Phosphirane and Thirane", I. Absar, L. Schad and J. Van Wazer, Theoret. Chem. Acta, 29, 173 (1973).

"Role of Sulfur d Orbitals in Isothiocyanic Acid and an Electronic-Structure Comparison with Isocyanic Acid", J. Howell, I. Absar and J. Van Wazer, J. Chem. Phys., 59, 5895 (1973)

"Electronic Structures of Dinitrogen Tetroxide and Diboron Tetrafluoride and an Analysis of Their Conformational Stabilities", J. Howell and J. Van Wazer, J. Amer. Chem. Soc., 96, 7902 (1974)

"Electronic Structures of Phosphorus Pentafluoride and Tetrafluorophosphorane", J. Howell, J. Van Wazer and A. Rossi, Inorg. Chem., 13, 1747 (1974).

"An Ab Initio Study of the Role of d Orbitals in Chlorosilane", J. Howell and J. Van Wazer, J. Amer. Chem. Soc., 96, 3064 (1974).

"DVMO (Directed-Valence Molecular Orbital) Method: A Rotationally Invariant Approximate MO Method Preserving Direct-Valence Effects", P. Coffey and J. Van Wazer, J. Chem. Phys., 61, 85 (1974)

"Electronic Density in Molecules and Molecular Orbitals", J. Van Wazer and I. Absar, Academic Press, New York, 1975

"A Pseudopotential SCF Method for Valence-Only Molecular Calculations", P. Coffey, C. Ewig and J. Van Wazer, J. Amer. Chem. Soc., 97, 1656 (1975)

"Use of Pseudopotential Theory to Study Molecular Structure: The Phosphorus Halides", C. Ewig, P. Coffey and J. Van Wazer, Inorg. Chem., 14, 1848 (1975)

"On Pseudopotential and Effective-Potential SCF Theory and Its Application to Compounds of Heavy Elements", C. Ewig and J. Van Wazer, J. Chem. Phys., 63, 4035 (1975)

"On the Use of Pseudopotential Theory to Study Molecular Structure: II. A NOCOR Calculation of the  $P_4$  and  $P_2$  Molecules and Their Interconversion", R. Osman, P. Coffey and J. Van Wazer, accepted by Inorg. Chem.

"Molecular Pseudopotential Calculations on Transition-Metal Complexes:  $Ni(CO)_4$ , and  $Pt(CO)_4$ ", R. Osman, C. Ewig and J. Van Wazer, submitted to Chem. Phys. Letters.

"The Use of Pseudopotentials in Calculating Barriers to Molecular Internal Rotation", C. Ewig and J. Van Wazer, submitted to J. Chem. Phys.

"Ab Initio Model Potentials in Molecular Pseudopotential Calculations", C. Ewig and J. Van Wazer, submitted to Chem. Phys. Letters.

"Applied Quantum Chemistry of Nonmetallic Materials", J. R. Van Wazer, Final Technical Report.

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The emphasis in the work carried out under this grant has been: (1) improved techniques for carrying out SCF calculations with the purpose of obtaining good quality molecular wavefunctions at much reduced cost and (2) computations on various molecules to obtain a better understanding of the electronic structure and physical properties of materials. In the first area, effort was first directed towards improved semi-empirical methods, but this approach was abandoned as not being very fruitful. Since a key savings in semi-empirical calculation results from the omission of the core orbitals from the calculation, various attempts were made to carry out ab initio calculations using a simplified treatment of the core orbitals. One of these approaches (later called the NOCOR method) based on a screening potential to replace the core-valence Coulombic and exchange interactions and a Phillips-Kleinman pseudopotential to replace orthogonality constraints turned out to be very successful in the preliminary studies and was chosen for further development.

During the period of this grant, two working versions of the NOCOR method were developed. The first, which is easy to set up and apply, assumed an exponential form for the screening potential, with a single function being used to describe the entire core of each of the constituent atoms as sensed by all of the different valence orbitals in the molecule. To the approximation of the minimum-Slater description of the constituent atomic orbitals in LCAO-SCF molecular calculation, this approach was quite satisfactory as shown by comparison of the NOCOR results on a number of different molecules with all-electron SCF calculations on the same molecules in the same basis set. This means that the agreement with experimental data was quite satisfactory; and, for those heavier molecules for which all-electron SCF calculations were not available, similar concordance with experimental data was also seen.

In order to obtain more accurate results in replacing the core electrons with a screening function and a pseudopotential operator, the NOCOR procedure was revised to include a manifold of screening functions - not necessarily exhibiting exponential forms. By employing a different screening function for each unique constituent atomic orbital in the valence shell a considerably more detailed description of the valence/core interaction is achieved - a description which ought to be suitable all the way to the Hartree-Fock limit. In order concomitantly to improve the action of the pseudopotential operator, the value of this operator is revised at each SCF iteration in order that the precise orthogonality conditions for the molecular orbitals be properly represented when reiteration is complete. In a calculation on the  $I_2$  molecule both of these improvements were shown to give better results in a minimum-Slater basis set than had been obtained previously.

While the theoretical work described above was going on, quantum chemical studies were being carried out on various molecules to give better insight as to their electronic structure. Several papers dealt with the thesis previously developed by this group that the delocalized molecular orbitals obtain from SCF calculations are about as readily understandable and interpretable in chemical terms as are the localized orbitals derived from them. Furthermore, certain delocalized orbitals of one molecule reappear practically unchanged in appropriately related other molecules. These "molecularly invariant" orbitals should be of great importance for prediction and interpretation in practical chemistry. Another interesting study, carried out on chlorosilane, showed that, when d character is allowed only to the silicon, the usual population analysis indicates a  $p\pi - d\pi$  transfer of charge from the chlorine to the silicon; but, when d character is allowed only to the chlorine, this approach shows just a polarization of the chlorine. On the other hand, electron-density plots demonstrated that the detailed distribution of charge between the chlorine and the silicon atoms in this molecule is about the same in these two cases (that are described so differently by the formality of a Mulliken population analysis). Electronic structures of a number of other molecules, using both the NOCOR and conventional SCF methods, were also calculated and interpreted.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Unsaturated Organosilicon Heterocycles
2. PRINCIPAL INVESTIGATOR: Professor William P. Weber  
Department of Chemistry  
University of Southern California  
Los Angeles, California 90007
3. INCLUSIVE DATES: 1 October 1972 - 30 September 1976
4. GRANT NUMBER: AFOSR 73-2424
5. COSTS AND FY SOURCE: \$37,242, FY73; \$33,062, FY74; \$25,402, FY75;  
\$29,357, FY76.
6. SENIOR RESEARCH PERSONNEL: Dr. Michael Dexheimer  
Dr. Thomas Ito  
Dr. Il Nam Jung
7. JUNIOR RESEARCH PERSONNEL:

Michael Childs  
Raymond Felix  
Karl Koenig  
Michelle Radcliffe

Bruce Rosen  
H. N. Soysa  
Phillip Valkovich

8. PUBLICATIONS:

"Synthesis and Mass Spectral Behavior of Representative 1, 1-Dichloro-2-phenyl-cyclopropanes and 1,1-Dichloro-2-ferrocenylcyclopropanes", G. Gokel, J. Shepherd, and Wm. Weber, H. Boettger, J. Holwick, and D. McAdoo, J. Org. Chem., **38**, 1913 (1973)

"Reaction of Deuterium Chloride with cis- and trans- $\beta$ -Trimethylsilylstyrene", K. Koenig and Wm. Weber, J. Am. Chem. Soc., **95**, 3416 (1973)

"Mass Spectrometry of Organosilicon Compounds - Some Examples of Interaction of the Silyl Center with Remote Functional Groups", Wm. Weber and H. Boettger, Intra-Science Reports, **7**, 107 (1973).

"The Reaction of Bromine with cis and trans- $\beta$ -Trimethylsilyl Styrene", K. Koenig and Wm. Weber, Tetrahedron Letters, 2533 (1973).

"Addition of H S to  $\alpha,\omega$ -Dienes to Yield Medium Sized Heterocycles 1,1-Dimethyl-1-sila-5-thiacyclooctane", Wm. Weber and K. Koenig, Tetrahedron Letters, 3151 (1973).

"Reaction of 1,2-Glycols with Dichlorocarbene Produced by Phase Transfer Catalysis", Wm. Weber, P. Stromquist, and M. Radcliffe, Tetrahedron Letters, 4523 (1973).

"Unsaturated Organosilicon Heterocycles", K. Koenig, R. Felix, and W. Weber, J. Org. Chem., 39, 1539 (1974)

"The Effect of a Neighboring Trimethylsilyl Group on the Photochemical and Mass Spectral Fragmentation Pathways of S-Alkyl Thioacetates", T. Ito and W. Weber, J. Org. Chem., 39, 1691 (1974).

"Synthesis and Mass Spectra of  $\omega$ -(Trimethylsilyl) Alkyl Methyl Sulfides and Sulfones", T. Ito and W. Weber, J. Org. Chem., 39, 1694 (1974).

"Observations on the Mechanism of Reduction of Sulfones to Sulfides", W. Weber, P. Stromquist, and T. Ito, Tetrahedron Letters, 2595 (1974).

"Pyrolytic and Photochemical Fragmentation of 1,1-Dimethyl-2-Phenyl-1-Silacyclobutane", P. Valkovich, T. Ito and W. Weber, J. Org. Chem., 39, 3542 (1974).

"Copyrolysis of 1,1-Dimethyl-2-phenyl-1-silacyclobutane and Acrolein", W. Weber and P. Valkovich, J. Org. Chem., 40, 229 (1975).

"Synthesis of Unsaturated Organosilicon Heterocycle-Reaction of Silylene with Cyclic Dienes", M. Childs and W. Weber, Tetrahedron Letters, 4033 (1974).

"A Convenient Synthesis of 1,2-Dimethyltetramethoxydisilane", M. Childs and W. Weber, J. Organometal. Chem., 86, 169 (1975)

"Pyrolysis of 1-Phenyl-1,3-Butadienes, A New Synthesis of 1,2-Dihydronaphthalenes", P. Valkovich, J. Conger, F. Castiello, T. Brodie, and W. Weber, J. Am. Chem. Soc., 97, 901 (1975).

"Synthesis and Pyrolysis of 1,1-Dimethyl-2-Phenyl-1-Silacyclobut-2-ene", P. Valkovich and W. Weber, Tetrahedron Letters, 2153 (1975).

"Copyrolysis of 1,1-Dimethyl-1-Silacyclobutane and Acrolein", P. Valkovich and W. Weber, J. Org. Chem., 99, 231 (1975).

"Radical Chain Reactions of Halomethyldimethylsilanes", I. Jung and W. Weber, J. Org. Chem., 41, 946 (1976)

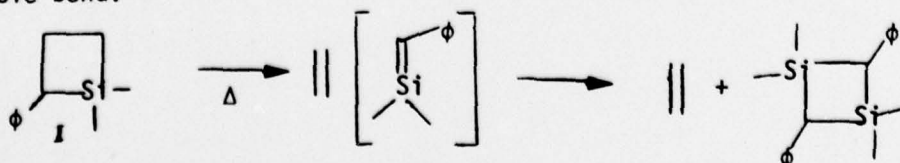
"Copyrolysis of Sym-Tetramethoxydimethyldisilane with 2,5-Dimethylfuran", M. Childs and W. Weber, J. Org. Chem., 41, 1799 (1976).

"Mercury Sensitized Photolysis of Pentamethyldisilane and Sym-Tetramethyldisilane", I. Jung and W. Weber, J. Org. Chem., 114, 257 (1976).

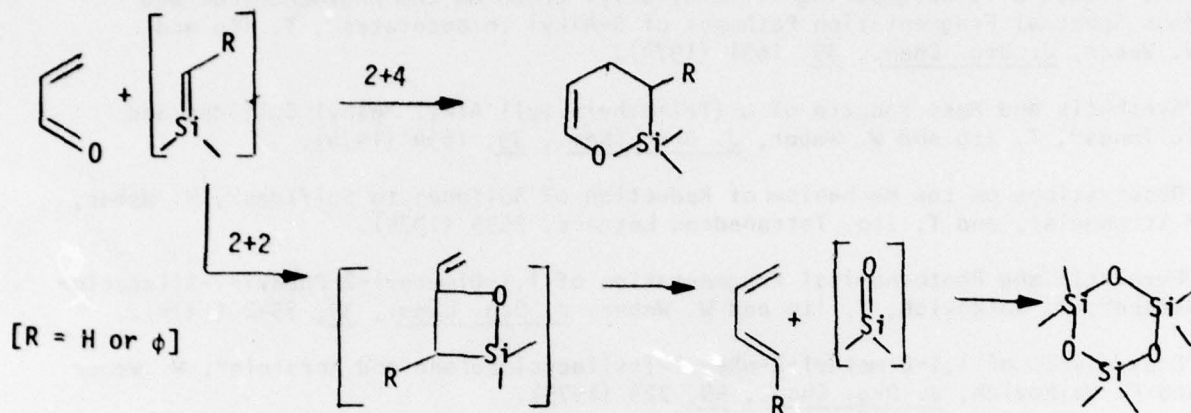
"Unsaturated Organosilicon Heterocycles", W. Weber, Final Technical Report.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

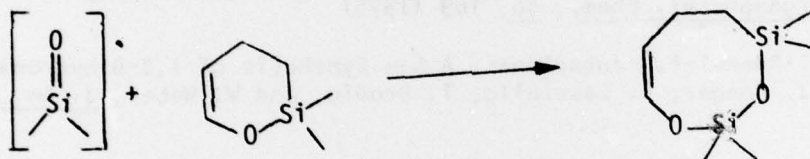
1,1-Dimethyl-2-phenyl-1-silacyclobutane (I) was prepared. Gas phase pyrolysis of I led to ethylene and a reactive intermediate possessing a carbon-silicon double bond.



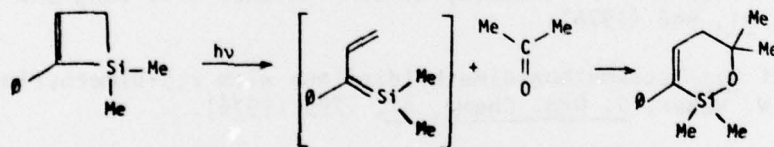
The cycloaddition reactions of such reactive carbon-silicon doubly bonded intermediates with acrolein were studied. It was found that carbon-silicon doubly bonded intermediates undergo both 2+2 and 2+4 cycloaddition reactions.



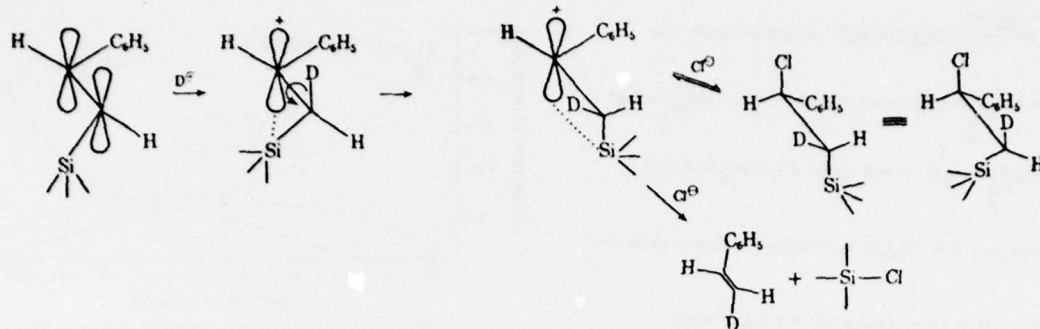
The insertion of silicon-oxygen doubly bonded intermediates into Si-O single bonds was observed. This is of potential importance since it may permit chemistry on the backbone of silicon polymers.



In order to generate intermediates possessing Si-C double bonds photochemically, we prepared 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene. On photolysis, ring opening occurs to yield an intermediate possessing a Si-Si double bond conjugated to a C-C double bond. The cycloaddition reactions of this intermediate with acetone were studied.



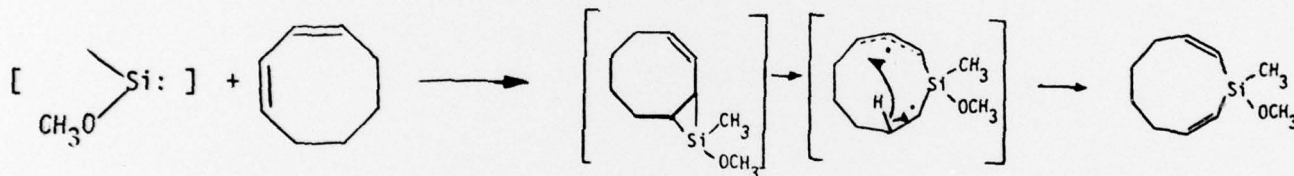
Work was done to determine the sensitivity of vinylic carbon-silicon bonds to electrophilic cleavage. The stereochemistry of such cleavage reactions provided insight into the mechanism by which such bonds are cleaved by electrophiles. Specifically, it was found that trans- $\beta$ -trimethyl-silylstyrene was cleaved by deuterium chloride to yield styrene in which the deuterium had replaced silicon. Similar results were obtained with cis- $\beta$ -trimethylsilylstyrene.



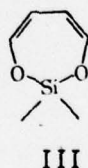
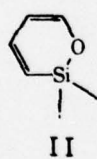
Cleavage of *cis*- and *trans*- $\beta$ -trimethylsilylstyrene with bromine likewise resulted in retention of stereochemistry. These results could be explained by a *cis* addition followed by a *trans* elimination mechanism.

Work on the effect of neighboring trimethylsilyl groups on the photochemical and mass spectral fragmentation pathways of *S*-alkyl thioacetates was carried out. Both sulfur-alkyl and sulfur-acyl bond scission were shown to be primary processes.

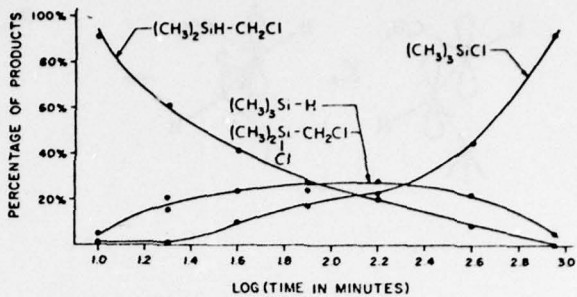
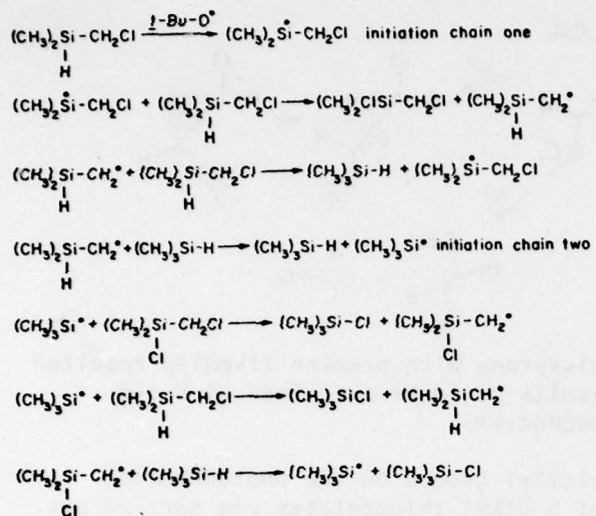
Insertion reaction of silylenes into unsaturated organic molecules was found to be a most direct synthetic approach to the preparation of unsaturated organosilicon heterocycles. Thus the reaction of methoxymethylsilylene with 1,3-cyclooctadiene led to 1-methoxy-1-methyl-1-sila-2,8-cyclononadiene.



The reaction of methoxymethylsilylene with 2,5-dimethylfuran yields two interesting compounds: 2-methoxy-2,3,6-trimethyl-1-oxo-2-silacyclohexa-3,5 diene (II) and 2-methoxy-2,4,7-trimethyl-1,3-dioxo-2-silacyclohepta-4,6-diene (III).



The photolysis of chloromethyldimethylsilane occurs by a pair of radical chain reactions leading to formation of trimethylsilane and chloromethyl-dimethylchlorosilane at short reaction times and trimethylchlorosilane at long reaction time. Similar results were found when the reaction was initiated by di-*t*-butyl peroxide decomposition.



Time dependence of the product ratios in the radical chain reactions of chloromethyl dimethylsilane initiated by di-tert-butyl peroxide.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Energies and Conformations of Molecules
2. PRINCIPAL INVESTIGATOR: Dr. Kenneth B. Wiberg  
Department of Chemistry  
Yale University  
New Haven, Connecticut 06520
3. INCLUSIVE DATES: 1 February 1972 - 31 August 1976
4. GRANT NUMBER: AFOSR 72-2239
5. COSTS AND FY SOURCE: \$52,186, FY72; \$29,850, FY73; \$40,925, FY74; \$40,871, FY75.
6. RESEARCH PERSONNEL:

Helen A. Cannon  
G. Barney Ellison

Kevin S. Peters  
John J. Wendoloski

7. PUBLICATIONS:

"Distorted Geometries at Carbon", K. Wiberg and G. Ellison, Tetrahedron, 30, 1573 (1974).

"Calorimetric Data Collection Using Computers", K. Wiberg, Computers & Chemistry, 1, 64 (1976)

"Electronic States of Organic Molecules. 1. Potential Functions for the Deformation of Methane", K. Wiberg, G. Ellison and J. Wendoloski, J. Am. Chem. Soc., 98, 1212 (1976).

"Correlation Between Ionization Potentials and MO Energy Levels", K. Wiberg, G. Ellison, C. Brundle and N. Kuebler, Chem. Phys. Lett., 41, 37 (1976).

"Enthalpy of the Metal Catalyzed Isomerizations of Quadricyclane and of Tricyclo [4.1.0.0<sup>2,7</sup>]heptane", K. Wiberg and H. Connon, J. Am. Chem. Soc., 98, 5411 (1976).

"Electronic States of Organic Molecules. 2. Vibrational Intensities for Ethylene", K. Wiberg and J. Wendoloski, J. Am. Chem. Soc., 98, 5465 (1976).

"Electronic States of Organic Molecules. 3. Photoelectron Spectra of Cycloalkenes and Methylenecycloalkanes", K. Wiberg, G. Ellison, J. Wendoloski, C. Brundle and N. Kuebler, J. Am. Chem. Soc., 98, 7179 (1976)

"Kinetics and Thermochemistry of the Rearrangement of Benzvalene to Benzene. An Energy Sufficient but Non-Chemiluminescent Reaction", N. Turro, C. Renner, T. Katz, K. Wiberg and H. Connon, Tetrahedron Letters, 4133 (1976).

"Infrared Intensities. Derivation of C-H Bond Moments from Out-of-Plane Bending Modes", K. Wiberg and J. Wendoloski, Chem. Phys. Lett., in press.

"Vibrational Spectrum of Bicyclo[1.1.0]butane", K. Wiberg and K. Peters, Spectrochim. Acta, in press.

"Electronic States of Organic Molecules. 4. Ultraviolet Spectrum of Bicyclobutane", K. Wiberg, G. Ellison and K. Peters, J. Am. Chem. Soc., in press.

"Electronic States of Organic Molecules. 5. High Resolution Spectrum of the A State of Cyclobutane", K. Wiberg, K. Peters, G. Ellison and F. Alberti, J. Am. Chem. Soc., in press.

"Rydberg States of Butadiene", K. Wiberg, K. Peters, G. Ellison and J. Dehmer, submitted to J. Chem. Phys.

"Energies and Conformations of Molecules", K. Wiberg, Final Technical Report.

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Energies and conformations of molecules were investigated in several different ways. The effect of angular distortion was studied by ab initio calculations of the energies of variously distorted methanes. The results could be related to the deformation energies found in small ring compounds. The photoelectron spectra of a series of cycloalkenes and methylenecycloalkanes were studied and the ionization potentials compared with the results of ab initio calculations. A remarkably good linear relationship was found, from which information on the reorganization energy and change in correlation energy on going to the ions could be derived.

Vibrational intensities in ethylene and related molecules were examined and led to information on the magnitudes of bond dipoles, and to charge distributions. Again, comparison with ab initio calculations provided the key to understanding the intensities.

The ultraviolet spectrum of bicyclobutane and of various deuterium substituted derivatives was examined. The high resolution spectrum of the first transition permitted determination of the equilibrium geometry of this state.

An automated calorimetric system was developed. The heats of isomerization of quadricyclane, tricyclo[4.1.0.0<sup>2,7</sup>]octane and benzvalene were determined.

AFOSR Program Manager: Dr. Anthony J. Matuszko

### COMPLETED PROJECT SUMMARY

1. TITLE: *State Identification of Reaction Products*
2. PRINCIPAL INVESTIGATOR: Richard N. Zare  
Department of Chemistry  
Columbia University  
New York, New York 10027
3. INCLUSIVE DATES: 1 June 1973 - 28 February 1977
4. GRANT NO: AFOSR 73-2551
5. COSTS AND FY SOURCE: \$40,350, FY73; \$77,000, FY74; \$78,000, FY75;  
\$75,000, FY76.

6. SENIOR RESEARCH PERSONNEL:

Dr. David Brewer  
Dr. Friedrich Engelke  
Dr. J. Gary Pruett  
Dr. Gregory P. Smith

Dr. Paul J. Dagdigian  
Dr. Ron C. Estler  
Dr. Robert S. Sander

7. JUNIOR RESEARCH PERSONNEL:

Mr. Henry U. Lee  
Mr. David Lubman  
Mr. John Choi

Mr. Charles R. Dickson  
Ms. Diane Welch

8. PUBLICATIONS:

"Radiative Lifetimes of the Alkaline Earth Monohalides", P. Dagdigian, H. Cruse and R. N. Zare, *J. Chem. Phys.* 60, 2330 (1974).

"Tunable Laser Fluorescence Method for Product State Analysis", P. Dagdigian and R. N. Zare, *Science* 185, 739 (1974).

"Primitive Angular Distribution Studies of Internal States in Crossed-Beam Reactions Using Laser Fluorescence Detection", P. Dagdigian and R. N. Zare, *J. Chem. Phys.* 61, 4450 (1974).

"Product State Analysis of BaO from the Reactions Ba + CO<sub>2</sub> and Ba + O<sub>2</sub>", P. Dagdigian, H. Cruse, A. Schultz and R. N. Zare, *J. Chem. Phys.* 61, 4450 (1974).

"Flame Emission Studies of Ozone with Metal Alkyls: Zn(CH<sub>3</sub>)<sub>2</sub> and Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>", H. Lee and R. Zare, *Combustion and Flame* 24, 27 (1975).

"Laser Fluorescence Study of AlO Formed in the Reaction Al + O<sub>2</sub>: Product State Distribution, Dissociation Energy, and Radiative Lifetime", P. Dagdigian, H. Cruse and R. N. Zare, *J. Chem. Phys.* 62, 1824 (1975).

"Lifetime-Separated Spectroscopy: Observation and Rotational Analysis of the BaO A' <sup>1</sup>Π State", J. Pruett and R. Zare, *J. Chem. Phys.* 62, 2050 (1975).

"A New Electronic Band System of PbO", R. Oldenberg, C. Dickson and R. N. Zare, *J. Mol. Spectrosc.* 58, 283 (1975).

"Efforts to Develop a Prototype Electronic-Transition Laser From the Chemical Reactions of Laser-Generated Metal Vapors", C. Dickson, H. Lee, R. Oldenberg and R. N. Zare, *Proceedings of the Second Summer Colloquium on Electronic Transition Lasers*, Woods Hole, Massachusetts, Sep 17-19, 1975 (MIT Press).

"State-to-State Reaction Rates: Ba + HF ( $v=0,1$ ) + BaF( $v=0-12$ ) + H", J. Pruett, and R. N. Zare, *J. Chem. Phys.* 62, 2050 (1975).

"Laser Fluorimetry", R. N. Zare, *Lecture Notes in Physics*, Vol. 43, (Springer-Verlag, New York, 1975) p. 112.

"Crossed-Beam Chemiluminescent Studies of Alkaline Earth Atoms with  $\text{ClO}_2$ ", F. Engelke, R. Sander and R. N. Zare, *J. Chem. Phys.* 65, 1146 (1976).

"The Four-Centre Reaction of  $\text{I}_2 + \text{F}_2$  Studied by Laser-Induced Chemiluminescence in Molecular Beams", F. Engelke, J. Whitehead and R. N. Zare, *General Discussion No. 62 on "Potential Energy Surfaces"*, Faraday Society, 1976 (in press).

"Crossed-Beam Chemiluminescence: The Alkaline Earth Rearrangement Reaction  $\text{M} + \text{S}_2\text{Cl}_2 \rightarrow \text{S}_2^* + \text{MCl}_2$ ", F. Engelke and R. N. Zare, *Chem. Phys.* 19, 327 (1977).

"Determination of Absolute Photon Yields Under Single-Collision Conditions", C. Dickson, S. George and R. N. Zare, *J. Chem. Phys.* (accepted for publication).

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Two major research objectives were set: (1) develop the necessary information to help assess the feasibility of a chemically-pumped electronic-transition laser; and (2) develop techniques to permit the study of state-to-state reaction rates. In the first case, we have shown that most chemiluminescent reactions under single-collision conditions have small ( $\leq 1\%$ ) yields of electronically excited products but with increasing pressure (on the order of a few Torr) the yields increase, and in some cases exceed 50%. Here the yield or branching ratio refers to the fraction of excited state molecules produced per metal atom consumed. With yields of this magnitude one can be assured that certain upper state vibrational levels show inversion with respect to other ground state vibrational levels, even without making gain measurements. Nevertheless, the task of creating a laser system by this manner seems to face a number of obstacles such as the characteristic short radiative lifetime compared to times of mixing, the difficulty of working with metal vapor without particle formation, and the difficulty of concentrating many excited-state molecules in a specific ( $v', J'$ ) level from reactive pumping.

Studies of the dynamics of chemical reactions using a crossed-beam or a beam-gas configuration have proved to be particularly fruitful when laser techniques are employed to either prepare the reactants, or to probe the products or both. The first experiments were demonstrated in which it was possible to measure the scattering angle of a product in a specific internal state ( $\text{Ba} + \text{KCl}$ ), to

measure the product internal state distribution as a function of reactant initial state [Ba + HF (v=0, or v=1)], or cause chemiluminescent reaction to proceed by laser preparation of the reactant ( $I_2^* + F_2$ ). Because of the generality of the laser techniques employed, it is anticipated that many other reaction systems can be similarly investigated.

AFOSR Program Manager: John T. Viola, Lt Col, USAF