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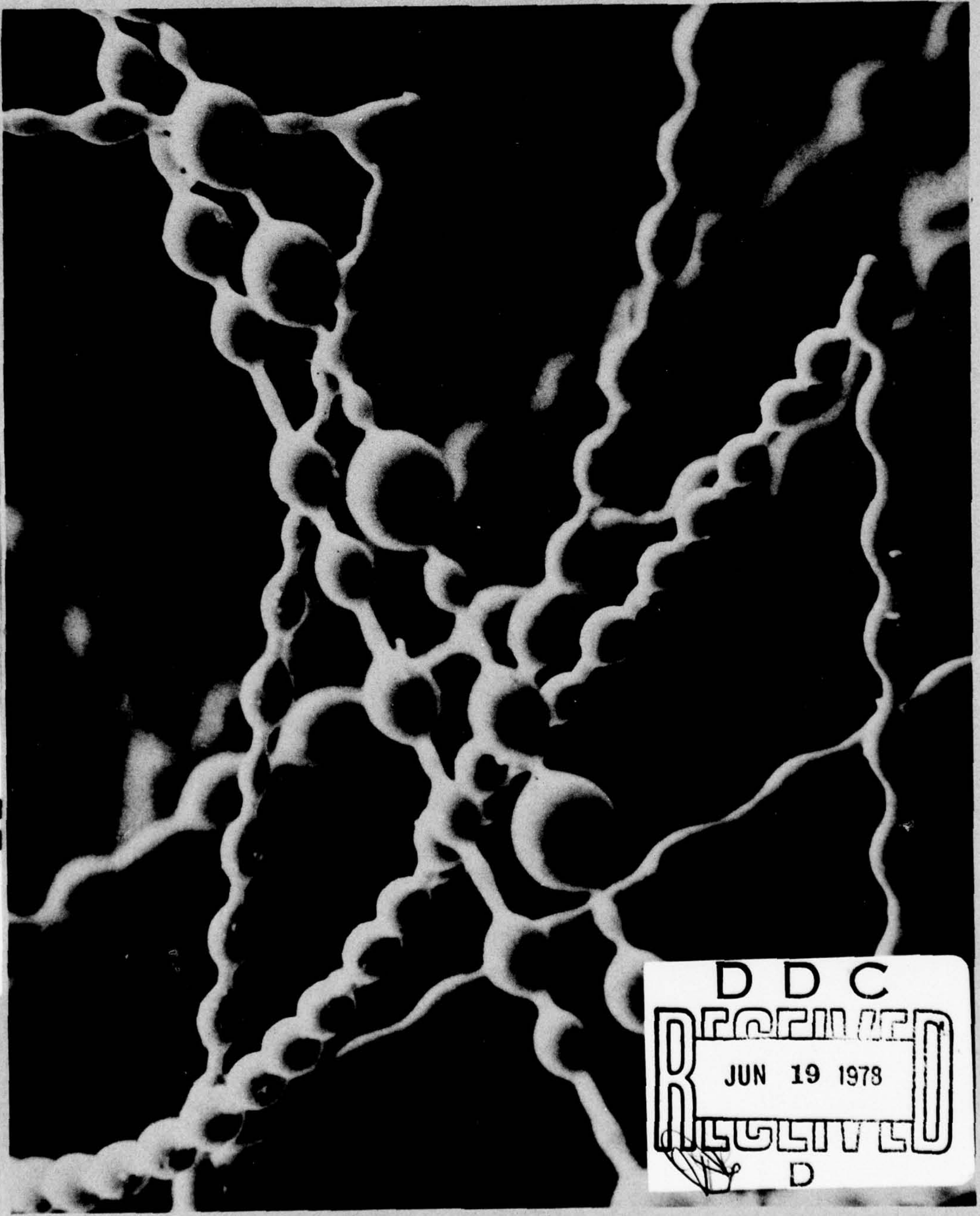

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COVER

When polymeric polysilane formed by Professor Robert West of the University of Wisconsin (AFOSR 74-2644), from a mixture of Me_2SiCl_2 and $PhMeSiCl_2$ was thermally decomposed by K. S. Mazdiyasni of the Air Force Materials Laboratory, very large and transparent greenish black whiskers of β-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 β-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. Mazdiyasni, Metals and Ceramics Division, AFML.)

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This review provides a record of research in progress, along with illustrative achievements resulting from the basic research program of the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFSC). The first section of the 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.

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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
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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.

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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 judgements 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 reams "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/$SOCl_2$ 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 (Southhampton 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)
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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.[19] 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 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 "Chloroaluminate Equilibria in AlCl$_3$-NaCl Melts".[9] 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.

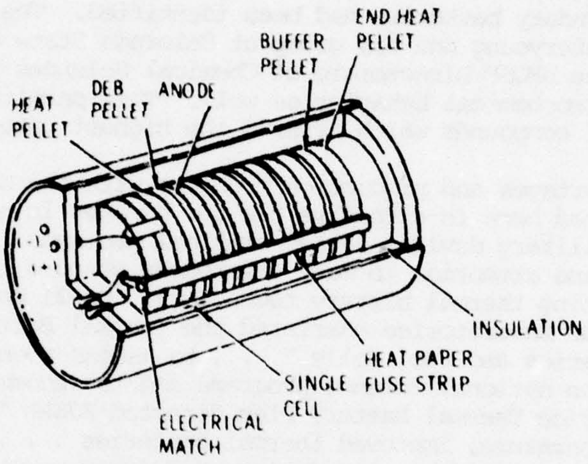
By 1972 numerous potential electrochemical couples (anodes and cathodes) for both primary and secondary batteries had been identified. The extensive work of Dr. Robert Osteryoung and his group at Colorado State University under support from the AFOSR Directorate of Chemical Sciences provided insight 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."

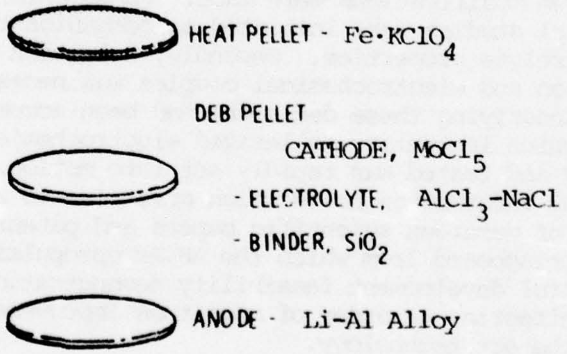
In response two program modifications were made. Fundamental anode and cathode electrochemical studies were initiated as companion to ongoing work on physical and electrolyte properties. Secondly, selection of optimum electrolyte composition and electrochemical couples was necessary. The fundamental 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

	$LiAl/NaAlCl_4/MoCl_5$			
	Single Cell[a]	Battery[b]		LiCl/KCl Battery[c]
	Achieved	Achieved	Projected	State of the Art
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 Density, mA/cm^2	35.5	43	350	50
Energy Density, Wh/lb	N/A	15	42	1.0

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[a] Ref. Nos. 16 and 21.

[b] Ref. No. 19.

[c] 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.

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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.

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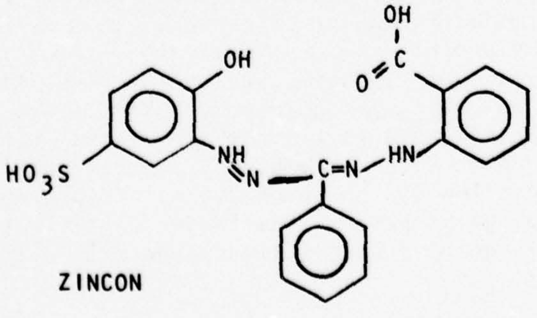
CHEMICAL TECHNIQUES

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 multicomponent 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.



ZINCON

(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 Cu^{++}, Zn^{++}, Hg^{++}, Fe^{+++}, Cd^{++}, AND 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 Zn^{++}, Cd^{++}, and Hg^{++} undergo rapid reaction.

$$\text{M(Zincon)} + \text{CyDTA} \xrightarrow{k_n} \text{M(CyDTA)} + \text{Zincon}$$

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.

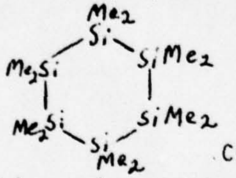
SILICON CARBIDE FROM ORGANOPOLYSILANES

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 organosilicons 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.[1] 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. Mazdiyasni, 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 Mazdiyasni 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.[2]



COMPOUND I

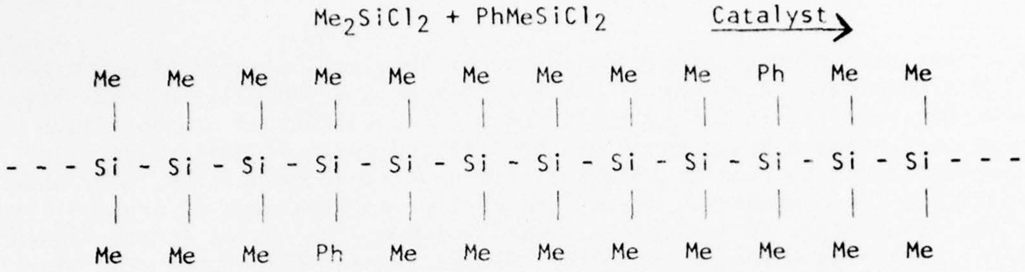
Me = $-CH_3$

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

In 1976, Yajima and coworkers[1] reported that melt spinning of permethylpolysilane or "polycarbosilane", $(Me_2Si)_n$, 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 $PhMeSiCl_2$ in the condensation polymerization of Me_2SiCl_2

leads to moderately high polymer as the direct product, thus eliminating the preparation of I and fractionation of the polymer. The resultant polymer must have phenyl groups at random positions along the chain.[3]



$$Me_2SiCl_2 + PhMeSiCl_2 \xrightarrow{\text{Catalyst}}$$

$$\begin{array}{ccccccccccccccccccccccccc} & Me & & Me & & Me & & Me & & Me & & Me & & Me & & Me & & Me & & Ph & & Me & & Me & \\ & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & \\ --- & Si & - & Si & - & Si & - & Si & - & Si & - & Si & - & Si & - & Si & - & Si & - & Si & - & Si & - & Si & --- \\ & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & \\ & Me & & Me & & Me & & Ph & & Me & & Me & & Me & & Me & & Me & & Me & & Me & & Me & \end{array}$$

COMPOUND II

Ph = Phenyl

The composition of the polymer (Compound II) depends on the amount of $PhMeSiCl_2$ introduced into the mixture. Samples of varying composition have been prepared for AFML by West. Mazdiyasni at AFML has pyrolyzed these polymeric polysilane samples in an inert atmosphere producing the interconnecting "rosary bead-like" whiskers shown below.

This work together with the results of pyrolyzing a mixture of porous Si_3N_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.[4]

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.

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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 Si_3N_4", K. Mazdiyasni 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, multicomponent 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.

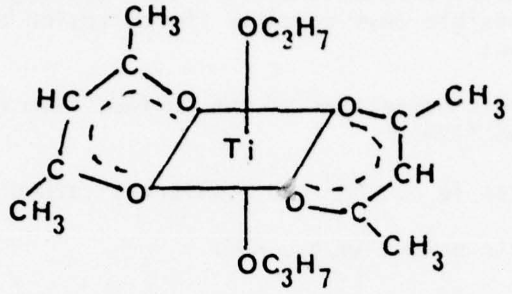
More detail about ongoing corrosion research programs follows:

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 ClO_3, $Na_2Cr_2O_7$ and 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:

$$4Al + 3O_2 + 2H_2O \rightarrow 4AlO(OH)$$

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:



Nibium and tantalum alkoxides will also be studied to determine if these metals form multioxide coatings with aluminum.[1]

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.

$$Ag|AgCl|MCl_n(C_1)|\text{membrane}|MCl_n(C_2)|AgCl|Ag$$

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.[2]

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 [illegible] 1000Å. 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.[3]

- Introduce a catalyst (e.g., Pb[3]) to accelerate cathodic reaction.

- Introduce a cathodic poison (e.g., Pb[4]).

- Induce the formation of a passive surface film by introducing elements such as Cr[5] or Ta[6].

- Extend the passive range of potentials by introducing elements such as 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).

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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.

Duration of Support	Number of "PIs"	Duration of Support	Number of "PIs"
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

FY	Expenditures (thousands)
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	George Burns Department of Chemistry University of Toronto Toronto, Canada M5S 1A1
Fast Ion Transport in Solids (DWE) AFOSR-77-3427, 2303/D1	Alan V. Chadwick and John H. Strange Department of Chemistry University of Kent Canterbury, Kent, U.K.
Nucleophillic Substitution Reactions of Alkyl, Vinyl, and Aryl Trifluoromethanesulfonates (AJM) AFOSR-77-3241, 2303/D9, ASEE Mini Grant	William D. Closson Department of Chemistry State University of New York Albany, New York 12222
Kinetics Studies Involving Electronically-Excited Interhalogens and Halogens (JTV) AFOSR-75-2843, 2303/B1	M. A. A. Clyne Department of Chemistry Queen Mary College London E1 4NS, England
Chemical Kinetic Studies Involving NF Radicals (RAO) AFOSR-78-3507, 2303/B1	M. A. A. Clyne Department of Chemistry Queen Mary College London E1 4NS, England
Novel Chemical Laser Systems (JTV) AFOSR-73-2550, 2303/B1	Terrill A. Cool School of Applied & Engineering Physics Cornell University Ithaca, New York 14853
Elastohydrodynamic Lubrication Studies (RWH) AFOSR-77-3229, 2303/D9, ASEE Mini Grant	John N. Crisp Department of Mechanical Engineering University of Dayton Dayton, Ohio 45469
Synthesis and Spectroscopic Investigation of Inorganic Materials Possessing Unusual Electronic Properties (DRU) AFOSR-76-2932, 2303/A3	Glenn A. Crosby Department of Chemistry Washington State University Pullman, Washington 99163
Chemical Reactions that Produce Electronically Excited Metal Atoms (JTV) AFOSR-75-2822, 2303/B1	Paul Davidovits Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167
Double Layer Structure and Electrode Kinetics (DWE) AFOSR-76-3027, 2303/A1	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	K. L. DeVries College of Engineering University of Utah Salt Lake City, Utah 84112
Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials (AJM) AFOSR-75-2749, 2303/B2	Michael J. S. Dewar Department of Chemistry University of Texas Austin, Texas 78712
Relation of Structure to Properties in Graphite Fibers (DRU) AFOSR-77-3436, 2303/A3	Russell J. Diefendorf Department of Materials Engineering Rensselaer Polytechnic Institute Troy, New York 12181
Investigation of Electron Attachment Processes in Polyatomic Molecules (JTV) F49620-77-C-0071, 2303/B1	Jerry T. Dowell IRT Corporation 7650 Convoy Court San Diego, California 92138
Evaluation of Chemical Research Relevant to Current and Projected U. S. Air Force Interests (DWE) F44620-75-C-0001, 2303/A1	Joseph E. Earley Department of Chemistry Georgetown University Washington, D.C. 20057
Picosecond Laser Studies of Excited State Proton Transfer (AJM) AFOSR-77-3407, 2303/B2	Kenneth B. Eisenthal Department of Chemistry Columbia University New York, New York 10027
Rates of Rapid Chemical Reactions (RWH) AFOSR-77-3255, 2303/A2	Edward M. Eyring Department of Chemistry University of Utah Salt Lake City, Utah 84112
One- and Two-Photon Optically Pumped Laser Devices: New Chemical Laser Diagnostics and Kinetic Probes (JTV) AFOSR-76-3056, 2303/B1	Robert W. Field Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
The Structure and Properties of Polymeric Materials (DRU) AFOSR-77-3293, 2303/A3	Paul J. Flory Department of Chemistry Stanford University Stanford, California 94305
Gordon Research Conference on Molecular Energy Transfer (JTV) AFOSR-77-3371, 2303/B1	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	Arthur Fontijn AeroChem Research Laboratories, Inc. Princeton, New Jersey 08540
Structural Studies of Monomeric Model Compounds and Related Ordered Polymer Systems (DRU) AFOSR-77-3267, 2303/D9, ASEE Mini Grant	Albert V. Fratini Department of Chemistry University of Dayton Dayton, Ohio 45469
Chemical and Physical Aspects of Mesophase Formation During Carbon-Carbon Composite Processing (DRU) F49620-78-C-0006, 2303/A3	J. J. Gebhardt Re-entry and Environmental Systems Division General Electric Company Philadelphia, Pennsylvania 19101
Theoretical and Computational Studies of Electronic Transitions in Molecular Collisions (JTV) F44620-74-C-0073, 2303/B1	Thomas F. George Department of Chemistry University of Rochester Rochester, New York 14627
Microscopic Theory of Electronic Transitions in Molecular Rate Processes (JTV) F49620-78-C-0005, 2303/B1	Thomas F. George Department of Chemistry University of Rochester Rochester, New York 14627
Absolute Rate Constants for Combustion Reactions Involving Free Radicals (JTV) F44620-75-C-0067, 2303/B1	D. M. Golden Stanford Research Institute Menlo Park, California 94025
Influence of Annealing on the Strengths of Secondary Relaxations in Glasses (DRU) AFOSR-73-2540, 2303/A3	Martin Goldstein Belfer Graduate School of Science Yeshiva University New York, New York 10033
Selective Chemical Pumping of Electronic States (RAO) AFOSR-78-3515, 2303/B1	James L. Gole School of Chemistry Georgia Institute of Technology Atlanta, Georgia 30332
New Materials for Electrochemical Cells (DWE) AFOSR-77-3402, 2303/A1	John B. Goodenough and Peter G. Dickens Inorganic Chemistry Laboratory Oxford University Oxford, OX1 3QR, England
Processing Mechanisms, Structure, and Morphology of High-Temperature Polymeric Alloys (DRU) F49620-77-C-0046, 2303/A3	Ian L. Hay Physics Research Department Celanese Research Co. Summit, New Jersey 07901

Structure-Property-Environmental Relations in Glass and Glass-Ceramics (DRU) AFOSR-77-3210, 2303/A3	Larry L. Hench Department of Materials Science University of Florida Gainesville, Florida 32611
Energy Disposal in Electronically Excited Halogen Atoms and Molecular Oxygen (RAO) AFOSR-78-3513, 2303/B1	Paul L. Houston Department of Chemistry Cornell University Ithaca, New York 14853
Solid State Materials Derived from Planar Metal Complexes (AJM) F44620-76-C-0006, 2303/B2	Leonard V. Interrante and John S. Kasper General Electric Co. Research & Development Center Schenectady, New York 12301
NMR Study of Viscoelastic Fluids and Elastomers Under Extreme Conditions of Temperature and Pressure (DRU) AFOSR-77-3185, 2303/A3	Jiri Jonas Department of Chemistry University of Illinois Urbana, Illinois 61801
Effect of Structure on Physical Polymer Interactions and Properties (DRU) AFOSR-76-2983, 2303/A3	Frank E. Karasz Polymer Science & Engineering University of Massachusetts Amherst, Massachusetts 01002
Phosphorus Chemiluminescence Feasibility Studies for an Ultraviolet and Visible Chemical Laser (JTV) AFOSR-77-3376, 2303/B1	Ahsan U. Khan and Brian Stevens Department of Chemistry University of South Florida Tampa, Florida 33620
Novel Organophosphorus and Organonitrogen Derivatives and their Use for the Synthesis of Unusual Transition Metal Complexes (AJM) AFOSR-75-2869, 2303/B2	R. Bruce King Department of Chemistry University of Georgia Athens, Georgia 30601
Post Doctoral Resident Research Associateship Program (RWH) F44620-76-C-0084, 2303/D8	R. W. Kinney Commission on National Resources National Research Council, NAS/NAE Washington, D.C. 20418
Spectroscopic Determination of Intermolecular Potentials of Gas Laser Components and of Major Atmospheric Constituents (JTV) AFOSR-77-3269, 2303/B1	William Klemperer Department of Chemistry Harvard University Cambridge, Massachusetts 02138
The Measurement of Vibrational Intensities for Infrared Active Exhaust Plume Species from Advanced Propellant Rocket Boosters (JTV) F49620-77-C-0075, 2303/B1	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	Aron Kuppermann *Division of Chemistry and Chemical Engineering* California Institute of Technology Pasadena, California 91109
Synthesis of Organofluorine Compounds by Direct Fluorination (AJM) AFOSR-76-3031, 2303/B2	Richard J. Lagow Department of Chemistry University of Texas Austin, Texas 78712
Analysis of Lubricant Films in Bearings Under Incipient Failure Conditions (RWH) AFOSR-78-3473, 2303/A2	James L. Lauer Department of Mechanical Engineering Rensselaer Polytechnic Institute Troy, New York 12181
Chemical Transfer Lasers (JTV) AFOSR-76-2959, 2303/B1	Paul H. Lee Department of Physics University of California Santa Barbara, California 93106
Solid Propellant Additives from Pentaborane-9 (AJM) AFOSR-77-3301, 2303/D9	Amos J. Leffler Department of Chemistry Villanova University Villanova, Pennsylvania 19085
Energy and Chemical Change (JTV) AFOSR-77-3135, 2303/B1	Raphael D. Levine and John M. Deutch Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Structure and Properties of Glasses (DRU) AFOSR-75-2764, 2303/A3	John D. Mackenzie Materials Department University of California Los Angeles, California 90024
Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants (RWH) F44620-76-C-0097, 2303/A2	L. R. Mahoney Fuels and Lubricants Department Ford Motor Co. Dearborn, Michigan 48121
Charge Transport Modes in Nickel Hydroxide Electrodes (DWE) AFOSR-76-2987, 2303/A1	Joseph T. Maloy Department of Chemistry University of West Virginia Morgantown, West Virginia 26506
Low Temperature Fluorine Chemistry of Electronegative Elements (AJM) AFOSR-77-3165, 2303/B2	Gleb Mamantov Department of Chemistry University of Tennessee Knoxville, Tennessee 37916

1977 Gordon Conference on Inorganic Chemistry (AJM) AFOSR-77-3370, 2303/A1	Dale W. Margerum Department of Chemistry University of Rhode Island Kingston, Rhode Island 02881
Anisotropic and Electro-Optical Effects in Liquid Crystals (DWE) F49620-77-C-0017, 2303/A1	J. David Margerum Hughes Research Laboratories Hughes Aircraft Co. Malibu, California 90265
Fabricable Polymers for Matrices and Adhesives Which Are Extremely Stable to Heat, Oxidation and Hydrolysis (AJM) AFOSR-77-3112, 2303/B2	Carl S. Marvel Department of Chemistry University of Arizona Tucson, Arizona 85721
Experimental Studies of the State-to-State Chemical Dynamics of Reactions Involving Air Triatomics (JTV) AFOSR-77-3348, 2303/B1	Robert J. McNeal and William H. Steier Graduate Center for Engineering and Computer Sciences University of Southern California Los Angeles, California 90007
Kinetics and Mechanisms of Reactions in the Sisler UDMH Process (AJM) AFOSR-MIPR-77-0002, 2303/B2	William McQuistion Propellant Sciences Department Naval Surface Weapons Center Silver Spring, Maryland 20910
Structure and Chemistry of Surfaces (RWH) F49620-77-C-0118, 2303/A2	Robert P. Merrill School of Chemical Engineering Cornell University Ithaca, New York 14853
Calculation of the Energetics and Collision Dynamics for Electronic Transitions (JTV) F49620-77-C-0064, 2303/B1	Harvey H. Michels United Technologies Research Center United Technologies Corporation East Hartford, Connecticut 06108
Energy Paths in Chemical Reactions (JTV) AFOSR-78-3535, 2303/B1	C. Bradley Moore Department of Chemistry University of California Berkeley, California 94720
The Relation Between the Chemical and Physical Structure and the Mechanical Response of Polymers (DRU) F44620-76-C-0075, 2303/A3	Robert P. Morgan McDonnell Douglas Research Labs McDonnell Douglas Corp. St. Louis, Missouri 63166
Ion Photofragment Spectroscopy - Potential Surfaces of Molecular Ions (JTV) F44620-76-C-0095, 2303/B1	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	Royce W. Murray Department of Chemistry University of Rhode Island Kingston, Rhode Island 02881
Chemical Physics of Charge Mechanisms in Nonmetallic Spacecraft Materials (DRU) F49620-77-C-0113, 2303/A3	Joseph E. Nanevicz Electromagnetic Sciences Laboratory Stanford Research Institute Menlo Park, California 94025
Investigation of Electrochromic Diphthalocyanines (AJM) F49620-77-C-0074, 2303/B2	M. M. Nicholson Electronics Research Division Rockwell International Corp. Anaheim, California 92803
Viscosity of Chloroaluminate Melts (DWE) AFOSR-77-3198, 2303/A1	Harald A. Øye Institute of Inorganic Chemistry University of Trondheim Trondheim-NTH, Norway
Synthesis of Phosphatriazines for Potential High Temperature Fluids Applications (AJM) F44620-76-C-0065, 2303/B2	Kay L. Paciorek Chemical & Materials Research Ultrasystems, Inc. Irvine, California 92664
High Resolution Vacuum Ultraviolet Spectroscopy of Small Molecules (JTV) F49620-77-C-0010, 2303/B1	W. H. Parkinson, D. E. Freeman and K. Yoshino Harvard College Observatory Cambridge, Massachusetts 02138
Cyclic Polyfluorosilicone Polymers and Copolymers (AJM) F49620-77-C-0012, 2303/B2	Ogden Pierce Contract Research & Development Lab Dow Corning Corporation Midland, Michigan 48640
Carbon-Carbon Composite Matrix Decomposition Reactions and Densification Response (DRU) F49620-78-C-0002, 2303/A3	J. P. Pope Material Sciences Division Science Applications, Inc. Santa Ana, California 92707
Experimental and Theoretical Studies of Intramolecular and Intermolecular Dynamics (JTV) F49620-76-C-0017, 2303/B1	Stuart A. Rice Department of Chemistry University of Chicago Chicago, Illinois 60637
Experimental and Theoretical Work in Chemical Dynamics and Nucleation (JTV) AFOSR-77-3214, 2303/B1	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 CU+, GA+, IN+ and 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	Ian W. M. Smith Department of Physical Chemistry The University of Cambridge Cambridge, U.K. England
Defect Chemistry of Crystalline Inorganic Materials (DRU) AFOSR-78-3505, 2303/A3	Donald M. Smyth Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015
Effects of Oxygen and Water Vapor on the Compressive Strength of Boundary Films on Iron Crystals (RWH) AFOSR-76-3051, 2303/A2	David K. Snediker Department of Tribomechanics Battelle Memorial Institute Columbus, Ohio 43201
Morphology and Mechanical Behavior of Isomeric Graft Polymers and Interpenetrating Polymer Networks (AJM) AFOSR-76-2945, 2303/B2	L. H. Sperling Department of Chemical Engineering Lehigh University Bethlehem, Pennsylvania 18015
Lithium Based Anodes for Solid State Batteries (RAO) AFOSR-77-3460, 2303/A1	B. C. G. Steele Department of Metallurgy and Materials Science Imperial College, University of London London, England
Formation and Deactivation Processes in Electronic Transition, Chemically Pumped Lasers (JTV) AFOSR-75-2758, 2303/B1	Jeffrey I. Steinfeld Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Synthesis of New Inorganic and Organometallic Materials (AJM) AFOSR-76-3102, 2303/B2	F.G.A. Stone Department of Chemistry University of Bristol Bristol, BS8 ITS, England
Multicomponent Oxide Systems for Corrosion Protection (RWH) AFOSR-77-3334, 2303/A2	Gary W. Stupian and William H. Steier Graduate Center for Engineering & Computer Sciences University of Southern California Los Angeles, California 90007
Molecular Beam Studies of Collisional Excitation and Energy Exchange in Polyatomic Studies (JTV) AFOSR-75-2863, 2303/B1	R. B. Subbarao and J. B. Fenn Department of Engineering Sciences Yale University New Haven, Connecticut 06520
Collisional Excitation and Ionization (JTV) F44620-76-C-0007, 2303/B1	Thomas O. Tiernan Department of Chemistry Wright State University Dayton, Ohio 45431

New Perfluoropolymer-Forming Reactions (AJM) F44620-76-C-0027, 2303/B2	Madeline S. Toy Science Applications, Inc. Sunnyvale, California 94086
Structural and Dynamic Studies of Materials Possessing High Energy Content (AJM) AFOSR-74-2589, 2303/B2	Nicholas J. Turro Department of Chemistry Columbia University New York, New York 10027
Microstructure of Amorphous and Semi-Crystalline Polymers (DRU) AFOSR-77-3226, 2303/A3	Donald R. Uhlmann Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Stabilization and Graphitization of Acrylic Fibers and Carbon Composite Matrices (DRU) AFOSR-77-3466, 2303/A3	Donald R. Uhlmann Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139
The Third International Summer Institute in Surface Science (ISISS 1977) (RWH) AFOSR-MIPR-77-0037, 2303/A2	Dr. Ralf Vanselow Department of Chemistry University of Wisconsin-Milwaukee Milwaukee, Wisconsin 53201
Development and Practical Application of the Theory of Materials (AJM) AFOSR-77-3145, 2303/B2	John R. Van Wazer Department of Chemistry Vanderbilt University Nashville, Tennessee 37203
Inhibitors for Corrosion Fatigue of High Strength Alloys (RWH) AFOSR-PD-77-0011, 2303/A2	Ellis Verink, Jr. Department of Materials Sciences and Engineering University of Florida Gainesville, Florida 32611
Radiation and Laser Potential of Homo- and Hetero-Nuclear Rare Gas Diatomic Molecules (JTV) AFOSR-77-3137, 2303/B1	W. C. Walker and Y. Tanaka Department of Physics University of California Santa Barbara, California 93106
Correlation of Electrode Kinetics With Molecular Structure (DWE) AFOSR-77-3408, 2303/A1	Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824
Organosilicon Chemistry (AJM) AFOSR-77-3123, 2303/B2	William P. Weber Department of Chemistry University of Southern California Los Angeles, California 90007

High Temperature Molecules and Molecular Energy Storage (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

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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. Hinchen 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
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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
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Wolfgang Henke
Daniel E. Klimek
Stephen K. Liu
Kammalathinna V. Reddy
William A. Tricumi, Jr.
Gary A. West

8. PUBLICATIONS:

"The F + H_2, D_2, 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_6 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. Cumm., 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 $\lambda \geq 200$ Å with high (digital) accuracy at resolution better than 0.3 Å, 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 ($\lambda \geq 1500$ Å), 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 ~ 3500°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 CaH_2 followed by a vacuum distillation. This procedure resulted in hydrazine with 0.05 percent water and less than 10 ppm 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 interferring 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:

$$2\ N_2H_5^+ + 2e \rightarrow 2\ N_2H_4 + H_2$$

The anodic reaction is activation controlled and proceeds according to:

$$5/2\ N_2H_4 \rightarrow 2\ N_2H_5^+ + 1/2\ N_2 + 2e$$

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
D. R. Fischell
D. R. Harris
R. A. Lucht
D. I. Rosen

A. C. Erlandson
N. R. Friedman
K. K. Hui
J. A. McGarvey, Jr.

8. PUBLICATIONS:

"Vibrational Deactivation of O_3 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_3", 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_2 and DF-CO_2 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_2, and DF-CO_2 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_2-D_2 and H_2-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_3-CO and O_3-OCS Systems", J. Chem. Phys. 65, 3536 (1976).

"Vibrational Energy Transfer in HF-HCN, DF, HCN, and H_2-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_3 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 ($> 10^{13}$ 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_2O and PH_3/N_2O 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 mear 4000 Å and weaker bonds 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^{-3}-10^{-5} seconds) for chemical laser operation.

Another system of potential importance was identified. Chemical reactions initiated by electrical discharges in PH_3/N_2O mixtures lead to strong visible chemiluminescence by the steps:

$$P(^4S) + N_2O(X^1\Sigma^+) \rightarrow PO\ (^4\pi) + N_2(X^1\Sigma^+)$$

$$PO(^4\pi) + PO(X^2\pi) \rightarrow (PO)_2^*$$

$$(PO)_2^* \rightarrow h\nu + PO(X^2\pi) + PO(X^2\pi)$$

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 $(PO)_2^*$ 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. Arthur L. Cummings
Dr. Michael M. Farrow
Dr. Johnathan E.C. Hutchins
Dr. J. Thomas Knudtson
Dr. Neil Purdie
Dr. Licesio J. Rodriguez
Dr. Ronald P. Rohrbach
Dr. F. Arce Vazquez
Dr. Robert D. White

6. JUNIOR RESEARCH PERSONNEL:

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

7. PUBLICATIONS:

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

"Molecular Associations in Non-Aqueous Solvents I. Thermodynamics of Dye-Dye Interactions in CCl_4 and C_6H_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-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 C_6H_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 Steroisomers in Thiacarbocyanine 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-αL-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 (α,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 ~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 Nd_2O_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. I. J. Westerman
Dr. A. M. Buyle	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 Fluorobicyclobutatnes 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 α-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. Hinchen
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 FY7T; $55,302 FY77

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:

$$OCl^- + H_2O_2 \rightarrow O_2 + Cl^- + H_2O$$

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 (β) 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 → 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 $H + H_2$", 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 $H + H_2$", G. Schatz and A. Kuppermann, J. Chem. Phys. 65, 4668 (1976).

"Large Quantum Effects in a Model Electronically Nonadiabatic Reaction: $Ba + N_2O \rightarrow BaO^* + N_2$", 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 $F + H_2 \rightarrow FH + H$, $F + D_2 \rightarrow FD + D$, $F + HD \rightarrow FH + D$, and $F + DH \rightarrow FD + H$

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-dimentional 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	<u>CURRENT ADDRESS</u>: 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 <u>21</u>, 153-158 (Sep, Oct 1976).

"Differential Infrared Fourier Emission Microspectrometer for Lubrication Studies. Paper No M.B.3. Presented at the 1977 Internation 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 Coblentz Symposium at the 29th Pittsburgh Conference, Session on Application of Fourier Transform Infrared Spectroscopy, Little Theater, Cleveland Convention Center, 2 March 1978.

9. INVENTIONS:

Name of Inventor	Title of Invention	Patent Application Ser. No.	Status
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 μm) and in the lattice region (>15 μm) 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 ∿ 2 μm, open area 0.25 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 725-735 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 Br($^2P_{3/2}$) + 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: $K + C_sF$" 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).

"Surprisal 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

$$F + HD \rightarrow \left\{ \begin{array}{l} H + DF \\ \\ D + HF \end{array} \right.$$

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 I($5p^5\ ^2P_{1/2}$) following Laser Photolysis of I_2 Near 5000Å", D. H. Burde, R. McFarland, J. Wiesenfeld, Phys. Rev. A10, 1917 (1974).

"Collisional Quenching of Excited Iodine Atoms I($5p^5\ ^2P_{1/2}$) 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 Transition Lasers, Sep 17-19, 1975, Woods Hole, Massachusetts.

"Collisional Quenching of Excited Iodine Atoms I($5p^5\ ^2P_{1/2}$) 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 I($5p^5\ ^2P_{1/2}$) 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	Current Address:
Dept of Chemical Engineering	School of Chemical Engineering
University of California	Cornell University
Berkeley, California	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, FY7T; \$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 CO + O_2, NO + CO, and H_2 + 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)

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"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).

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

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"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 chemi-sorption, H_2 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. Spacial resolution of this beam is 0.4° 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° resolution out of plane and 0.135° 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 form 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 or 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_2 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_2, NO, CO, H_2, and O_2 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 7T; $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 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 ArF and Ar_2F," 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 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 (BeO-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 $F+H_2$ Chemical Lasers: V→V and V→R,T Energy Transfer Corrections", O. Krogh, D. Stone, and G. Pimentel, J. Chem. Phys. 66, 368 (1976).

"ClF_x-H_2 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_2O, Ca + N_2O + CO, and Sr + N_2O + 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_2 in Cryogenic Samples", Y. Lee and G. Pimentel (in preparation).

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

"ClF_x-H_2 Chemical Lasers: Vibration-Rotation Emission by HCl", O. Krogh and G. Pimentel (in preparation).

"HF Rotational Laser Emission by the ClF-H_2 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_3, in the presence of fluorinated methanes and argon produces hydrofluoric acid, HF, through imine (NH, probably a $^1\Delta$) 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_4, CF_3H, CF_2H_2, and CFH_3. Part of the HF is evidently produced by NH(a $^1\Delta$) 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_3 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_x-H_2 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 ClF_5-H_2 system. The ClF-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→R deactivation with large ΔJ coupled with V→V pumping in $HF^{\dagger}$-$HF^{\dagger}$ 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 20μ spectral region. With rather large pressures, 80-100 torr of rather concentrated mixtures, ClF:H_2: Ar = 1:1:10, laser emission is seen in the spectral region 985-810 cm^{-1} with extremely long durations, up to 70 μsec. This corresponds to HF rotational transitions J=22→21 and J=24→23. The available energy in the F + 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→24 up to J=30→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 H_2-Cl_2 explosion was inititated 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, $Ba(g) + N_2O(g) \rightarrow BaO^* + N_2$, gain on certain barium stomic transitions was detected but only absorption in the BaO transitions. In the corresponding reaction with Sn atoms, no positive gain was detected. Evidently, there is more 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 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=o→4, using a 70 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 D_2 were exposed to 10^4 dye laser flashes. Unfortunately, the D_2 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_2H_4 with and without a few percent O_2 impurity were flash photolyzed. In the presence of the O_2 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 $C_2H_4^*$, O_2^*, 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:

$$HCO + O_2 \rightarrow HO_2 + CO \quad k = (4.0 \pm .8) \cdot 10^{-12}\ cm^{-3}/molecule\ sec.$$

$$HCO + NO \rightarrow HNO + CO \quad k = (1.45 \pm .2) \cdot 10^{-11}\ cm^{-3}/molecule\ sec.$$

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_2 are observed when solid $N_2O/Ar = 1/100$ 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_6 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_2 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_2 $A' \rightarrow X$ transition. A variety of arguments lead to a rather definite assignment of the other, weaker progression to the S_2 $c \rightarrow a$ transition.

The observation of electronic transitions never before detected for a molecule as well known as S_2 suggests that this thermoluminescence technique will be of particular interest. We already have detected cryogenic thermoluminescence from SO_2, 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(fluoroorganophosphozenes)

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, FY7T; $23,187, FY77.

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 $R_f = \underline{n}\text{-}C_3F_7$.

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 fatigues polycarbonate films showed a shift of α and β 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

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

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

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"Formation of closo- and nido-Metallocarboranes from closo-C_2B_9 and -C_2B_7 Carboranes; Molecular Structures of closo-1,1-$(Me_2PhP)_2$-2,4-Me_2-1,2,4-$PtC_2B_9H_9$ and nido-10,10-$(Et_3P)_2$-2,8-Me_2-10,2,8-$PtC_2B_7H_7$", M. Green, J. Spencer, F. Stone and A. Welch. J.C.S. Chem. Comm., 571 (1974)

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"Cyclopentadienylruthenium Phosphine Complexes. Some Complexes Derived from 1-Alkynes: Molecular and Crystal Structure of the Cumulene Derivative $[\overbrace{\mathrm{Ru\{C(CF_3){:}C(H)C(CF_3){:}C}}\mathrm{{:}C{:}CH(CF_3)\}(PPh_3)(\eta^5\text{-}C_5H_5)}]$", 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 $[\mathrm{Ni_4(CO)_4(\mu_3\text{-}CF_3C_2CF_3)_3}]$ and $[\mathrm{Ni_3(CO)_3(\mu_3\text{-}C_8H_8)(\mu_3\text{-}CF_3C_2CF_3)}]$. In the latter, a planar C_8 ring bridges a nickel triangle, whereas in the former structure three acetylene ligands bridge faces of a Ni_4 tetrahedron.

Several new cyclometallation reactions have been identified, particularly involving the group $[\mathrm{Ru(Ph_3P)(\eta^5\text{-}C_5H_5)}]$ and azobenzene derivatives. Numerous fluorocarbon metal complexes have been prepared by oxidative-addition reactions of d^8 and d^{10} 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 $[\mathrm{MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}]$ (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. Patrick Coffey
Dr. James Eberhardt
Dr. Carl Ewig
Dr. Raymond Gangi
Dr. James Howell
Dr. Roman Osman

7. PUBLICATIONS:

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

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"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 psuedopotential 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 psuedopotential 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 psuedopotential 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-phenylcyclopropanes 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*-β-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*-β-Trimethylsilyl Styrene", K. Koenig and Wm. Weber, *Tetrahedron Letters*, 2533 (1973).

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"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)

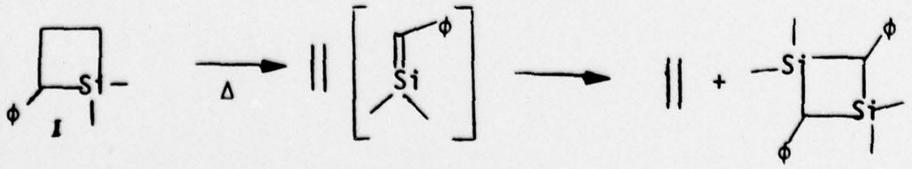
"Copyrolysis of Sym-Tetramethoxydimethyldisilane with 2,5-Dimethylfuran", M. Childs and W. Weber, J. Org. Chem., 41, 1799 (1976).

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

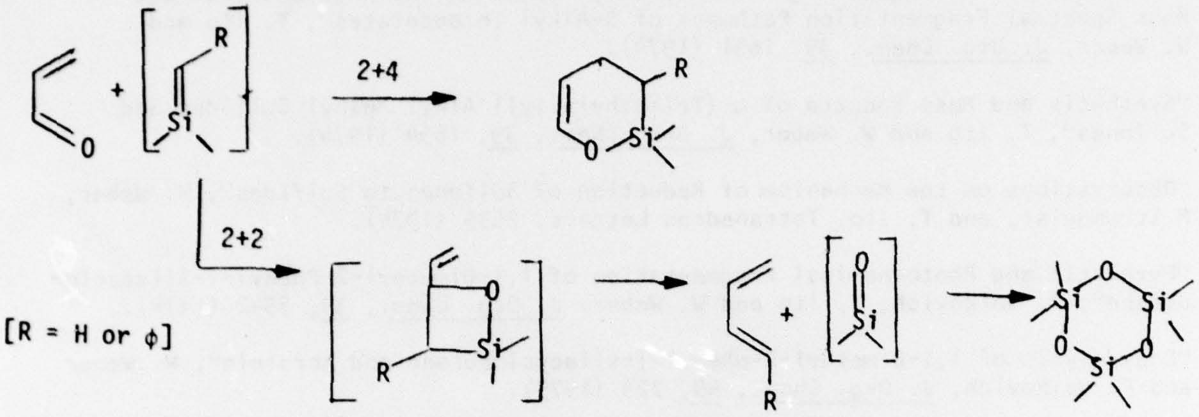
"Unsaturated Organosilicon Heterocycles", W. Weber, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

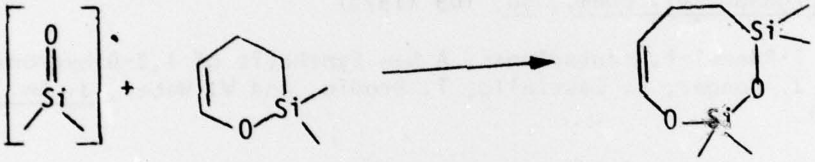
1,1-Dimethyl-2-phenyl-1-silacyclobutane (I) was prepared. Gas phase pyrolysis of I led to ethylene and a reactive intermediate possessing a carbon-silicon double bond.



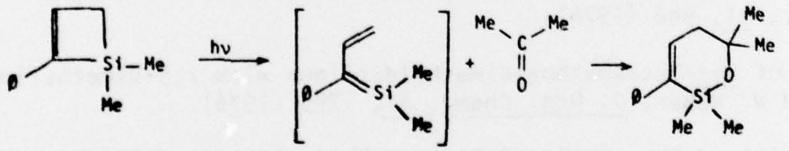
The cycloaddition reactions of such reactive carbon-silicon doubly bonded intermediates with acrolein were studied. It was found that carbon-silicon doubly bonded intermediates undergo both 2+2 and 2+4 cycloaddition reactions.



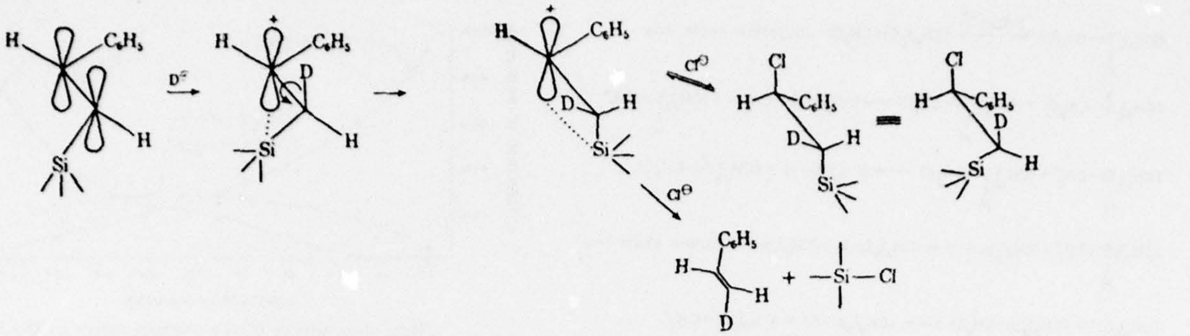
The insertion of silicon-oxygen doubly bonded intermediates into Si-O single bonds was observed. This is of potential importance since it may permit chemistry on the backbone of silicon polymers.



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 Ci-Si double bond conjugated to a C-C double bond. The cycloaddition reactions of this intermediate with acetone were studied.



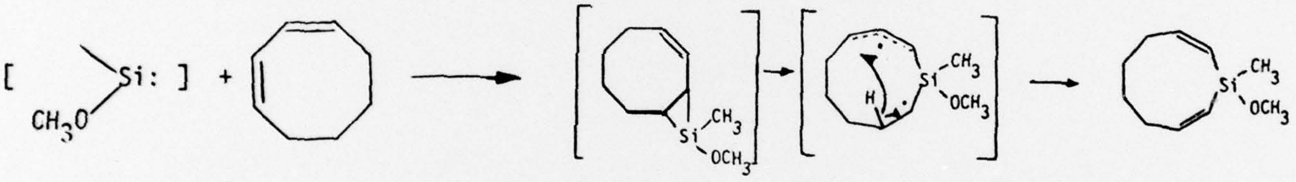
Work was done to determine the sensitivity of vinylic carbon-silicon bonds to electrophilic cleavage. The stereochemistry of such cleavage reactions provided insight into the mechanism by which such bonds are cleaved by electrophiles. Specifically, it was found that <u>trans</u>-β-trimethyl-silylstyrene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



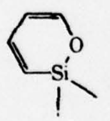
Cleavage of *cis*- and *trans*-β-trimethylsilylstyrene with bromine likewise resulted in retention of stereochemistry. These results could be explained by a *cis* addition followed by a *trans* elimination mechanism.

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.

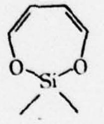
Insertion reaction of silylenes into unsaturated organic molecules was found to be a most direct synthetic approach to the preparation of unsaturated organosilicon heterocycles. Thus the reaction of methoxymethylsilylene with 1,3-cyclooctadiene led to 1-methoxy-1-methyl-1-sila-2,8-cyclononadiene.



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).

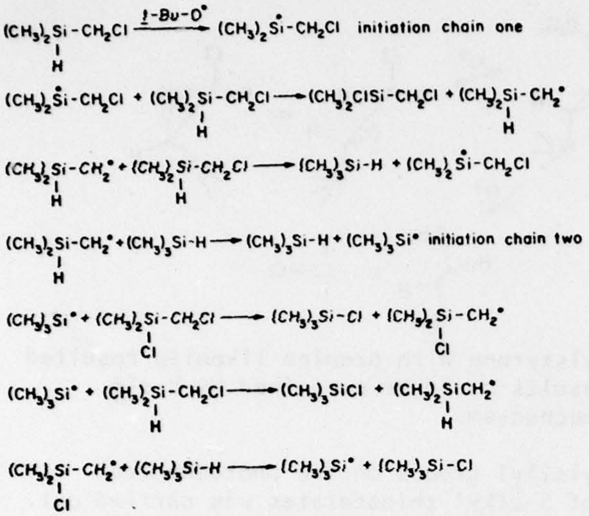


II



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.



$$(CH_3)_2\underset{H}{Si}-CH_2Cl \xrightarrow{t\text{-}Bu\text{-}O^\bullet} (CH_3)_2\overset{\bullet}{Si}-CH_2Cl \quad \text{initiation chain one}$$

$$(CH_3)_2\overset{\bullet}{Si}-CH_2Cl + (CH_3)_2\underset{H}{Si}-CH_2Cl \longrightarrow (CH_3)_2ClSi-CH_2Cl + (CH_3)_2\underset{H}{Si}-CH_2^\bullet$$

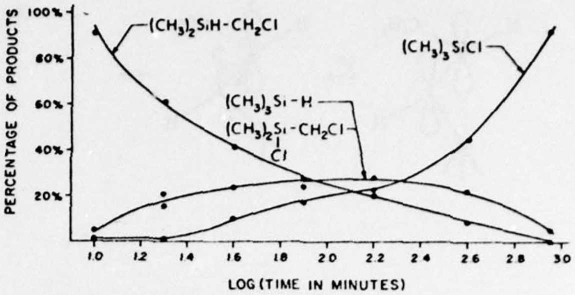
$$(CH_3)_2\underset{H}{Si}-CH_2^\bullet + (CH_3)_2\underset{H}{Si}-CH_2Cl \longrightarrow (CH_3)_3Si-H + (CH_3)_2\overset{\bullet}{Si}-CH_2Cl$$

$$(CH_3)_2\underset{H}{Si}-CH_2^\bullet + (CH_3)_3Si-H \longrightarrow (CH_3)_3Si-H + (CH_3)_3Si^\bullet \quad \text{initiation chain two}$$

$$(CH_3)_3Si^\bullet + (CH_3)_2\underset{Cl}{Si}-CH_2Cl \longrightarrow (CH_3)_3Si-Cl + (CH_3)_2\underset{Cl}{Si}-CH_2^\bullet$$

$$(CH_3)_3Si^\bullet + (CH_3)_2\underset{H}{Si}-CH_2Cl \longrightarrow (CH_3)_3SiCl + (CH_3)_2\underset{H}{Si}CH_2^\bullet$$

$$(CH_3)_2\underset{Cl}{Si}-CH_2^\bullet + (CH_3)_3Si-H \longrightarrow (CH_3)_3Si^\bullet + (CH_3)_3Si-Cl$$



. Time dependence of the product ratios in the radical chain reactions of chloromethyldimethylsilane 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
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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	Kevin S. Peters
G. Barney Ellison	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).

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"Enthalpy of the Metal Catalyzed Isomerizations of Quadricyclane and of Tricyclo $[4.1.0.0^{2,7}]$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).

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"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.

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"Electronic States of Organic Molecules. 5. High Resolution Spectrum of the A State of Cicyclobutane", 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^{2,7}]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_2 and Ba + O_2", P. Dagdigian, H. Cruse, A. Schultz and R. N. Zare, J. Chem. Phys. 61, 4450 (1974).

"Flame Emission Studies of Ozone with Metal Alkyls: $Zn(CH_3)_2$ and $Zn(C_2H_5)_2$", H. Lee and R. Zare, Combustion and Flame 24, 27 (1975).

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"Efforts to Develop a Prototype Electronic-Transition Laser From the Chemical Reactions of Laser-Generated Metal Vapors", C. Dickson, H. Lee, R. Oldenborg 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: $Ba + HF (v=0,1) \rightarrow BaF(v=0\text{-}12) + H$", 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 $C\ell O_2$", F. Engelke, R. Sander and R. N. Zare, J. Chem. Phys. 65, 1146 (1976).

"The Four-Centre Reaction of $I_2 + F_2$ 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 $M + S_2C\ell_2 \rightarrow S_2^* + MC\ell_2$", 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 ($Ba + KC\ell$), 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.

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