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AIR FORCE OFFICE OF SCIENTIFIC RESEARCH BOLLING AFB DC
AFOSR CHEMISTRY PROGRAM REVIEW (25TH) FY-80, (U)
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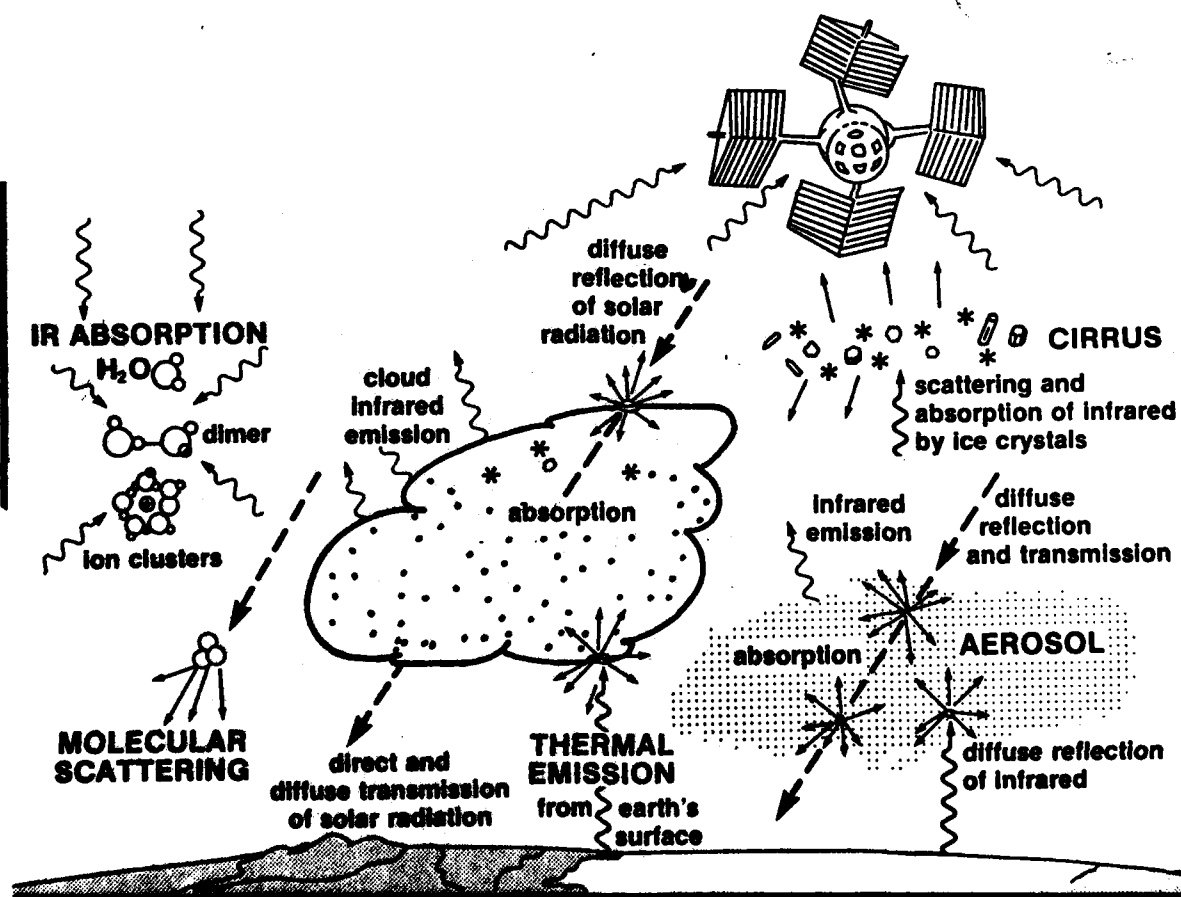
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AFOSR Chemistry Program Review FY-80



Air Force Office of Scientific Research

Air Force Systems Command

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COVER

The cover is illustrative of the inextricable links between chemistry and atmospheric sciences. The graphic depicts specific effects of the natural atmosphere on visible and infrared radiation propagation. The net impact of these effects is determined by the general chemical and physical history of the air mass itself; aerosol composition determines absorption and scattering properties, aerosol and haze size distributions are functions of history, age and current conditions, chemical and physical behavior of water molecules determines infrared absorption characteristics. Outside of radiation effects, clouds and fogs are possibly nature's most complex chemical laboratories. At high altitudes the chemical balance of the atmosphere is crucial to atmospheric phenomenology and behavior. Aurora are detectable evidence of excited state chemical processes. The maintenance of the protective ozone sheath is a direct product of photo ionization chemistry. The presence of heavy metallic ions from meteoric debris is catalytic to naturally occurring chemical processes. The list of chemically based atmospheric phenomena goes on. It is critical to the operation of USAF surveillance and communications to fully understand the behavior of the upper atmosphere and its chemical balance and processes. At all altitudes the performance of visible and infrared devices is degraded by atmospheric processes not yet well enough understood. This knowledge must be pursued and is a variable dependent upon chemistry as well as classical meteorological considerations.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR-81-0448 ✓	2. GOVT ACCESSION NO. AD A100 137	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 25TH ANNIVERSARY EDITION AFOSR CHEMISTRY PROGRAM REVIEW FY-80		5. TYPE OF REPORT & PERIOD COVERED Scientific Special
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Lorelei A. Krebs, Editor Sylvia A. Stallings, Managing Editor		8. CONTRACT OR GRANT NUMBER(s) In-House
9. PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Office of Scientific Research, AFSC Directorate of Chemical & Atmospheric Sciences Bolling AFB, Washington, DC 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2303/2310 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS same as above		12. REPORT DATE 1 March 1981
		13. NUMBER OF PAGES 226
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Air Force Office of Scientific Research Mesoscale Weather Forecasting Chemical Sciences Chemical Dynamics Radar Atmospheric Research Chemical Techniques Chemical Synthesis Meteorology Surface Chemistry Atmospheric Sciences Upper Atmosphere Chemical Structures Cloud Physics		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A review is presented of research efforts sponsored by the Directorate of Chemical and Atmospheric Sciences which have completed their period of support. Illustrated accounts resulting from the basic research programs in the Atmospheric and Chemical Sciences are highlighted. The Atmospheric Sciences is concerned with meteorology and upper atmospheric structure and dynamics. The meteorology focuses on mesoscale meteorology, cloud physics, and atmospheric dynamics. The Chemical Sciences deal with Chemical Techniques, Chemical Structures, Surface Chemistry, Chemical Dynamics, and Synthesis and properties of Materials.		

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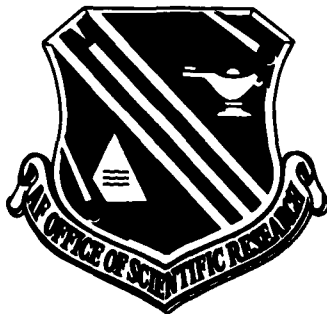
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CHEMISTRY PROGRAM REVIEW (257)

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LORELEI A. KREBS, EDITOR
SYLVIA A. STALLINGS, MANAGING EDITOR

111 MAR 1981

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
DIRECTORATE OF CHEMICAL AND ATMOSPHERIC SCIENCES
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MISSION

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

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

TECHNICAL STAFF

Dr. Donald L. Ball
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Chemical Structures

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Molecular Dynamics

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

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Program Manager
Surface Chemistry

Lt Col Ted S. Cress
Program Manager
Atmospheric Sciences

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Mrs. Eugenia L. Woodman

Mrs. Martha P. Bloom



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

March 1981

TO: FRIENDS OF AFOSR

This issue of the "Program Review" marks a quarter of a century of its publication. Perhaps this warrants some kind of recognition to those individuals who have participated in the AFOSR research programs from its beginning.

Since 1951, the Chemistry Directorate has supported 545 principal investigators in 143 colleges and universities, representing 44 states in the United States. In addition, there were 75 principal investigators in 49 universities and colleges in 16 foreign countries. Added to those were 61 principal investigators in 37 industrial organizations representing 15 states, plus 44 principal investigators in 14 non-profit and government organizations in seven different states. This gives one some idea where the taxpayer's money has been invested. Elsewhere in the book one may note the amount of money spent annually by this directorate for research in the area of chemistry.

Obviously, all this could not have been accomplished without a lot of combined effort. In this issue we feel it only appropriate to list the program managers who gave impetus and direction to the programs throughout the years, and to the Research Evaluation Panel members who willingly gave of their time and expertise to evaluate the scientific merit and technical aspects of the proposals.

With the 25th publication anniversary issue, it also marks the first in-depth review of the on-going AFOSR Atmospheric Sciences program, now combined with the former Directorate of Chemical Sciences. Project summaries from the last four or so years of the Atmospheric Sciences program are included, as well as several survey articles addressing specific aspects of the research program.

Based on the strong foundation built by the people cited, I feel confident that we shall be able to maintain a progressive and high quality basic research program for the Air Force for even another twenty-five years in the Chemistry and Atmospheric Sciences.

Sincerely,

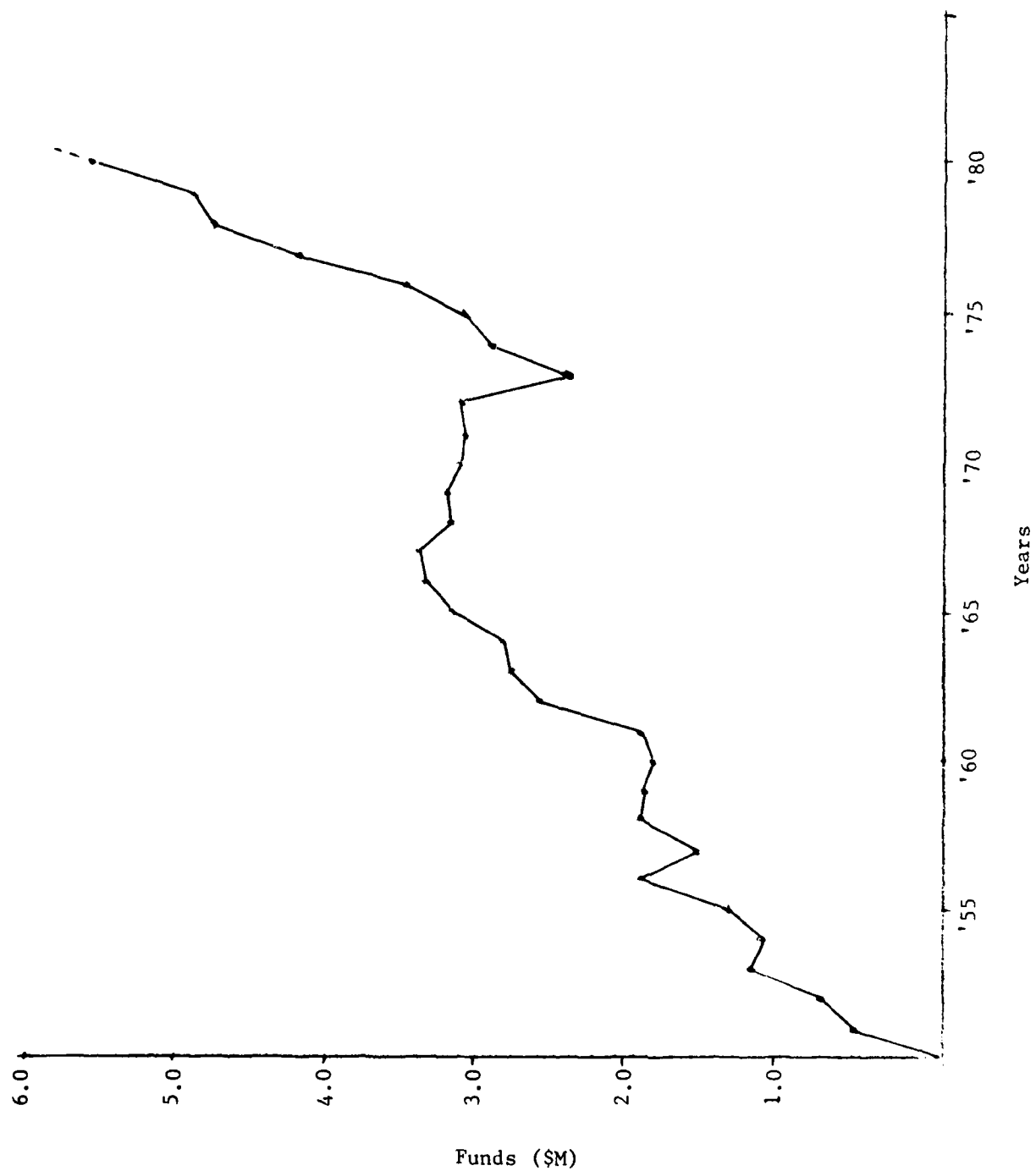
DONALD L. BALL
Director, Chemical &
Atmospheric Sciences

CHEMISTRY FUNDS (THOUSANDS) 1951-1980

<u>FY</u>	<u>Funding (thousands)</u>	<u>FY</u>	<u>Funding (thousands)</u>
1951	596	1967	3,480
1952	835	1968	3,329
1953	1,284	1969	3,338
1954	1,102	1970	3,169
1955	1,432	1971	3,205
1956	2,043	1972	3,210
1957	1,664	1973	2,512
1958	2,084	1974	3,080
1959	2,063	1975	3,213
1960	1,966	1976	3,620
1961	2,084	1977	4,364
1962	2,700	1978	4,884
1963	2,922	1979	5,045
1964	2,959	<u>1980</u>	<u>5,777</u>
1965	3,356		
1966	3,475	TOTAL	84,889

FY80 CHEMISTRY PROGRAM STATISTICS

Total number of proposals received.....	263
Total number of inquiries received.....	173
New work efforts initiated.....	36
Renewals.....	83
Proposals declined.....	77
Proposals withdrawn.....	3
Proposals transferred.....	2
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CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY 80 with funds provided in part or wholly by the Directorate of Chemical and Atmospheric Sciences as a means of furthering areas of scientific research of particular interest to the Air Force.

Air Force/Navy Second Rocket Nozzle Technology and Processing Science Meeting

Dr. D. R. Ulrich and Dr. J. Patton
Williamsburg, Virginia
2-3 October 1979

Gordon Research Conference on Electrochemistry

Dr. Donald E. Smith
Santa Barbara, California
27 January-1 February 1980

ACS National Symposium on Polymers in the Service of Man

Dr. Robert S. Shane
Washington, D.C.
9-11 June 1980

Second Symposium on Applied Surface Analysis

Dr. John T. Grant
University of Dayton Research Institute
Dayton, Ohio
11-13 June 1980

Problems in Chemical Toxicology

Dr. Richard E. Lindstrom
Storrs, Connecticut
19-20 June 1980

International Conference on Frontiers of Glass Science

Dr. John D. Mackenzie
University of California, Los Angeles
Los Angeles, California
16-18 July 1980

Gordon Research Conference on Corrosion

Dr. R. Latanision
Colby Sawyer College
New London, New Hampshire
21-25 July 1980

Workshop on Recent Experimental and Theoretical Approaches
to the Study of the Electrical Double-Layer

Dr. Douglas Henderson
IBM Research Division
San Jose, California 95193
23-25 July 1980

Gordon Research Conference on Inorganic Chemistry

Dr. Jack Williams
New Hampton School
New Hampton, New Hampshire
4-8 August 1980

PROGRAM MANAGERS - 1951-1980
(Chronologically Listed)

Horney, Amos G. (Director 1951-1972)
Borum, Olin (Major)
Elliott, Denton W.
Hertzfeld, Simon H.
Haas, Eugene
Leiserson, Lee
Shipp, John (Major)
Stanbaugh, Claude K. (Lt Col)
Harper, Robert S. (Lt)
Ruigh, William L.
Barneyback, William (Capt)
Wyatt, William H. (Lt Col)
Smith, Brandes H. (Lt)
Pierce, Elliott S.
Weissler, Alfred
Matuszko, Anthony J.
Sprinkle, Milton S. (Lt Col)
Ball, Donald L. (Director 1973 - Present)
Walford, Edward T. (Lt Col)
Whipple, Loris D. (Lt Col)
Cole, Alan R. (Major)
Comerford, Jack (Col, Acting Director '73)
Masi, Joseph F.
Olson, David S. (Major)
Ulrich, Donald R.
Haffner, Richard W. (Lt Col)
Viola, John T. (Lt Col)
Armstrong, Russell A. (Capt)
Osteryoung, Robert A.
Wodarczyk, Frank J.
McKechney, William J. (Lt Col)
Krebs, Lorelei A. (Capt)
Cress, Ted S. (Lt Col)
Thorpe, William G. (Capt)

RESEARCH EVALUATION PANEL*
(1951-1980)

Harry R. Allcock, Penn State U.
Fred Anson, Cal Tech
Richard Arnold, A. P. Sloan Foundation
Allen J. Bard, U. of Texas
Fred Basola, Northwestern U.
Jesse L. Beauchamp, Cal Tech
Edwin Becker, NIH
Jacob Bigeleisen, Brookhaven N.L.
A. H. Blatt, Queens College
John R. Bowman, Northwestern U.
Ronald Breslow, Columbia U.
Wallace Brode, NBS
S. B. Brummer, Tyco
Melvin Calvin, U. of Calif, Berkeley
Bryce Crawford, J., U. of Minn.
Dwaine O. Cowan, Johns Hopkins
Carol Creutz, Brookhaven N. L.
Paul C. Cross, U. of Washington
D. D. Cubicciotti, Stanford Rsch
Lawrence F. Dahl, U. of Wisconsin
Joseph E. Earley, Georgetown U.
James Economy, IBM
Gert Ehrlich, U. of Ill
Mostafa F. A. El-Sayed, UCLA
James Espenson, Iowa State
Paul Flory, Cornell
Francis Frary, ALCOA
William Gentry, U. of Minn.
J. Calvin Giddings, U. of Utah
Peter R. Girardot, Pittsburgh Plate Glass
Mary L. Good, U. of Louisiana
W. E. Hanford, Olin Mathieson
John P. Howe, Atomics International
Clyde A. Hutchinson, Jr. U. of Chicago
James A. Ibers, Northwestern U.
Ralph K. Iler, DuPont
George Jura, U. of Calif, Berkeley
Frederick Kaufman, U. of Pittsburgh
I. M. Kolthoff, U. of Minn.
Herbert A. Laitinen, U. of Ill.
Yuan T. Lee, U. of Calif, Berkeley
William A. Lester, Jr. IBM
Franklin A. Long, Cornell U.
Dale W. Margerum, Purdue
John L. Margrave, Rice U.
Arther E. Martell, Texas A&M

Donald R. Martin, Olin Mathieson
Lynne L. Merritt, U. of Indiana
J. w. Mitchell, U. of Virginia
Earl R. Muetterties, DuPont
Melvin S. Newman, Ohio State
Donald Noyce, U. of Calif, Berkeley
Robert Parr, Johns Hopkins
Rowland Pettit, Texas U.
Charles U. Pittman, Jr., U. of Alabama
Benton S. Rabinovitch, U. of Washington
Howard Reiss, UCLA
Guy E. Rindone, Penn State
John D. Roberts, Cal Tech
L. B. Rogers, Purdue U.
John Ross, MIT
Wayne S. Scanlon, Naval Ordnance Lab
Donald W. Setser, Kansas State U.
Jean'ne Shreeve, U. of Idaho
Andrew Streitwieser, Jr. U. of Calif, Berkeley
Henry Taube, Stanford U.
E. C. Taylor, Princeton
John C. Tully, Bell Labs
Ervin R. Van Artsdalen, Union Carbide
Arnold C. Wahl, Argonne National Lab
Warren Watanabe, Roehm & Haas
George W. Watt, U. of Texas
Frank H. Westheimer, Harvard U.
Kenneth B. Wiberg, Yale
Field W. Winslow, Bell Labs
S. Winstein, UCLA
Mark S. Wrighton, MIT
Bruno H. Zimm, General Electric

*Affiliations of the above are at the time of their selection to the panel. These panel members were selected initially through a contract with Cornell University, and at present with Georgetown University.

ATMOSPHERIC SCIENCES

Lieutenant Colonel Ted S. Cress

As the "single manager" for the Air Force basic research program, AFOSR supports atmospheric research both in-house at AF laboratories and through an extramural research program. While AFOSR maintains an active extramural program, the basic research program is dominated by the total in-house and contractual program at the Air Force Geophysics Laboratory (AFGL). In contrast to the AFGL basic research goals which support, directly, the exploratory development efforts at the laboratory, the AFOSR sponsored extramural program is more widely ranging and futuristic, looking towards the creation of the knowledge base that will serve problem solving efforts in the 10-15 year time frame. Close coordination between efforts at AFOSR and AFGL is observed to insure complementary programs and avoidance of duplicative efforts.

The wide variety of research supported by AFOSR encompasses physical processes in the atmosphere between the earth's surface and approximately 400 kilometers altitude. This domain includes nearly all geophysical processes influencing the use and performance of Air Force current and proposed ground-based and airborne systems. Space-based systems, performance and environmental physics, with the exception of ionospherically induced scintillations in transionospheric radio-wave communications signals, generally fall into other AFOSR program areas.

The Atmospheric Sciences program is structured in two major task areas; Meteorology and Upper Atmospheric Structure and Dynamics. Within these general environmental categories, areas of emphasis are imbedded and see a concentration of effort. In Meteorology during FY80, the program was focused into three areas; mesoscale meteorology, cloud physics, and atmospheric dynamics. In the Upper Atmosphere, the areas of emphasis were upper atmospheric dynamics, dynamic coupling in the vertical, and ionospheric morphology as it relates to radio wave systems performance.

In mesoscale meteorology, AFOSR frequently cooperates with NSF, funding specific efforts within much larger NSF sponsored programs. Studies being conducted with multi-agency sponsors include those of Dr. Peter Hobbs at the University of Washington and Dr. Bernice Ackermann at the Illinois state Water Survey; both are very interesting and suggest striking similarities in seemingly distinct and unrelated precipitation systems. Dr. Hobbs in studying winter-time cyclonic storms approaching the West Coast has determined that these systems are largely characterized by a band-like structure in which the precipitation elements have well defined characteristics. Dr. Ackermann's work, in conjunction with the University of Virginia and NOAA, on summer season mesoscale convective complexes (MCCs) in the midwest has noticed a similar structure to precipitation cells developing along a synoptically

ill-defined line of instability. As the individual precipitation cells develop they become characterized by a multi-cellular structure oriented at a preferred orientation to the axis of the larger pattern with characteristics similar to the winter cyclonic storm mesoscale structure.

In cloud physics, the major effort during 1980 was the continued development of a precision controlled 3-meter cloud simulation chamber under the guidance of Dr. James Kassner at the University of Missouri-Rolla. AFOSR's interest in cloud microphysics as well as aerosol physics and optical/infrared propagation will be well served by the completion of this facility in 1982-83. This is an effort supported in cooperation with the Army Research Office and the Office of Naval Research.

In an exciting developmental effort, AFOSR has been following closely the development, under NSF sponsorship, of the so-called MST radar (Mesospheric-Stratospheric-Tropospheric) by Dr. Ben Balsley of NOAA. AFOSR is sponsoring several studies of lower atmospheric dynamics with this facility and in the future may sponsor investigations of vertical dynamic coupling and this radar's utility for synoptic or mesoscale meteorological programs. If successful, the suggestion of potential tactical utility for operational mesoscale forecasting is most intriguing.

In the Upper Atmosphere, progress under AFOSR sponsorship has been equally exciting. In dynamics research efforts, Dr. Arthur Belmont of Control Data Corporation has been using satellite radiance data to investigate the character of temperature field wave-1 and wave-2 phenomenology from 10 mb to .4 mb. Combined with other data sources such as ozone distributions, Dr. Belmont's results promise to shed new light on the behavior of upper stratospheric dynamic processes. Dr. Jeffrey Forbes of Boston College has been investigating the tidal structure of the mesosphere and lower thermosphere to generate an excellent model of thermospheric tidal behavior. Dr. Forbes is expanding his area of concern to investigate the role of atmospheric dynamic motion in the upper atmospheric chemical balance. As a result of his tidal work, Dr. Forbes' inputs into other upper atmospheric dynamic programs (e.g., mesosphere wind behavior) is highly valued.

Ionospheric morphology and scintillation causing irregularities have been a focus of much effort under AFOSR sponsorship. Dr. Ed Fremouw, Physical Dynamics, Inc., is concluding his statistical investigation of DNA Wideband Satellite Data and has confirmed the sheet-like structure of electron density irregularities in the auroral zone and identified the probable change to a "rod-like" structure south of the auroral zone. Dr. James Vickery at SRI and Dr. John Evans at Haystack Observatory independently investigated the morphological structure of ionospheric electron densities using the high powered Incoherent Scatter (ICS) radars at Chatanika, Alaska, and Millstone Hill, Massachusetts.

Dr. Vickery has looked more specifically at the behavior of F-region "blobs" of electron densities as well as the behavior of Hall and Pederson current systems while Dr. Evans is looking at the diurnal variation of the F-region electron densities in the auroral zone and the auroral trough. All of these phenomena are important to the performance of existing and potential Air Force systems.

Though not directly tied to solving immediate problems, the research investments made by AFOSR in Atmospheric Sciences are tied to a foreseen or forecast relevance. Requirements for basic research are identified from many sources in the Air Force, but the dominant sources continue to be Air Weather Service and the Air Force Laboratories.

In the future AFOSR is looking forward to sponsoring additional work in cloud microphysical processes, mesoscale meteorology, dynamics and the 2-dimensional behavior of auroral zone parameters over long periods of time. AFOSR will continue to cooperate with other Federal agencies to sponsor larger research efforts not compatible with the relatively lean Atmospheric Sciences budget. Where advantageous and advisable AFOSR will sponsor research efforts on the periphery of larger programs sponsored by other agencies. We are willing to consider all proposals based on good science, but will obviously weigh our programs towards foreseeable AF applications.

EXPERIMENTAL CLOUD PHYSICS RESEARCH

A BACKGROUND SURVEY FOR AFOSR

James I. Metcalf
Capt., USAF Reserve

Historical Development

Meteorological research has always been impeded by the difficulties of experimental measurements. The nature of the atmosphere is such that discrete physical processes are difficult or impossible to separate, that field experiments are not usually repeatable except in a statistical sense, and that measurements are often unobtainable at temporal or spatial scales that are obviously relevant to a particular problem. Cloud physics exemplifies these difficulties better than other areas of meteorology, particularly as it deals with the microphysics of water condensation and freezing. Cloud microphysics links the chemistry and physics of atmospheric aerosols, the thermodynamics of water phase changes, the physics and aerodynamics of interactions between liquid or solid water particles, the formation of precipitation, and the cloud-scale dynamics. Theoretical and experimental research has shown that the early stages of cloud condensation have direct effects on the subsequent development of clouds and precipitation. Quantitative understanding of the condensation process and the initial growth of cloud water drops is therefore essential to successful forecasting or modification of precipitation.

One of the earliest developments in cloud physics was the identification of two precipitation-forming mechanisms. The so-called warm process involves the growth of cloud water drops (tens of micrometers in diameter) to precipitation size (diameters larger than a few hundred micrometers) by collision and coalescence with other drops. This auto-conversion of cloud water to precipitation is not fully understood, since clouds with maximum drop sizes about 20 micrometers are known to be colloidally stable. Relatively broad distributions of drop sizes in maritime clouds, presumably due to the characteristics of maritime condensation nuclei, are thought to yield sufficient differential fall speeds to permit the growth of precipitation. The failure of numerical models to predict drop size distributions as broad as are observed is believed to be due to lack of quantitative knowledge of the composition and activation characteristics of the condensation nuclei.

The cold process involves the presence of ice crystals in a cloud of supercooled liquid water, so that the ice crystals grow at the expense of the liquid water, first by preferential water vapor deposition and subsequently by riming due to collision and coalescence with cloud water drops. This process is the physical basis for most attempts at

precipitation augmentation, since ice crystals can be introduced into a supercooled cloud or the freezing process can be initiated by artificial "seeding" materials. Quantitative evaluation of weather modification attempts has been thwarted by lack of detailed knowledge of the natural course of the precipitation-forming process. Numerical simulation has shown that it is possible to over-seed clouds, so that an excessive number of ice particles compete for insufficient water to permit their growth to precipitation size. The optimum number concentration of ice particles (either naturally present or artificially induced) depends on parameters such as the size and number concentration of water drops, which depend in turn on the inflow of water vapor and condensation nuclei at cloud base.

Measurements in situ of the characteristics of nuclei or of cloud water drops are difficult to obtain because of natural variability of the relevant parameters, limitations imposed by positioning or movement of the measurement platform (aircraft or balloon), and limited response characteristics of the instrumentation. Significant progress has been made in instrumentation in recent years, and field measurements provide valuable guidance for the development of numerical models and the design of laboratory experiments. Even in the laboratory, measurements have been difficult to obtain for a variety of reasons, including accurate and repeatable control of temperature, humidity, and nucleus characteristics or the time scales imposed on the observations by the experimental equipment. Hence, there is great value in a research facility large enough and well enough controlled to permit the conducting of quantitatively accurate and repeatable experiments on cloud condensation and freezing processes.

Current Status

Large gaps exist in our understanding of water and ice nucleation processes and the subsequent growth of water drops and ice crystals. While the characteristics of condensation nuclei are known to affect and perhaps to determine the size distribution of water drops in clouds, the quantitative aspects of the relationship are not well defined. This includes the distribution of critical supersaturation of condensation nuclei as related to nucleus size and chemical composition. The deficiency of numerical models in predicting cloud drop size spectra was noted above.

The "auto-conversion" of cloud liquid water to liquid precipitation is thought to depend on locally enhanced number concentrations of cloud liquid water drops associated with variations of liquid water content due to turbulence and entrainment of environmental air into the cloud. Numerical modeling can determine the conditions required to initiate this process, but only controlled experiments can determine whether these conditions are physically reasonable.

Ice crystals are known to play a key role in the development of most non-tropical precipitation and particularly in the development of hail. The origin of ice particles coexisting with liquid water drops is a subject of great significance to weather modification, especially precipitation enhancement and hail suppression. The processes of condensation-freezing and contact nucleation are processes thought to be dominant requiring the presence of insoluble particles to act as freezing nuclei.

In summary, a large portion of the framework of knowledge of cloud and precipitation processes is in place, and most aspects of precipitation formation are understood qualitatively. There remain key areas in which quantitative understanding is limited or non-existent. To a considerable extent this is due to the difficulties of field measurements and of achieving unambiguous and repeatable conditions and measurements in laboratory experiments.

Prospects

As the foregoing discussion suggests, there is a great need for a major experimental facility for cloud physics research, capable of supporting research on fundamental processes of water and ice nucleation and the initial stages of precipitation development. The cloud chamber proposed by the University of Missouri appears to meet this need, as it will have well-controlled temperature and humidity conditions as well as precise definition of sizes and chemical compositions of nuclei. These characteristics will permit repetition of experiments for verification and well-documented variation of one or more parameters for comparative purposes.

The proposed facility should yield valuable contributions to crucial scientific problems identified by the cloud physics community. These include the relative significance of water drop coalescence and ice processes in producing rain, the interactions of aerosols (natural or anthropogenic) with atmospheric water, the study of cloud seeding materials, and the development of measuring techniques.

Two related areas, which have heretofore received less scientific emphasis than precipitation physics but which are of equal or greater concern to the Air Force, are also amenable to research in the University of Missouri cloud chamber. These are the physics of fog and the propagation of electromagnetic signals through clouds and fog. The proposed cloud chamber can support research relating to the onset and dissipation of fog and the effects of fog and non-precipitating clouds on optical and infrared signals.

Air Force Benefits and Involvement

The most obvious benefit of this research facility to Air Force operations will result from its contributions to the predictability and possible modification of clouds and precipitation. Atmospheric prediction, both at the cloud scale and mesoscale, requires accurate representation of water transport and phase changes and interactions with the dynamics. Thus, the experimental capability will contribute to understanding of severe storm development and to forecasting of clouds and fog. While the effects of precipitation on microwave communications and guidance systems are well known, the effects of water vapor, clouds, and fog at optical and infrared wavelengths are only partially understood. Instrumentation development associated with the cloud chamber will provide not only improved techniques of documenting cloud physical parameters but also increased understanding of electromagnetic absorption and scattering processes.

The capability of controlling the characteristics of nucleating materials will also permit research on environmental impacts of Air Force operations. Possible effects which could be investigated include both local and global effects on clouds and precipitation and detectability of aerospace vehicles by their emissions or contrails.

Recommendations

The facility being built at the University of Missouri-Rolla will be one of the most significant advances in cloud physics research facilities in recent years. AFOSR should encourage a broad-based cooperative spirit in the research community.

The cloud simulation facility should be viewed as a quasi-national facility whereby the Graduate Center for Cloud Physics at Rolla can cooperate with diverse interested research groups in cloud, aerosol, and optical physics to get the most out of this very expensive and sophisticated installation.

MESOSCALE WEATHER FORECASTING

A BACKGROUND SURVEY FOR AFOSR

James I. Metcalf
Capt, USAF Reserve

Historical Development

Numerical techniques for forecasting the weather were first investigated intensively in the 1920's, on the hypothesis that a quantitative description of the state of the atmosphere at any future time could be obtained by integration of the thermodynamic and dynamic equations from a known initial state. It was recognized at the outset that the number of computations required would preclude the generation of a true forecast, i.e., that the numerical model would run slower than real time. This major deficiency was alleviated by the advent of high-speed, large-capacity computers. From the earliest one-layer models evolved more complex models incorporating the variations of the atmosphere in height and including surface topography and air-sea interactions. These have proven to be fairly successful in forecasting the development and movement of large-scale features of the general circulation of the atmosphere.

Problems remain, however, in the specification of the initial state of the atmosphere and in the representation of atmospheric processes at time and space scales smaller than the time step and grid size used in the model computations. The initialization problem is particularly severe over the oceans, where relatively few upper air soundings are taken. Furthermore, the lack of temporal and spatial resolution of the models has prevented their use for reliable forecasting of "weather," i.e., ceiling, visibility, icing, amount of precipitation, and time of precipitation, and the development of severe storms since these phenomena involve or are dominated by small-scale physical processes.

In order to incorporate these processes into the numerical forecast, atmospheric models have been developed with denser grids and, for computational economy, limited areas. Whereas the global models have grid point spacing of 200-400 km, the so-called mesoscale models have grid point spacing as small as about 20 km, and cover areas typically 2000 km on a side. The mesoscale, as defined by the meteorological community, includes three subsets of scale sizes: 2500-250 km, 250-25 km, and 25-2.5 km. The two larger scales are also called "regional" scales whereas the smallest scale is the "storm" scale, with reference to individual severe storms. The following discussion deals mainly with the use of regional models for weather forecasting, although these models are also applicable to weather modification experiments and to air quality studies.

Current Status

A variety of mesoscale meteorological models have been developed for the investigation of various types of regional weather phenomena. Two-dimensional models have been applied to the flow of air over mountain ridges or near coastlines, where uniformity in one horizontal dimension may be assumed as a first approximation. A representation of the atmospheric boundary layer in two horizontal dimensions has been used to predict the development of convective clouds, based on low level convergence of heat and moisture flux. In general, however, mesoscale models must be three-dimensional in space, since the phenomena they are designed to investigate tend to have significant variability both horizontally and vertically.

Mesoscale modelling problems fall into two general categories: those associated with physical processes and those which are essentially numerical. Physical processes include the accurate representation of heat and moisture flux divergence and the budget of total water, including its transitions from vapor to cloud to precipitation. Also the modeler must be concerned with the representation of physical processes which occur at size scales less than the grid point spacing, such as cumulus convection and turbulence. Boundary conditions on the model determine substantially the effects of larger-scale motions on regional-scale weather developments. The lower boundary must be capable of admitting surface heat and moisture and accommodating turbulent energy dissipation and mixing. The specification of upper boundary conditions is particularly difficult. For some applications a fixed "lid" is satisfactory, but in general the upper boundary must permit a flux of energy and momentum into or out from the model domain, without fictitious reflection of waves propagating upward.

The numerical problems are mainly associated with the quantity and variety of data used to initialize and to update the model. Types of data include satellite depiction of cloud locations and top heights (from infrared temperature data), radar reflectivity distributions which approximate the distribution of precipitation, and radiosonde observations of upper air winds, temperature, and humidity. In working toward particular research or operational goals, consideration must also be given to the grid spacing, domain size, and input data density as these factors relate to computational cost and forecast accuracy.

Prospects

Continuing development of mesoscale meteorological models should yield improvements in forecast parameters and increase in the potential breadth of application on a time scale of 1-2 days. Major factors governing the advance of mesoscale forecasting are computational power, development of sensors and interpretive techniques, and the availability of large data sets with which to test the models and verify their

output. Computational volume and speed have increased significantly in the past few years and are likely to continue to do so. Temperature soundings from satellites are supplementing conventional radiosoundings, and new instruments are being developed for measurement of water vapor profiles from satellites. Use of the mesosphere-stratosphere-troposphere (MST) radar technique for wind measurements can provide increased data for forecast verification or more detailed definition of winds for the upstream boundary conditions of the model domain, depending on the locations and mode of operation of these radars. Large data sets have been generated for extratropical cyclonic storms through the CYCLES project, directed by the University of Washington, and are being generated for severe convective storms through the SESAME project, directed by NOAA.

A Drexel University regional scale model developed under Dr. Kreitzberg is designed primarily for the forecasting of clouds and precipitation, both stratiform and convective. It involves a numerical grid approximately 2000 km on a side with 35-km horizontal spacing and approximately 1-km vertical spacing up to 16 km. Its potential for forecasting "weather" parameters of concern to Air Force operations is based on the fact that the model includes both "cloud" water content, i.e., non-precipitating water, and "precipitation" at each grid point. The model software is designed to permit integration of data from a variety of sources (surface instruments, rawinsondes, satellites, and radar). The availability of large data sets from the SESAME and CYCLES projects provide an unparalleled opportunity for research with this model, in that the model can be initialized with greater accuracy and detail than previously and model output parameters verified and/or modified at relatively short time intervals.

A version of a model by Anthes and Warner at the Pennsylvania State University operates with a horizontal grid spacing of 60 km and 6 layers in the vertical and is designed to forecast the development and release of latent instability which is associated with the development of severe storms. This process is thought to involve the interaction of warm moist tropical air at low levels and warm dry air masses of Mexican and southwest US desert origins aloft. The resulting instability is usually released gradually by convection at a variety of scales but occasionally released very rapidly in severe storms. The availability of the SESAME data sets will facilitate research aimed at defining the conditions under which the rapid release occurs.

Air Force Benefits and Involvement

The major benefit to the Air Force from this research is through improved prediction of cloud and precipitation development. Parameters such as time and quantity of precipitation, and the occurrence of icing in stratiform clouds should be forecast with greater accuracy and reliability. While regional scale models will not be capable of

detailed forecasts of severe storm development and movement, they should yield more precise indications of areas likely to be affected and the probable intensity of storms, a day or two in advance

Models developed for air quality applications should be valuable in assessing the environmental effects of Air Force operations. Models including both dynamics and chemistry can describe the transport and diffusion of trace constituents, their chemical reactions, and their scavenging by precipitation. Models can be run for individual situations or can be used to generate regional-scale climatologies which may be useful for long-range planning purposes.

Recommended Research Areas

Active support of research efforts to improve the basic understanding of mesoscale processes and to develop improved models of mesoscale phenomenology is strongly recommended. While the breadth of specific research topics could well be termed limitless, in the near future, it is recommended that AFOSR consider actively supporting basic research in the following listed areas for the most immediate benefit to military interests:

1. Development of nested fine-mesh models from synoptic scales down to 10 km resolution.
2. Inclusion in mesoscale models of the total water budget from vapor through precipitation.
3. Inclusion of effects of cumulus convection on mesoscale dynamics.
4. Planetary boundary layer effects in heat, moisture and momentum transfer.
5. Inclusion of other small-scale effects on dynamics such as radiation and turbulence as well as heat, moisture and momentum exchange through model boundaries.
6. Determination of the effects of higher temporal resolution data on mesoscale model capabilities (e.g., MST radar continuous wind data).
7. Improved initialization techniques.
8. Effect of incorporation of available and anticipated satellite data on mesoscale model performance.

RADAR ATMOSPHERIC RESEARCH AT AFOSR

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1. Introduction

Radar techniques, i.e., the detection and evaluation of electromagnetic signals resulting from the scattering of a transmitted signal, have been applied to the research of a great variety of atmospheric phenomena. These phenomena differ widely in essential characteristics, ranging from ionization in the upper atmosphere to the structure of turbulence in the earth's planetary boundary layer; and the radar techniques used to observe them differ correspondingly. The purpose of this survey is to place these techniques and research areas in perspective, comparing measurement capabilities of different types of radars and relating these to attainable scientific objectives.

Concepts of radar reflectivity and design are discussed with reference to operations at very high frequency (VHF, 30-300 MHz or 1-10 m wavelength), ultra-high frequency UHF, 300-3000 MHz or 10-100 cm wavelength), extremely high frequency (EHF, 3-30 GHz or 1-10 cm wavelength) and superhigh frequency (SHF, 30-300 GHz or 1-10 mm wavelength). The SHF, EHF, and upper UHF regions of the electromagnetic spectrum constitute the microwave region, defined in terms of the techniques of generating and transmitting signals at these frequencies, although the SHF region is more commonly referred to as the "millimeter wavelength" region. Specific applications of these techniques are discussed in relation to different classes of atmospheric phenomena and the atmospheric science research subspecialties which make use of radar as an observational tool. Finally, the involvement of AFOSR in these areas is presented, with the objective of showing the interrelationships of some of these programs and the different scientific results expected from different research groups, some of which use similar types of equipment.

2. Radar Reflectivity

Variations of refractive index in a propagation medium result in scattering of electromagnetic signals, which can then be detected remotely and used to characterize the medium. Variations result from the presence of water drops or ice crystals, gradients of temperature or humidity, or gradients of electron density. Scatter also arises from the random motion of electrons in a medium in thermodynamic equilibrium. The processes that produce electromagnetic scattering can be characterized by appropriate physical parameters, which can then be related to spatial or temporal characteristics of these processes in the atmosphere. Since the scattering involves the interaction of

electromagnetic signals with the physical process, the formulations of reflectivity typically include the wavelength or frequency of the incident signal, and the wavelength thus becomes a potentially important radar design parameter.

2.1. Clouds and Precipitation

Reflectivity of clouds or precipitation is usually formulated in terms of scattering from spheres or ellipsoids which are small relative to the wavelength. This assumption permits use of the Rayleigh approximation for the scattered signals, where backscatter reflectivity is dependent on the summation or integration over a collection of particles at a specific wavelength. The wavelength dependence makes shorter wavelengths (higher frequencies) more desirable for remote detection if scattering effects alone are considered. Increasing signal attenuation is encountered with increasing frequency across the EHF and SHF regions, especially in rain. Analysis of the detectability of rain through a rain propagation medium results in the identification of an optimum frequency which, depending on the rainfall rate, is between 3 and 10 GHz.

The reflectivity of clouds or precipitation is related to the water content or precipitation rate through the drop size distribution. Measurements at two wavelengths or at two orthogonal polarizations can be used to derive improved estimates of water content or precipitation rate, since the two measured parameters can be related analytically to a size parameter and a number density parameter. The use of Doppler radar permits measurement of the distribution of velocities within the scattering medium and thus permits the derivation of wind fields within clouds and the estimation of atmospheric turbulence.

2.2. Clear Atmosphere

Reflectivity in the clear atmosphere results from refractive index fluctuations associated with gradients of temperature and humidity. In some cases the echoes are "specular", i.e., due to differences of refractive index across layers that are much smaller than the radar wavelength. More commonly they are due to mechanical turbulence in layers of refractive index gradient. In this case the refractive index is describable in terms of a spectrum of fluctuations; reflectivity is due to fluctuations at a scale of half the radar wavelength, the variance of refractive index and the "outer scale" of the turbulence which produces the fluctuations. This formulation is strictly valid in the "inertial subrange" of the refractive index spectrum, where the transfer of energy to smaller scales is accomplished only by inertial forces. At small scales, where viscous dissipation of energy is significant, the turbulent energy and hence the intensity of refractive index fluctuations decreases rapidly with decreasing length scale. Thus there is a wavelength at which the clear air reflectivity is maximized for given values of the variance of refractive index and the outer scale

of the turbulence. This wavelength is also related to the "inner scale" of the inertial subrange, and because the scale associated with viscous dissipation of turbulent kinetic energy increases with altitude, the optimum wavelength for detection of echoes from the electrically neutral clear atmosphere increases approximately logarithmically with altitude, from a value near 2 cm (frequency 15 GHz) at the surface to about 200 m (frequency 1.5 MHz) at 100 km.

Analytical techniques have been developed to relate the clear-air reflectivity to the thermal stability and (approximately) to turbulence intensity, although the latter is more accurately determined if a Doppler radar is used. Since the small-scale refractive index structure is carried with the larger-scale flow, the clear air reflectivity can act as a tracer of wave motions in the atmosphere.

2.3. Ionized Atmosphere

Reflectivity due to electron density gradients becomes increasingly significant above about 60 km altitude, as the electron density increases with altitude. The reflectivity is dependent on the variance of refractive index expressed in terms of the variance of electron density fluctuations. The wavelength dependence is reversed from the previous cases, so that the reflectivity increases rapidly with increasing wavelength. Because no other physical factors are involved, there is no optimum wavelength for detection, and the only limits are those due to radar system design. Because of reduced electron density at night, backscatter due to electron density gradients is detectable only during the day.

At altitudes above about 80 km, scattering due to random thermal motion of electrons becomes significant and reflectivity is a function of the electron density, but is independent of radar wavelength. Below about 100 km, however, scattering due to electron thermal motion is combined with that due to mechanical turbulence so that if the so-called "thermal scatter" is to be resolved from turbulent scatter the wavelength must be chosen to be less than twice the "inner scale" of the turbulent velocity spectrum. Thus wavelengths of less than about 1 m (frequencies above 300 MHz) can be used to observe thermal scatter at altitudes of 65 km or even less.

In addition to yielding values of electron density and (with Doppler radar techniques) electron drift velocity, measurements of thermal scatter can be interpreted in terms of the ionospheric conductivity. In the lower portion of the ionosphere, electron motion is coupled to the motion of the heavier, electrically neutral, constituents, while at higher altitudes the electrons tend to follow magnetic field lines since their mean free path increases with height. Under these conditions, the measured electron drift velocity can be interpreted in terms of the convection of the geomagnetic field.

Scientific Applications

Research in atmospheric science has always been somewhat stratified, corresponding to the different physical processes that dominate at different altitudes. The science is further subdivided according to interest in various scales of dynamics and in the physics of radiative transfer, molecular or sub-molecular interactions, and the formation of clouds and precipitation. The radar techniques useful for measurements of these processes differ widely so that to the extent that research in each of these sub-areas proceeds independently of other research, the radar-oriented investigators in one sub-area may have limited communication with radar-oriented investigators in another.

For the observation of electron density in the ionosphere, for example, radars have been developed at wavelengths from about 20 cm to several meters. These have little or no value for the observation of clouds or precipitation, and except for the shorter-wavelength radars, with fully steerable antennas, they are not capable of observing the two or three dimensional structure of backscatter associated with atmospheric turbulence. Radars for the observation of precipitation and clouds in the troposphere operate at wavelengths from about 8 mm to 10 cm, and radars of 10 cm wavelength are used also for the observation of backscatter from refractive index fluctuations associated with turbulence. These radars, operating in the EHF and SHF regions, are not useful for the observation of backscatter associated with ionization processes in the middle and upper atmosphere.

In each of these scientific sub-areas, radar is used as an observational tool in conjunction with associated theoretical and analytical research. Thus the use of different types of radars has resulted in a dissociation of what might otherwise be viewed as the "atmospheric research radar" community. It is interesting to note that while "meteorology" is defined broadly as the science of the atmosphere, it is traditionally applied more restrictively to the troposphere. The biennial Radar Meteorology Conferences of the American Meteorological Society have illustrated this restrictiveness, as they have traditionally been dominated by researchers of cloud and precipitation physics, storm dynamics, and turbulence in the troposphere.

The emergence of the mesosphere-stratosphere-troposphere (MST) radar technique in the past few years has had the effect of bridging the gap between the study of tropospheric dynamics and the study of the upper atmosphere. As more data becomes available on a routine basis, this research should develop closer collaboration between individuals and groups which have heretofore pursued research in the dynamics of the lower and upper atmosphere as mostly separate disciplines. Ultimately, the dynamical interactions between different regions of the atmosphere can be related to physical processes such as radiative transfer in the upper atmosphere and its effects on atmospheric dynamics at all altitudes.

AFOSR Programs in Radar Atmospheric Research

Because of the diversity of research sub-areas that rely substantially on radar for experimental data, it appears impossible to present the AFOSR support of radar-related atmospheric research as a completely unified program. The selection of particular facilities, individuals, or research groups for support inevitably depends on criteria such as the identification of worthy new ideas, the maximizing of scientific return on initial investments in existing equipment, and the availability or interest of individuals to pursue research in areas identified as important by AFOSR.

Research in traditional tropospheric radar meteorology has been funded largely by National Science Foundation, with support also by NASA, AF Geophysics Laboratory, ONR, ARO, NOAA, FAA, the Water and Power Resources Service, and few other agencies. The state of research in this area will be of importance during the next few years because of the need for developing specifications and data processing techniques for the Next-Generation Weather Radar (NEXRAD). Most of the research required by the NEXRAD will be system-oriented and hence not strictly appropriate for AFOSR support. Development of new radar techniques will continue, and while some may not be incorporated in the NEXRAD they should yield more and better information on physical and dynamical processes in clouds and precipitation. As opportunities appear for the use of these radar techniques in basic atmospheric research, AFOSR should consider funding some components of the proposed research efforts.

Because physics and dynamics of the upper atmosphere are of particular concern to military operations, especially those of the Air Force, it is appropriate that AFOSR take a leading role in supporting research in this region. Research currently receiving OSR funds includes both experimental and theoretical projects.

Current projects related to the physics and dynamics of the ionosphere include studies of gravity waves in the 170-280 km region based on data from the Chatanika radar, of electron density variations, and of the auroral zone energy budget. The latter is oriented toward understanding the ionospheric energy budget and neutral winds using long-duration observations from Chatanika. The former project is aimed primarily at understanding the phenomenon of magnetospheric convection, as revealed by the Millstone Hill radar. The locations of the two radars involved in these studies permit observations of the auroral and sub-auroral regions from directly underneath the auroral zone and from about 15° south.

OSR funding permitted the early initiation of construction of the NOAA MST radar at Poker Flat. Involvement in this research has continued in the form of data analysis as well as model development. Additionally, AFOSR supports theoretical research in upper atmospheric structure and dynamics. Most closely related to the experimental efforts are studies

of planetary waves in the stratosphere and of tidal motions in the ionosphere. These research programs enhance the theoretical basis for interpreting radar data and designing future experiments. Research in tidal motions, for example, will permit the removal of this component of motion from radar-derived measurements and thus permit the more accurate interpretation of spatial and temporal variations which are of non-tidal origin.

Recommendations

AFOSR should remain deeply involved in both experimental and theoretical radar studies of the atmosphere. Support of ionospheric radar studies to confirm and improve existing ionospheric prediction models is urged as such improvements will immediately impact the predictive capability of the currently operational Air Weather Service models. AFOSR should continue support for the development and evaluation of MST radar capabilities. From the surface to 100 km the MST radar offers the potential for understanding the vertical transfer of energy and the coupling of dynamics at different altitude regimes. At low altitude the continuous data base available from a small (surface to 15 km capability) offers promise to improving synoptic and mesoscale forecasting of significant weather events.

ACTIVE RESEARCH EFFORTS

ATMOSPHERIC SCIENCES

As of 1 Oct 1980

Alphabetical by Principal Investigator

Low Level Convergence and the
Production of Convective Pre-
cipitation (TSC)
AFOSR-ISSA-80-00029, 2310/A1

Bernice Ackermann
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Modelling the Ionospheric and
Plasmaspheric Effects Produced
by a Simulated Saturn V Launch
(TSC)
AFOSR-ISSA-81-0020, 2310/A2

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Analysis and Prediction of Severe
Storm Environment (TSC)
AFOSR-79-0125, 2310/A1

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T. N. Carlson
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The Morphology of Stratospheric
Planetary Waves (TSC)
F49620-79-C-0160, 2310/A2

Arthur D. Belmont
Control Data Corporation
Minneapolis, Minnesota 55440

Remote Lidar Measurement of Wind,
Turbulence and Convective Structure
in the Planetary Boundary Layer
(TSC)
AFOSR-MIPR-80-00041. 231-/A1

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Latitudinal and Altitudinal Dis-
tribution of Ionospheric Parameters
(TSC)
F19628-80-C-0002, 2310/A2

J. V. Evans
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Structure of the Upper Atmosphere
(TSC)
AFOSR-77-3223, 2310/A2

Jeffrey M. Forbes
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Analysis of Coherent Satellite
Scintillation Data (TSC)
F49620-78-C-0014, 2310/A2

Edward J. Fremouw
Physical Dynamics Inc.
Bellevue, Washington 98005

Analysis of Severe Weather Using
Digital Doppler and Noncoherent
Radar Data (TSC)
AFOSR-80-0063, 2310/A1

George Huebner
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Construction of University of
Missouri-Rolla's Full Scale Cloud
Simulation Chamber (TSC)
N00014-79-C-0545, 2310/A1

James J. Kassner, Jr.
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Analysis of the NOAA Alaskan MST
Radar System Data (TSC)
AFOSR-80-0020, 2310/A2

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Light Scattering and Absorption
Properties of Ice Clouds for Visible
and Infrared Laser Wavelengths (TSC)
F49620-79-C-0198, 2310/A1

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Kenneth Sassen
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University of Utah
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Propagation of Transient Signals
through Non-Linear Ionized Media
(TSC)
AFOSR-78-3729, 2310/A2

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Computer Engineering
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Shear-Induced Turbulence by MST
Radar (TSC)
AFOSR-80-0286, 2310/A1

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High Time Resolution Thermospheric
Temperature and Wind Studies in the
Arctic (TSC)
AFOSR-80-0240, 2310/A2

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Scattering by Non-Spherical
Particulates (TSC)
AFOSR-MIPR-80-00015, 2310/A1

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Atmospheric Absorption of Radiation
by Water (TSC)
AFOSR-80-0058, 2310/D9

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Latitudinal Variations of Auroral
Zone Ionization Distributions (TSC)
F49620-80-C-0014, 2310/A2

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Phase Fluctuations of Trans-
ionospheric Signals under
Multiple Scattering Conditions (TSC)
AFOSR-80-0187, 2310/A2

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Auroral-Region Dynamics Determined
with the Chatanika Radar (TSC)
F49620-78-C-0018, 2310/A2

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RESEARCH EFFORTS COMPLETED IN FY77

ATMOSPHERIC SCIENCES

Alphabetical by Principal Investigator

Propagation of an EMP Pulse
Pulse through the D-Region
of the Ionosphere (TSC)
AFOSR-76-2949; AFOSR-76-0436,
2310

R. N. Carlile
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Analysis of Severe Storms Using
Digital Radar Data (TSC)
AFOSR-77-3146, 2310/A1

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Summer Programs in Geophysical
Fluid Dynamics (TSC)
AFOSR-MIPR-77-0030, 2310

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RESEARCH EFFORTS COMPLETED IN FY78

ATMOSPHERIC SCIENCES

Alphabetical by Principal Investigator

Develop a Mesosphere-Stratosphere-
Troposphere Radar System (TSC)
AFOSR-ISSA-78-0028, 2310

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Energy Input to the Auroral
Ionosphere (TSC)
AFOSR-77-3435, 2310/A2

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Satellite Sensing and Radiative
Transfer (TSC)
AFOSR-78-3576, 2310/A1

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Tracking and Monitoring Hurricanes
by HF Skywave Radar Over the Gulf
of Mexico (TSC)
F49620-76-C-0023, 2310/A1

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HARP Data Analysis (TSC)
AFOSR-77-3320, 2310/A2

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Error Growth in General
Circulation Models (TSC)
AFOSR-76-3164; AFOSR-78-3531
2310/A1

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RESEARCH EFFORTS COMPLETED IN FY79

ATMOSPHERIC SCIENCES

Alphabetical by Principal Investigator

Studies of Upper Air Motions
by VHF Backscatter (TSC)
AFOSR-ISSA-79-0031, 2310

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Nonlinear Transfer of Kinetic
Energy in the Atmosphere Using
One- and Two-Dimensional
Spectral Representation (TSC)
AFOSR-78-3492, 2310

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Solar-Terrestrial Predictions
Workshop (TSC)
AFOSR-ISSA-79-0019, 2310

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The Nature and Derived Climatology
of Thunderstorm Electrical Activity
over a Large Geographic Area (TSC)
AFOSR-79-0003, 2310

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Spectroscopic Investigation of the
Upper Atmosphere in the Plasma-
pause Region (TSC)
AFOSR-ISSA-79-0032, 2310

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Laser Induced Lightning
Investigation (TSC)
AFOSR-78-3722, 2310

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RESEARCH EFFORTS COMPLETED IN FY80

ATMOSPHERIC SCIENCES

Alphabetical by Principal Investigator

Extratropical Cyclonic Storms -
The Cycles Project (TSC)
F49620-77-C-0057, 2310/A1

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Corona from Ice, Thunderstorm
Electrification and Lightning
Suppression (TSC)
AFOSR-77-3429, 2310/A1

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Near-Infrared Spectrometric Airglow
Measurements During the Total Solar
Eclipse of 26 Feb 1979 (TSC)
AFOSR-79-0040, 2310/A2

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Stratospheric Residence Times from
Contrail Observations by Satellite
(TSC)
F49620-79-C-0180, 2310

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Auroral-Region Dynamics Deter-
mined with the Chatanika Radar
(TSC)
F49620-78-C-0018, 2310/A2

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COMPLETED PROJECT SUMMARY

1. TITLE: Propagation of an EMP Pulse through the D-Region of the Ionosphere

2. PRINCIPAL INVESTIGATOR: Dr. R. N. Carlile
Department of Electrical Engineering
University of Arizona
Tucson AZ 85721

3. INCLUSIVE DATES: 1 October 1975 - 30 September 1977

4. GRANT NUMBER: AFOSR-76-2949; AFOSR-76-0436

5. COSTS AND FY SOURCE: \$64,744, FY76; \$77,399, FY77

6. PUBLICATIONS:

"Absorption of Energy from a Large Amplitude Electromagnetic Pulse by a Collisionless Plasma," R. N. Carlile, A. Cavalli, W. L. Cramer, Richard M. Hyde, and William A. Seidler, IEEE Transactions on Antennas and Propagation, V. AP-27, N. 5, pp. 596-603 (1979).

"Final Report on Grant AFOSR-76-2949," R. N. Carlile, AFOSR-TR-80-0001 (1979).

"A Note on the Absorption of Energy from an EMP by a Plasma at a Moderate Neutral Pressure," R. N. Carlile and Alexander Cavalli, submitted to the IEEE Transactions on Antennas and Propagation.

"Propagation of an EMP through a Collisional Plasma," R. N. Carlile and Alexander Cavalli, submitted to IEEE Transactions on Antennas and Propagation.

"A Simple, Inexpensive Laboratory Plasma Machine, R. N. Carlile and Alexander Cavalli, submitted to the IEEE Transactions on Plasma Science.

"Anomalous Enhanced Ionization of a N₂ Plasma by a Transient Electromagnetic Pulse," R. N. Carlile and Alexander Cavalli, submitted to the IEEE Transactions on Antennas and Propagation.

"Computer Simulation of the Propagation of a EMP Through a Plasma," R. N. Carlile, submitted to the IEEE Transactions on Antennas and Propagation.

"A Structurally Simple Baffle which Allows Differential Pumping of a Vacuum System," R. N. Carlile and Alexander Cavalli, submitted to the Review of Scientific Instruments.

"The Evolution of the Electron Distribution Function in Time for Electrons in the Presence of a Transient Electromagnetic Pulse, R. N. Carlile, submitted to the IEEE Transactions on Plasma Science.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project attempted to verify theoretical calculations of electromagnetic pulse (EMP) propagation in the ionosphere. Experiments using existing and new equipment used dimensional similarity between the D-region of the ionosphere and a laboratory-generated plasma wave guide to test the theoretical calculations. During the course of this grant, a series of experiments in which an electromagnetic pulse (EMP) was propagated through a nitrogen plasma were conducted. The pulse had the general characteristics of an EMP. The pulse was observed as it emerged from the plasma as a function of the plasma parameters. As the electron number density increased, it was found that energy was increasingly absorbed from the pulse, a process due to joule heating. In addition, at higher number densities, ringing of the pulse occurred. The nitrogen pressure in these experiments was sufficiently low so that collisions played only a minor role. Also developed was a theoretical model based on the fluid transport equations. This theory predicted that the electrons of the plasma attain a temperature of about 15 eV in that part of the system where the DC magnetic field was about 80 G. More importantly, it predicted the output pulse quite well under the conditions that the ambient nitrogen pressure and the electron number density were low. The theory appeared to fail as these parameters were increased.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Analysis of Severe Storms Using Digital Radar Data

2. PRINCIPAL INVESTIGATOR: Dr. George L. Huebner
Department of Meteorology
Texas A&M University
College Station, TX 77840

3. INCLUSIVE DATES: 1 October 1976 - 30 June 1977

4. GRANT NUMBER: AFOSR-77-3146

5. COSTS AND FY SOURCE: \$3,500, FY77

6. JUNIOR RESEARCH PERSONNEL: Thomas E. Sieland

7. PUBLICATIONS:

"Real-Time Computer Techniques in the Detection and Analysis of Severe Storms from Digital Radar Data," T. F. Sieland, Final Technical Report , AFOSR-TR-78-0123 (1978).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In order to improve models of severe storm structure, digital radar data were analyzed to determine (1) the vertical distribution of liquid water content; (2) atmospheric conditions when storm vertical development occurs; and (3) the location where tornadoes appear in the storm.

An improved computer method was developed by which multi-tilt digital radar data can be interpolated in three dimensions and reduced to a two-dimensional display of partially vertically-summed reflectivity (Z) maps (PVSZ) in near real time. Digital radar data from the 10-cm radar at the National Severe Storms Laboratory in Norman, Oklahoma, was used to evaluate the numerical techniques. Various combinations of interpolation schemes were used in the new method, and the resultant products were compared to determine whether or not significant features of a severe storm evident in constant altitude reflectivity maps are retained. In addition, the number of PVSZ layers was varied to determine the minimum needed for adequate depiction of the tilt of the storm core.

Severe storm data from New England were processed using the new techniques to compare Oklahoma storms to those evident in the New England digital radar data. A tornadic storm in Maine presented many severe-storm signatures that have been observed in analyses of Oklahoma tornadoes.

The new computer method developed during this investigation resulted in significant savings of computer time and memory as compared to previous methods and yet retains all of the significant features of the severe storm complex. Three PVSZ layers appear to be sufficient to depict adequately the tilt of the storm core.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Summer Programs in Geophysical Fluid Dynamics
2. PRINCIPAL INVESTIGATOR: Dr. George Veronis
Department of Geology and Geophysics
Yale University
New Haven, CT 06520
3. INCLUSIVE DATES: 1 June 1977 - 15 August 1977
4. GRANT NUMBER: AFOSR-MIPR-77-0030
5. COSTS AND FY SOURCE: \$6,000, FY77
6. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

AFOSR provided partial support for the conduct of a 10-week summer workshop on turbulence theory and the incorporation of recent theoretical advances into models of geophysical flows. Primary funding was provided by the Office of Naval Research. Twenty professional scientists and 14 pre-doctoral and post-doctoral fellows participated in the workshop. The workshop provided the opportunity to evaluate recent research in turbulence theory and modeling, identify new and promising areas of research, and to plan future research programs.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Develop a Mesosphere-Stratosphere-Troposphere Radar System
2. PRINCIPAL INVESTIGATOR: Dr. Ben B. Balsley
Aeronomy Laboratory
NOAA
Boulder, CO 80303
3. INCLUSIVE DATES: 15 June 1978 - 30 September 1978
4. GRANT NUMBER: AFOSR-ISSA-78-0028
5. COSTS AND FY SOURCE: \$54,541, FY78
6. SENIOR RESEARCH PERSONNEL:

Warner L. Ecklund
K. S. Gage
7. PUBLICATIONS:

"The Poker Flat MST Radar: First Results," B. B. Balsley,
W. L. Ecklund, D. A. Carter, and P. E. Johnston, Geophys. Res. Lett., **6**,
921 (1979).

"The Poker Flat MST Radar: An Outline of the Primary Echoing Mechanisms
and a Description of the Facility," B. B. Balsley, W. L. Ecklund, and
D. A. Carter, Preprints 19th Conf. Radar Meteor., Amer. Meteor. Soc.,
549 (1980).

"The Poker Flat MST Radar: Preliminary Results Between 3-20 km,"
W. L. Ecklund, B. B. Balsley, and D. A. Carter, Preprints 19th Conf.
Radar Meteor., Amer. Meteor. Soc., 557 (1980).

"The Poker Flat MST Radar: Signal Analysis and Data Processing
Techniques with Examples," D. A. Carter, B. B. Balsley, and
W. L. Ecklund, Preprints 19th Conf. Radar Meteor., Amer. Meteor. Soc.,
563 (1980).

"The MST Radar Technique: Potential for Middle Atmospheric Studies,"
B. B. Balsley and K. S. Gage, Pure and Appl. Geophys., **118**, 452 (1980).

"The MST Radar at Poker Flat, Alaska," B. B. Balsley, W. L. Ecklund,
D. A. Carter, and P. E. Johnston, Radio Sci., **15**, 213 (1980).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The NOAA Aeronomy Laboratory proposed to National Science Foundation the construction of a radar at Poker Flat, Alaska, operating at a frequency of 50 MHz and capable of detecting signals backscattered from the clear atmosphere at all heights up to 100 km. Backscatter is due to turbulence in layers of refractive index gradient. Backscatter from the surface to near 50 km is due to temperature and humidity fluctuations, and backscatter from greater altitudes is due to fluctuations of electron density. The signals are processed to obtain the radial wind component, and observations at several beam angles allow determination of vertical and horizontal wind components.

Early results with a prototype radar in Colorado showed the capability of observing short-period (few minutes) wind fluctuations associated with atmospheric gravity waves and showed good agreement between winds measured by radar and those obtained by conventional sounding techniques. AFOSR contributions to the building of the radar at Poker Flat permitted construction of the radar antenna to begin before the winter of 1978-79. Further system development proceeded through the winter, and the first wind measurements were obtained during February and March of 1979, with about 1/4 of the antenna array installed. With continued support from NSF, the installation is now being completed.

In conjunction with the radar construction project, AFOSR has also supported data-analysis research efforts at several locations.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Energy Input to the Auroral Ionosphere
2. PRINCIPAL INVESTIGATOR: Dr. Joseph R. Doupnik
Center for Atmospheric and Space Sciences
Utah State University
Logan, UT 84322
3. INCLUSIVE DATES: 1 September 1977 - 31 August 1978
4. GRANT NUMBER: AFOSR-77-3435
5. COSTS AND FY SOURCE: \$32,000, FY77
6. SENIOR RESEARCH PERSONNEL:

J. C. Foster
G. S. Stiles
D. J. Baker
7. PUBLICATIONS:

"A Review of Incoherent Scatter Radar Measurements of Magnetospheric Electric Fields," J. R. Doupnik, Chapman Conf. Magnetospheric Substorms, Los Alamos (1978).

"Large Scale Convection of the High Latitude Ionosphere," J. R. Doupnik, J. C. Foster, and G. S. Stiles, Amer. Geophys. Union Fall Meeting, San Francisco (1978).

"Incoherent Scatter Radar Studies of the Dayside High Latitude Ionosphere," J. R. Doupnik, J. C. Foster, and G. S. Stiles, Amer. Geophys. Union Fall Meeting, San Francisco (1978).

"Detailed Comparison of Ionospheric Convection and Density," J. R. Doupnik, J. C. Foster, and G. S. Stiles, Amer. Geophys. Union Fall Meeting, San Francisco (1979).

"Chatanika Radar Electric Field Observations: Measurements in Important Boundary Regions," J. R. Doupnik, J. C. Foster, and G. S. Stiles, Amer. Geophys. Union Fall Meeting, San Francisco (1979).

"A Review of Magnetospheric Electric Fields," J. R. Doupnik, Intl. Union of Geodesy and Geophys. Meeting, Camberra, Australia (1979).

"Prolonged Radar Observations of an Auroral Arc," G. S. Stiles, J. C. Foster, and J. R. Doupnik, accepted by J. Geophys. Res.

"High Latitude Convection: Comparison of a Simple Model with Incoherent Scatter Observations," J. J. Sojka, J. C. Foster, W. J. Raitt, R. W. Schunk, and J. R. Doupnik, accepted by J. Geophys. Res.

"Energy Input to the Auroral Ionosphere," J. R. Doupnik, Final Report, AFOSR-TR-80-0261 (1980).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research was designed to investigate the role of Joule heating processes in the high latitude ionosphere. The strength of the electric field and the motions of the ionospheric plasma through the nearly stationary neutral gas have been found to be the dominant physical factors in the energy input to the atmosphere by Joule heating. Both the conductivity and electric field change by large factors but the dependence of the Joule heating rate on the square of the electric field strength makes the electric field the most critical factor. In experiments with a steerable dish antenna the conductivities are obtained from electron densities in the E region of the ionosphere while the electric fields are obtained from the F region. In this work, to cover a wide range of latitudes with acceptable time resolution, the E region measurements were curtailed. Two series of experiments were conducted with the Chatanika radar in Alaska: one in January 1978 and the second in June 1978. An objective of the June series was to study the global pattern versus temporal fluctuation by simultaneously operating the Millstone Hill radar located in Massachusetts. The raw radar data were recorded on tape and processed at the CASS Computer Facility to give geophysical parameters of plasma densities and drift velocities.

A finding from these and subsequent similar experiments is that the electric field pattern (strength and direction) is surprisingly smooth over large ranges of latitudes and over long periods of local time. The local afternoon sector (22 hours UT is local noon at Chatanika) is characterized by very strong electric fields which increase rapidly with latitude. Small changes in the diameter of the auroral oval due to substorms or fluctuations in the solar wind produce large variations of the field strength over Chatanika without necessarily altering the overall electric field pattern. This means the Joule heating during the afternoon is greatest at higher latitudes. From the repetitive nature of the observed pattern the heating rate is consistently large in that local time sector. The morning sector has high speed plasma flow also but generally not as large as the afternoon sector. Thus, the large increases in heating rate observed previously directly over Chatanika are due in large part to simple expansions and contractions of the auroral oval. Further, since Chatanika is typically in the lower part

of the oval the heating rates should be much greater in the poleward part of the oval. Preliminary results of the comparisons of Millstone Hill and Chatanika radar data indicate that on average the electric fields observed from Millstone Hill are somewhat smaller than those observed at the same magnetic latitudes from Chatanika. A suggestion from model studies is that the offset of the geomagnetic pole from the geographic pole and a further offset of the center of the oval, several degrees antisunward of the geomagnetic pole, introduces a strong longitudinal variation in the magnetic latitude of the oval. Hence some longitude sectors, such as Chatanika, penetrate more deeply into the oval than other locations with the same magnetic latitude.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Satellite Sensing and Radiative Transfer
2. PRINCIPAL INVESTIGATOR: Dr. Kuo-Nan Liou
Department of Meteorology
University of Utah
Salt Lake City, UT 84112
3. INCLUSIVE DATES: 15 March 1978 - 30 September 1978
4. GRANT NUMBER: AFOSR-78-3576
5. COSTS AND FY SOURCE: \$5,000, FY78
6. JUNIOR RESEARCH PERSONNEL:

Grant Aufderhaar
Allan Duff
Gerard Wittman

James Hatch
P. Nipko

7. PUBLICATIONS:

"Parameterization of the Radiative Properties of Clouds," K.-N. Liou and G. D. Wittman, Final Report, AFOSR-TR-79-0428.

"Parameterization of the Radiative Properties of Clouds," K.-N. Liou and G. D. Wittman, J. Atmos. Sci., 36, 1261 (1979).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was the development of empirical and theoretical equations describing the reflection, transmission, and absorption of solar radiation by clouds of different types as functions of solar zenith angle and cloud liquid water content. Parameterization of the effects of surface reflection and absorption by water vapor between the cloud and the earth's surface in terms of the water vapor absorptivity, ground reflection, and average cloud reflection was developed. The range of the solar spectrum considered was from 0.2 to 3.4 micrometers wavelength (visible and near infrared). The parameterization also included gaseous absorption and aerosol scattering.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Tracking and Monitoring Hurricanes by HF Skywave Radar Over the Gulf of Mexico
2. PRINCIPAL INVESTIGATOR: Joseph W. Maresca, Jr.
SRI International
333 Ravenswood Ave.
Menlo Park, CA 94025
3. INCLUSIVE DATES: 14 July 1976 - 30 November 1978
4. CONTRACT NUMBER: F49620-76-C-0023
5. COSTS AND FY SOURCE: \$12,493, FY77; \$87,496, FY77; \$25,210, FY78;
\$4,390, FY79
6. SENIOR RESEARCH PERSONNEL: Christopher T. Carlson
James R. Barnum
7. PUBLICATIONS:

"Tracking and Monitoring Hurricanes by HF Skywave Radar over the Gulf of Mexico, J. W. Maresca, Jr and C. T. Carlson, Technical Report 1, Contract F49620-76-C-0023 (1977).

"Tracking and Monitoring Hurricanes by HF Skywave Radar over the Gulf of Mexico, J. W. Maresca, Jr. and C. T. Carlson, Final Report, AFOSR-TR-79-0042 (1979).

"HF Skywave Radar Measurement of Hurricane Winds and Waves, J. W. Maresca, Jr. and C. T. Carlson, Proc. 16th Conf. Coastal Engr., Hamburg, Germany, Sept. 1978, 190-208.

"High-Frequency Skywave Radar Measurements of Waves and Currents Associated with Tropical and Extra-Tropical Storms, J. W. Maresca, Jr., Ocean Wave Climate, (Earle and Malahoff, Eds.), Plenum Pub. Co., 1979.

"HF Skywave Radar Estimates of the Track, Surface Wind and Waves of Hurricane Anita," J. W. Maresca, Jr. and C. T. Carlson, Advisory Group for Aerospace Research and Development (AGARD), Conference Proceedings No. 263, Special Topics in HF Propagation (edited by V. J. Coyne) Technical Editing and Reproduction Ltd., London, Chapter 34, 1-12, 1979.

"Remote Measurement of the Position and Surface Circulation of Hurricane Eloise by HF Skywave Radar," J. W. Maresca, Jr. and J. R. Barnum, Mon. Wea. Rev., pp 1648-1652, 1979.

"A Comment on 'Longshore Currents on the Fringe of Hurricane Anita' by Ned P. Smith," J. W. Maresca, Jr. and C. T. Carlson, J. Geophys. Res. - Oceans and Atmosphere, pp. 1640-1641, 1980.

"HF Skywave Radar Track of Tropical Storm Debra," J. W. Maresca, Jr. and C. T. Carlson, accepted by Mon. Wea. Rev.

"High-Frequency Skywave Radar Measurements of Hurricane Anita," J. W. Maresca, Jr. and Christopher T. Carlson, Science, 8, p. 1189, 1980.

"HF Skywave Radar Estimates of Track and Wind Velocity During Hurricane Anita," J. W. Maresca and C. T. Carlson, Transactions-American Geophysical Union, p. 1099-1100, 1978.

"HF Skywave Radar Measurement of Significant Wave Height During Hurricane Anita," C. T. Carlson, J. W. Maresca, Jr. and T. M. Georges, Transactions-American Geophysical Union, p. 1099-1099, 1978.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research was planned to evaluate the effectiveness of a high-frequency (HF) skywave radar used to determine (1) the track of a hurricane, and (2) hurricane wind velocity and wave height throughout all regions of a storm. Experimental data were collected using the SRI-operated Wide Aperture Research Facility (WARF) located in central California. The WARF radar is a high-resolution skywave radar capable of forming a 0.5° beam at 15 MHz. HF skywave radar sea-echo Doppler spectra were recorded for: Hurricanes Anita (1977), Caroline (1975), and Eloise (1975); tropical storms Babe (1977) and Debra (1978), in the Gulf of Mexico; and Hurricane Kate (1976) in the Pacific Ocean. Both day and night measurements were made, as well as one- and two-ionospheric-hop measurements ranging out from 2800 to 4000 km.

Surface wind direction maps were computed for all six tropical storms. In situ measurements were available for Anita and Eloise for comparison to the WARF radar wind maps. The radar-derived wind directions coincident in time and space with National Data Buoy Office (NDBO) moored buoys for Anita and Eloise showed agreement to within 10° . The spatial distribution of the wind directions within the hurricane were computed from NDBO buoys during Eloise and Anita using the buoy data compiled over 22 hours and 36 hours, respectively, and were compared to the WARF radar wind maps. Agreements to within 10° for Eloise and 20° for Anita was found despite the different time and space scales.

The center of the hurricane was estimated from each WARF wind map and was compared to the official track compiled by the National Hurricane Center (NHC). A track was developed for Hurricane Anita from 17 wind maps compiled over a 5-day period. The mean difference between the WARF radar positions and the interpolated positions along the NHC track was

19 km. A track for Tropical Storm Debra was similarly developed from seven wind maps computed during a two-day tracking experiment. The WARF position fixes for Debra were compared to the reconnaissance aircraft position fixes and agreement was within 25 km.

WARF measurements of ocean wind speed and wave height were made during Hurricanes Anita and Babe. A parametric wave prediction model developed previously was used to compute wind speeds from rms wave height and the radial fetch. The wind speeds and significant wave heights measured at NDBO EG71 during Anita were also plotted with respect to the radar measured center and were compared to the radar estimates and a wave prediction model forecast. Significant wave-height and wind speed estimates made at WARF were within 0.5 m and 2 m/s, respectively, of the buoy-derived measurements.

AFOSR Program Manager: Ted. S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: HARP Data Analysis
2. PRINCIPAL INVESTIGATOR: Dr. W. Sharp
Department of Atmospheric &
Ocean Sciences
Space Physics Research Laboratory
University of Michigan
Ann Arbor, MI 48109

3. INCLUSIVE DATES: 1 April 1977 - 31 January 1978

4. GRANT NUMBER: AFOSR-77-3320

5. COSTS AND FY SOURCE: \$8,032, FY77

6. SENIOR RESEARCH PERSONNEL: T. Donahue

7. PUBLICATIONS:

"Coordinated Rocket and Satellite Measurements of an Auroral Event - The Rocket Observations and Analysis," W. E. Sharp, M. H. Rees and A. I. Stewart, J. Geophys. Res., 85 (1979).

"Auroral Electron Fluxes," Final Report, AFOSR-TR-79-0037 (1978).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

One of the goals of the research efforts being conducted by the group at Space Physics Research Laboratory is to arrive at an understanding of the energetics of the Earth's atmosphere. The particular objective of the research effort funded by this grant was to further the understanding of energy deposition by energetic electrons at high altitudes by analyzing the electron energy distributions obtained on an auroral rocket flight.

The primary instrumentation consisted of a low energy electron spectrometer (HARP), a high energy electron spectrometer (ESA) and a group of high energy particle detectors which measured the total flux above a given energy threshold. These are described in an Air Force Technical Report, AFCRL-TR-75-0023.

The rocket was launched along the geomagnetic meridian to the North during a negative magnetic bay. The payload crossed the Harang

discontinuity and documented changing electron energy fluxes (1 eV to 30 KeV) in a bright auroral arc over an altitude range from 110 km to 185 km. The data acquired represented the first available for such an extensive energy range at an instant of time and for a number of altitudes.

Two peaks in the flux distribution were measured at about 5 eV and near 4 KeV. The peak at 4 KeV represented a monoenergetic beam incident on the top of the atmosphere which above 150 km was essentially unattenuated. The peak at 5 eV was due to "secondary" electrons produced in collisions between the primary electrons and the atmospheric gases. The peak was produced by the apparent absence of a strong loss process for the electrons in this energy region.

The general altitude behavior of the fluxes was found to decrease in magnitude with decreasing altitude below 162 km. This was reasonable due to increasing atmospheric density. Increasing density reduces the primary flux as well as resulting in a large loss for the "secondary" electrons produced in the ionizing events.

Examination of the HARP spectra revealed no pitch angle dependence over 0-32 degrees. The fluxes measured by ESA showed some broadening of the peak region between 1 and 5 KeV and this was presumed to indicate some pitch angle dependence. The HARP and ESA were not set up on the payload to gather good pitch angle information.

Examination of .7 KeV to 20 KeV fluxes indicated three types of auroral features. The first was a weak steady precipitation encountered between 110 km and 165 km. Here the peak fluxes were centered at 2 KeV. The second was a rapid increase in flux recorded at 165 km when crossing the Harang discontinuity. The increase amounted to an order of magnitude enhancement at energies less than 10 KeV with the largest increase in flux between 500 eV and 4 KeV on a relative basis. The third occurred between 170 km and over apogee. An active arc (maybe series of arcs) was crossed with the characteristic signature of an arc, the "inverted - V", being evident. The peak beam flux moved from near 2 KeV to about 7 KeV and then back to near 2 KeV. The high energy tail above the peak fell off much faster at high altitude than at low altitude, and the fluxes tended to remain high until the northern edge of the arc. An obvious feature of the data was a "bump" in flux at 5 eV, which remained pretty well defined throughout the flight. The rate of decrease of flux with increasing energy was not constant throughout the flight. Below 120 km for example, the flux decreased as $1/E^2$ above 10 eV. Above 180 km the flux above 35 eV decreased as $1/E$.

The flux magnitude for energies greater than 1 KeV was found to change more slowly as a function of altitude when compared with the flux magnitude for energies less than 1 KeV. Also, the slowly changing character of the high energy flux was almost mirrored by the flux for

energies less than 10 eV. The reason for this was that within both the high energy and very low energy regions there was structure. The structure may have been modified by wave-particle interaction producing changes in the 15 eV to 1 KeV region as well as the region less than 3 eV.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Error Growth in General Circulation Models
2. PRINCIPAL INVESTIGATOR: Professor J. R. Spreiter
Division of Applied Mechanics
Stanford University
Stanford, CA 94305
3. INCLUSIVE DATES: 1 September 1976 - 30 September 1978
4. GRANT NUMBERS: AFOSR-76-3164; AFOSR-78-3531
5. COSTS AND FY SOURCES: \$15,558, FY7T; \$46,632, FY77; \$24,785, FY78
6. SENIOR RESEARCH PERSONNEL: John A. Laurmann
7. JUNIOR RESEARCH PERSONNEL: John Dunec
8. PUBLICATIONS:

"A Small Perturbation Approximation for Stochastic Dynamic Weather Prediction," J. A. Laurmann, Final Technical Report, AFOSR-TR-78-0742 (1977).

"A Small Perturbation Approximation for Stochastic Dynamic Weather Prediction," J. A. Laurmann, Tellus, 30, 404 (1978).

"Error Growth in General Weather Circulation Models," Final Technical Report, AFOSR-TR-79-0018 (1978).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The stochastic dynamics method for optimum weather forecasting and forecast variance estimation suffers from computational complexity sufficient to obviate its utility as an operational tool. The work conducted under this contract was designed to test the suggestion that the use of a linear approximation for a perturbed set of stochastic dynamic equations could reduce computational time significantly. The linearization was based on an assumption of small departures of the stochastic dynamic solution from the usual deterministic forecast. The resultant linear scheme was tested by evaluating its predictions for a simple mathematical model of the atmosphere, that described by Lorenz's "minimum hydrodynamic equations."

The linearization was found to be as effective as was the standard non-linear stochastic dynamics method, which approximates the exact stochastic dynamic solution by ignoring third-order moments. The

problem of developing efficient numerical algorithms that take advantage of the simplification attendant upon linearization was studied at depth. However, it was found that all standard numerical techniques for solving the stochastic dynamic weather forecasting systems of equations were insensitive to their degree of non-linearity. To the extent that it was possible to investigate the numerical evaluation process, it was concluded that, contrary to our initial expectations, only a minor amount of computation time could be saved by the linearization.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of Upper Air Motions by VHF Backscatter
2. PRINCIPAL INVESTIGATOR: Dr. S. A. Bowhill
Department of Electrical Engineering
University of Illinois
Urbana, IL 61801
3. INCLUSIVE DATES: 15 April 1979 - 30 September 1979
4. GRANT NUMBER: AFOSR-ISSA-79-0031
5. COSTS AND FY SOURCE: \$35,000, FY79
6. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS"

AFOSR contributed to a research project principally funded by National Science Foundation with the objectives of performing systematic observations of winds and wave motions in the stratosphere and mesosphere, estimating mesospheric eddy diffusion coefficients by means of scattering models in conjunction with available electron density information, and developing a general description of mid-latitude circulations in the stratosphere and mesosphere and their relationship to the transport of trace constituents at various scales.

Early analytical results show the existence of a semi-diurnal tidal component of motion in the mesosphere, driven from below by the solar heating of stratospheric ozone and having a characteristic vertical wavelength about 15 km. This wavelength is interpreted as evidence of strong influence by the mesosphere on the propagation of atmospheric tidal motions. Moderate changes in the mesosphere with resulting changes in its wave propagation characteristics may explain a problem that has puzzled researchers for years--the variability and apparent contradiction between observations of the phase of tidal motion over France and similar observations over the northeastern United States. The observations at the University of Illinois revealed considerable day-to-day variability in the prevailing mesospheric winds.

AFOSR Program Manager: Ted S. Cress, Lt Col. USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Nonlinear Transfer of Kinetic Energy in the Atmosphere Using One- and Two-Dimensional Spectral Representation
2. PRINCIPAL INVESTIGATOR: Dr. Dusan Djuric
Department of Meteorology
Texas A&M University
College Station, TX 77843
3. INCLUSIVE DATES: 1 January 1978 - 31 March 1979
4. GRANT NUMBER: AFOSR-78-3492
5. COSTS AND FY SOURCE: \$3,500, FY78
6. JUNIOR RESEARCH PERSONNEL: Frank H. Bower
7. PUBLICATIONS:

"Nonlinear Transfer of Kinetic Energy in the Atmosphere Using One- and Two-Dimensional Spectral Representation," D. Djuric, Final Report, AFOSR-TR-80-0159 (1980).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The representation of the nonlinear transfer of kinetic energy in forecasting models was investigated to determine whether the forecast models are correctly handling this transfer process and whether comparable results could be obtained by one- and two-dimensional spectral representations. It was found that the hemispheric meteorological data from Air Force Global Weather Center (AFGWC) and Air Force Environmental Technical Applications Center (AFETAC) have serious gaps that hinder the calculation of nonlinear kinetic energy transfer. Alternative recommendations to permit successful computations were (1) to introduce an interpolation technique to formally fill the data gaps or (2) to acquire new data sets without such gaps.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Solar-Terrestrial Predictions Workshop
2. PRINCIPAL INVESTIGATOR: Dr. Richard F. Donnelly
Space Environment Laboratory
NOAA
Boulder, CO 80302
3. INCLUSIVE DATES: 15 November 1978 - 30 September 1979
4. GRANT NUMBER: AFOSR-ISSA-79-0019
5. COSTS AND FY SOURCE: \$5,000, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. S. I. Akasofu, Univ of Alaska
Dr. S. D. Dehpande, India
Dr. K. Harvey, Kitt Peak Observatory
Dr. R. Hedeman, McMath Observatory
Dr. R. Hunsucker, Univ. of Alaska
Dr. A. P. Mitra, NPL, New Delhi, India
Dr. W. R. Piggott, England
Dr. K. Schatten, Boston Univ.
Dr. E. Thrane, Norway

7. PUBLICATIONS:

"Solar-Terrestrial Predictions, Proceedings, Vol. I, Prediction Group Reports; Vol. II, Working Group Reports and Reviews; Vol. III, Contributed Papers," R. F. Donnelly, editor, US Government Printing Office, SD Stock No. 003-023-00041-9.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A workshop on solar-terrestrial predictions was held on 23-27 April 1979 in Boulder, Colo., for the purposes of facilitating the transition of research and development on techniques to ultimate application and to document the current state and future needs of the science. AFOSR funds were used to partially fund secretarial support and foreign travel.

Most solar-terrestrial forecast centers provide monitoring measurements, warnings of solar-terrestrial disturbances, and short and long term predictions. In the last two decades, significant improvements have been made in satellite monitoring measurements and in disturbance detection and warning services. However, the advances in solar-terrestrial predictions have been relatively minor. There was a

great need for a coordinated attempt to improve prediction techniques. The success of the workshop will be determined mainly by the degree of improvement of predictions in the next few years as a consequence of discussions initiated at this workshop.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: The Nature and Derived Climatology of Thunderstorm Electrical Activity over a Large Geographic Area
2. PRINCIPAL INVESTIGATOR: Dr. George Huebner
Department of Meteorology
Texas A&M University
College Station, TX 77843
3. INCLUSIVE DATES: 1 October 1978 - 30 September 1979
4. GRANT NUMBER: AFOSR-79-0003
5. COSTS AND FY SOURCE: \$3,000, FY79
6. JUNIOR RESEARCH PERSONNEL: William B. Freeman, Jr.
7. PUBLICATIONS:

"A Study of the Variability of Thunderstorm Electrical Events Based on Very Low Frequency Electromagnetic Data," W. B. Freeman, Jr. ; Final Report, AFOSR-80-TR-0115 (1980)

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Sferics counts were used to estimate the incidence of lightning discharges in order to study the relationship of lightning-flash density to thunderstorm days, and explore the variability of cloud-to-ground discharges. Areal and global discharge incidence estimates were generated from sferics data, yielding a global estimate of $1.3 \times 10^{-5} \text{ km}^{-2} \text{ sec}^{-1}$. Gridded monthly values were computed for much of the Eastern Hemisphere. The Southern Hemisphere tropics were found to have a higher average incidence of discharge than the Northern Hemisphere tropics. The linear regression relationship between flash density and thunderstorm days indicated lower estimates of flash density, relative to estimates from previous studies, when based on particular data stratifications. Selected data from the Eastern Hemisphere were studied by linear regression techniques for causes of large-scale variability of cloud-to-ground discharges. In order of importance the regressors were the height of the freezing level, the planetary geomagnetic index, a parameterized freezing level height, the precipitable water in the 1000-850 mb layer, the dew-point depression at 850 mb, K index of stability, and the departure of the H-component of the magnetic force vector from its means.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Spectroscopic Investigation of the Upper Atmosphere in the Plasmapause Region
2. PRINCIPAL INVESTIGATOR: Dr. J. S. Kim
Department of Atmospheric Sciences
State University of New York at Albany
Albany, NY 12222
3. INCLUSIVE DATES: 1 June 1979 - 30 September 1979
4. GRANT NUMBER: AFOSR-ISSA-79-0032
5. COSTS AND FY SOURCE: \$26,000, FY79
6. SENIOR RESEARCH PERSONNEL: S. Okano
7. PUBLICATIONS:

"Photometric and Interferometric Observations of the SAR Arc Event of September 25/26, 1978," S. Okano and J. S. Kim, J. Geophys. Res., **84**, 4441 (1979).

"Measurements of Thermospheric Temperatures during Geomagnetic Storms and the Concurrent Auroral Events," S. Okano and J. S. Kim, Amer. Geophys. Union Spring Meeting (1979).

"The Design and Application of a Multiple Zone Aperture to the Fabry-Perot Interferometer," S. Okano, J. S. Kim, and T. Ichikawa, Appl. Optics, **19**, 1622 (1980).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Under funding from National Science Foundation and AFOSR, a Fabry-Perot interferometer previously developed at SUNYA was modified by the use of a multiple zone aperture (MZA) to replace the conventional pinhole aperture. This modification increases the throughput of the instrument, thereby greatly increasing the sensitivity. The modified instrument was used to observe emissions from atomic oxygen in the upper atmosphere under various geomagnetic conditions. Emissions at 6300 Å and 5577 Å correspond to heights of approximately 100 and 275 km, respectively. The Doppler shift of the lines provides a measure of wind speed, which can be correlated with wind speeds measured in the same altitude regions by incoherent-scatter radar. The spread of the lines is related to temperature.

Results from observations with the interferometer with the multiple-zone aperture are not yet available, as the research is continuing under NSF sponsorship. One example of the use of the unmodified interferometer was its use in conjunction with a scanning photometer to observe a stable auroral red (SAR) arc. Analysis of these measurements yielded an unusually short time constant for the intensity growth rate, about 20 min, a rather high southward drift velocity, about 240 km hr^{-1} , and a temperature enhancement of about 200°K within the arc. Further observations of auroral phenomena and airglow are being conducted.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Laser Induced Lightning Investigation

2. PRINCIPAL INVESTIGATOR: Dr. C. B. Moore
Langmuir Laboratory
New Mexico Institute of Mining
and Technology
Socorro, NM 87801

3. INCLUSIVE DATES: 1 July 1978 - 30 June 1979

4. GRANT NUMBER: AFOSR-78-3722

5. COSTS AND FY SOURCE: \$20,500, FY78; \$15,000, FY79

6. PUBLICATIONS:

"Radar and Acoustic Studies of Lightning," C. R. Holmes,
E. W. Szymanski, S. E. Szymanski, and C. B. Moore, accepted by
J. Geophys. Res.

"Local Charge Concentrations in Thunderclouds," J. E. Griswold,
D. N. Holden, C. R. Holmes, C. B. Moore, W. P. Winn, and J. W. Cobb, VI
Intl. Commission on Atmos. Electricity, Manchester, England (1980).

"Measurement of Electromagnetic Properties of Lightning with 10
Nanosecond Resolution," C. E. Baum, E. L. Breen, J. P. O'Neill,
C. B. Moore, and D. L. Hall, Symp. Lightning Technology, Langley Rsch.
Ctr. NASA-CP-2128, FAA-RD-80-30, 39 (1980).

"Electromagnetic Sensors for General Lightning Application," C. E. Baum,
E. L. Breen, J. P. O'Neill, C. B. Moore, and G. D. Sower, Symp.
Lightning Technology, Langley Rsch. Ctr., NASA-CP-2128, FAA-RD-80-30, 85
(1980).

"The Cloud Effects Phase of the Laser Induced Lightning Investigation,"
C. B. Moore, D. N. Holden, and J. Griswold, Final Report,
AFOSR-TR-80-0454 (1980).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A high power laser system was used to enhance the probability of
triggering a natural lightning discharge, so that parameters of the
discharge could be measured by ground-based instrumentation. By this
means it is possible to determine the time history of a lightning
discharge and the frequency spectrum of the emitted radiation in much
more detail than could be done with airborne instruments and without the

attendant flight safety problems. The triggering of the discharge increases the number of discharges available for measurement in a given period of time, providing more reliable statistics on the variability of lightning parameters.

The ionization produced by the laser was effective in triggering of lightning; it was found that the electric field measured about 600 m above the surface by an electric field meter carried beneath a captive balloon provided a better choice for the optimum times for triggering lightning, due to the absence of the corona discharge effects that occur near the surface. A significant result of the research was the discovery that lightning deposits positive charge on precipitation low in the cloud, and that this charge then dominates the electric field below the cloud for a radius of about 1 km as the precipitation falls out. The fall of this charged precipitation aids in the further electrification of the cloud and usually results in the occurrence of another lightning flash. Lightning was also successfully triggered by means of a wire carried aloft by a rocket. Analysis of the lightning measurements has been reported in preliminary form and is continuing under other funding.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of Extratropical Cyclonic Storms--The CYCLES Project
2. PRINCIPAL INVESTIGATOR: Dr. Peter V. Hobbs
Department of Atmospheric Sciences
University of Washington
Seattle, WA 98195

3. INCLUSIVE DATES: 1 February 1977 - 30 October 1980

4. CONTRACT NUMBER: F49620-77-C-0057

5. COSTS AND FY SOURCE: \$16,500, FY77; \$43,794, FY78; \$40,912, FY79;
\$44,822, FY80

6. SENIOR RESEARCH PERSONNEL:

R. A. Houze, Jr.	J. D. Locatelli
L. F. Radke	K. R. Biswas
R. R. Weiss, Sr.	

7. JUNIOR RESEARCH PERSONNEL:

T. J. Matejka	O. Persson
P. H. Herzegh	M. Kruidenier
D. B. Parsons	C. Glantz
S. A. Rutledge	

8. PUBLICATIONS:

"Air Motions and Precipitation Growth in a Mesoscale Precipitation Band Associated with a Warm Front," P. H. Herzegh and P. V. Hobbs, Preprints, 18th Conf. Radar Meteor., Amer. Meteor. Soc., 23 (1978).

"Airborne Measurements of the Size Distributions of Precipitation Particles in Frontal Clouds," R. A. Houze, Jr., P. V. Hobbs, P. H. Herzegh, and D. B. Parsons, Preprints, Conf. Cloud Physics and Atmos. Electricity, Amer. Meteor. Soc., pp. 168-172 (1978).

"The University of Washington's CYCLES Project An Overview," P. V. Hobbs, Preprints, Conf. Cloud Physics and Atmos. Electricity, Amer. Meteor. Soc., pp. 271-276 (1978).

"Air Motions, Mesoscale Structure, and Cloud Microphysics Associated with a Cold Front," P. V. Hobbs, J. D. Locatelli, T. J. Matejka, and R. A. Houze, Jr., Preprints, Conf. Cloud Physics and Atmos. Electricity, Amer. Meteor. Soc., pp. 277-283 (1978).

"Generating Cells and Precipitation Growth in Mesoscale Rainbands," P. H. Herzegh and P. V. Hobbs, Preprints, Conf. Cloud Physics and Atmos. Electricity, Amer. Meteor. Soc., pp. 284-291 (1978).

"Microphysical and Dynamical Structure of Mesoscale Cloud Features in Extratropical Cyclones," T. J. Matejka, R. A. Houze, Jr., and P. V. Hobbs, Preprints, Conf. Cloud Physics and Atmos. Electricity, Amer. Meteor. Soc., pp. 292-299 (1978).

"Studies of Extratropical Cyclonic Storms--The CYCLES Project," P. V. Hobbs, Interim Report, Contract F49620-77-C-0057 (1978).

"Organization and Structure of Clouds and Precipitation on the Mesoscale and Microscale in Cyclonic Storms," P. V. Hobbs, Rev. Geophys. Space Phys., 16, 741 (1978); AFOSR-TR-79-0767 (1979).

"A Technique for Obtaining Detailed Wind Fields in a Frontal System from a Single Doppler Radar," J. D. Locatelli and P. V. Hobbs, J. Appl. Meteor., 17, 1076 (1978).

"Size Distributions of Precipitation Particles in Frontal Clouds," R. A. Houze, Jr., P. V. Hobbs, P. H. Herzegh, and D. B. Parsons, J. Atmos. Sci., 36, 156 (1979).

"The Cellular Structure of Narrow Cold-Frontal Rainbands," P. V. Hobbs and K. R. Biswas, Quart. J. Roy. Meteor. Soc., 105, 723 (1979).

"Simultaneous Observations of Cloud and Precipitation Particles with Vertically Pointing X- and K_a -band Radars," R. R. Weiss, Sr., J. D. Locatelli, and P. V. Hobbs, IEEE Trans. Geosci. Electr., GE-17, 151 (1979).

"Studies of Extratropical Cyclonic Storms--The CYCLES Project," P. V. Hobbs, Interim Report, Contract F49620-77-C-0057 (1979).

"Microphysics and Dynamics of Clouds Associated with Mesoscale Rainbands in Extratropical Cyclones," T. J. Matejka, R. A. Houze, Jr., and P. V. Hobbs, Quart. J. Roy. Meteor. Soc., 106, 29 (1980).

"The Mesoscale and Microscale Structure and Organization of Clouds and Precipitation in Mid-Latitude Cyclones, I: A Case Study of a Cold Front," P. V. Hobbs, T. J. Matejka, P. H. Herzegh, J. D. Locatelli, and R. A. Houze, Jr., J. Atmos. Sci., 37, 568 (1980).

"The Mesoscale and Microscale Structure and Organization of Clouds and Precipitation in Mid-Latitude Cyclones, II: Warm Fronts," P. H. Herzegh and P. V. Hobbs, J. Atmos. Sci., 37, 597 (1980).

"Doppler Radar Study of a Warm-Frontal Rainband," R. A. Houze, Jr., S. A. Rutledge, T. J. Matejka, and P. V. Hobbs, Preprints, 19th Conf. Radar Meteor., Amer. Meteor. Soc., 23 (1980).

"Studies of Extratropical Cyclonic Storms--the CYCLES Project," P. V. Hobbs, Final Report, AFOSR-TR-80-1279 (1980).

"The Mesoscale and Microscale Structure and Organization of Clouds and Precipitation in Mid-Latitude Cyclones, III. Air Motions and Precipitation Growth in a Warm-Frontal Rainband," R. A. Houze, Jr., S. A. Rutledge, T. J. Matejka, and P. V. Hobbs, accepted by J. Atmos. Sci.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The CYCLES Project of the University of Washington was designed to observe and understand the physical and dynamical processes in extratropical cyclonic storms including the interactions and energy balances of these processes. Principally funded by National Science Foundation, it included several seasons of operations in northwest Washington state and subsequent analysis of data obtained by instrumented aircraft, conventional and Doppler radars, surface weather instrumentation, balloon-borne sounding instrumentation (rawinsondes) and meteorological satellites. Operations were conducted during November and December of 1976 and 1977 and during February and March of 1979.

The most significant result was the identification of rainbands in cyclonic storms. These have been classified into six types, according to their location in the different air masses or relative to the principal air mass fronts. The motion of these rainbands relative to the motion of the surface fronts or upper-level winds was documented. Wind measurements by Doppler radar made possible the description of the interactions of dynamical and microphysical processes in the rainbands. The heaviest precipitation in the rainbands occurs in "cores" which may occupy areas as large as 100 km^2 and which are in turn composed of individual precipitation cells. Precipitation efficiency (the relative conversion of inflowing water vapor to precipitation) is very high in some of the rainbands, approaching 100%, while efficiency of other types of rainbands ranges from 40% to 80%. Airborne measurements of cloud and precipitation particle sizes, shapes, and number concentrations were essential to the explanation of the physical processes of precipitation development. Real-time display of wind speeds measured by the Doppler radars were essential for the effective coordination of radar and aircraft operations. Valuable data were also generated by simultaneous observation of clouds and precipitation by 3-cm and 8.5-mm wavelength radars.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Thunderstorm Electrification and Lightning
2. PRINCIPAL INVESTIGATOR: Dr. John Latham
Physics Department
University of Manchester
Manchester, England M60 1QD
3. INCLUSIVE DATES: 1 September 1977 - 30 September 1980
4. GRANT NUMBER: AFOSR-77-3429
5. COSTS AND FY SOURCE: \$12,980, FY78; \$19,004, FY79
6. SENIOR RESEARCH PERSONNEL: A. J. Illingworth
7. JUNIOR RESEARCH PERSONNEL:

R. Warwicker
W. Gaskell

8. PUBLICATIONS:

"Airborne Studies of Electric Fields and the Charge and Size of Precipitation Elements in Thunderstorms," W. Gaskell, A. J. Illingworth, J. Latham, and C. B. Moore, Quart. J. Roy. Meteor. Soc., 104, 447 (1978).

"Electric Fields and Particle Charges in Thunderstorms," W. Gaskell, A. J. Illingworth, B. J. P. Marshall, and J. Latham, Preprints, Conf. Cloud Physics and Atmos. Electricity, Amer. Meteor. Soc., pp. 635-640 (1978).

"Corona from Ice, Thunderstorm Electrification and Lightning Suppression," J. Latham, Interim Report, Grant AFOSR-77-3429 (1979).

"Corona from Ice, Thunderstorm Electrification and Lightning Suppression," J. M. Caranti and A. J. Illingworth, Nature, 284, 44 (1980)

"Corona from Ice, Thunderstorm Electrification and Lightning Suppression," W. Gaskell and A. J. Illingworth, Quart. J. Roy. Meteor. Soc., 106 (1980).

"Airborne and Ground-Based Studies of Thunderstorms in the Vicinity of Langmuir Laboratory," H. Christian, C. R. Holmes, J. W. Bullock, W. Gaskell, A. J. Illingworth, and J. Latham, Quart. J. Roy. Meteor. Soc., 106, 159 (1980).

"Charge Transfer Accompanying the Splashing of Supercooled Raindrops on Hailstones," J. Latham and R. Warwicker, Quart. J. Roy. Meteor. Soc., 106, 559 (1980).

"Corona from Ice, Thunderstorm Electrification, and Lightning Suppression," J. Latham, Final Report, AFOSR-TR-80-1285 (1980).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Five distinct avenues of research relating to thunderstorm electrification were pursued in this project: (1) airborne studies of thunderstorm electrification, (2) charge transfer accompanying collisions between hailstones and supercooled raindrops in the presence of an electric field, (3) charge transfer accompanying collisions between ice particles, (4) growth of positive streamer systems, and (5) theoretical studies of the raingush phenomenon. The airborne observations were conducted in New Mexico during the summers of 1976, 1977, and 1979, as part of the Thunderstorm Research International Project (TRIP). It was found that significant electrical currents are often carried by precipitation, but that the charges on individual precipitation particles are not explicable by the inductive mechanism of thunderstorm electrification. The dependence of charge transfer on impact parameter was defined by laboratory experiments. Splashing of raindrops colliding with hailstones was found not to assist electric field growth and to impede it in some circumstances. Cold-room wind tunnel experiments revealed that charge transfer was proportional to both temperature and impact velocity but not dependent on ice purity or surface roughness. Theoretical studies of the enhancement of raindrop collision efficiency associated with lightning channels led to the development of a model of the raingush phenomenon.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Near-Infrared Spectrometric Airglow Measurements during the Total Solar Eclipse of 26 Feb 1979
2. PRINCIPAL INVESTIGATOR: Dr. William R. Pendleton, Jr.
Electro-Dynamics Laboratory
Utah State University
Logan, UT 84322
3. INCLUSIVE DATES: 1 February 1979 - 30 September 1980
4. GRANT NUMBER: AFOSR-79-0040
5. COSTS AND FY SOURCE: \$35,929, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. Doran Baker
Dr. Allan Steed

7. JUNIOR RESEARCH PERSONNEL: Lee Davis

8. PUBLICATIONS:

"Residual Dayglow and Twilight-Glow Measurements in Conjunction with the 26 February 1979 Solar Eclipse, W. R. Pendleton, Jr., D. J. Baker, and A. J. Steed, EOS, Vol. 61, No. 17, April 22, 1980.

"Temporal Variation of Residual Dayglow Features during the Total Phase of the 26 February 1979 Eclipse," W. R. Pendleton, Jr., D. J. Baker, and A. J. Steed, to be submitted to either Applied Optics or Journal of the Optical Society of America.

"Spectrally Resolved [NI] 3F Emissions in Sunlit and Normal Aurora," W. R. Pendleton, Jr., D. J. Baker, and A. J. Steed, to be submitted to Journal of Geophysical Research or Geophysical Research Letters.

"Near-Infrared Spectrometric Airglow Measurements during the Total Solar Eclipse of 26 Feb 1979," W. R. Pendleton, Final Report, to be submitted, Grant AFOSR-79-0040.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The solar eclipse of 26 February 1979, visible in parts of North America, provided a rare opportunity to observe infrared emissions from the atmosphere during daytime. Such measurements are essential to the testing of models of the excitation and emission characteristics of

atmospheric molecules. During the eclipse, measurements of infrared emissions of OH and O₂ were made using a near-infrared field-widened interferometer-spectrometer and a coaligned dual-channel radiometer. Short-term trends for the chemical species of interest were established by a series of measurements for one week prior to the eclipse and four days following.

Near-IR spectrometric (0.8-1.65 μm) and radiometric (λ 1.27 μm ; λ 1.70 μm) measurement of the terrestrial airglow were made during the eclipse. Twilight-transition and nightglow data were acquired on February 23, 24, and 26. The temporal variations of the dominant features were similar on the three nights, but relatively large differences in the emission levels were apparent, with airglow intensities significantly lower on February 26.

First-of-a-kind time-resolved spectra of the near-IR residual dayglow were made with a spectral resolution of $\leq 3 \text{ cm}^{-1}$ and a temporal resolution $\approx 20 \text{ sec}$. With the possible exception of the OH Meinel features, the features behaved as predicted from photochemical models of the mesosphere and lower thermosphere.

It was aurorally active in the late evening and night on the day of the eclipse. Sunlit auroral spectra during the twilight have yielded a value of ≈ 0.03 for the number of [NI] 3F photos per N₂⁺ ion. The [NI] 3F emissions exhibited striking changes with respect to the other auroral features, presumably due to changes in the auroral altitude.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Stratospheric Residence Times from Contrail Observations by Satellite

2. PRINCIPAL INVESTIGATOR: Dr. Norman Rosenberg
Department of Interdisciplinary Studies
Tel-Aviv University
Ramat-Aviv
Tel-Aviv 69978 Israel

3. INCLUSIVE DATES: 1 July 1979 - 30 June 1980 (Continuation transferred to Air Force Geophysics Laboratory)

4. CONTRACT NUMBER: F49620-79-C-0180

5. COSTS AND FY SOURCE: \$4,955, FY79; \$14,860, FY80 (AFGL)

6. PUBLICATIONS:

"Estimation of Stratospheric Residence Times from Satellite Observations of Contrails," N. Rosenberg, Interim Report, Contract F49620-79-C-0180 (1979).

"Estimation of Stratospheric Residence Times from Satellite Observations of Contrails," N. Rosenberg, Interim Report, Contract F49620-79-C-0180 (1980).

"Stratospheric Residence Times," N. Rosenberg, Interim Report, Contract F49620-79-C-0180 (1980).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The original plan of this research was to use images of aircraft contrails observed by LANDSAT to determine stratospheric turbulence coefficients and evaluate the feasibility of using such data to develop a statistical model of eddy diffusivities and stratospheric residence times. A search of about 10,000 LANDSAT images revealed only nine contrail images suitable for analysis. These were analyzed to determine the radial growth characteristics, and relationship to atmospheric parameters, and to derive the eddy diffusivity for each case. The small number of suitable images precluded the continuation of the original plan, since no statistically significant results could be obtained. A new plan was developed to derive stratospheric residence times from measurements of high-frequency relative wind velocity by AFGL coronagraph balloon flights and from other wind measurements such as conventional rawinsonde data and smoke trail data. The continuation of the research was transferred from AFOSR to AFGL.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Auroral-Region Dynamics Determined with the Chatanika Radar
2. PRINCIPAL INVESTIGATOR: Dr. Vincent B. Wickwar
Radio Physics Laboratory
SRI International
333 Ravenswood Ave.
Menlo Park, CA 94025
3. INCLUSIVE DATES: 1 October 1977 - 30 September 1980
4. CONTRACT NUMBER: F49620-78-C-0018
5. COSTS AND FY SOURCE: \$49,850, FY78; \$49,194, FY79; \$49,630, FY80
6. SENIOR RESEARCH PERSONNEL: Dr. John Meriwether, Univ of Mich
7. PUBLICATIONS:

"Auroral Region Dynamics," V. B. Wickwar, Final Report, Contract F49620-78-C-0018 (1981).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Archived data recorded by the Chatanika incoherent-scatter radar for the period 1971 through 1978 were used to determine the altitude and time dependence of the quasi-steady-state neutral winds in the lower F region (175-275 km) of the ionosphere, to investigate the correlation between dynamical effects and precipitating particle effects and the departure of the neutral winds from their value under quiet conditions, and to evaluate the use of the radar in the observation of gravity waves. Ancillary data were acquired with the Michigan Auroral Observatory Fabry-Perot Interferometer in 1972 and 1973.

For the first time winds in the magnetic meridian determined from these independent techniques were compared and found to agree well. The radar data alone were used to determine the meridional wind pattern throughout a 24-hour period. With increased magnetic activity, the most pronounced change was a stronger wind to the south at night. With season, the variation was not inconsistent with theory. The radar and Fabry Perot data were combined to identify a transient phenomenon involving large vertical neutral velocities of order 50 to 100 M/S, most likely part of a medium scale gravity wave. The two data sets were again combined to examine the neutral zonal wind and the influence of ion drag and joule heating on that wind. Under magnetically quiet conditions, the zonal wind was to the east in the early evening. Under active conditions evidence was found for significant roles of both ion drag and joule heating in reversing the wind direction.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

CHEMICAL TECHNIQUES

Denton W. Elliott

In the AFOSR Chemical Techniques program the exploitation of new methods and the improvement of current trace chemical analysis methods are of importance to a variety of Air Force problems. Some of the problems include efforts to improve material purity, the monitoring of environmental contamination, applications involving chemical monitoring, problems requiring chemical surveillance, as well as a host of other irritants.

Gas phase electronic spectroscopy has been a principal technique involved in investigations of atmospheric gases, chemical processes, and radiation effects.

In the selection of optimum trace vapor analysis methods, molecular electronic spectroscopy seems to offer the best opportunity to approach single molecule detection limits under the mandatory condition of minimum sampling handling.

The visible and ultraviolet spectral regions provide minimum interference from bulk atmospheric constituents and provide maximum sensitivity based on quantum mechanical considerations.

Visible and ultraviolet spectrophotometry are simple and sensitive standard analytical approaches that suffer from lack of specificity. Most compounds have broad, featureless gas phase absorption spectra that span appreciable intervals of the available optical spectrum. Even though nitrogen, oxygen, water and carbon dioxide have distinctive spectra located far in the ultraviolet, thereby providing no interference, most substances of interest have spectra that are virtually indistinguishable from large classes of similar compounds.

To obtain really good sensitivity, a high intensity ultraviolet tunable light source is required. Laser derived sources are not yet available in the critical region from 200 to 250 nm. Therefore, sensitivity of analysis for molecules that absorb in this region is poor. A notable exception to this trend is atomic absorption spectrometry. Atoms, unlike molecules, have a few discrete absorption transitions in which they compress all the transition strength. Since high intensity atomic emission light sources can be obtained by exciting the element of interest in an electronic discharge, the atomic absorption of an unknown sample can be measured with high sensitivity and excellent selectivity. Therefore, atomic absorption has become the most successful bulk trace elemental analysis method.

Measurement of absorption by detecting the fluorescence excited by it provides the opportunity to attain much higher sensitivity than can be

achieved by direct absorption. This is based on ability to detect single fluorescence quanta emitted from a molecule. The technique is equally applicable to atoms and molecules; however, not all molecules fluoresce and molecular fluorescence is subject to the spectral discrimination problem. For atoms, strong transitions have absorption cross-sections in the range 10^{-10} cm², strong molecular transitions have absorption cross sections as large as 10^{15} cm². Therefore, given a laser intensity of 1 watt/cm², (c.a. 10^{18} photons/cm². sec) each atom will generate up to 10^8 fluorescence quanta per second and each molecule about 10^3 per second. Unfortunately for complex molecules, fluorescence is ordinarily broad and provides poor discrimination.

A potential method to overcome this limitation was provided by the method of Doppler-free two-photon spectroscopy proposed by Russian theorists. Recently several academic research groups at Harvard, the University of Paris, and Stanford demonstrated that the new method was capable of greatly improving spectral resolution in atomic spectroscopy research. The Aerospace Corporation recognized the potential importance of the Doppler-free method for overcoming the severe problem of spectral congestion in large molecule electronic spectroscopy. A program was initiated to explore its application to trace vapor detection and it was demonstrated that extremely high analytical specificity can be achieved for complex molecules in the gas phase.

Investigations arising from Doppler-free two-photon atomic spectroscopy have suggested an approach which should overcome some of the limitations while simultaneously providing higher sensitivity. The Doppler-free method of two-photon absorption is based on use of a single laser excitation frequency, which is not normally resonant with a one-photon transition of the system. However, if the laser frequency is in resonance with a one-photon transition, the two-photon absorption strength can be increased a billion-fold, as has been demonstrated for sodium. In these experiments one laser is tuned to resonance with a one-photon transition and the second is adjusted to the energy difference between the final two-photon excited state and the intermediate state excited by the first photon. The overall transition is Doppler broadened in proportion to the mismatch of laser frequencies, nonetheless, high specificity is retained because of the two-fold requirement for resonances. Detection limits of one molecule per cm³ can be envisioned using this approach, which also provides high selectivity.

Dr. John E. Wessel and his group at Aerospace Corporation undertook a thorough investigation of resonance enhanced molecular multiphoton absorption as a means of improving capability for optical excitation and detection of trace gas species. The investigations included resonance enhanced two-photon absorption, resonance enhanced multiphoton photoionization, and the influence of coherence effects on the processes.

Several significant accomplishments resulted from this work. Studies of the two-photon photoionization method applied to trace mixtures of the aromatic hydrocarbon naphthalene in an ambient pressure buffer gas led to firm demonstration of a detection limit of 5×10^4 molecules/cm³, which represents a one-thousandfold improvement with respect to the most sensitive methods available previously. Detection of other molecular species with differing excited state properties was studied as a function of laser pulse duration. The results indicate that photoionization excitation conditions can be selected so that there is little compromise in sensitivity of detection for species that undergo rapid radiationless decay from excited states. Therefore the method will be widely applicable to diverse molecular species. The results to date support the feasibility of further extending detection toward the single molecule limit.

Detection under low pressure conditions was investigated using an ion multiplier detector. With this device it is easy to detect formation of single ions. It was also found that time-of-flight mass spectra can be attained with little additional effort and no loss of sensitivity using this device. Ionization occurs in the small, well defined region of the laser beam and the time required for ions formed in this region to drift into the ion multiplier is dependent on the ion mass. Therefore by time resolving the ion signal following each laser pulse, mass spectra are generated. At low laser intensities the parent ion (molecule less one electron) was formed. At higher intensities fragment ions are formed. The fragmentation pattern is characteristic of the molecular species and can provide highly useful analytical characterization in addition to the spectroscopic signature.

One of the most exciting results of this research was the innovation of a novel method of high resolution multiphoton spectroscopy based on interference between ionization and stimulated emission channels. The method, called "Ion Dip Spectroscopy (IDS)," is based on use of two excitation wavelengths. The first wavelength induces a multiphoton ionization signal. A second source (usually of longer wavelength) is tuned to a wavelength which causes depopulation of the intermediate state involved in the multiphoton process. Under these conditions, the ionization signal declines. The first wavelength selects a specific well-defined intermediate quantum state. Therefore the second wavelength interacts specifically with this state and the process is thus highly selective. It is anticipated that this method will be advantageous for detection and spectroscopy of complex molecules.

The two wavelength IDS detection process is described in Fig. 1. Four molecular energy levels consisting of ground state $|0\rangle$, excited vibrational state $|1\rangle$, excited electronic state $|2\rangle$, and ionized state $|3\rangle$ are involved.

Two photons at frequency ω_1 induce efficient ionization because resonance enhancement occurs through state $|2\rangle$. A high intensity probe at $\omega_2 < \omega_1$ is introduced. When $\omega_1 - \omega_2$ matches suitable ground state vibrational frequencies, stimulated emission (stimulated Raman if ω_1 is out of resonance with $|2\rangle \rightarrow |0\rangle$) competes with ionization. This decreases the effective population in $|2\rangle$ and reduces the ionization signal, provided population inversion occurs between $|2\rangle$ and $|1\rangle$. The effective reduction in ion signal under resonance conditions is estimated by $R = r/(r + r')$, where r is the rate of depopulation of $|2\rangle$ in the absence of ω_2 and r' is the rate of stimulated emission from $|2\rangle$ induced by ω_2 (clearly the process can also operate in principle if $|1\rangle$ is above $|2\rangle$). Consideration of stimulated emission cross sections leads to the conclusion that the rate r' can easily be made to dominate r . Therefore the IDS process can be readily implemented for large molecules, given current pulsed dye laser technology.

The method measures ground state vibrational properties, thereby avoiding potential problems encountered in excited electronic states such as dissociation or of rapid radiationless decay. Measurements are made by selecting an ω_1 resonant with a rotational-vibrational transition to electronic state $|2\rangle$ (designated here as a rovibronic transition). The ionization signal due to absorption of two ω_1 photons is monitored. Then ω_2 is scanned across the spectral region corresponding to the stimulated emission transition from $|2\rangle$ to $|1\rangle$. When the exact resonance is achieved a decrease is recorded in the two-photon ionization signal. This is termed an ionization dip due to its resemblance to the Lamb Dip that is recorded in saturation spectroscopy when counterpropagating beams interact simultaneously with the same zero velocity group of the Doppler profile.

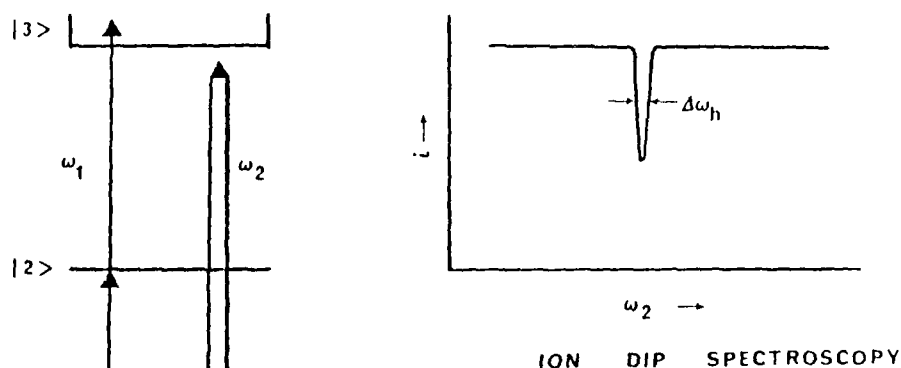


Fig. 1. The energy level scheme for IDS is shown on the left hand side of the figure. A low intensity excitation beam at frequency ω_1 induces resonance enhanced two-photon photoionization by way of intermediate electronic state $|2\rangle$. A high power beam at ω_2 stimulates the transition $|2\rangle \rightarrow |1\rangle$, thereby depleting $|2\rangle$ and reducing the ionization signal. This reduction is depicted on the right hand side of the figure for a spectral scan across the $|2\rangle \rightarrow |1\rangle$ resonance. The homogeneous linewidth, $\Delta\omega_h$, is measured.

SURFACE CHEMISTRY

DENTON W. ELLIOTT

In the surface chemistry program the ever-present problems of corrosion involve protection, inhibition, and prevention of this insidious monster.

Program emphasis in the study of corrosion is focused on using the most modern techniques and instrumentation available in the collection of information that will give us a handle to the understanding of the beast.

At Georgia Institute of Technology, Drs. Keith Legg, Martin Ribarsky, and members of their groups are exploiting a recent development of a new metallurgical process of high dose "ion implantation" with the hope of focusing some light on the corrosion process.

Ion implantation is the process of modifying the properties of a solid by embedding into it appropriate atoms in the form of a beam of ionized particles. The solid may be in crystalline, polycrystalline or amorphous form and need not be homogeneous. Alternative techniques such as diffusion or co-evaporation may often be impractical; in which case ion implantation offers a straightforward and reproducible means of achieving what is required. Being a non-equilibrium process one may incorporate any kind of ion without the need for developing a set of diffusion conditions or the appropriate chemical combination method.

The early work in ion implantation has been overwhelmingly concerned with the fabrication of semi-conductor compounds for electronic devices. In this case one introduces a relatively low concentration of the implant species into the substrate; doses of 10^{13} to 10^{15} ions per cm^2 of surface area are typical. It is however well known that as doses are increased to levels of 10^{15} to 10^{18} ions per cm^2 of surface area one can also modify the chemical and mechanical properties; for example the coefficient of friction may be increased or decreased, hardness can be altered and corrosion rate retarded. These high density implants differ somewhat from the low level implants used for electronic device preparation; for example at a high dose level there will be substantial radiation damage to the substrate causing radiation enhanced diffusion and therefore perturbation of the expected depth distribution. Moreover the high density implant may cause precipitation of crystallites. At Georgia Tech their attention is directed on the high density implants in titanium and aluminum substrates and their alloys. Areas of interest include the chemical modification of the implanted region, the physical change in the depth profile with temperature cycling, changes in grain size distribution, and changes in the growth kinetics of oxide and nitride formation.

Ion implantation will modify the properties of a material to a depth of some thousands of Angstroms, depending of course on the mass and energy of the implant species as well as the nature of the substrates. For example a 100 keV Ti^+ ion implant will penetrate to a depth of the order of 400 Å and at a beam current of $10 \mu\text{A}/\text{cm}^2$ will attain an implant density of 1% in 10 seconds, lighter projectiles will penetrate further and a 100 keV H^+ projectile will implant to a depth of 5000 Å.

Implantation would be expected to modify such properties as hardness, friction, oxidation, and corrosion, but there will be no change to bulk properties. Implantation depths may appear to be small, but there is ample evidence that surface mechanical and chemical properties are influenced to a depth of many tens of microns. The depth of the implant is important data to be collected. The study includes depth profile of the implanted species and the kinetics of this profile with temperature cycling, grain size distribution, and during oxide and nitride formation. The growth kinetics of oxide and nitride formation is followed in ion implanted specimens to identify the important mechanisms controlling the kinetics.

Analysis of the depth profile of the implanted ion is accomplished by using the Rutherford Backscattering (RBS) technique. The ion implanter is used to supply a He^{2+} beam to the implanted sample and the energy distribution of backscattered particles in a particular direction can be analyzed. The recoil energy is related to the mass of the target atom involved in the collision and to the depth at which it is located. The flux of recoils at an energy is related absolutely to the density of the target species via the Rutherford scattering cross section.

The RBS technique is described quantitatively by Townsend, Kelly and Hartley, "Ion Implantation, Sputtering and Their Application," Academic Press, 1976, in application to obtaining the depth profile of an implanted species. Schematically the experiment is shown in Figure 1. The energy of particles scattered from the surface is given by

$$E = K E_0 \quad (1)$$

where

$$K = \frac{M_1^2}{(M_1 + M_2)^2} \left[\cos^2 \theta_s + \left(\frac{M_2^2}{M_1^2} - \sin^2 \theta_s \right)^2 \right] \quad (2)$$

M_1 is the mass of the incident ion and M_2 is the mass of the scattering center. As seen from equations (1) and (2) the energy of the scattered ion at fixed detector angle depends on the mass of the atomic scattering center. The analysis of the energy of the scattered ions at fixed detector angle will thus serve as a mass analyzer of the target.

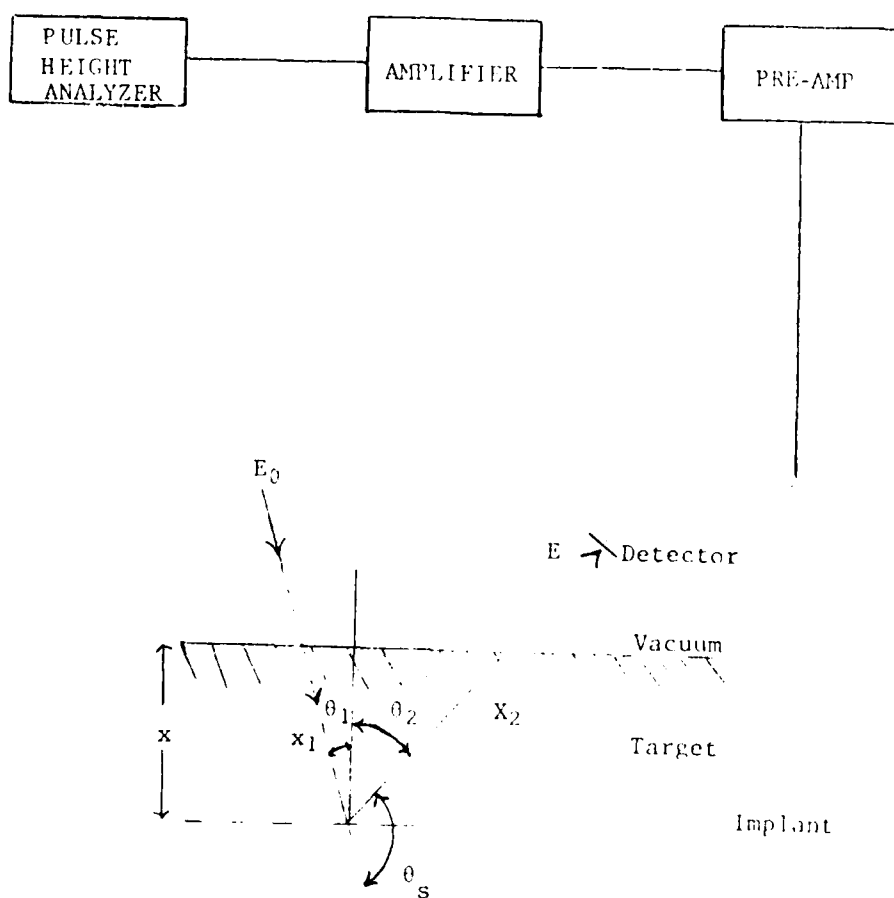


Figure 1. Schematic of Rutherford Backscattering Experiment

During the year that this work has been in effect, noted progress has been made, resulting in the publication of two papers and five presentations:

Publications:

"Optical Properties of Titanium and Titanium Oxide Surfaces," W. E. Wall, M. W. Ribarsky and James R. Stevenson, Journal of Applied Physics, 51, 661 (1980).

"Design Considerations for the Parasitic Use of Synchrotron Radiation in the Infrared," James R. Stevenson and J. Michael Cathcart, Nuclear Instruments and Methods (to be published).

Presentations:

"Design Considerations for Parasitic Use of Synchrotron Radiation in the Infrared," James R. Stevenson and J. Michael Cathcart, National Conference on Synchrotron Radiation Instrumentation, National Bureau of Standards, Gaithersburg, Maryland, June 4-6, 1979.

"Synchrotron Radiation as an Infrared Source," James R. Stevenson, Seminar Northern Illinois University, DeKalb, Illinois, September 21, 1979.

"Synchrotron Radiation in the Infrared," James R. Stevenson and J. Michael Cathcart, Eleventh Annual Synchrotron Radiation Users Group Conference, University of Wisconsin, October 23, 1979.

"Inhibition of Grain Growth in Titanium by Ion Implantation," J. Michael Cathcart, Keith O. Legg, James R. Stevenson, Materials Research Society, Cambridge, Mass, November 30, 1979.

"Surface Grain Growth and Oxidation in Ion Implanted Titanium" J. Michael Cathcart, Keith O. Legg, James R. Stevenson, American Physical Society, Washington, D.C., April 29, 1980.

The preceding research is just an example of the importance of pursuing work in ion implantation of metals. Besides the inroad to the understanding of corrosion, ion implantation gives us a way of creating better surface-related properties, especially for critical components (e.g., engine bearings, turbine blades and spacecraft components). A component with good bulk properties but poor surface properties can be

ion implanted to prove its characteristics. For example, ion plating with platinum improves fatigue and corrosion of titanium alloy turbine blades.

Ion implantation works very well in some industrial applications, such as wire-drawing dies, but its full potential can be realized only if we understand how it works.

CARBON-CARBON COMPOSITE PROCESSING SCIENCE

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and

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Introduction

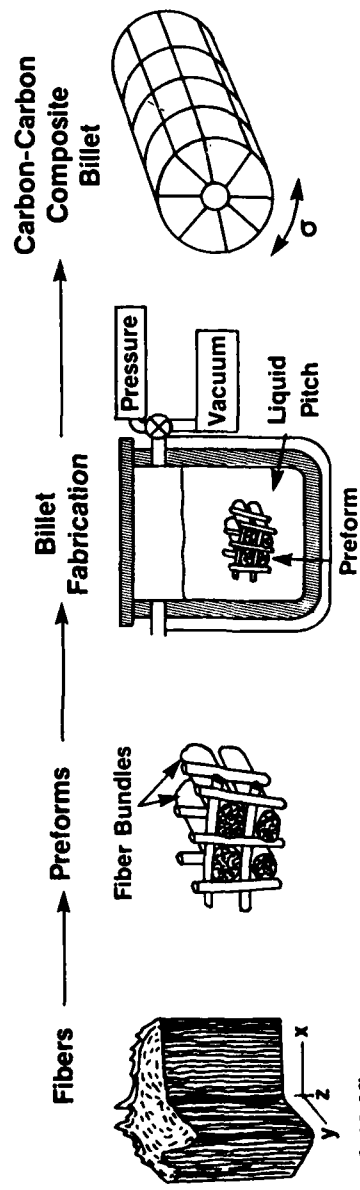
In 1977 the Air Force Office of Scientific Research and the Air Force Wright Aeronautical Laboratory/Materials Laboratory undertook a processing science program in carbon-carbon composite materials for rocket nozzles. These are multi-directional fiber-reinforced composites with excellent thermomechanical and thermalchemical properties. They are now being employed by the Air Force in Integral Throat and Entrance (ITE) rocket nozzles and exit cones and used in all three stages of the MX missile.

The composite materials for modern solid rocket design are the product of complex, multiple-step processes. To process a carbon-carbon composite, single carbon fibers are formed into yarn bundles, which are woven into preforms (Figure 1). The preforms are impregnated with liquid coal tar pitch under pressure in an autoclave to form a billet. Several steps of impregnation, graphitization, and carbonization constitute one densification cycle. These are repeated until a target density is achieved. However, several serious manufacturing survivability problems result when following this empirical process, particularly cracked billets. Some demonstrate catastrophic failure.

Thus, before carbon-carbon composites could be reliably produced for future propulsion systems the Air Force had to develop a capability to manufacture materials repeatably with consistently acceptable physical properties regardless of size. As a result research was undertaken to establish a 3-D Composite analytical program to predict the processing conditions for acceptable billets. Basic research, addressing process chemistry, fundamental properties, residual stress distribution, and the fluid mechanics of carbon (PAN or Polyacrylonitrile precursor) fibers and coal tar pitch composite matrix, iteratively interacted with model development. The approach is illustrated in Figure 2. The basic research part of the program will be highlighted here with emphasis on the fundamental process chemistry of carbon fibers and carbon fiber-matrix systems.

Carbon-Carbon Rocket Nozzle

• Processing Science



← 8-10 Micron →
Polyacrylonitrile

Problem:

- Manufacturing Survivability

Circumferential Stress →

- Cracks
- Catastrophic Failure



FIGURE 1

CARBON-CARBON COMPOSITE PROCESSING SCIENCE APPROACH

FIBER RESEARCH

- POLYACRILONITRILE
- STABILIZATION MECHANISM
- RESIDUAL STRESS DISTRIBUTION
- MICROSTRUCTURE-PROPERTY-

PROCESSING RELATIONS

- OPTIMUM TIME, TEMPERATURE

TENSION

MATRIX RESEARCH

- COAL TAR PITCH
- IN-SITU FUNDAMENTAL PROPERTIES
- DECOMPOSITION KINETICS
- PYROLYSIS AND MESOPHASE REACTIONS
- FLUID MECHANICS

3-D COMPOSITE

ANALYTICAL PROCESSING

MODEL

- PROCESS ENVIRONMENT

MODEL

- 3D THERMAL/DIFFUSION

PROPERTY PREDICTION

MODEL

- MECHANICAL MODEL

ANALYTICAL PROCESSING GUIDANCE

- TIME

- TEMPERATURE

- PRESSURE

- CYCLES

- PREFORM

CONSTRUCTION

FIGURE 2

Carbon Fiber Research

Under AFOSR-77-3466, Professor Donald R. Uhlmann of the Massachusetts Institute of Technology systematically studied how process variables influence the chemical reactions and structural changes which take place in the conversion of acrylic fibers to carbon fibers and the influence of the fibers on the composite matrix mesophase precursor. His research focused on: (1) The tension, time and temperature conditions and concentration of the oxidizer in the atmosphere during the various stages of oxidative stabilization of acrylic fibers and the effect on chemical and physical structure; (2) the translation of the structural features of the stabilized fibers through the firing step into the final carbon fibers, the influence of the carbonizing temperature range on the stabilized fiber structures, and the extent to which stabilization orientation is reflected in the carbon fiber properties; (3) the influence of the fiber structural and surface chemistry on the composite matrix precursor, fiber-matrix interface, and graphitic matrix; and (4) the development and testing of models to describe these phenomena.

Important information was revealed regarding the role of stabilization in producing stabilized fibers suitable for conversion into carbon fibers with improved properties. The internal structure of fibers, particularly those which contain a weak acid which acts as a stabilization catalyst, is quite dependent upon the process parameters used during stabilization. The chemical steps of stabilization can be split into two broad categories: (a) prefatory reactions which lead up to and include nitrile polymerization; and (b) sequent reactions which follow nitrile polymerization. Oxygen is involved in both categories, but the predominant oxygen uptake occurs during the sequent reactions. These reactions can occur by two different mechanisms: (a) reaction-controlled, where the prefatory reactions are slow and sequent reactions follow immediately; and (b) diffusion-controlled, where the prefatory reactions are faster and the sequent reactions are limited by diffusion of oxygen to the reaction sites. Usually the mechanisms are differentiated by transmission optical microscopy on thin sections, e.g., diffusion-controlled reactions exhibit a dark mantle surrounding a lighter colored core. In the reaction-controlled case, the fiber darkens uniformly throughout its cross-section. Fibers which undergo the diffusion-controlled mechanisms also show other mantle-core structures, including a polished mantle, a fracture mantle and an etched mantle. These mantles have various initial thicknesses and vary with time. These different mantles and their rates of thickening give evidence that the assorted reactions occurring within the uniformly colored zone of the dark mantle do not proceed at the same rate. The chromophores responsible for the dark mantle are formed at a faster rate than the crosslinks thought to be responsible for the insoluble etched mantle. Furthermore, the various reactions do not go rapidly to completion. Bleaching studies on fibers show that the colored material is rapidly digested leaving behind essentially unaltered original polymer. The

bleaching and etching studies lead to the conclusion that the partially stabilized fiber exists as a series of interpenetrating networks; and the mechanisms of stabilization given earlier are only part of the story. The formation of the mantles and their rate of movement is controlled by cracks formed at high temperature due to differences in Poissons ratio between the oxidized mantle and unoxidized core. Thus proper attention must be paid to the time, temperature, and tension at various stages as the fiber undergoes stabilization in order to produce stabilized fibers suitable for conversion into carbon fibers with improved properties.

Studies of the formation, growth and coalescence of mesophase material during the firing of pitches on contact with carbon fibers have indicated that alignment of the mesophase material with a substrate is primarily controlled by motion of the mesophase droplets in flow. Such droplets generally do not wet the carbon fibers. When dynamic motion is restricted, as in the interstices of a yarn, the formation and growth of the mesophase material is also restricted. These results appear to have significant implications for the processing of fiber-carbon composites.

Concurrent with Professor Uhlmann's research, Professor R. J. Diefendorf of Renssaeler Polytechnic Institute investigated the relations of structure to properties of high performance carbon reinforcement filaments with emphasis on strength improvements under Grant AFOSR-77-3436. The location and origin of strength limiting flaws in carbon fibers and how they relate to ultimate fiber performance in composites were determined. This research contributed to the establishment of the process science data base essential to carbon fiber availability and processability and composite reliability.

The approach was to: (1) determine if preferred orientation measurements made on carbon fibers in finished carbon-carbon composites in yarn bundles could be used with crystal properties to calculate, or at least, correlate with axial properties; (2) ascertain if transverse moduli and coefficient of thermal expansion can be calculated from preferred orientation measurements; and (3) identify and eliminate the sources of critical flaws and injurious residual carbon fibers to increase tensile strength.

The axial properties of carbon fibers were found to correlate well with preferred orientations determined by either x-ray diffraction or optical techniques. High modulus carbon fibers were found to have significant gradients in preferred orientation. For HMS fiber, the modulus of the surface layers is about twice the average fibers modulus, while the interior modulus is only about one-half the average. This modulus gradient suggests that higher modulus fibers, with good strength, could be produced, if the modulus at the interior of these fibers could be increased. The gradient in preferred orientation produces high residual stresses in HMS fibers. While the high surface compressive stresses minimize the effect of surface flaws, the high axial tensile stresses in the interior may decrease strength by causing fracture to initiate at

flaws in the interior rather than at the surface. Similarly, the high axial compressive stressed outer layers of a fiber may initiate buckling when the fiber is compressively loaded. Modifications of the residual stress pattern might allow increased tensile and/or compressive strengths to be obtained in high modulus carbon fibers.

Many correlations between properties and fiber diameter, reported in the past, may be in error because it is very difficult to determine the fiber diameter precisely and accurately.

Carbon Matrix Research

The advent of carbon-carbon composites has brought about a need for more rapid, precise and controlled graphite formation from liquid precursors within the voids and interstices of arrays of preassembled fiber bundles than has heretofore been required. Simultaneously, variations in pitch raw stocks, not unusual for an industrial 'natural' product, have made it more difficult to predict composite fabrication and performance on the basis of the properties of 'typical' available raw materials. A further requirement for shortened production schedules has led to impregnation and coking of the pitch within the preforms at elevated pressures while at the same time expanded use of carbon-carbon composites has increased not only the volume to be processed, i.e., densified, but also preform sizes and geometries.

As a consequence there has arisen a need to know more precisely some of the physical and chemical responses of polynuclear molecules and mixtures, such as coal tar pitch at elevated pressures and temperatures. This is particularly so of transport property data such as viscosity and thermal diffusivity and conductivity needed to permit prediction of processing parameters and rates of change to be used in impregnation and pyrolysis within relatively fragile and expensive preforms. Rates of heating, pressure application, impregnation and penetration, gas formation and percolation, liquid exudation and finally coke yield and distribution within the preform can be expected to be influenced by changes in pitch properties with time at temperature and pressure. Preform strength and integrity can also be compromised by unexpected internal stress buildup due to imbalances in the pressure-temperature response of the impregnated, reacting pitch.

The purpose of the research of Dr. J. J. Gebhardt of General Electric Company under Contract F49620-78-C-0006 was to generate an understanding of the nature and composition of coal tar and petroleum with respect to mesophase and graphite formation at atmospheric as well as elevated pressure. This was accomplished by direct determination of selected transport properties of an accepted coal tar pitch standard as well as observations of its behavior during the early phases of mesophase formation under pressure.

Experimental work performed included: (1) studies of mesophase formation in three coal tar pitches at near atmospheric and moderately high pressure, which included determination of molecular weight distribution, quinoline insoluble measurement and microscopic examination; (2) measurement of sound velocity of phenanthrene up to 101 MPa (15,000 psi) and coal tar pitch at one atmosphere and calculation of adiabatic compressibilities; (3) measurement of viscosity of naphthalene, phenanthrene and 277-15V pitch up to 101 MPa using a falling needle viscometer; and (4) measurement of thermal diffusivity and conductivity of coal tar pitches in the as-received as well as partially pyrolyzed condition. In view of the aforementioned variations in properties with the ultimate origin of natural pitches, two experimental reproducible and 'tailored' pitches were included in some of the measurements to assess how their 'typical' properties vary with pressure and time at temperature relative to the 'natural' product. In addition, phenanthrene and naphthalene were studied as pure, polynuclear aromatics, related to pitches, but free of the side chains, suspended particulates and molecular weight distribution typical of pitch mixtures.

Pyrolysis studies were carried out at 0.5, 3.5 and 6.2 MPa (50, 500 and 900 psig) and 723 and 748K (450 and 475°C) for 2, 4 and 7 hours on Allied 277-15V coal tar pitch and on two developmental Koppers Co. pitches, types A and B. Determination of quinoline insolubles and coking values showed a generally positive effect of pressure on conversion. The developmental pitches gave higher conversions to coke and less gas evolution than 277-15V. The greatest variation in kinetics appears to occur during the first two hours and at temperatures between about 698 and 748K. Examination of pyrolyzed products by optical and scanning microscopy indicated that smaller particles tend to be formed at elevated pressure and that coalesced mesophase areas are more uniform and less perturbed by gas formation and percolation.

Thermal diffusivity and conductivity measurements were made as a function of temperature on as-received as well as outgassed 277-15V pitch using a laser flash diffusivity technique. Similar measurements were also made at room temperature on partially pyrolyzed specimens of 277-15V and the two Koppers Co. developmental pitches. Specific heats were determined by differential scanning calorimetry. Thermal conductivity of the partially pyrolyzed materials decreased during the first two hours of pyrolysis, then increased gradually thereafter. No sudden or large changes were noted; the presence of bubbles in both solid and liquid specimens probably accounts for the observed scatter.

Sound velocity was measured in liquid phenanthrene up to 101 MPa and in liquid 277-15V pitch at one atmosphere; adiabatic compressibilities at one atmosphere were computed for both materials.

Relative viscosities of naphthalene, phanthrene and 277-15V pitch were measured up to 101 MPa; freezing point measurements were also made from observed temperature changes during freezing and melting. This permitted establishing an estimated freezing point of 393K for phanthrene at 69.4 MPa and a full pressure-melting point curve for naphthalene up to 101 MPa and 390K. Viscosities increased by a factor of up to two for the two pure compounds at pressures up to 101 MPa and up to six for 277-15V pitch. Quantitative evidence of partial solidification at around 50-60 MPa was also observed for 277-15V pitch.

Performance models which relate the microstructure of the composites to their environmental response are limited since the fundamental relationships between process chemistry, in-process events and microstructure formation have not been defined. While the GE program concentrated on thermophysical and thermomechanical properties of pitch, the objective of the research of Mr. James P. Pope (F49620-79-C-0068) at Science Applications, Inc. was to define the critical chemical phenomena and kinetics occurring in composite matrix decomposition as a function of pressure under simulated fabrication conditions. The intent was to contribute to the establishment of a science base which would permit tailoring of the carbon-carbon composite processing cycle to optimize carbon yield, obtain desired microstructures for achieving improved thermochemical and thermostructural response, and obtain high quality composites via low pressure processing. The approach included three tasks: (1) Definition of the reaction rates of the decomposition of matrix pitches without the presence of fibers, powders or mechanical constraints through determination of time-temperature-pressure relationships; (2) investigation of matrix decomposition as modified by the presence of active surfaces and mechanical constraints in fluid flow; and (3) analysis of decomposition reactions and solid state products through consideration of microstructure, chemical structure, crystallographic orientation and degree of ordering, fluid dynamics, heat conduction, diffusion and mechanical environment.

A mini hot isotatic pressure (MIP) autoclave was fitted with thermal and external diagnostic apparatus for monitoring decomposition rates and events of pressure-temperature-time scheduled carbonization of coal tar pitch. Carbonization cycles based upon the Air Force's Equivalent Industrial Standard Process (EISP) were conducted for the full time-temperature-pressure schedule as well as for process runs interrupted in the liquid-solid transformation temperature range of the pressure decomposition of coal tar pitch (450° - 490°C). Thermogravimetric analysis, high pressure liquid chromatography, gel permeation, and compositional analysis techniques were used to parametrically study critical events of coal tar pitch carbonization.

Pitch matrix decomposition reaction rates were identified and density data at temperature and pressure were obtained which iteratively interacted with process environment model development. Microstructure development after carbonization and graphitization of various carbonization cycles and its relation to densification, decomposition, pressure and temperature dependence, properties, and autoclave can location were systematically studied for the first time. Research was performed on Allied 15 pitch, Koppers 15V equivalent and several Koppers experimental pitches.

Based on the results of this study, the following conclusions can be drawn in the areas of coal tar pitch characterization, the heat treatment of pitch and the decomposition reactions of pitch and mechanical properties of pitch:

1. Characterization specifications for coal tar pitches used in the Air Force Equivalent Industrial Standard Process (EISP) should be rewritten to take into account the change in the characteristics of coal tar pitch material over long periods of time and also the increase in softening point in the thermally pretreated pitches.

2. Thermal pretreatment of pitch combined with mechanical agitation of the pitch can result in: (a) More reproducible batches for impregnation; (b) increase in char yield; (c) increase in temperature range where the decomposition occurs and reduction of gas evolution during liquid state; (d) deduction in average molecular weight by reducing long chain polymers; and (e) reduction in maximum rate of decomposition.

3. Studies of the decomposition of coal tar pitch established the following: (a) The apparent and bulk densities of coal tar pitch at the liquidus-solidus transition temperatures are on the order of 1.10 to 1.25 gm/cm³; (b) stratification of variant properties and microstructure of carbonized coal tar pitch occurs in sealed cans at all processing pressures; (c) the weight loss of decomposing coal tar pitch in sealed cans appears to be independent of pressure and a linear function of ultimate temperature during carbonization; and (d) evaluation of coal tar pitch carbonized at 5000 psi and 15,000 psi indicate that the complete carbonization occurs at temperatures greater than 620°C. The 15,000 psi process is slightly more efficient in terms of char yield at 620°C but probably is not as efficient at lower temperatures.

4. The elastic modulus and ultimate strength from flexure tests of carbonized pitch is on the order of $.4 \times 10^6$ psi and 1200 psi, respectively. Partially carbonized pitch (to 470°C at 15,000 psi) appears to have similar properties.

Analytical Modeling for Improved Composites

Dr. W. C. Loomis, Dr. D. A. Eitman and several associates at Science Applications, Inc. conducted an analytical modeling and experimental program for processing effects in carbon-carbon composites under contract F33615-77-C-5094. Model development and demonstration addressed the definition of processing effects on constituent material behavior, the development of an analytical model including mechanical effects, fluid/thermal effects and interactions, and the demonstration of analytical model capability for composite property prediction against controlled composite.

The research included the experimental fabrication of an ideal 3-D composite. Standard fabrication conditions were developed as a baseline followed by fabrication of 3D composites where variables in processing and materials were introduced. Process environment, mechanical and 3D thermal/diffusion property prediction models were developed to predict and show observed results from the processing variables. The analytical code work was directed at modeling the processing of the 3D composite using input data developed in the experimental modeling work and under the aforementioned programs at GE, SAI, MIT and RPI. Work was also directed at following dimensional changes and cracks via computer modeling during processing of the composites.

Payoff

This research told nozzle designers how to weave, impregnate and graphitize carbon-carbon billets without cracking. The analytical guidance predicted safe and failure zones for the fabrication of cracked or acceptable billets in terms of graphitization temperature and preform construction as shown in Figure 3.

An acceptance criteria for the processing of carbon-carbon billets was determined from the final processing cycle - the graphitization cycle. Cracking occurs during this cycle as carbon is converted to graphite. The circumferential stresses were determined analytically as a function of preform geometry and graphitization temperature for billets that had cracked. The billets were then redesigned in terms of maximum stress graphitization temperature so that circumferential stresses were reduced to an acceptable level. This prediction was based upon newly determined properties of fibers and the flow and other fundamental properties of the Allied 15V pitch. These process predictions were utilized in the fabrication of MX Manufacturing Technology billets with a high degree of success. The MX Systems Projects Office is now exploring the feasibility of using this model as part of the MX nozzle materials review bid.

Theoretical Billet Design Process

- Process for MX Nozzles
 - High Yield
 - Low Stress

Theory — Experiment Confirmation

Stress vs Process Temperature: Experimental Result

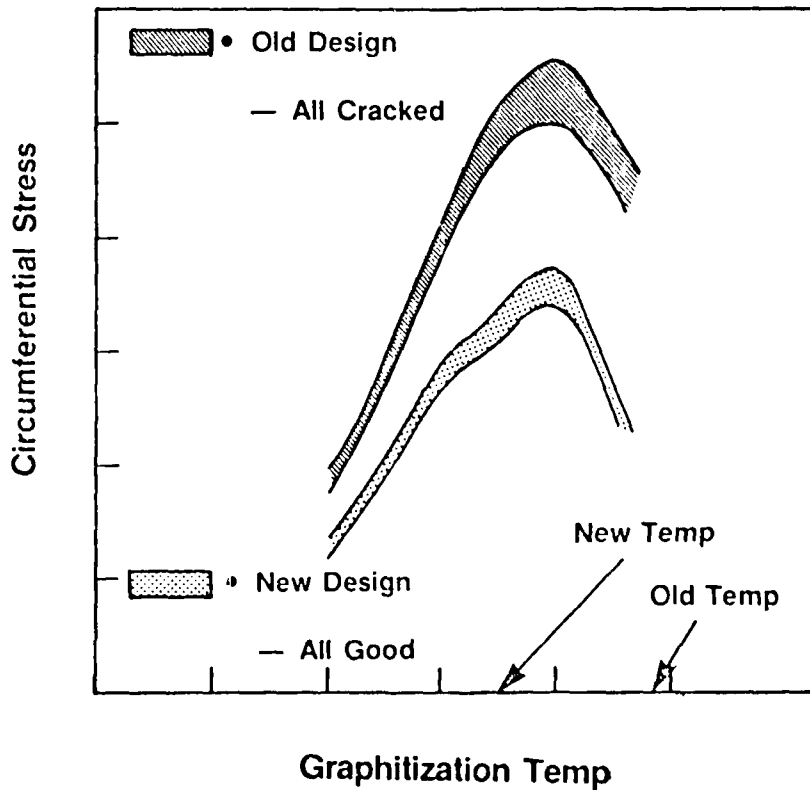


FIGURE 3

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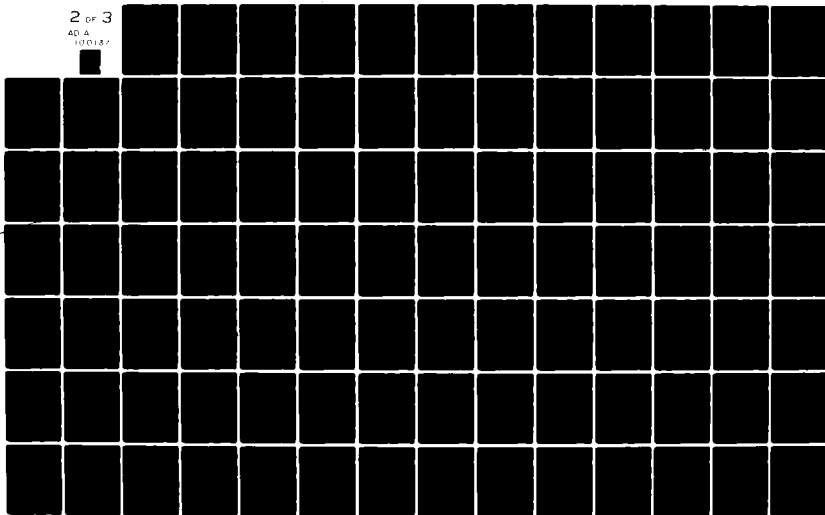
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AFOSR SPONSORED RESEARCH IN MOLECULAR DYNAMICS

Capt William G. Thorpe

Within the context of the AFOSR program, molecular dynamics encompasses the study of the molecular mechanism of elementary chemical and physical rate processes occurring in or among species in the gas phase. Such a broad area in chemical physics - or physical chemistry is too large for the scope and resources of one program. The scope of this program is focused by two criteria, the impact of the sponsored research on the scientific discipline and on future Air Force technology needs. The goal is to support that research which will significantly advance the state of the art in molecular dynamics. Air Force technological needs are implicit in the titles of the four subareas: chemical lasers, chemistry of the upper atmosphere, plume and wake chemistry, and interactive dynamics.

The chemical laser subarea has historically involved a search for chemical laser candidates by screening exoergic reactions with respect to population inversions and competing reaction channels. The Air Force continues to have a strong interest in electronical transition chemical lasers. The oxygen-iodine chemical laser is undergoing development at the Air Force Weapons Laboratory (AFWL). However, much basic research is needed to fundamentally understand the mechanistic chemistry in the production of $O_2(^1\Delta)$ and in the dissociation of molecular iodine by excited oxygen. Also at AFWL, Dr. Steve Davis is currently studying the possibility of a chemical laser based on the molecule IF. This exciting work is an outgrowth of past AFOSR supported work of Dr. Michael Clyne at Queen Mary College, London.

The atmospheric chemistry subarea is concerned primarily with optical and chemical processes occurring in the upper atmosphere. A deeper understanding must be developed of the radiation processes and chemical reactions occurring in the upper atmosphere in order to exploit new communication and detection technologies. The Air Force Geophysics Laboratory (AFGL) is actively involved in this area. New studies of the chemistry in the upper atmosphere is needed where one or more of the reactant species are state selected. It is expected that support in this subarea will continue to grow.

The plume and wake chemistry subarea is certainly the most focused. Its goal is to understand translational to vibrational energy transfer processes in order to predict, detect, and minimize rocket and aircraft plume signatures. During the past year, AFOSR sponsored programs involved experimental efforts at Yale (Dr. John Fenn) and AFGL (Dr. Al Rahbee) and theoretical efforts at Harvard (Dr. Dudley Herschbach) and Battelle (Dr. Michael Redmon).

The interactive dynamics subarea is built about a basic understanding of the interaction of optical radiation with chemical species and the study of energy transfer mechanisms both within and among these species. It encompasses some of the most long range research and enhances the above, more directed efforts. Included in this area are studies of multiphoton processes, unimolecular decomposition kinetics, and state selected reactions wherein one or more of the reactants are placed in a specified state prior to reaction with a subsequent identification of product states.

An AFOSR sponsored contractors meeting was held at AFGL this past year. The highlights of these meetings are the informal communications fostered within this group of distinguished scientists and their interaction with AFGL scientists. The program manager was extremely happy to observe and learn that this distinguished research group felt the meeting to be one of the better scientific meetings of the year and not a mandatory attendance symposium.

A good research program necessitates a continuity in research goals and support. Consequently, it is planned to continue this strong AFOSR program in much the same mold in which it has been cast over the past several years. It is both stimulating and challenging to work with such a group of top-notch scientists in academia, industry, and the Air Force laboratories. One looks forward to many more years of such interaction. Fiscal Year 81 has started in a budget-cutting atmosphere which will serve to increase the challenge of this job.

FOCUSSING IN ON DYE LASERS

DR. ANTHONY J. MATUSZKO

A little over a decade ago Lankard and Sorokin at IBM observed stimulated emission from organic dyes which produced a frequency tunable laser. Since a large variety of organic dyes is available, each fluorescing at specific wavelengths, this discovery lead to the possibility of designing lasers to cover the entire range of the visible spectrum. As an added advantage, each of the laser dye systems could be individually tunable over a range of wavelengths.

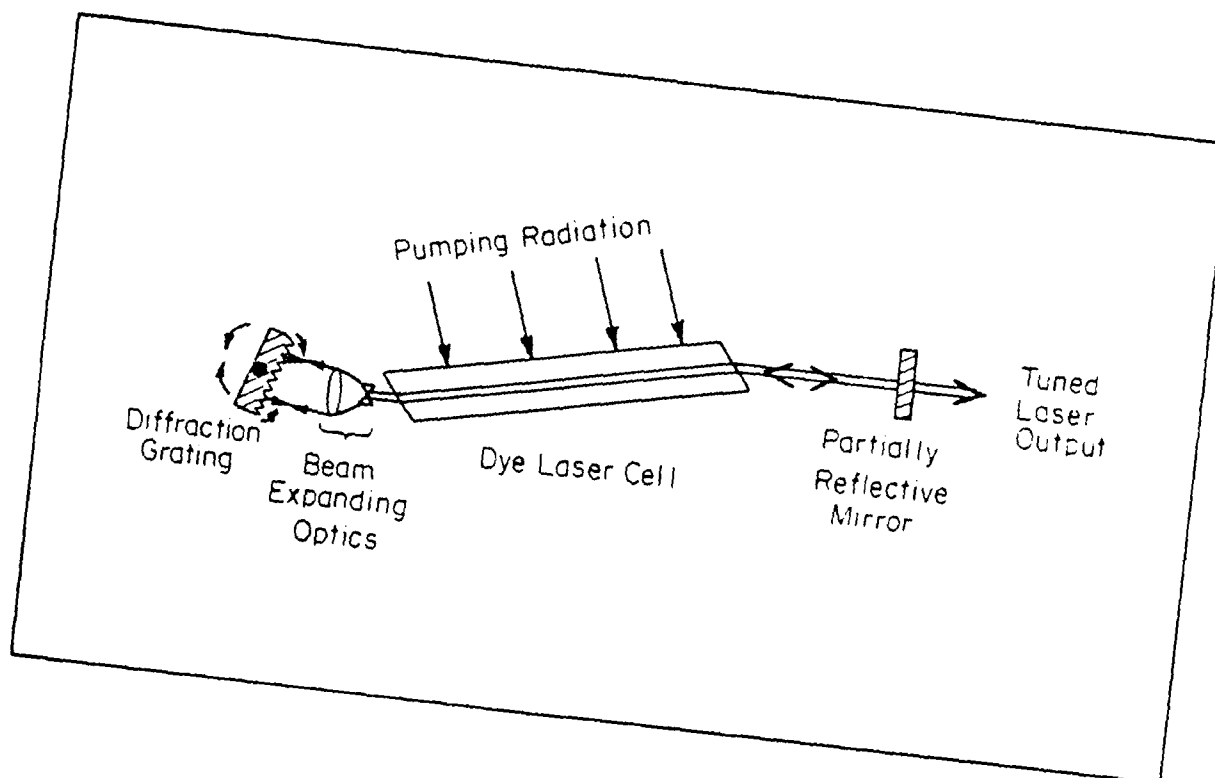


FIGURE 1. SCHEMATIC ILLUSTRATION OF A DYE LASER

The Air Force became interested in tunable dye lasers in the early 1970s as one approach to fill requirements for a multi-line laser source over a waveband of from 0.5 to 0.9 μm (500-900 nm). Flashlamp pumped dyes were seen as possible candidates for certain airborne laser applications.

However, dyes pumped with a flashlamp have short lifetimes due to the harmful photochemical effects of the ultraviolet light from the lamp. This photochemical deterioration occurs to a greater or lesser degree with all classes of laser dyes, with the result that the efficiency of a dye laser typically drops more or less continuously as the laser is operated. Laser action eventually ceases unless the dye is replenished. Research was needed to study ways in which dye photochemical instability could be minimized, while at the same time maintaining the overall efficiency derived from flashlamp pumped laser systems.

By pumping the dye with another laser emitting in the spectral region of the peak dye absorption, dye instability is nearly eliminated for dyes lasing in the visible region. Unfortunately, the addition of another laser to pump the dye adds complexity, weight, and size to the system.

A convenient measure of the useful lifetime of a given laser dye system is the total input energy (in Joules) which will produce a 50 percent decrease in the initial output of a given dye solution. The units of "lifetime" are thus Joules/liter. Most laser dyes available today have lifetimes of 10^3 to 10^5 Joules/liter, which corresponds to several hundred shots of a flashlamp-pumped dye laser. Such dye lifetimes, while suitable for applications in which the dye solutions can be changed periodically, are unacceptably short for other applications requiring long-term stability of laser output.

In 1974, the Air Force Avionics Laboratory initiated an in-house research program aimed at studying decomposition mechanisms of laser dyes with the ultimate objective of extending their lifetimes. This work was done by Capt Sid Johnson and his group at the Avionics Laboratory along with a cooperative effort with Dr. Ernie Dorko of the Air Force Institute of Technology. AFOSR Chemistry initiated a program in support of this work in 1977 with research efforts at Battelle Columbus Laboratories, University of Virginia and Columbia University.

The research at Battelle was under the direction of Dr. Robert Schwerzel and involved mechanisms of photochemical degradation in xanthene laser dyes. The objectives included mechanistic studies on Kiton Red S and other xanthene dyes and an evaluation of solvent effects. The research performed in the course of this program has led to the discovery of an unprecedented excited state pathway for the photodegradation of Kiton Red S, a sulforhodamine laser dye, in which the reactive, lowest energy excited triplet state of the molecule is populated by preferential intersystem crossing from upper singlet excited states, not from the singlet state nearest in energy to the triplet. The mechanism is shown schematically in Figure 2.

The results obtained have led to a tentative chronology of the first several stages in the photodegradation process (Figure 3).

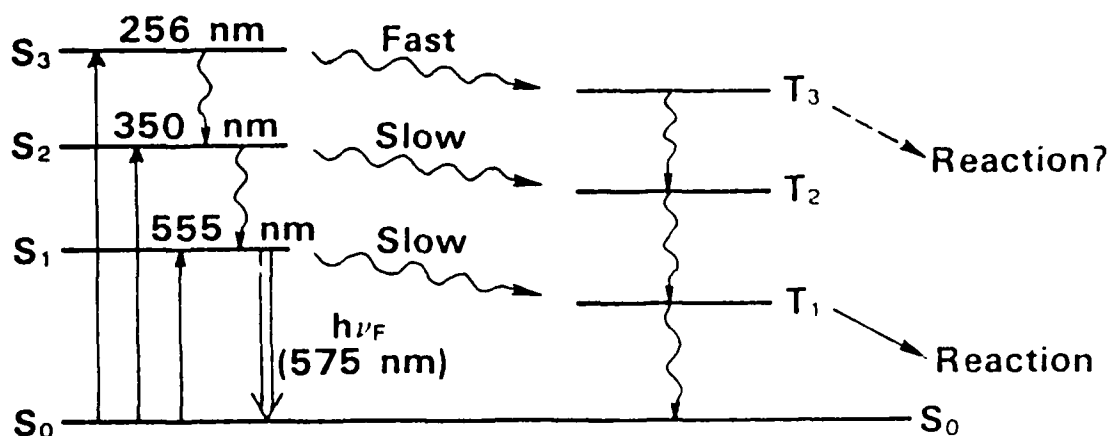


FIGURE 2. SCHEMATIC ENERGY-LEVEL DIAGRAM FOR THE PHOTOCHEMICAL DECOMPOSITION OF KITON RED S.

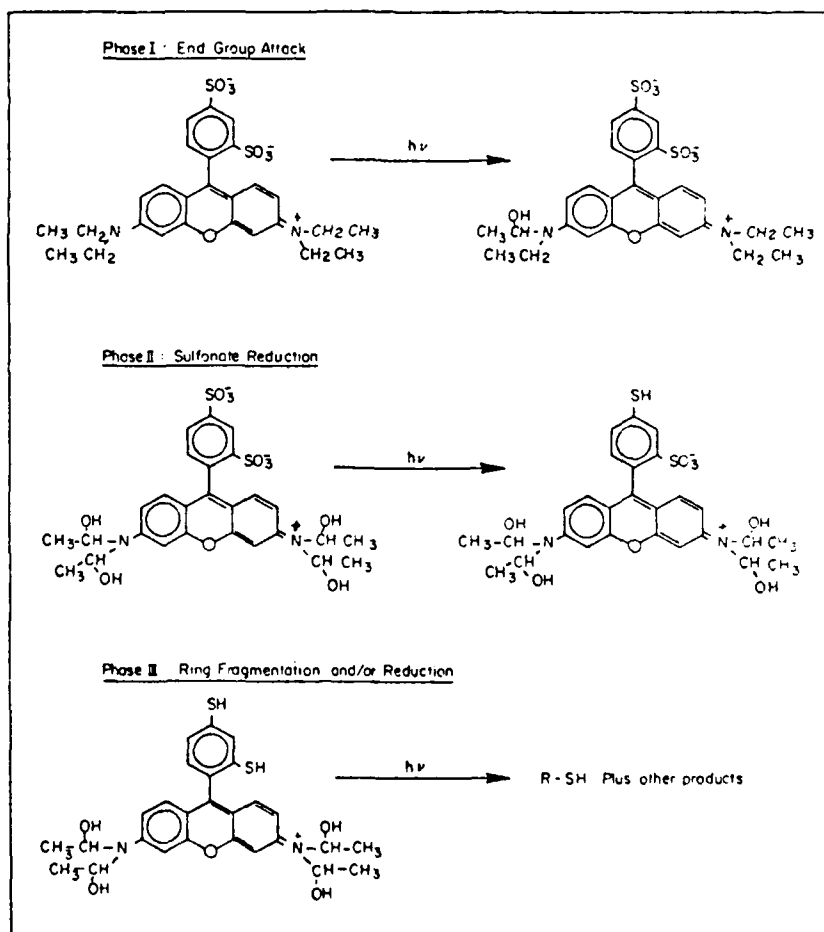


FIGURE 3. POSTULATED CHRONOLOGY OF PHOTODEGRADATION OF KITON RED S

While much remains to be learned about the details of the chemical reactions involved in the photodegradation of Kiton Red S and other xanthene dyes under various conditions, the research performed during this program has achieved significant progress toward this goal. In particular, enough has been learned about the degradation of these dyes that it is now possible to suggest new strategies for slowing their degradation under lasing conditions. These include, in particular, the removal of excitation wavelengths below 240 nm by selective filtering, and the use of improved triplet quenchers.

Several aspects of the photodegradation process remain incompletely understood. These include the detailed identity of the photodegradation products formed from Kiton Red S and the other xanthene laser dyes, the role of peroxides in the photodegradation process, and the factors which result in the loss of lasing capability of dye solutions before appreciable degradation has occurred (as measured by chromatographic and spectroscopic analysis of the dye). These problems could form the basis for future research in this field.

The objectives of the research by Dr. Jim Demas of the University of Virginia included obtaining a better understanding of the mechanisms of energy and electron transfer between metal complexes and laser dyes, and utilization of the energy transfer for developing new and improved binary laser dye systems with enhanced stability, efficiency and narrower line widths.

Demas has reported the first example of singlet energy transfer from a charge transfer (CT) excited state of a metal complex $[\text{Ru}(\text{bpy})_3]^{2+}$, (bpy=2,2'-bipyridine). The acceptor was the laser dye Rhodamine 101 and the energy transfer efficiency extrapolated to total quenching was $100 \pm 5\%$. The current evidence points to the transfer proceeding by a contact rather than long range Förster mechanism, at least in low viscosity solvents.

Demas and his coworkers have found very efficient (up to 80%) energy transfer from $[\text{Ru}(\text{bpy})_3]^{2+}$ to rhodamine and oxazine dyes in sodium laurylsulfate micelles. The significance of this result is that the micelles concentrate the acceptor and the sensitizer into localized regions, and thus much lower concentrations are required. For example, the methanol solution work required 10^{-3} M in dye concentrations while only 10^{-5} M was required in the micelle work. An added advantage might be the non-flammability of the aqueous micellar system as compared to the methanol solution.

The fundamental picture of the excited state interactions of metal complexes is not yet complete. Essential to this understanding is dynamic lifetime information and accurate broad wavelength studies of energy transfer efficiencies in optically dilute systems. In particular,

the micellar systems show great complexity of behavior. Demas and his coworkers are continuing to work on these problems and hope to come up with some answers.

Dr. Ken Eisenthal of Columbia University has been developing and utilizing picosecond laser techniques to obtain information on ultrafast molecular processes in liquids. From these studies, primarily of organic molecules, he and his research group have gained insight into the physical and chemical pathways by which excited state molecules dissipate their energy by proton and electron transfer phenomena, the nature of intermolecular motions (cage effects in chemical reactions) and intramolecular motions about methylene groups, and photodissociation of excited molecules and energy relaxation in the fragments generated. The information the Columbia group has obtained, particularly the proton transfer work, has important implications in the photostability of dye lasers and polymer systems, as well as in the development of new lasers based on the generation of large excited state populations in transient species and the general effects of intense lasers on materials.

Research on better understanding and improving dye laser systems has been widespread since their discovery. Among the many individuals making early contributions to the area from government laboratories should be mentioned A. Fletcher, E.J. Schimitschek, A. D. Britt and W. B. Moniz of the Navy Laboratories, and S. Johnson and E. Dorko of the Air Force. Basic research supported by AFOSR has provided added knowledge to a better understanding of these unique systems.

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1. "New Laser Dye Systems Based on Luminescent Transition Metal Complexes," AFOSR Grant 78-3590 with University of Virginia, Dr. James N. Demas, Principal Investigator (June 1, 1978 - Present).
3. "Picosecond Laser Studies of Excited State Proton Transfer," AFOSR Grant 77-3407 with Columbia University, Dr. Kenneth B. Eisenthal, Principal Investigator (Sept 1, 1977 - Sept 30, 1980).

ACTIVE RESEARCH EFFORTS

CHEMISTRY

As of 1 Oct 1980

Alphabetical by Principal Investigator

Photoionization of Molecular Clusters (WGT) AFOSR-78-3638, 2303/B1	Ronald P. Andres Joseph M. Calo Department of Chemical Engineering Princeton University Princeton, New Jersey 08540
Transport Properties and Structure of Extended-Chain Polymers (DRU) AFOSR-80-0014, 2303/A3	R. Edward Barker, Jr. Kenneth R. Lawless Department of Materials Science University of Virginia Charlottesville, VA 22901
Rates of Intramolecular Conversions Over Low Barriers (WGT) AFOSR-80-0046, 2303/B1	Simon Bauer Department of Chemistry Cornell University Ithaca, New York 14853
Diagnostics and Chemical Applications of Multiphoton Absorption Processes (WGT) AFOSR-77-3279, 2303/B1	Sidney W. Benson Department of Chemistry University of Southern California Los Angeles, CA 90007
Low Frequency Light Scattering in Extended Chain Polymers (DRU) AFOSR-77-3317, 2303/A3	Elliot R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521
Property-Structure-Processing Relations in Polymeric Materials (DRU) AFOSR-77-3404, 2303/A3	Guy C. Berry Herschel Markovitz Department of Chemistry Carnegie-Mellon University Pittsburgh, PA 15218
New Approaches to the Synthesis of Novel Organosilanes (AJM) AFOSR-80-0239, 2303/B2	Philip Boudjouk Department of Chemistry North Dakota State University Fargo, ND 58105

Underpotential Metal Deposition
and Trace Analysis Using Solid
Electrodes (DWE)
AFOSR-78-3621, 2303/A1

Molten Salt Electrochemical
System (DWE)
AFOSR-80-0173, 2303/A1

New Approaches to Functionalized
Fluorocarbons (AJM)
AFOSR-80-0259, 2303/B2

Model Studies of Energetic
Compounds (AJM)
AFOSR-80-0104, 2303/D9

Chemical Kinetic Studies Invol-
ving NF and PF Radicals (WGT)
AFOSR-78-3507, 2303/B1

Excited State Chemistry of
Halogen Azides (WGT)
F49620-79-C-0053, 2303/B1

Structural Electronic Relation-
ships in Polymeric Solids (DRU)
AFOSR-80-0038, 2303/A1

Theoretical Studies of Metal
Oxides (WGT)
AFOSR-78-3677, 2303/B1

Chemiluminescence and Laser
Induced Fluorescence of Boron
Atom Reactions (WGT)
AFOSR-80-0061, 2303/B1

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Electrosorption of Organic
Molecules (DWE)
AFOSR-80-0262, 2303/A1

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New Laser Dye Systems Based on
Luminescent Transition Metal
Complexes (AJM)
AFOSR-78-3590, 2303/B2

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Development of Practical MO
Techniques for Prediction of the
Properties and Behavior of
Materials (AJM)
AFOSR-79-0008, 2303/B2

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Evaluation of Photochemical Atmos-
pheric Processes of Environmental Relevance
for the Proposed U.S. Air
Quality Criteria (DWE)
AFOSR-79-0144, 2303/A1

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Picosecond Laser Studies of Excited
State Proton and Electron Transfer
Phenomena (AJM)
AFOSR-81-0009, 2303/B2

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High Resolution Electron Energy
Loss Studies of Chemisorbed
Species on Aluminum and Titanium
(LAK)
AFOSR-80-0154, 2303/A2

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Time Resolved Spectroscopy of
Reactive Chemical Systems (DWE)
AFOSR-78-3617, 2303/A1

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Collisional Energy Exchange in
Polyatomic Molecules (WGT)
F49620-80-C-0026, 2303/B1

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Preparation of
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Structural and Chemical
Properties (WGT)
AFOSR 80-0254, 2303/B1

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

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

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

Exploratory High Pressure
Chemistry (AJM)
AFOSR-79-0092, 2303/B2

Spectroscopic Studies of the
Products of the Reactions of
Noble-Gas Atoms (WGT)
AFOSR-79-0089, 2303/B1

Multiphoton Dynamics: Energy
Disposal During Decomposition of
Molecules (WGT)
F49620-78-C-0107, 2303/B1

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

Spectroscopic Investigations of
PbF (WGT)
AFOSR-80-0019, 2303/D9

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Ultrastructure Processing and
Environmental Stability of
Advanced Structural and Elec-
tronic Materials (DRU)
F49620-80-C-0047, 2303/A3

Ion-Molecule Reactions Involving
Atmospheric Cluster Ions (WGT)
AFOSR-80-0116, 2303/D9

Theoretical Study of the Ener-
getics and Dynamics of High
Energy Inelastic Collision
Processes (WGT)
F49620-80-C-0017, 2303/B1

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

Synthesis and Characterization
of Transition Metal Complex
Systems with Novel Solid State
Properties (AJM)
F49620-79-C-0051, 2303/B2

Molecular Order and Solifidifica-
tion Processes in Organic Liquids
and Solutions (LAK)
AFOSR-80-0166, 2303/A2

NMR Study of Disordered Materials
under Extreme Conditions of Pres-
sure and Temperature (DRU)
AFOSR-81-0010, 2303/A3

Electrochemical Impregnation for
the Fabrication of Cadmium
Electrodes (DWE)
AFOSR-79-0104, 2303/D9

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Effect of Structure on Physical
Properties of Polymers (DRU)
AFOSR-80-0101, 2303/A3

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Measurement of Rate Constants of
Elementary Gas Reactions of
Importance to Upper Atmosphere
and Combustion Systems (WGT)
AFOSR-80-0207, 2303/B1

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Computer Modeling of Pulsed
Chemical Lasers (WGT)
AFOSR-80-0003, 2303/B1

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An Approach to Molecular Composites
(DRU)(AJM)
AFOSR-79-0080, 2303/A3 & 2303/B2

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The Quantum Dynamics of Chemical
Reactions (WGT)
F49620-79-C-0187, 2303/B1

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Chemically Modified Electrodes
and Oxygen Electrocatalysis
(DWE)
AFOSR-78-3672, 2303/A1

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Studies of Polymer-Bound
Macrocyclic Polytertiary
Phosphines (AJM)
AFOSR-79-0090, 2303/B2

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Synthesis of Novel Fluorine
Compounds - New Experimental
Challenges in Elemental Fluorine
Chemistry (AJM)
AFOSR-78-3658, 2303/B2

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

Infrared Chemiluminescence Studies
of Ion-Molecule Reactions in a
Flowing Afterglow (WGT)
AFOSR-78-3565, 2303/B1

Laser Hole Burning and Coherent
Transient Spectroscopy of Glass
and Macromolecular Materials (DRU)
F49620-79-C-0108, 2303/A3

Preparation & Properties of
Halide Glasses and Glass-Polymer
Composites (DRU)
AFOSR-80-0059, 2303/A3

Time-Temperature Studies of
High Temperature Deterioration
Phenomena in Lubricant Systems:
Synthetic Ester Lubricants (LAK)
F49620-80-C-0061, 2303/A2

Chemical Structure by Laser-
Produced X-Rays (DWE)
AFOSR-78-3575, 2303/A1

Theoretical Studies of Relatively
Rigid Polymer Chains (DRU)
AFOSR-78-3683, 2303/A3

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

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Fundamental Studies of the Structure
and Chemistry of Solid Surfaces
(LAK)
AFOSR-80-0103, 2303/A2

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Energetic and Collision Dynamics
of Electronic Transition Laser
Systems (WGT)
F49620-80-C-0095, 2303/B1

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A Search for New Fuel Components
in Explosive Mixtures with Ammon-
ium Nitrate (AJM)
AFOSR-80-0134, 2303/D9

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Mechanisms and Kinetics of
Diphthalocyanine Electrode
Processes (AJM)
F49620-80-C-0060, 2303/B2

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Electronically Excited Molecular
Oxygen (WGT)
AFOSR-79-0088, 2303/B1

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Electrochemistry and Electrochemical
Methodology in Molten Salts (DWE)
AFOSR-81-0007, 2303/A1

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Synthesis of Phosphotriazines for
Potential High Temperature Fluids
and Elastomers Applications (AJM)
F44620-79-C-0037, 2303/B2

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

Solid State Reactions in
Polymeric Materials (DRU)
AFOSR-80-0287, 2303/A3

Studies of Non-Radiating Species
in Metal + Oxidant Chemiluminescent
Flames (WGT)
F49620-79-C-0023, 2303/B1

Studies in Non-Equilibrium
Statistical Mechanics (WGT)
AFOSR-78-3724, 2303/B1

Computational Study of Nonadiabatic
Effects in Atom-Molecule Reactive
Scattering (WGT)
F49620-79-C-0050, 2303/B1

Experimental and Theoretical
Studies of Molecular Dynamics
(WGT)
AFOSR-81-0029, 2303/B1

Theory and Experiments on Chemical
Dynamics and Instabilities (WGT)
AFOSR-80-0094, 2303/B1

Nonlinear Interactions Between
the Pumping Kinetics, Fluid
Dynamics and Optical Resonator
of CW Fluid Flow Lasers (WGT)
AFOSR-80-0133, 2303/B1

Organosilicon Compounds and
Organosilicon Polymer Inter-
mediates (AJM)
AFOSR-79-0007, 2303/B2

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Impact Initiated Damage in Laminated Composites (DRU)
F49620-80-C-0050, 2303/A3

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

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

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Detection by Gas Chromatography (DWE)
AFOSR-80-0011, 2303/A1

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Synthesis of Monomethylhydrazine and Problems Relating to the Protection of the Environment from Hydrazine Vapors (AJM)
AFOSR-80-0007, 2303/B2

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Reactive Atomic Species Generated at High Temperatures and Their Low Temperatures Reactions to Form Novel Substances (AJM)
AFOSR-79-0063, 2303/B2

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Studies of Energy Transfer and Selective Chemical Reaction Using Tunable IR Radiation (WGT)
AFOSR-77-3240, 2303/B1

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Composition and Electrical Property Relationships in Glass-Ceramic and Polycrystalline Materials (DRU)
AFOSR-78-3505, 2303/A3

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

Spectroscopy and Chemistry of
Molecules with High Vibrational
Energy Content (WGT)
AFOSR-78-3725, 2303/B1

High Dose Ion Implantation of
Aluminum and Titanium Alloys
(LAK)
AFOSR-79-0011, 2303/A2

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

Effects of Surface Morphology
and Chemical Composition on the
Durability of Adhesively Bonded
Aluminum Structures (LAK)
F49620-78-C-0097, 2303/A2

The Role of Coupling Agents in
Metal-Polymer Adhesion (LAK)
F49620-79-C-0085, 2303/A2

Structural and Dynamic Studies
of Materials Possessing High
Energy Content (AJM)
AFOSR-81-0013, 2303/B2

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Microstructure of Amorphous and
Semi-Crystalline Polymers (DRU)
AFOSR-81-0011, 2303/A3

Applied Quantum Chemistry of
Nonmetallic Materials (AJM)
AFOSR-77-3145, 2303/B2

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

Correlation of Electrode Kinetics
with Surface Structure (DWE)
AFOSR-80-0271, 2303/A1

Organosilicon Chemistry (AJM)
AFOSR-80-0006, 2303/B2

High Temperature Molecules and
Molecular Energy States
AFOSR-76-2901

Phase Spectroscopy
AFOSR-77-3438, 2303/A1

Chemical Reactions and Properties
of Organosilicon Compounds
Related to New Materials (AJM)
AFOSR-78-3570, 2303/B2

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

Atomic and Molecular Gas Phase
Spectrometry (DWE)
F49620-80-C-0005, 2303/A1

X-Ray Photoelectron Spectroscopy
(XPS) and Secondary Ion Mass
Spectrometry (SIMS)
AFOSR-80-0000, 2303/B1

Gas Phase Free
Radical Spectrometry
AFOSR-78-3693, 2303/B1

Alkaline Earth - Noble Gas Excimers
(WGT)
F49620-79-C-0049, 2303/B1

A First Principles Approach to
Electronic Energy Transfer Processes
in Reactions of the Form $Me + O-A =$
 $MeO + A$ (WGT)
AFOSR-79-0073, 2303/B1

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

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RESEARCH EFFORTS COMPLETED IN FY80

CHEMISTRY

Alphabetical by Principal Investigator

Reactions and Energy Transfer
of Excited Molecules (WGT)
AFOSR-78-3643, 2303/B1

Philip R. Brooks
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Energy Transfer and Chemical
Reactions Important in Molecular
Lasers (WGT)
AFOSR-75-2856, 2303/B1

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Fast Ion Transport in Solids
(DWE)
AFOSR-77-3427, 2303/A1

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

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

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

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Investigation of Electron Attach-
ment Processes in Polyatomic
Molecules (WGT)
F49620-77-C-0071

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Intramolecular Energy Exchange by
Infrared Radiometry (WGT)
F49620-79-C-0036, 2303/B1

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

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Energy Transfer and Optical
Spectroscopy of Diatomic
Molecules in Chemically Reacting
Systems (WGT)
AFOSR-77-3138, 2303/B1

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

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Structure-Property-Environmental
Relations in Glass and Glass-
Ceramics (DRU)
AFOSR-77-3210, 2303/A3

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

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

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Controlled Structural Adhesive
Interphases (LAK/DRU)
AFOSR-78-3692, 2303/A2 and 2303/A3

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

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

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

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

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Investigation of Electrochromic
Diphthalocyanines (AJM)
F49620-79-C-0104, 2303/B2

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

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

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Carbon-Carbon Composite Matrix
Decomposition Reactions and
Densification Response (DRU)
F49620-79-C-0068, 2303/A3

Computational Study of Nonadia-
batic Effects in Atom-Molecule
Reactive Scattering (WGT)
F49620-79-C-0050, 2303/B1

Experimental and Theoretical Studies
of Intramolecular and Intermolecular
Dynamics (WGT)
F49620-80-C-0004, 2303/B1

Inorganic Reactants for
Synthesis of Novel Fluorocarbon
Derivatives (AJM)
F49620-77-C-0038, 2303/B2

Electron Paramagnetic Resonance
Spectroscopy of Vanadium (IV)
Complexes and Related Species
(DWE)
AFOSR-77-3368, 2303/A1

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

Photofragment Momentum
Spectroscopy of NSO^+ and D2^+ at
334.1 nm (WGT)
F49620-79-C-0167, 2303/B1

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

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

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High Energy Sources and
Materials: High-Temperature
Molecules and Molecular Energy
Storage (WGT)
AFOSR-76-2906, 2303/B1

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Gas-Surface Dynamics, High
Power Laser-Solid Interactions (LAK)
AFOSR-77-3186, 2303/A2

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X-Ray Photoelectron
Spectroscopic Studies of
Electrode Surfaces (DWE)
AFOSR-76-2974, 2303/A1

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Polybenzothiazoles: Synthesis
and Characterization (DRU)
F49620-78-C-0110, 2303/A3

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COMPLETED PROJECT SUMMARY

1. TITLE: Energy Transfer and Optical Spectroscopy of Diatomic Molecules in Chemically Reacting Systems
2. PRINCIPAL INVESTIGATORS: Dr. H. P. Broida
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Santa Barbara, California 93106
3. INCLUSIVE DATES: 1 August 1976 - 31 December 1979
4. GRANT NUMBER: AFOSR-77-3138
5. COSTS AND FY SOURCE: \$57,499, FY77; \$89,129, FY78; \$19,319, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. M. Lambropoulos
Dr. W. P. West
7. JUNIOR RESEARCH PERSONNEL:

R. E. Steele
J. C. Wyss
A. Adams
8. PUBLICATIONS:

"Flame Spectroscopy of TiO: Chemiluminescence," C. Linton and H. P. Broida, J. Mol. Spectrosc., 64, 382-8 (1977).

"Flame Spectroscopy of TiO: Photoluminescence of the $\alpha(C^3\Delta - X^3\Delta)$ System," C. Linton and H. P. Broida, J. Mol. Spectrosc., 64, 389-400 (1977).

"Flame Spectroscopy of TiO: Radiative Lifetimes and Oscillator Strengths of the $\alpha(C^3\Delta - X^3\Delta)$ System, R. E. Steele and C. Linton, J. Mol. Spectrosc., 69, 66-70 (1978).

"Chemiluminescence, Photoluminescence and Radiative Lifetimes of Diatomic Copper Fluoride," R. E. Steele, Ph. D. Thesis, University of California, Santa Barbara (Oct 1977).

"Chemiluminescent and Excitation Spectra of CuF," R. E. Steele and H. P. Broida, Journal of Chemical Physics, 69, 2300-2305 (1978).

"Optically Pumped Vapor Phase Bi_2 Laser," W. P. West and H. P. Broida, Chemical Physics Letters, 56, 283-285 (1978)

"Photoluminescence of Calcium Molecules," J. C. Wyss, Ph.D. Thesis, University of California, Santa Barbara (Dec 1978).

"Long Range Energy Levels of Ca_2 ," J. C. Wyss, R. Belanger and H. P. Broida, in preparation for submission to J. Chem. Phys.

"Calcium Molecules -- A New Ground State," J. C. Wyss, in preparation for submission to J. Chem. Phys.

"Luminescence and Nonradiative Energy Transfer to Surfaces," A. Adams, R. W. Rendell, W. P. West, H. P. Broida, P. K. Hansma and H. Metiu, Phys. Rev. B (scheduled June 15, 1980).

"Effect of Metal Film Thickness on Surface-Atom Coupling," A. Adams, R. W. Rendell, R. W. Garnett, P. K. Hansma and H. Metiu, Optics Communications (Amsterdam, submitted May 1980).

"Practical Range and Energy Loss of 0.1-3 keV Electrons in Thin Films of N_2 , O_2 , A, Kr and Xe," A. Adams and P. K. Hansma, Phys. Rev. B (submitted May, 1980).

"Nonradiative Energy Transfer from Atoms to Surface Plasmons," A. Adams, dissertation, University of California at Santa Barbara (May, 1980).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Increased capabilities in remote sensing, communication and several other areas depend on developments in laser technology. Chemical lasers indicate a high probability of fulfilling these needs through their properties of different wavelengths, high power, high operating efficiency and lower weight. Additionally, optically pumped metal dimers are attractive systems for visible, tunable gas lasers. The development of new improved chemical laser systems and optically pumped laser systems requires an increased understanding and knowledge of the properties and characteristics of candidate reactions and molecules.

Detailed spectroscopic studies on both CuF and Ca_2 have been carried out. Use of laser photoluminescence has produced spectroscopic information previously unobtainable. Improved molecular constants and dissociation energies, radiative lifetimes, and quenching cross-sections for electronically excited products have been obtained. In addition previously unknown electronic states have been identified.

Using spectroscopic information previously obtained in this laboratory, we have demonstrated that the Bi_2 molecule can be used as an optically pumped laser. Other molecules have been investigated as optically pumped laser media without success: these include Rb_2 and Ca_2 .

An ultrahigh vacuum system with He recirculating cryogenic refrigerator has been constructed along with a bake-out oven, and an elaborate gas handling system. This system has been thoroughly tested and preliminary matrix isolation studies of N_2 have been carried out.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Reactions and Energy Transfer of Excited Molecules

1. PRINCIPAL INVESTIGATOR: Dr. Philip R. Brooks
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3. INCLUSIVE DATES: 1 June 1978 - 31 October 1979

4. GRANT NUMBER: AFOSR 78-3643

5. COSTS AND FY SOURCE: \$42,000, FY78

6. SENIOR RESEARCH PERSONNEL: Dr. H. F. Pang

7. JUNIOR RESEARCH PERSONNEL:

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8. PUBLICATIONS:

"Molecular Beam Reaction of K with HCl: Effect of $v=1$ state of HCl," H. H. Dispert, M. W. Geis, and P. R. Brooks, J. Chem. Phys., **70**, 5317 (1979).

"Reaction of Magnetically State Selected NO with O: Effect of fs States and Rotational States on Reactivity," S. L. Anderson, P. R. Brooks, J. Dispert, and O. V. Nguyen, J. Chem. Phys., to be published.

"Reactions and Energy Transfer of Excited Molecules," P. R. Brooks, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Most molecular collisions do not result in chemical reaction, even for species which are potentially reactive. Tradition and much indirect evidence suggest that certain pre-conditions must be met before reaction can occur: that the reagents must be in some unknown critical (or "activated") configuration. This critical configuration is expected to be highly dependent on orientation and interatomic distance and one expects (and observes) that energy of the reagents strongly affects reaction probability. The goal of this research has been to learn how this energy may be most efficiently supplied.

By studying chemical reactions in crossed molecular beams we are able to eliminate the randomizing collisions which are responsible for Boltzmann equilibrium in dense phases. We can consequently prepare reagents with different speeds and different internal energy states to see how reaction probability depends on translational [T], rotational [R], vibrational [V], and electronic [E] energy. We have previously shown for the prototype reaction $K + HCl \rightarrow KCl + H$ that one quantum (100 Kcal/mole) of [V] increases reaction probability a hundred fold, while an equivalent amount of energy in [T] increases reaction probability only a modest ten-fold. Further increase in [R] causes reaction probability to decrease. The consequence is that the chemical reaction is thus highly specific.

We have now studied the effect of rotation [R] on reaction probability. Differences are small at normal temperatures, but the role played by rotation has largely been neglected. We have studied reaction of HCl in various J levels of the v=0 state by irradiating the HCl beam with a HCl chemical laser tuned to oscillate by various P-branch transitions. We find that reactivity is strongly inhibited by rotation, and that the reactive cross section decreases by roughly a factor of two for each value of J in the range J = 1 to 4.

Electronic states are most widely separated in energy and it is tempting to believe that electronic excitation of a reagent could have really drastic effects on reactivity. We have not yet investigated the effect of adding [E] to our prototype reaction, but we have investigated the effect of [E] on the reaction $NO + O_3 \rightarrow NO_2^* + O_2$. The ground state of NO is a doublet, $2\pi_{3/2}$ and $2\pi_{1/2}$, separated by 121 cm⁻¹. It had been suggested that the upper component of this doublet ($2\pi_{3/2}$) was mainly responsible for reaction to NO_2^* , electronically excited NO_2 in the $2B_1$ or $2B_2$ state while NO ($2\pi_{1/2}$) reacted to yield mainly NO_2^* , vibrationally excited ground ($2A_1$) electronic state.

We have directly tested and disproved this hypothesis by magnetically state selecting a NO beam and then observing the chemiluminescence of this state selected beam as it traverses a scattering chamber containing a very low pressure of O_3 . The magnetic-state selection enhances the population of upper electronic state molecules which were alleged to be mainly responsible for reaction, but the increase in beam intensity is observed to far surpass the increase in chemiluminescence. Both electronic states are involved in reaction to give chemiluminescence. Other experiments have rather conclusively shown, however, that heating the NO increases chemiluminescence so that populating higher internal states clearly increases reactivity. We have been able to reconcile all of the experiments by assuming that reactivity of the two fs states is (roughly) equal, but that higher rotational states react more rapidly.

It is clear that reagent rotation plays a crucial role in chemical reaction. This is not yet understood, and further experiments are underway.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Study in Molecular Lasers
2. PRINCIPAL INVESTIGATOR: Professor George Burns
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3. INCLUSIVE DATES: 1 June 1975 - 15 December 1979
4. GRANT NUMBER: AFOSR 75-2856
5. COSTS AND FY SOURCE: \$11,908, FY75; \$13,715, FY76; \$15,340, FY77;
\$20,150, FY78
6. SENIOR RESEARCH PERSONNEL:

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7. JUNIOR RESEARCH PERSONNEL:

R. G. Macdonald
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8. PUBLICATIONS:

"Shock Dissociation of Bromine in Krypton," R. K. Boyd, George Burns and R. G. Macdonald, Modern Developments in Shock Tube Research, Tenth Intern. Shock Tube Symp., p. 552-557, Shock Tube Research Soc. Japan (1975).

"Study of Atomic Recombination," George Burns, Proceeding of the Third International Congress, Ir. Chem. Society, p. 271-277 (1975).

"Recombination of Iodine Atoms by Flash Photolysis over a Wide Temperature Range. VII. Recombination between 206 and 300° K," H. W. Chang and George Burns, J. Chem. Phys., 64, 349-353 (1976).

"Trajectory Study of Atomic Recombination Reactions. VII. Recombination of I and Br Atoms," D. T. Chang and George Burns, Can. J. Chem., 54, 1535-1542 (1976).

"Diatom Potential Curves and Transition Moment Functions from Continuum Absorption Coefficients: Br₂," R. J. LeRoy, R. G. Macdonald and George Burns, J. Chem. Phys., 65, 1485-1500 (1976).

"Trajectory Study of Dissociation Reactions. Br₂ in Ar at 3500 K," D. T. Chang and George Burns, Can. J. Chem., 55, 380-382 (1977).

"Recombination of Iodine Atoms by Flash Photolysis over a Wide Temperature Range. VIII. I₂," R. E. Antrim, George Burns, and J. K. K. Ip, Can. J. Chem., 55, 749-756 (1977).

"Dissociation of Br₂ in Shock Waves," R. G. Macdonald, George Burns and R. K. Boyd, J. Chem. Phys., 66, 3598-3608 (1977).

"Halogen Recombination-Dissociation Reactions. Current Status," R. K. Boyd and G. Burns, J. Phys. Chem., 83, 88-98 (1979).

"On Heteronuclear Recombination of Chlorine and Iodine Atoms," George Burns and F. W. Lampe, J. Phys. Chem., 83, 3308 (1979).

"Experimental Study of Dissociation-Recombination Reactions," R. K. Boyd and G. Burns, Shock Waves in Chemistry, Assa Lifshitz, ed., Marcel-Decker Inc. (in press).

"Trajectory Study of Dissociation Reactions. The Single-Ensemble Method," H. D. Kutz and G. Burns, J. Chem. Phys., March 15 Issue (in press)(1980).

"Trajectory Study of Atomic Recombination Reactions. The Energy Transfer Mechanism," G. Burns and A. W. Young, J. Chem. Phys., March 15 Issue (in press)(1980).

"Study in Molecular Lasers," G. Burns, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Reaction, occurring in chemical lasers, with special emphasis on atomic recombination-dissociation, were investigated using shock wave and flash photolysis techniques.

In order to extend the temperature range over which recombination-dissociation reactions were studied, the dissociation of Br₂ in Kr and Ar up to 3000°K, was investigated in shock waves. This is a temperature range about twice as wide as that of previous investigators. Three different techniques - laser schlieren, absorption spectroscopy, and emission spectroscopy - were used to follow the rate of the dissociation reaction in the same shock tube. The obtained measured rate constants showed much less scatter than those of previous

investigators. Present shock wave results are in agreement with the most reliable flash photolysis data of recombination reactions obtained earlier. Smooth, continuous shock wave-flash photolysis rate constant data on the recombination-dissociation of bromine between 300 and 3000°K are now available.

It was found that even such a simple recombination reaction as $2\text{I} + \text{O}_2 \rightarrow \text{I}_2 + \text{O}_2$, which was studied over a wide temperature range, involved about twelve different reactions which proved to be more or less important depending upon the temperature and the excitation conditions. It was possible to elucidate these reactions over a wide temperature range. Atomic recombination rate constants for iodine, k_r , were measured down to 206°K by flash photolyzing HI in the presence of an excess of inert gas. Hydrogen atoms produced in photolysis of HI reacted with undissociated HI within the duration of the flash, yielding H_2 and additional quantities of I atoms. Recombination occurred on a time scale much faster than the formation of solid I_2 ; no other side reaction interfered with recombination. The recombination rate constants displayed a pronounced negative temperature coefficient between 206° and 300°K, and yielded, for all third bodies studies, a smooth $\log k_r$ vs $\log T$ curve between 206 and 1150°K.

Much effort was put into reviewing available data to pin-point the most promising future avenues of research.

To interpret the results of recombination-dissociation studies of I_2 and Br_2 , 3-D trajectory calculations were conducted over a wide temperature range. As the precision of trajectory studies improved, it became clear that trajectory data agreed reasonably well with experiment only at the intermediate temperature range (about 1000°K for I and Br). At the lowest temperatures, trajectory data consistently underestimated the experimental results. At the highest temperatures, trajectory rate constants exceeded the experimental k_r . Therefore, although trajectories did yield a reasonably good overall agreement with experiment, they failed to provide quantitative explanation of the negative temperature coefficient of atomic recombination rate constants. To eliminate remaining uncertainties in trajectory studies on recombination, an improved set of interaction potentials between the recombining atom and inert gas was used. These were obtained by independent workers in cross molecular beam experiments. The energy transfer (ET) mechanism of atomic recombination reactions, which has been used for the past forty years, was studied using the trajectory calculation technique. It was found that even in one of the most favorable cases where the ET mechanism is predominant, i.e., for the $2\text{I} + \text{He} \rightarrow \text{I}_2 + \text{He}$ reaction, the error introduced by the ET mechanism is of the order of two in the rate constant. For this reason, new methods of calculation of rate constants via ET mechanism are being developed.

One of the most difficult parts of trajectory calculations is the estimation of corrections for non-equilibrium effects, which may change the magnitude of the rate constant by a factor of as much as ten. For this reason we developed a multiple collision technique, which was tested in a study of Br_2 dissociation in Ar at 3500°K.

Unfortunately the fluctuations in the cross-section values were so large that the rate constant could not be determined even within an accuracy of a factor of four. Therefore, a new method for calculating non-equilibrium effects in diatom dissociation was developed. Statistical fluctuations which in the past had prevented accurate determination of such observables as steady-state rate constants and reaction cross sections, were reduced by a factor of ten.

A program for calculating diatomic molecule absorption coefficients using exact numerically computed radial wave functions was developed and employed to examine the approximations used in absorption coefficient calculations. This program was applied to the analysis of the visible absorption continuum of Br_2 and its temperature dependence.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Fast Ion Transport in Solids Using Conductivity and NMR
2. PRINCIPAL INVESTIGATORS: Dr. A. V. Chadwick
Dr. J. H. Strange
Department of Chemistry
University of Kent
Canterbury, Kent, England
3. INCLUSIVE DATES: 15 September 1977 - 14 September 1980
4. GRANT NUMBER: AFOSR-77-3427
5. COSTS AND FY SOURCE: \$15,311, FY77; \$20,920, FY78; \$10,000, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. David S. Hope
Dr. George Jaroszkiewicz
7. JUNIOR PERSONNEL: None
8. PUBLICATIONS:

"NMR and Conductivity Studies of Ionic Transport in LaF_3 ,"
A. V. Chadwick, D. S. Hope, G. Jaroszkiewicz and J. H. Strange in Fast Ion Transport in Solids, editors Vashishta, Munday and Shenoy (North Holland, New York), 683, 1979.

" ^{19}F NMR Studies of LaF_3 ," G. Jaroszkiewicz and J. H. Strange,
Journal de Physique, 41, C-6, 246 (1980).

"An Investigation of Fast Ion Transport in Solids Using Conductivity and N.M.R.," Alan V. Chadwick, David S. Hope, George Jaroszkiewicz and John H. Strange, Final Technical Report, AFOSR-TR-80-1337.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Materials, which are termed "solid electrolytes" or "fast-ion conductors" or "superionic conductors," are currently one of the most active areas of scientific research. This report describes the work performed with the study of fast ion conduction in lanthanide fluorides and related materials. The study was aimed at the evaluation of the parameters affecting the ion transport with a view to understanding how they might be controlled with a view to the design of materials with optimum properties.

Three types of fluoride were chosen in which to study transport by the combined conductivity - N.M.R. approach. These are as follows:

A. Rare Earth Fluorides (LnF_3):

At elevated temperatures these materials can be classed as fast F^- ion conductors. LaF_3 , CeF_3 , PrF_3 , NdF_3 and PmF_3 all have the hexagonal tysonite LaF_3 structure. These materials have been grown as good single crystals. YF_3 and the heavier rare earths fluorides are dimorphic; the room temperature form has an orthorhombic structure and there is a transition to the LaF_3 structure at high temperatures. Large crystals of the room temperature form have not been grown. LaF_3 and YF_3 were chosen for study. Other rare earth fluorides, with the exception of LuF_3 , would not be suitable for N.M.R. diffusion studies since their La^{3+} ion is paramagnetic.

B. Tysonite-Related Fluorides ($\text{Ln}_{1-x}\text{B}_x\text{F}_{3-x}$):

- where B is an alkaline earth ion.

The few systems that have been studied show extremely high conductivities (e.g., $\text{La}_{0.95}\text{Sr}_{0.05}\text{F}_{2.95}$ has a conductivity of $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature). These were chosen for study and of particular interest is the relationship between conductivity and composition.

C. Mixed Fluorides (ALn F_3):

- where A is an alkali ion.

The structure of these materials depends on A and Ln. Of particular interest are the materials like KLa F_4 which have a low temperature hexagonal scheelite structure which transform to a cubic fluorite structure at high temperatures. In these compounds F^- is very mobile and there is the possibility that A^+ is mobile. The current research effort into the fluorites makes these systems additionally attractive.

The aim was to use techniques to gain the following information:

- A. Accurate diffusion parameters for the constituent ions from room temperature to near the melting point;
- B. An identification of the mechanisms of diffusion;
- C. Information on the point defect structure;
- D. The relevance of the phase transitions and their effect on ionic transport.

This study of ionic conductivity and N.M.R. in tysonite fluorides is the most thorough study of transport in these materials that has been reported.

Crystal growing facilities were developed for the production of good samples of these materials and the results showed the necessity of single crystals for reliable transport studies.

Procedures were developed for the quantitative interpretation of both the N.M.R. and the conductivity results.

On the basis of a Schottky model of point defect disorder the energies of defect formation and migration were evaluated. A discussion was presented of the effect on defect energies if it was assumed that the predominant point defects in tysonites were anion Frenkel defects.

The tysonites doped with divalent metal cations are good F^- ion conductors. It was shown that doped LaF_3 is as good a conductor as any of the other tysonite fluorides. Their use in battery systems would be governed more by the selection of suitable electrode systems than by the ionic conductivity of the systems.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Kinetic Studies Involving Electronically-Excited Interhalogens and Halogens
2. PRINCIPAL INVESTIGATOR: Dr. Michael A. A. Clyne
Chemistry Department
Queen Mary College
Mile End Road, London E1 4NS UK
3. INCLUSIVE DATES: 1 June 1975 - 30 November 1979
4. GRANT NUMBER: AFOSR-75-2843
5. COSTS AND FY SOURCE: \$26,500, FY76; \$32,891, FY77; \$36,753, FY78;
\$35,158, FY78
6. SENIOR RESEARCH PERSONNEL:

Dr. I. S. McDermid	Professor S. Toby
Dr. J. P. Liddy	Professor S. Jaffe
Dr. E. Martinez	Dr. D. J. Smith
7. JUNIOR RESEARCH PERSONNEL:

P. D. Whitefield
M. C. Heaven
8. PUBLICATIONS:

"The $B^3\Pi(0^+)$ States of IF, ICl and IBr. Part 1 - Calculation of RKR Turning Points and Franck-Condon Factors for the B-X Systems. Part 2 - Observation and Analysis of the Excitation Spectra of IF and ICl," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 72, 2242 and 2252 (1976).

"Kinetics of Excited $B^3\Pi(0^+)$ States of BrF, ICl and IF. Fluorescence Decay Lifetimes and Quenching Cross-Sections," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 73, 1094 (1977).

"Studies of BrCl by Laser-Induced Fluorescence. Part 1 - Excitation Spectra and Predissociation in the Excited $B^3\Pi(0^+)$ State," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 74, 796 (1978).

"Studies of BrCl by Laser-Induced Fluorescence. Part 2 - State-Selected Kinetics in the Excited $B^3\Pi(0^+)$ State of BrCl," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 74, 807 (1978).

"Quantum-Resolved Dynamics of Excited States. Part 1 - Predissociation in the $B^3 \Pi(0^+)$ State of BrF," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 74, 644 (1978).

"Quantum-Resolved Dynamics of Excited States. Part 2 - Stable Levels of the $B^3 \Pi(0^+)$ State of BrF," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 74, 664 (1978).

"Non-Reversed Source of Br Atom Resonance Radiation and Its Application to the Measurement of Br Atom Concentrations," M. A. A. Clyne and D. J. Smith, J. C. S. Faraday II, 74, 263 (1978).

"Quantum-Resolved Dynamics of Excited States. Part 3 - Collision-Free Lifetimes of BrF (B)," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 74, 1376 (1978).

"Quantum-Resolved Dynamics of Excited States. Part 4 - Radiative and Predissociative Lifetimes of IF $B^3 \Pi(0^+)$," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 1979, 74, 1644 (1978).

"Kinetics of Excited States of Br₂ Using Laser Excitation. Part 1 - System Description and Rotationally-Dependent Lifetimes in Br₂ (B)," M. A. A. Clyne and M. C. Heaven, J. C. S. Faraday II, 74, 1992 (1978).

"Laser-Induced Fluorescence Studies: B-X Transitions of Cl₂. Part 1 - Rotationally-Resolved Excitation Spectra and Predissociation in the Excited $B^3 \Pi(0^+)$ State," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 74, 1935 (1978).

"Kinetics of Formation of Electronically-Excited Cl₂, BrCl and Br₂ in the Recombination of Ground-State Halogen Atoms," M. A. A. Clyne and D. J. Smith, J. C. S. Faraday II, 75, 704 (1979).

"Laser-Induced Fluorescence Studies: B-X Transition of Cl₂. Part 2 - Transition from Bound to Unbound Excited States," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 1979, 75, 280 (1979).

"Laser-Induced Fluorescence Studies: B-X transition of Cl₂. Part 3 - Collisional Energy Transfer Rates in the $B^3 \Pi(0^+)$ State of Cl₂," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 75, 1313 (1979).

"Formation of Excited BrCl $B^3 \Pi(0^+)$ in the Reaction of Bromine with Chlorine Dioxide," M. A. A. Clyne and S. Toby, J. Photochem., 11, 87 (1979).

"Atomic Resonance Fluorescence for Rate Constants of Rapid Bimolecular Reactions. Part 7 - Sulphur Atom Reactions: $S + O_2 \rightarrow SO + O$ and $S + NO \rightarrow SO + NO$ from 296 to 410 K," M. A. A. Clyne and P. D. Whitfield, J. C. S. Faraday II, 75, 1327 (1979).

"Laser-Induced Fluorescence Studies: B-X Transition of Cl_2 . Part 4 - Predissociation in the B State," M. A. A. Clyne and I. S. McDermid, J. C. S. Faraday II, 75, 1677 (1979).

"Quantum-Resolved Dynamics of Excited States. Part 5 - The Long-Lived $A^3\Pi(1_u)$ State of Br_2 ," M. A. A. Clyne, M. C. Heaven and E. Martinez, J. C. S. Faraday II, 76, 177 (1980).

"Laser-Induced Fluorescence of IBr : the $B^3\Pi(0^+)$ Excited State," M. A. A. Clyne and M. C. Heaven, J. C. S. Faraday II, 76, 49 (1980).

"Studies of $BrCl$ by Laser-Induced Fluorescence. Part 3 - Dynamics of Quantum-Resolved Levels in the Excited $B^3\Pi(0_u^+)$ State," M. A. A. Clyne and I. S. McDermid, Faraday Disc. Chem. Soc., 67, 316 (1979).

"Laser-Excitation Studies of Br_2 . Collisional Energy Transfer Involving Resolved Quantum States of Excited Br_2 $B^3\Pi(0_u^+)$," M. A. A. Clyne, S. J. Davis and M. C. Heaven, J. C. S. Faraday II, 76, in press.

"Laser-Induced Fluorescence Studies: The B-X Transition of Cl_2 . Part 5 - Radiative Lifetime of the B State," M. A. A. Clyne and E. Martinez, J. C. S. Faraday II, 76, in press.

"Kinetics of Excited States of Br_2 Using Laser Excitation. Part 2 - Radiative Lifetime and Collisional Deactivation of the $B^3\Pi(0_u^+)$ State," M. A. A. Clyne, M. C. Heaven and E. Martinez, J. C. S. Faraday II, 76, in press.

"Laser-Induced Fluorescence Studies: the B-X transition of Cl_2 . Part 6 - Rotationally-Dependent Predissociation," M. A. A. Clyne and E. Martinez, J. C. S. Faraday II, 76, submitted.

"Quantum-Resolved Dynamics of Excited States. Part 6 - Radiative Lifetime and Collisional Deactivation Rates in $BrF(B)$," M. A. A. Clyne and J. P. Liddy, J. C. S. Faraday II, 76, submitted.

9 ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A. Kinetics of Chemiluminescent Reactions Involving Excited B States of Halogens and Interhalogens:

The kinetics of the chemiluminescent atom-recombination reactions $\text{Cl} + \text{Br} + \text{M} \rightarrow \text{BrCl}(\text{B}) + \text{M}$, $\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2(\text{B}) + \text{M}$ and $\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M}$ have been determined. Branching ratios for forming the excited states were determined; all lie in the range 0.01 to 0.1.

The kinetics of the chemiluminescent reaction of Br_2 with OClO have been studied. The overall reaction was characterized as a branched-chain process. The branching ratio for forming excited $\text{BrCl}(\text{B})$ is > 0.05 .

New spectroscopic data on the B and X states of BrCl are reported.

B. Measurement of Halogen Atom Concentrations:

Methods based on atomic resonance absorption and fluorescence have been developed for measuring Br and $\text{Cl}^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ atom concentrations over a wide range of densities, and in mixtures of different halogen atoms. The variation of oscillator strength within the $(\text{N} + 1)\text{s}-\text{np}^5$ resonance multiplets has been exploited in wavelength-resolved atomic resonance studies.

C. Studies of Halogens and Interhalogens by Laser-Induced Fluorescence (LIF):

A state-of-the-art narrow-band, pulsed dye laser has been used to study the quantum-resolved dynamics of excited $\text{B}^3\Pi(0^+)$ states of Cl_2 , Br_2 , BrCl , BrF , IF , ICl and IBr and the $\text{A}^3\Pi(1_u)$ state of Br_2 . The first observation of quantum-resolved LIF is described for all of these molecules other than $\text{Br}_2(\text{B})$. The first direct determinations of radiative lifetimes by LIF is described for the B states of Cl_2 , BrF , Br_2 , IF and for the A state of Br_2 . Detailed studies of predissociation dynamics are reported. Measurements of rate constants for electronic quenching, collisional predissociation and ro-vibrational transfer are reported. In most cases, quenching of the B states is slow, but vibrational transfer is fast, thus favouring the B-X transitions as electronic-transition laser candidates.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Double Layer Structure and Electrode Kinetics
2. PRINCIPAL INVESTIGATOR: Dr. Robert de Levie
Department of Chemistry
Georgetown University
Washington, DC 20057
3. INCLUSIVE DATES: 15 May 1976 - 30 September 1980
4. GRANT NUMBER: AFOSR-76-3027
5. COSTS AND FY SOURCE: \$42,980, FY76; \$58,907, FY77; \$51,359, FY79;
\$53,263, FY80
6. SENIOR RESEARCH PERSONNEL:

Dr. T. Ohsaka	Prof. S. K. Rangarajan
Dr. S. Sarangapani	Dr. P. F. Seelig
7. JUNIOR RESEARCH PERSONNEL:

R. Acerete	R. J. Atwell, Jr.
C. Chang	P. S. Czekaj
J. F. Garvey	M. Krishnan
J. W. Smuda	R. Sridharan
8. PUBLICATIONS:

"Ionic Adsorption and the Conductance of Ultrathin Lipid Membranes,"
R. de Levie, J. Electroanal. Chem., 82, 361 (1977).

"Numerical Differentiation by Fourier Transformation as Applied to
Electrochemical Interfacial Tension Data," R. de Levie, S. Sarangapani,
P. Czekaj and G. Behnke, Anal. Chem., 50, 110 (1978).

"Mathematical Modeling of Transport of Lipid-Soluble Ions and
Ion-Carrier Complexes through Lipid Bilayer Membranes," R. de Levie, in
Advances in Chemical Physics (I. Prigogine and S. A. Rice, eds.) 37, 99
(1978).

"On the Ionic Displacement Current in Lipid Bilayer Membranes,"
S. K. Rangarajan and R. de Levie, Biophys. J., 25, 235 (1979).

"On the Adsorption of Phloretin onto a Black Lipid Membrane,"
R. de Levie, S. K. Rangarajan, P. F. Seelig and O. S. Andersen, Biophys.
J., 25, 295 (1979).

"Tetrathionate Adsorption onto Mercury," T. Ohsaka and R. de Levie, J. Electroanal. Chem., 99, 255 (1979).

"On the Admittance of Lipid Bilayer Membranes I: Membrane-Permeable Ions," S. K. Rangarajan, P. F. Seelig and R. de Levie, J. Electroanal. Chem., 100, 33 (1979).

"On Some Problems of Diffusion towards a Circular Disk," S. Sarangapani and R. de Levie, J. Electroanal. Chem., 102, 165 (1979).

"The Use of Kinetic Probes in Concentrated Electrolytes: the Reduction of Perbromate in KF," in Proceedings of the Third Symposium on Electrode Processes (S. Bruckenstein, J. D. E. McIntyre, B. Miller and E. Yeager, eds.), 422 (1980).

"Adsorption of Alkaline Earth Cations on Mercury as Studied with the Perbromate Kinetic Probe," T. Ohsaka and R. de Levie, Bull. Chem. Soc. Japan, 53, 344 (1980).

"Double Layer Capacitance Measurements with Digital Synchronous Detection at a Dropping Mercury Electrode," P. F. Seelig and R. de Levie, Anal. Chem., 52, 1506 (1980).

"Sampling Error in Fourier and Hadamard Transform Capacitance Measurements," R. de Levie, Anal. Chem., 52, 1535 (1980).

"On the Admittance of Lipid Bilayer Membranes II: Uncouplers and Ion-Carriers," R. de Levie and P. F. Seelig, J. Electroanal. Chem., in press.

"The Structure of Charged Interfaces," R. de Levie, Sensors and Actuators, in press.

"Transport of Dipicrylamine across Lipid Bilayer Membranes: Evidence for Ion Pairing," R. de Levie and R. J. Atwell Jr., Biophys. J., submitted.

"On the Adsorption of Sucrose from Aqueous NaCl Solutions," M. Krishnan and R. de Levie, in preparation.

"On Subequivalent Specific Adsorption of Ions," R. de Levie and M. Krishnan, in preparation.

"Double Layer Structure and Electrode Kinetics," R. de Levie, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The program encompassed theory, development of new instrumental methods as well as experimentation.

The modular "systems" formalism for the description of the admittance of electrode kinetics was applied to membranes, especially to the cases in which membrane-soluble ions cross the membrane, or where ion transport is facilitated by cation carriers, or proton transport by weak acids. The expressions include the effects of the ionic displacement current, which was studied separately in greater detail. Two manuscripts surveyed double layer effects on membranes and at electrodes, while an extensive review discussed the mathematical modeling of ion transport through membranes. Some problems were treated which occur in the application of admittance measurements to a fixed or rotating disk electrode.

A new method to analyze electrocapillary data was developed, based on Fourier transformation. This efficient method has since been applied extensively in the work on sucrose adsorption. The sampling problem of measurements on a dropping mercury electrode was addressed. It was found that the usual errors involved in sampling on the growing mercury surface can be reduced more than an order of magnitude, from over one percent to less than one per mille, by either using averaging over the sampling interval or, for "instantaneous" measurements, by taking into account the transfer function of the specific detector used.

A novel method was devised and tested to obtain admittance data on time-varying objects such as a dropping mercury electrode. The technique is the digital analog of synchronous detection, with the additional advantages of high speed (even faster than Fourier transformation) and simultaneous detection at a number of different frequencies. It uses the Hadamard transform algorithm.

Extensive double layer studies were made at the water-membrane and water-mercury interfaces. The effect of the neutral compound phloretin, which can modify membrane permeability more than thousandfold by changing the existing dipole potential, could be interpreted quantitatively. The effect was used to determine the nature of the phloretin adsorption isotherm.

A boxcar integration method was developed which allows one to measure shortlived transients with the PDP-11 minicomputer. The method yields a time resolution of 0.1 microsecond and has been used effectively to establish that the anomalous behavior of dipicrylamine is due to ion pairing.

Extensive ion probe measurements using perbromate, and a combination of dc, ac and pulse polarography, were made in order to measure possible specific adsorption of both fluoride anions and alkaline earth cations on mercury. The fluoride data tested whether the method is useful up to high ionic strengths, where the more classical methods fail; no internal inconsistencies were observed. In the case of the alkaline earth cations, the method appears to yield results which are too high, most

likely as the result of a "dynamic discreteness-of-charge effect," whereby the probe ion is attracted to the vicinity of the oppositely charged, specifically adsorbed ion, and hence oversamples its presence.

During efforts to find additional probe ions it was found that tetrathionate, a likely candidate, is specifically adsorbed onto mercury even at very low (10^{-4} to 10^{-5} M) concentrations, and is therefore not useful as a probe.

Using the fully computer-controlled maximum bubble pressure instrument, the adsorption of sucrose on Hg from aqueous NaCl solutions was studied. Sucrose was selected because it is adsorbed over the entire range of experimentally accessible potentials, and NaCl because activities of the ternary system sucrose-NaCl-water are available. The data obtained show that the mutual effects of sucrose and chloride adsorption are very small, and can be neglected to a first approximation. These measurements also confirm, at least qualitatively, the earlier probe results on specific adsorption of alkali cations.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Relation of Structure to Properties in Graphite Fibers
2. PRINCIPAL INVESTIGATOR: Dr. R. J. Diefendorf
Department of Materials Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181
3. INCLUSIVE DATES: 30 September 1977 - 30 September 1980
4. GRANT NO: AFOSR-77-3436
5. COSTS AND FY SOURCE: \$48,070, FY77; \$53,000, FY78; \$55,650, FY80
6. SENIOR RESEARCH PERSONNEL: None
7. JUNIOR RESEARCH PERSONNEL:

K. J. Chen
W. P. Seagraves
J. J-H Wang

8. PUBLICATIONS:

"Residual Stresses in High Modulus Carbon Fibers," W. C. Stevens, J. H. Wang and R. J. Diefendorf, Carbon '80, 598-602, Deutchen Keramischen Gesellschaft, Bad Honnef, West Germany, 1980.

"Relation of Structure to Properties in Graphite Fibers, R. J. Diefendorf, Final Technical Report, 1981.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Advanced strategic missile systems will employ carbon-carbon structural composite materials for nozzles, nosetips and heatshields. The relations of structure to properties of high performance carbon reinforcement filaments with emphasis on strength improvements are not understood. The location and origin of strength limiting flaws in carbon fibers and how they relate to ultimate fiber performance in composites were determined. This research contributed to the establishment of the process science data base essential to carbon fiber availability and processability and composite reliability.

The approach was to: (1) determine if preferred orientation measurements made on carbon fibers in finished carbon-carbon composites in yarn bundles could be used with crystal properties to calculate, or at least, correlate with axial properties; (2) ascertain if transverse

moduli and coefficient of thermal expansion can be calculated from preferred orientation measurements; and (3) identify and eliminate the sources of critical flaws, and injurious residual carbon fibers to increase tensile strength.

The axial properties of carbon fibers were found to correlate well with preferred orientations determined by either x-ray diffraction or optical techniques. High modulus carbon fibers were found to have significant gradients in preferred orientation. For HMS fiber, the modulus of the surface layers is about twice the average fibers modulus, while the interior modulus is only about one-half the average. This modulus gradient suggests that higher modulus fibers, with good strength, could be produced, if the modulus at the interior of these fibers could be increased. The gradient in preferred orientation produces high residual stresses in HMS fibers. While the high surface compressive stresses minimize the effect of surface flaws, the high axial tensile stresses in the interior may decrease strength by causing fracture to initiate at flaws in the interior rather than at the surface. Similarly, the high axial compressive stressed outer layers of a fiber may initiate buckling when the fiber is compressively loaded. Modifications of the residual stress pattern might allow increased tensile and/or compressive strengths to be obtained in high modulus carbon fibers.

Many correlations between properties and fiber diameter, reported in the past, may be in error because it is very difficult to determine the fiber diameter precisely and accurately.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Investigation of Electron Attachment in Polyatomic Molecules
2. PRINCIPAL INVESTIGATOR: Jerry T. Dowell
IRT Corporation
P.O. Box 80817
San Diego, CA 92138
3. INCLUSIVE DATES: 1 April 1977 - 31 March 1980
4. CONTRACT NUMBER: F49620-77-C-0071
5. COSTS AND FY SOURCE: \$38,000, FY77; \$77,000, FY78; \$96,987, FY79;
\$40,988, FY80
6. SENIOR RESEARCH PERSONNEL: Dr. Jerry T. Dowell
7. JUNIOR RESEARCH PERSONNEL: J. A. Rutherford
8. PUBLICATIONS:

"Investigation of Electron Attachment in Polyatomic Molecules,"
Jerry T. Dowell, Final Technical Report, AFOSR-TR-80-0549.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research program was concerned with the investigation of two-body electron attachment processes in molecules. Emphasis in the program was on the study of reactions that appear to have high rates in plasmas and that involve species with high electron affinities. Such reactions were of interest for two reasons: advancement of the theoretical understanding of resonant electron-molecule scattering for other than diatomic molecules, and possible application to plasma engineering (e.g., wake modification).

A crossed beam apparatus has been developed that is well suited for investigation of two-body electron attachment down to very low electron energies. Excellent electron beam energy resolution was achieved. Through variation of the target molecule temperature, it was found that internal energy plays a very important role in attachment processes for polyatomic molecules, even at room temperature.

Attachment in SF_6 and MoF_6 was studied in detail in this program, and some measurements were done on attachment in the very difficult WO_3 polymer system. Some significant new results were obtained in SF_6 , and it is intended that a paper on them be submitted soon to the Journal of Chemical Physics. Although not enough information is available for full interpretation of the MoF_6 data, a short paper on

that material will also be submitted to the same journal. It is expected that the WO_3 work will be published as a short note in Chemical Physics Letters.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Intermolecular Energy Exchange by Infrared Radiometry
2. PRINCIPAL INVESTIGATOR: Dr. J. B. Fenn
Department of Engineering and Applied
Science
Yale University
New Haven, Conn 06520
3. INCLUSIVE DATES: 15 June 1975 - 31 December 1979
4. GRANT NUMBER: AFOSR 75-2863 and F49620-79-C-0036
5. COSTS AND FY SOURCE: \$43,512, FY76; \$51,827, FY77; \$44,109, FY78;
\$142,000, FY79; \$4,975, FY80
6. SENIOR RESEARCH PERSONNEL:

Dr. G. L. Haller	Dr. J. C. Polanyi
Dr. S. P. Venkateshan	Dr. S. B. Ryali
Dr. Ryali Subbarao	Dr. D. R. Miller
Dr. C. E. Kolb	
7. JUNIOR RESEARCH PERSONNEL

M. Labowsky
D. A. Mantell
C. G. M. Quah
8. PUBLICATIONS:

"Internal Energy Relaxation Rates from Observations on Free Jets,"
C. G. M. Quah, J. B. Fenn and D. R. Miller, Rarefied Gas Dynamics 11th
Symposium, Vol II 885, (Ed. R. Campargue - Commissariat a L'Energie
Atomique, Paris 1979).

"Internal Energy Relaxation in Methane and Its Chlorinated Derivatives,"
R. J. Gallagher and J. B. Fenn, " ibid. page 935.

"Internal Energy Relaxation Rates from Seeded Supersonic Beams with a
Monatomic Host Gas," C. G. M. Quah, Chem. Phys. Letters, 63, 141 (1979).

"Collisional Excitation of CO₂ by N₂, O₂ and Ar," S. B. Ryali,
J. B. Fenn and C. E. Kolb, to be submitted to Journal of Chemical
Physics.

"Relaxation of Internal Energy During Free Jet Expansion," M. Labowsky, D. R. Miller, S. B. Ryali and J. B. Fenn, submitted for presentation at the 12 International Symposium on Rarefied Gas Dynamics to be held at the University of Virginia in July 1980.

"Energy Transfer as a Function of Collision Energy IV: State to State Cross Sections for Rotation to Translation Energy Transfer in HF plus Ne, Ar and Kr," J. A. Barnes, M. Kiel, R. E. Kutina and J. C. Polanyi, to be submitted to Journal of Chemical Physics.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Excitation by translational energy of the asymmetric stretch vibrational mode of ground state carbon dioxide molecules in collision with nitrogen, oxygen and argon molecules has been studied by intersecting two slightly collimated molecular beams in the field of view of an InSb photovoltaic detector which monitored resulting radiation in the 4.3 micrometer band. The excitation cross sections for all three combinations of partners were of similar magnitude and showed a strong dependence upon collision velocity. For nitrogen the measured cross sections ranged from about 0.0008 square Angstroms at 2 km/s to about 0.5 square Angstroms at 5 km/s. A similar but separate experiment determined an upper limit of 0.1 square Angstroms for the collisional excitation of hydrogen fluoride by krypton at energies up to 1.7 times the threshold requirement. Bulk relaxation rates for molecules in free jet expansion were also investigated. Results obtained from experimental data with the frequently used Sudden Freeze Model have been compared with those obtained by Numerical Integration. Success has been achieved in obtaining Method-of-Characteristics solutions for the free jet expansion with a varying specific heat ratio. This development provides the best description yet of relaxation in free jet expansion for any internal mode which can be characterized by a Boltzmann distribution of energy.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: One- and Two-Photon Optically Pumped Laser Devices: New Chemical Laser Diagnostics and Kinetic Probes
2. PRINCIPAL INVESTIGATOR: Dr. Robert W. Field
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139
3. INCLUSIVE DATES: 15 June 1976 - 31 August 1980
4. GRANT NUMBER: AFOSR-76-3056
5. COSTS AND FY SOURCE: \$50,738, FY76; \$50,474, FY77; \$54,795, FY78;
\$83,571, FY79
6. SENIOR RESEARCH PERSONNEL:

Roger Bacis
Daniel Katayama
Francis J. Wodarczyk
7. JUNIOR RESEARCH PERSONNEL:

J. Brooke Koffend	Carter Kittrell
Peter F. Bernath	Evan Abramson
Gunjit Chawla	Steve McDonald
Philip G. Cummins	David E. Reisner
Michael Dulick	Philip Brucat
Richard A. Gottscho	Alain Drooz
Precila Ip	Jeffrey Manni
Ronald F. Marks	Hrvoje Petek
Bernard Pinchemel	Andrew Ralston
Ingemar Renhorn	Paul S. Weiss
Hartmut S. Schweda	Michael Wilson
8. PUBLICATIONS:

"Optical-Optical Double Resonance Laser Spectroscopy BaO. II,"
R. A. Gottscho, J. B. Koffend, J. R. Lombardi, and R. W. Field,
J. Chem. Phys., 68, 4110-4122 (1978).

"Assignment of Extra Lines in a Perturbed Band Spectrum Using Power
Broadened Line Widths," R. A. Gottscho and R. W. Field, Chem. Phys.
Lett., 60, 65-68 (1978).

"CW Optically Pumped Iodine Laser II. Spectroscopy and Long Range Analysis of the $X^1\Sigma$ Ground State of I_2 ," J. B. Koffend, R. Bacis, and R. W. Field, J. Mol. Spect., 77, 202-212 (1979).

"CW Optically Pumped Molecular Iodine Laser," J. B. Koffend and R. W. Field, J. Appl. Phys., 48, 4468-4472 (1977).

J. B. Koffend, F. J. Wodarczyk, and R. W. Field, pages 96-109, High Power Lasers and Applications, K. L. Kompa and H. Walther (editors), Springer Verlag (1978).

"Pulsed and CW Optically Pumped Lasers for Novel Applications in Spectroscopy and Kinetics," J. B. Koffend, R. W. Field, D. R. Guyer, and S. R. Leone, Laser Spectroscopy III, 382-393, J. L. Hall and J. L. Carlsten (editors), Springer Verlag (1977).

"Transitions Near Dissociation Limits by Optical Optical Double Resonance and Optically Pumped Laser Spectroscopy," R. W. Field, États, Atomiques et Moléculaires Couplés a un Continuum. Atomes et Molécules Hautement Excités, Editions du CNRS No. 273, 143-155 (1977).

"Doppler-Free Emission Spectroscopy and Secondary Frequency Standards Using an Optically Pumped Laser," J. B. Koffend, S. Goldstein, R. Bacis, R. W. Field, and S. Ezekiel, Phys. Rev. Lett. 41, 1040-1045 (1978).

"The Electronic Transition Moment of the $BO_u^+-X^1\Sigma_g^+$ System of I_2 Through Gain Measurements of an I_2 Optically Pumped Laser," J. Brooke Koffend, R. Bacis and Robert W. Field, J. Chem. Phys., 70, 2366-2372 (1979).

"Stimulated Emission Spectroscopy with an Optically Pumped I_2 Laser," J. Brooke Koffend, Roger Bacis, and Robert W. Field, SPIE Proceedings for the International Conference on Lasers '78, 168 (1979).

"Collisional Relaxation of Highly Excited Vibrational Levels of the $I_2 X^1\Sigma_g^+$ State Using an I_2 Optically Pumped Laser," J. B. Koffend, F. J. Wodarczyk, R. Bacis, and R. W. Field, J. Chem. Phys., 72, 478-483 (1980).

"Optical-Optical Double Resonance Spectroscopy of CaF: The $E^2\Sigma^+$ and $E'^2\Pi$ States," P. F. Bernath and R. W. Field, J. Mol. Spectry., accepted for publication (1980).

"High Resolution and Sub-Doppler Fourier Transform Spectroscopy: Iodine Molecular Fluorescence Excited by the 514.5 and 401.7 nm Ar^+ Laser Lines," R. Bacis, S. Churassy, R. W. Field, J. B. Koffend, and J. Verges, J. Chem. Phys., 72, 34-42 (1980).

"Rotational and Vibrational Analysis of the $\text{CaF } B^2\Sigma^+ - X^2\Sigma^+$ System," M. Dulick, P. F. Bernath, and R. W. Field, Can. J. Phys. **58**, 703-712 (1980).

"Laser Excited Fluorescence of CS_2 ," P. F. Bernath, M. Dulick, R. W. Field, and J. Hardwick, J. Mol. Spectrosc., accepted for publication (1980).

"Intermodulated Fluorescence Spectroscopy of $\text{CaF } A^2\Pi - X^2\Sigma^+$," P. F. Bernath, P. G. Cummins, and R. W. Field, Chem. Phys. Lett., **70**, 618-620 (1980).

"Laser Spectroscopy of $\text{CaBr: } A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ Transitions," P. F. Bernath, R. W. Field, B. Pinchemel, Y. Lefebvre, and J. Schamps, manuscript in preparation for submission to J. Mol. Spectrosc.

"The Hyperfine Structure of the Calcium Halides," P. F. Bernath, B. Pinchemel, and R. W. Field, manuscript in preparation for submission to J. Chem. Phys.

"Simultaneous Fitting of Optical and Microwave Data: CaBr as Example," P. F. Bernath, B. Pinchemel, R. W. Field, K. Möller, and T. Törring, manuscript in preparation for submission to J. Mol. Spectrosc.

"Optical-Optical Double Resonance Spectroscopy of $\text{BaF: } E^2\Sigma^+$ and $F^2\Pi$ States," P. Ip, P. F. Bernath, and R. W. Field, manuscript in preparation for submission to J. Mol. Spectrosc.

"Laser Spectroscopy of $\text{CaI: } A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ Transitions," D. Reisner, P. F. Bernath, and R. W. Field, manuscript in preparation for submission to J. Mol. Spectrosc.

"The Electronic Structure of the Calcium Halides," P. F. Bernath and R. W. Field, manuscript in preparation for submission to J. Chem. Phys.

"The $\text{CaO } a^3\Pi$ and $A^1\Pi$ States from Partial Analysis of the 'Orange' Band System," R. F. Marks and R. W. Field, manuscript in preparation for submission to J. Chem. Phys.

"The I_2 0_g^+ and 1_g States by LIF-FTS," R. Bacis, S. Churassy, J. Vergès, and R. W. Field, manuscript in preparation for submission to J. Chem. Phys.

"Assignment and Kinetic Mechanism for $\text{N}_2\text{W}^3\Delta - B^3\Pi$ and $B^3\Pi - \text{W}^3\Delta$ Lasing Lines," R. Bacis, D. Cerny, R. W. Field, and R. A. McFarlane, manuscript in preparation for submission to J. Mol. Spectrosc.

"Stimulated Emission Pumping of $I_2Bo_u^+-X^1\Sigma_g^+$,"

C. Kittrell, E. Abramson, D. H. Katayama, S. McDonald, D. E. Reisner, and R. W. Field, manuscript in preparation for submission to J. Chem. Phys.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A. Optically Pumped Lasers.

A cw, optically pumped, I_2 laser was demonstrated, characterized, and exploited for various spectroscopic and kinetic measurements. Highlights include development of novel methods for determination of the electronic dipole transition moment function for I_2 B-X, measurement of hyperfine structure in highly excited vibrational levels of the electronic ground state of I_2 , and determination of total population removal rates for highly excited and nonfluorescing rotation-vibration levels of I_2 . The I_2 laser experiments have suggested several major new research programs: Stimulated Emission Pumping (Section C below), the combination of Fourier Transform Spectroscopy with Laser Induced Fluorescence, use of an Na_2 optically pumped laser to prepare vibrationally excited molecules and then detect cw dye laser excitation of these molecules (Section D below).

B. Spectroscopy of Alkaline Earth Halides.

A variety of laser spectroscopic techniques (excitation, fluorescence, optical-optical double resonance, intermodulation spectroscopy) have been applied to CaF, CaBr, CaI, and BaF. Two kinds of structural interrelationships have been explored: properties of the corresponding X, A, and B states of all alkaline earth halides were compared in order to characterize the factors controlling s/p/d hybridization; the states of CaF and BaF were fitted into Rydberg series in order to examine the predictive utility of n^* (the effective principal quantum number) for spin-orbit and other fine structural constants and transition strengths.

C. Stimulated Emission Pumping.

A new technique has been demonstrated by which highly excited rotation-vibration levels of small polyatomic molecule electronic ground states may be selectively and significantly populated. This technique involves two Nd:YAG pumped pulsed dye lasers and has been tested on the I_2 B-X system. Applications of this technique will form the major thrust of a new AFOSR research program (jointly with Professor J. L. Kinsey).

D. Optically Pumped Na_2 Laser

An optically pumped laser is simultaneously a source of population in selected, thermally unpopulated v'' , J'' levels (particularly those at $v'' \gg 0$, thus with outer turning point at $R > 5\text{\AA}$) and a probe of

kinetic processes which depopulate this selected lower level of the lasing transition. A series of experiments is underway, combining the Ar^+ laser pumped Na_2 laser with a cw dye laser, the initial purpose which is to characterize bound and unbound ungerade excited electronic states near their dissociation asymptote.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Measurement of Vibrational Intensities for Infrared Active Exhaust Plume Species from Advanced Propellant Rocket Boosters
2. PRINCIPAL INVESTIGATORS: Dr. Michael E. Gersh
Dr. Charles E. Kolb
Center for Chemical and Environmental
Physics
Aerodyne Research, Inc.
Crosby Drive
Bedford, MA 01730
3. INCLUSIVE DATES: 1 April 1977 - 31 March 1980
4. CONTRACT NUMBER: F49620-77-C-0075
5. COSTS AND FY SOURCE: \$33,000, FY77; \$66,901, FY78; \$79,131, FY79
\$35,641, FY80
6. SENIOR RESEARCH PERSONNEL:

Dr. Mark S. Zahniser
Dr. Lawrence S. Bernstein
7. JUNIOR RESEARCH PERSONNEL:

Robert G. Brown
8. PUBLICATIONS:

"Infrared Spectral Measurements of Species in a High Temperature Flow Tube," M. E. Gersh and C. E. Kolb, in PROCEEDINGS OF THE 10TH MATERIALS RESEARCH SYMPOSIUM ON CHARACTERIZATION OF HIGH TEMPERATURE VAPORS AND GASES, J. Hastie, ed., National Bureau of Standards Special Publication 561 (1979), 679-693.

"Measured and Predicted Band Model Parameters of BF_3 (ν_3) at High Temperatures," M. E. Gersh, L. S. Bernstein, and L. M. Peterson, submitted to J. Chem. Phys.

"A Versatile High Temperature Flow Reactor for Kinetic and Spectroscopic Studies," M. E. Gersh, J. A. Silver, M. S. Zahniser, C. E. Kolb, R. G. Brown, C. M. Gozewski, S. Kallelis, and J. C. Wormhoudt, submitted to Rev. Sci. Instr.

"Measurement of the Vibrational Band Strength of ^{11}BF Using a Tunable Diode Laser," M. S. Zahniser and M. E. Gersh, submitted to J. Chem. Phys.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research is the performance of quantitative infrared spectroscopic measurements of boron fluorides and oxides in the gas phase. The measurement program is designed to determine infrared absorption coefficients and absorption line spacings in order to facilitate the construction of infrared radiation band models.

In order to carry out these measurements an apparatus which permits the performance of quantitative spectroscopic measurements of transient species over the temperature range of 300 to 1500K was constructed. The capability of this apparatus to perform these measurements over its designed range of operating parameters was demonstrated.

The infrared absorption coefficients of the ν_3 band of BF_3 were measured over the range of 300 to 1500K. These measurements were combined with flame measurements at 2400K to develop and verify a radiation band model for BF_3 . The formalism developed for this band model is more comprehensive than previous treatments and is generally applicable to perpendicular bands of symmetric top molecules.

The infrared band strength of BF was measured and found to be $650 \pm 200 \text{ cm}^{-2} \text{ amagat}^{-1}$. The band strength was determined by measuring the absorption cross section of a single vibration-rotation line using a tunable diode laser as the light source. The BF number density was measured in-situ using ultraviolet absorption spectroscopy.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Structure-Property-Environmental Relations in Glass and Glass-Ceramics
2. PRINCIPAL INVESTIGATOR: Dr. Larry L. Hench
Department of Materials Science and Engineering
University of Florida
Gainesville, FL 32611
3. INCLUSIVE DATES: 1 March 1977 - 29 February 1980
4. GRANT NUMBER: AFOSR-77-3210
5. COSTS AND FY SOURCE: \$39,971, FY77; \$41,915, FY78; \$96,738, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. David E. Clark
Dr. Paul H. Holloway
7. JUNIOR RESEARCH PERSONNEL:

E. Lue Yen-Bower
W. J. McCracken
J. M. Barrett
F. Ohuchi
8. PUBLICATIONS:

"Surface Characterization of Ceramed Composites and Environmental Sensitivity," presented at the Conference on Composites and Advanced Materials, Cocoa Beach, Florida, January 1978.

"Aqueous Corrosion of Lithia-Alumina-Silicate Glasses," Am. Ceram. Soc. Bull., 57[11], 1040 (1978)

"Effects of Glass Surface Area to Solution Volume Ratio on Glass Corrosion," J. Phys. & Chem. Glasses, 20[2], 35 (1979).

"Ceramic Surface Degradation," presented at 70th Annual Meeting of American Institute of Chemical Engineers, New York City, November 1977.

"Role of Ca^{+2} in the Mixed Alkali Effect," submitted to the J. Am. Ceram. Soc.

"Mechanical Properties of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Glass," submitted to J. Am. Ceram. Soc.

"Infrared Reflection Analysis of Thermal Changes in Si_3N_4 Surfaces," submitted to the J. Am. Ceram. Soc.

"Physical Chemistry of Glass Surfaces," J. Non-Crystalline Solids, 28, 83 (1978)

"Physical Chemistry of Glass Surfaces," Survey Lecture for the XIth International Congress of Glass Conference, Prague, Czechoslovakia, July 4, 1977.

"Physical Chemistry of Glass Surfaces," Glass '77, A Survey of Contemporary Glass Science and Technology, Jeri Gotz, ed., published by CVTS-DUM Techniky, Praha, 343-370, July 1977.

"Surface Analysis of Si_3N_4 Oxidation," paper presented at the Conference on Composites and Advanced Materials, Cocoa Beach, Florida, January 24, 1978.

"Effects of Heat Treatment Time on the Oxidation of Pressed Si_3N_4 as Determined by Infrared Reflection Analysis," presented at the Conference on Composites and Advanced Materials, Merritt Island, Florida, January 21-24, 1979.

"Corrosion Behavior of Lithia Disilicate Glass in Aqueous Solutions of Aluminum Compounds," Am. Ceram. Soc. Bull., 58[11], 1111 (1979).

"Aqueous Corrosion of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Glass-Ceramics," submitted to the J. Am. Ceram. Soc.

"Determination of Fatigue Parameter for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Glass and Partially Crystallized $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$," presented at the 80th Annual Meeting of the American Ceramic Society, Detroit, Michigan, May 6-11, 1978.

"Effect of Crystallization on the Auger Electron Signal Decay in a $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Glass and Glass-Ceramic," J. Am. Ceram. Soc., 62[9-10], 500 (1979).

"Durability of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Glass-Ceramics," presented at the 80th Annual Meeting of the American Ceramic Society, Detroit, Michigan, May 6-11, 1978.

"Compositional Analysis of Alkali Glasses Using Auger Electron Spectroscopy," presented at the 80th Annual Meeting of the American Ceramic Society, Detroit, Michigan, May 6-11, 1978.

"Fatigue Properties of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Glass and Glass-Ceramics," J. Am. Ceram. Soc., 62[5-6], 319 (1979).

"Corrosion of Glass Surfaces," accepted by Surface Science.

"Aqueous Corrosion of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaO} \cdot \text{SiO}_2$ Glass-Ceramics," submitted to J. Am. Ceram. Soc.

"Use of New Surface Physics for Controlling the Physical Properties of Ceramics," presented at the Science of Ceramics 10, Munich, Germany, September 2-4, 1979.

"Use of New Surface Physics for Controlling the Physical Properties of Ceramics," published in the Proceedings Science of Ceramics 10 (1980).

"Surface Characterization of Ceramed Composites and Environmental Sensitivity," published in Ceramic Engineering and Science Proceedings, No. 7-8, July-Aug (1980).

"Surface Analysis of Si_3N_4 Oxidation," published in Ceramic Engineering and Science Proceedings, No. 7-8, July-Aug (1980).

"Effects of Heat Treatment Time on the Oxidation of Pressed Si_3N_4 as Determined by Infrared Reflection Analysis," published in Ceramic Engineering and Science Proceedings, No. 7-8, July-Aug (1980).

"Durability and Strength of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaO} \cdot \text{SiO}_2$ Glass-Ceramics," presented at 81st Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, April 29-May 2, 1979.

"Effects of Solution pH on Corrosion Behavior of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Glass-Ceramics," presented at 81st Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, April 29-May 2, 1979.

"Nondestructive Evaluation of Surface Flaws Using Infrared Reflection Spectroscopy," presented at 81st Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, April 29-May 2, 1979.

"Corrosion of Glass Surfaces," an invited paper presented at the Seventh Canadian Seminar on Surfaces, Pinawa, Canada, July 1979.

"Electron Beam Effects during Analysis of Glass Thin Film with Auger Electron Spectroscopy," published in J. of Surface and Interface Analysis, Aug./Sept. (1980).

"Electron Beam Effects during Analysis of Glass Thin Film with Auger Electron Spectroscopy," presented at the 8th International Conference on Surface Science, Cannes, France, September 1980.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall objectives of this study of glass, glass-ceramics, Si_3N_4 and SiC was aimed at developing predictive relationship for the lifetime of materials under various combinations of chemical, mechanical, and thermal environments. Several analytical surface techniques were routinely applied to the characterization of glass and glass surfaces.

While emphasis of the application of surface sensitive techniques for characterizing surfaces was placed on glass and glass-ceramics, analysis of Si , SiC , Si_3N_4 , and Al_2O_3 indicated that the techniques can be used for surface characterization of these important ceramic materials as well. The major thrust was the correlation of structure with mechanical and chemical properties, and the development of models for predicting long-term behavior of ceramics in a variety of environments. Glass-ceramics have provided a good model system due to the wide range of possible microstructures attainable with these materials. Preliminary results suggest that glass-ceramics may be used as analogs for understanding the chemical and physical properties of more complicated polyphase, polycrystalline ceramic materials. Additionally, concepts developed in this three year program may be utilized in achieving better correlations between ceramic processing, surface structure, and properties.

A clearer understanding of corrosion mechanisms and kinetics emerges when a combination of surface and solution analyses is employed. Glass corrosion mechanisms and kinetics, plus analytical techniques and testing methods used for measuring glass corrosion were reviewed. Application to both simple binary and complex multicomponent glass systems was illustrated. The corrosion behavior of stoichiometric $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (33L) glass and glass-ceramics in acidic, neutral and basic solutions has been studied using infrared reflection spectroscopy, scanning electron microscopy and solution analyses. Glass-ceramics containing a volume fraction of crystallization ranging from 0-90% were investigated. Selective Li^+ leaching and glass network dissolution are major mechanisms of corrosion in 33L glass and glass-ceramics. In addition, attack of the glass at the glass crystal phase boundary contributes significantly to surface deterioration of the glass ceramics. The relative importance of network dissolution, a Li^+ leaching and phase boundary attack is dependent on the extent of crystallization and solution pH.

In the corrosion study of a non-stoichiometric system, a $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaO} \cdot \text{SiO}_2$ glass was heat treated to provide various stages of crystallization. The glassy phase was much richer in alkaline and alkaline earth species than the crystalline phase. The corrosion behavior of the resulting glass-ceramics was studied using infrared reflection spectroscopy (IRRS), scanning electron microscopy, and solution analyses. The mechanisms controlling corrosion vary depending

on the degree of crystallization (V_V). The higher V_V glass-ceramics exhibited poorer resistance to aqueous attack than did the low V_V glass-ceramics even though the crystalline phase itself was more durable.

Migration of sodium in thin films of soda-silica glass deposited on a stainless steel substrate has been studied. The amounts of charge trapping and local heating were a strong function of beam parameters for thin films. The rearrangement of sodium due to charge trapping was calculated and compared to experimental data. The calculated and experimental data agree well and indicate that fields of 10^5 V/cm exist during analysis. The depth distribution of sodium indicates that either electrons or ion bombardment can cause sodium migration during analysis. The cross-section for electron induced desorption was measured to be 3×10^{-20} cm for sodium in this glass, thus it is only important at very high current densities.

It is proposed that progress in improving the properties of technical ceramics will require improved understanding of ceramic processing, especially the surfaces, interfaces and agglomeration of powders, and the interaction of surfaces with the environment. New surface analysis instruments such as infrared reflection spectroscopy (IRRS) and Auger electron spectroscopy are used to describe surface compositional changes of SiC, Si₃N₄, and Al₂O₃. Preferred crystallographic pathways of surface attack are observed for both SiC and Si₃N₄ single and polycrystalline samples. Formation of an oxynitride surface phase on Si₃N₄ powders significantly alters the surface charge distribution and decrease the isoelectric point of the powders. Variations in processing of dense Al₂O₃ result in a deep surface layer of preferred orientation detection by IRRS methods.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: NMR Study of Viscoelastic Fluids and Elastomers Under External Conditions of Temperature and Pressure
2. PRINCIPAL INVESTIGATOR: Dr. Jiri Jonas
Department of Chemistry
University of Illinois
Urbana, IL 61801
3. INCLUSIVE DATES: 1 January 1977 - 30 September 1980
4. GRANT NUMBER: AFOSR-77-3185
5. COSTS AND FY SOURCE: \$41,961, FY77; \$44,592, FY78; \$44,967, FY79; \$38,000, FY80
6. JUNIOR RESEARCH PERSONNEL

Michael Stephen Wolfe
Edward Arndt
Donald Brown
Jeffrey Bonekamp
7. PUBLICATIONS:

"Density and Temperature Effects on Some Transport Properties of Perfluorocyclobutane," R. J. Finney, M. Fury and J. Jonas, J. Chem. Phys., 66, 760 (1977).

"NMR Study of Angular Momentum Relaxation in Fluids. I. Compressed CF₄," R. J. Finney, M. Wolfe and J. Jonas, J. Chem. Phys., 67, 4004 (1977).

"NMR Study of Angular Momentum Relaxation in Fluids. II. Mixtures of CF₄ with Inert Gases," M. Wolfe, E. Arndt, and J. Jonas, J. Chem. Phys., 67, 4012 (1977).

"Magnetic Resonance Spectroscopy at High Pressure," J. Jonas, Proceedings NATO ASI, High Pressure Chemistry, held at Corfu, Greece, 1977, 65 (D. Reidel Publ. Co., Dordrecht, Holland, 1978).

"¹³C and ¹H Relaxation in Viscous Liquid of Di-(2-Ethylhexyl) Phthalate," J. Jonas and E. Arndt, J. Magn. Resonance, 32, 297 (1978).

"Transport and Relaxation in Mesophase of Organic Salt Melt," M. Wolfe, J. Bonekamp and J. Jonas, J. Chem. Phys., 70, 3993 (1979).

"Reorientational Motions in Compressed Viscous Fluids: Selectively Deuterated Glycerol," M. Wolfe and J. Jonas, J. Chem. Phys., 71, 3252 (1979).

"Molecular Motions in Dense Liquids," J. Jonas, Proceedings Joint ACS and JCS Meeting, Hawaii, April 1979 Nankodo Publ. Tokyo, Japan 1979, Kagaku No Ryoiki, 33, 987 (1979).

"NMR in Chemistry - An Evergreen," J. Jonas and H. S. Gutowsky, Prefatory Chapter, Ann. Rev. Phys. Chem., 31, 1 (1980).

"²³Na NMR Study of Ionic Mesophases of Molten Sodium Carboxylates," J. Bonekamp, T. Eguchi and J. Jonas, Chem. Phys. Lett., 75, 360 (1980).

"High Resolution Probe for NMR Measurements at High Pressures and High Fields," J. Jonas, D. L. Hasha, W. J. Lamb, G. A. Hoffman, T. Eguchi, J. Magn. Resonance, 42, Jan. issue (1981).

"Nuclear Magnetic Resonance Studies at High Pressures," J. Jonas, Rev. Phys. Chem. JAPAN, 50, 0000 (1980).

"¹H and ²D NMR Study of Isopropylbenzene Ring Motions in the Supercooled Liquid State," E. Arndt and J. Jonas, J. Phys. Chem., submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Advanced aircraft systems employ viscoelastic fluids, elastomers and amorphous polymers as elastohydrodynamic lubricants, sealants, fuels and matrices which are subject to operation at high pressures and temperatures. The basic principles and parameters governing the behavior of viscoelastic fluids and materials, their dependence upon temperature and pressure and their correlations with molecular structure are not understood. Using nuclear magnetic resonance relaxation techniques the dynamic structure of viscoelastic materials and fluids were studied over wide ranges of temperature, pressure and viscosity.

The dynamic structure of three main disordered systems: (1) viscous fluids, (2) ionic mesophases of melts of alkali metal carboxylates, and (3) selected polymer systems were investigated. The results obtained contributed towards the goal of better understanding the relationship between the molecular behavior and the macroscopic properties of the system studied. Experiments on fluids helped to bridge the current gap between molecular dynamics and hydrodynamics. In addition, considerable effort was devoted to the development of new instrumentation necessary for NMR experiments at extreme conditions of pressure and temperature.

In the case of viscous fluids, new insights were gained concerning applicability of hydrodynamic equations at the molecular level. One of the objectives of this project was to provide a solid foundation for the systematic investigation of highly viscous fluids building on studies of low viscosity fluids. For several specific viscous fluids such as glycerol, di-(2-ethyl hexyl) phthalate, supercooled isopropylbenzenes a detailed investigation of the molecular dynamics was carried out, data interpreted in terms of available theoretical models and new interpretations of specific aspects of the motional behavior proposed.

In the studies of alkali metal carboxylates, research efforts focused on the dynamic structure of the mesophase and solid of sodium isovalerate and sodium n-butyrate. Results in the liquid-crystalline ionic mesophase indicated that cation diffusion is very rapid and is independent of the rapid anion diffusion. Polarization microscopy experiments performed imply the ionic mesophase found in these melts consist of randomly oriented domains of macroscopic dimensions having two-dimensional, smectic A (neat) structure. It is proposed that planes of diffusing ions affectively stabilize by electrostatic forces these unusual, long-lived mesophases. Results on solid sodium n-butyrate show the cation sublattice to be dynamically disordered. Analogies existing in the ^{23}Na NMR data between the superionic conductor, sodium β -alumina, and solid sodium n-butyrate suggest solid sodium n-butyrate to resemble a fast ion conductor.

The exploratory experiments on elastomers dealt mainly with polybutadienes investigating various dynamic properties of elastomers under extreme conditions of high temperature and high pressure. A very useful information about the behavior of spin-spin relaxation times at high temperature in the motional narrowed region offers a possibility for diagnostic measure of the extent of crosslinking and/or presence of entanglements in polymeric systems investigated.

In a collaborative effort with Mr. Warren Griffin, Fluids, Lubricants and Elastomers Branch, AFWAL/ML, NMR experiments on fluorosilicone integral fuel tank sealants were conducted. The proton spin-spin relaxation time measurements and a detailed investigation of proton and fluorine free induction decays indicate the effects of non-zero averaging of dipolar interactions due to anisotropic motions of the chain segments at high temperatures in the motionally narrowed region. The measurements of ^{13}C spectra at natural abundance and of ^{29}Si spectra confirmed that the high resolution spectroscopy at high magnetic fields has a great promise as an analytical tool to study fluorosilicone sealants. The ^{13}C experiments showed that in the motionally narrowed region, the fluorosilicone polymers can be studied by using the standard ^{13}C high resolution techniques without the need of the multiple pulse techniques.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Effect of Structure on Physical Properties of Polymers
2. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz
Polymer Science and Engineering
University of Massachusetts
Amherst, MA 01003
3. GRANT NUMBER: AFOSR-76-2983
4. INCLUSIVE DATES: 1 January 1976 - 31 December 1979.
5. COSTS AND FY SOURCE: \$35,995, FY76; \$44,900, FY77; \$50,042, FY78;
\$44,900, FY79

6. SENIOR RESEARCH PERSONNEL:

Dr. P. Couchman
Dr. B. Das
Dr. R. Galkiewicz

Dr. K. Takamizawa
Dr. A. Teramoto

7. JUNIOR RESEARCH PERSONNEL:

P. Alexandrovich
J. R. Fried
L. Kleiner

P. Moy
C. Ryan
S. Wunder

8. PUBLICATIONS:

"Physical Properties of Compatible Polymer Mixtures," F. E. Karasz and W. J. MacKnight, Second Annual Cleveland Symposium on Macromolecules, A. G. Walton, ed. (in press).

"Problems in Compatibility Structures," F. E. Karasz and W. J. MacKnight, Contemporary Topics in Polymer Science, 2, 143 (1977), E. M. Pearce and J. R. Schafgen, eds. Plenum Press, N.Y., 1977.

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"Heats of Polymer Mixing," F. E. Karasz and W. J. MacKnight, Pure and Appl. Chem., 52, 409 (1980).

C. L. Ryan, Ph.D. Thesis, University of Massachusetts (1979).

"Compatible Glassy Polyblends: Tensile Modulus Studies," L. W. Kleiner, F. E. Karasz, and W. J. MacKnight, Polymer Eng and Sci., 19, 519 (1979).

L. W. Kleiner, Ph.D. Thesis, University of Massachusetts (1978).

"Modeling of Tensile Properties of Polymer Blends," J. R. Fried, W. J. MacKnight, F. E. Karasz, J. Appl. Phys., 50, 6052 (1979).

"Dielectric Study of Polymer Compatibility," P. Alexandrovich, F. E. Karasz, W. J. MacKnight, J. Macromol. Sci., (in press).

"Compatibility in PPO/PS Copolymers; Dielectric Study of Critical Composition Range," R. E. Wetton, W. J. MacKnight, J. R. Fried, F. E. Karasz, Macromolecules, 11, 158 (1978).

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"Thermally Stimulated Discharge in Polymer Blends," J. Appl. Phys., 47, 4251 (1976).

"Epoxy-Water Interactions," P. Moy and F. E. Karasz, Polymer Eng. and Sci., 20, 315 (1980).

"Test Methods and Experimental Research," The Effects of Relative Humidity and Elevated Temperatures on Composite Structures, J. R. Vinson, R. B. Pipes, W. J. Walker, D. R. Ulrich, eds. AFOSR Report TR-77-0030, Center for Composite Materials, University of Delaware.

S. Wunder, Ph.D. Thesis, University of Massachusetts (1978).

"Quasi-Electric Light Scattering from a Sodium Salt of Ethyl Acrylate - Acrylic Acid Copolymer," S. Wunder, N. C. Ford, Jr., F. E. Karasz, J. Coll. and Interface Sci., 63, 290 (1978).

"Viscoelastic Characterization of Isotropic Solids," R. Galkiewicz and F. E. Karasz, J. Appl. Phys., 49, 5233 (1978).

"On the Entropy of Fusion," F. E. Karasz, P. R. Couchman, D. Klempner, Macromolecules, 10, 88 (1977).

"Domain Size Dependence of Glass Transition Temperature," F. E. Karasz and P. Couchman, J. Polym. Sci., Polym. Phys. Ed., 15, 1037 (1977).

"Some Domain Size Effects in Polymer Transitions," J. Polym. Sci., Polym. Symp., 63, 271 (1978).

"On Relations Between Surface Energy, Melting Temperature and Interatomic Separations," C. L. Reynolds, P. Couchman, F. E. Karasz, Philosophical Mag., 34, 659 (1976).

"Effect of Particle Size on Debye Temperatures," P. Couchman and F. E. Karasz, Physics Letters, 62A, 59 (1977).

"Classical Thermodynamic Discussion of the Effect of Composition on T_g ," F. E. Karasz and P. Couchman, Macromolecules, 11, 117 (1978).

"Glass Transition of Linear Polyethylene," C. L. Beatty and F. E. Karasz, J. Macromol. Sci., - Rev. Macromol. Chem., C17, 37 (1979).

"Effect of Stereoregularity on Bulk Properties of Polymers," Preparation and Properties of Stereoregular Polymers, R. W. Lenz and F. Ciardelli, eds., p. 449, D. Reidel (1979).

"Solid State Transition Behavior of Blends," Polymer Blends, D. Paul and S. Newman, Eds. (1978).

"Effect of Structure on Physical Properties of Polymers," F. E. Karasz, Final Technical Report, ADA086199, 1 January 1980.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall objective of this research program was to investigate the physical nature of macromolecular systems as a function of the chemical and stereochemical structure of the macromolecule. A potential improvement in important facets of polymer properties was an underlying premise in the design and execution of the research. The work performed included investigations of the behavior of polymers in solution, as well as in the solid state and was accompanied by a program of theoretical studies to complement the experimental work. One focus of the research was the area of polymer-polymer interactions in binary blends, in which factors influencing compatibility, i.e., mutual solubility, were systematically investigated by a number of thermodynamic techniques. Heats of polymer mixing were obtained for selected systems and shown to be useful in predicting phase behavior otherwise obscured by non-equilibrium effects. The latter were also investigated theoretically in studies of the effect of domain size and composition on glass transition temperatures and allied phenomena. Another area of research concerned the physical properties of model epoxy network systems, and, in particular, the effect of water on these properties. A

characteristic of cross-linked polymers is their ready plasticization by relatively small amounts of low molecular weight materials and the basis of this observation has been explained on a thermodynamic basis. Solution properties of polymers were studied by means of quasi-elastic light scattering. The effect of an ionic structural component on macromolecular conformation was examined in some detail in model copolymers of acrylic acid and ethyl acrylate. This technique was also employed in studies of solubilized stiff chain polymers of high persistence length, while a complementary theoretical investigation dealt with this problem in more general terms as part of an investigation of rigid and near-rigid rod conformations using the so-called n -broken rod approximation.

Mechanical properties of polymers were studied in a newly developed apparatus which measured the resonant vibrational frequencies of rigid beams in an extremely precise manner. From this it was possible to determine elongational and shear moduli on the same sample (as a function of temperature and, in principle, pressure, etc.) and hence Poisson's ratio for the polymer, a parameter important in composite theory and practice.

In addition, a number of miscellaneous investigations and advances, including the development of a precision high pressure differential thermal analysis apparatus capable of measurements up to 7000 kbars, were conducted.

AFOSR Program Manager: Dr. Donald R. Ulrich

PROJECT SUMMARY

1. TITLE: Controlled Structure Adhesive Interphases
2. PRINCIPAL INVESTIGATORS: Dr. Jerome B. Lando
Dr. Charles E. Rogers
Dept of Macromolecular Science
Case Western University
Cleveland, Ohio 44106
3. INCLUSIVE DATES: 1 September 1978 - 30 September 1980
4. GRANT NO: AFOSR-78-3692
5. COSTS AND FY SOURCE: \$53,780, FY78; \$57,330, FY79
6. JUNIOR RESEARCH PERSONNEL:

Kevin O'Brien
Eric Rahnenfueher

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this study was to determine adhesion-related properties of monolayers and multilayers of coupling agents formed with known and controlled compositions and structural packing configurations upon well-characterized glass, pyrolytic graphite, and resin substrates. The effects of exposure to water on interphase structure and properties were related to performance characteristics.

Variations in the composition of the coupling agent and its mixtures and in the technique of layer deposition were employed to introduce specific layer sequence structures and defect/void regions in the interphase. The interphase was characterized by electron microscopy, an unique micromechanical tensile test, and other techniques (e.g., argon ion laser Raman and Fourier Transform infrared spectroscopies, and electron and x-ray diffraction) as deemed appropriate to establish the nature and perfection of interphase structures and component interactions.

AFOSR Program Manager: Lorelei A. Krebs, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Energy and Chemical Change
2. PRINCIPAL INVESTIGATORS: Dr. Raphael D. Levine
Dr. James L. Kinsey
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139
3. INCLUSIVE DATES: 1 November 1976 - 31 October 1980
4. GRANT NUMBER: AFOSR-77-3135
5. COSTS AND FY SOURCE: \$16,863, FY76; \$34,312, FY77; \$18,392, FY78;
\$19,262, FY79
6. JUNIOR RESEARCH PERSONNEL: Y. Alhassid
7. PUBLICATIONS:

"The Information Theoretic Approach: An Interim Progress Report,"
R. D. Levine, in ACS Symposium Series 'State-to-State Chemistry,' Philip
R. Brooks and Edward F. Hayes, Editors, p. 226 (1977).

"Connection between the Maximal Entropy and the Scattering Theoretic
Analyses of Collision Processes," Y. Alhassid and R. D. Levine, Phys.
Rev., A18, 89 (1978).

"Entropy and Chemical Change III: The Maximal Entropy (Subject to
Constraints) Procedure as a Dynamical Theory," Y. Alhassid and
R. D. Levine, J. Chem. Phys., 67, 4321 (1977)

"Thermochemical Properties of Atoms and Molecules in Specific Quantum
States," W. C. Gardiner, Jr. and R. D. Levine, J. Chem. Phys., 68, 4524
(1978)

"An Algorithm for Finding the Distribution of Maximal Entropy,"
N. Agmon, Y. Alhassid and R. D. Levine, J. Comput. Phys., 30, 250 (1979).

"The Thermal Rate Constant of Elementary Reactions: Does Specificity of
Energy Disposal Require a Concomitant Lowering of Its Magnitude?"
F. Kaufman and R. D. Levine, Chem. Phys. Lett., 54, 407 (1978).

"Information Theory Approach to Molecular Reaction Dynamics,"
R. D. Levine, Ann. Rev. Phys. Chem., 29, 59 (1978)

"The Application of Information Theory to Molecular Collisions," in Atom-Molecule Collision Theory: A Guide for the Experimentalist, R. B. Bernstein, editor (Plenum, 1979), Chapter 22.

"Information Theoretic Analysis of Multiphoton Excitation and Collisional Deactivation of Polyatomic Molecules," C. C. Jensen, J. I. Steinfeld, and R. D. Levine, Abstracts 10th Intl. Q. E. Conference (1978).

"Microscopic and Macroscopic Analysis of Nonlinear Master Equations: Vibrational Relaxation of Diatomic Molecules," M. Tabor, R. D. Levine, A. Ben-Shaul and J. I. Steinfeld, Mol. Phys., 37, 141 (1979).

"Information Theoretic Analysis of Multiphoton Excitation and Collisional Deactivation of Polyatomic Molecules," C. C. Jensen, J. I. Steinfeld and R. D. Levine, J. Chem. Phys., 69, 1432 (1978)

"Structure, Energy and Reactivity," R. D. Levine, Abstracts, Symposium on Current Status of Kinetics of Elementary Gas Reactions: Predictive Power and Accuracy of Measurement, National Bureau of Standards, June (1978).

"Maximal Entropy Procedure for Molecular and Nuclear Collisions," R. D. Levine in The Maximum Entropy Formalism (MIT Press 1979), p. 247.

"An Algorithm for Determining the Lagrange Parameters," N. Agmon, Y. Alhassid and R. D. Levine, in The Maximum Entropy Formalism (MIT Press, 1979), p. 207.

"Collision Experiments with Partial Resolution of Final States: The Maximum Entropy Procedure and Surprisal Analysis," Y. Alhassid and R. D. Levine, Phys. Rev., C20, 1774 (1979).

"Heavy Ion Transfer Reactions to the Continuum: Surprisal Analysis and the Condition of Maximal Entropy," R. D. Levine, S. G. Steadman, J. S. Karp and Y. Alhassid, Phys. Rev. Letters, 41, 1537 (1978).

"Information Theoretic Analysis of Energy Disposal in Heavy Ion Transfer Reactions," Y. Alhassid, R. D. Levine, J. S. Karp and S. G. Steadman, Phys. Rev., C20, 1789 (1979).

The Maximum Entropy Formalism, R. D. Levine and M. Tribus, Editors, (MIT Press, 1979) 500 p.

"Information Theoretic Analysis of Gamma-Ray Multiplicities in Deep Inelastic Collisions," R. D. Levine and S. G. Steadman, Phys. Letts.

"The Information Theoretic Approach to Intramolecular Dynamics," R. D. Levine, in Photoselective Chemistry, J. Jortner, R. D. Levine and S. A. Rice, eds., (Wiley, NY, 1980).

"Reactions and Relaxations in Gaseous Molecular Systems - The Information Theoretic Approach," R. D. Levine, (O. Laporte Memorial Lecture) in Proceedings XII Int'l Symposium on Shock Tubes and Waves (Magnes Press, Jerusalem, 1979).

"A Performance Criterion for Information Theoretic Data Analysis," J. L. Kinsey and R. D. Levine, Chem. Phys. Letters, 65, 413 (1979).

"Distribution of HX Vibrational States in Four-Center Elimination Reactions: A Surprisal Analysis and Synthesis," E. Zamir and R. D. Levine, Chem. Phys. Letters, 67, 237 (1979).

"Nonlinear Transport Processes: Hydrodynamics," I. Oppenheim and R. D. Levine, Physica, 99A, 383 (1979).

"On the Rotational Relaxation of Hydrogen Halides," R. D. Levine, J. Chem. Phys., 72, 3845 (1980).

"Photoselective Chemistry," J. Jortner and R. D. Levine in Photoselective Chemistry, J. Jortner, R. D. Levine and S. A. Rice, eds. (Wiley, NY, 1980).

"Heavy-Ion Transfer Reactions to Highly Excited States," Y. Alhassid, R. D. Levine, J. S. Karp and S. G. Steadman in Proceedings Int'l Symp. Continuum Spectra of Heavy Ion Reactions.

"Experimental and Inherent Uncertainties in the Maximum Entropy Formalism," Y. Alhassid and R. D. Levine, Chem. Phys. Letts., 73, 16 (1980).

"Energy Disposal in Unimolecular Reactions," E. Zamir and R. D. Levine, Chem. Phys.

"The Role of Internal Excitation in Collision Experiments," A. Ben-Shaul and R. D. Levine, Chem. Phys. Letts., 73, 263 (1980).

"A Reduced Phase Space Approach to Collision Processes," Y. Alhassid and R. D. Levine, Chem. Phys. Letts., 72, 401 (1980).

"Laser Enhanced Addition Reactions Between Hydrogen Halides and Unsaturated Hydrocarbons: An Information-Theoretic Approach," E. Zamir, Y. Haas and R. D. Levine, J. Chem. Phys., 73, 2680.

Lasers and Chemical Change, A. Ben-Shaul, Y. Haas, K. L. Kompa and R. D. Levine (Springer, Berlin, 1980).

"Chemical Photophysics," R. D. Levine in Atomic and Molecular Collision Theory, NATO ASI Series, Cortona 1980 (Plenum, NY, 1981).

"Does Chaotic Time Evolution Rule Out Selective Processes in Isolated Molecules?", R. D. Levine, Chem. Phys. Letts.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Work under this project has been directed both at the development of the information-theoretic methodology and at its application to specific problems of experimental interest, with special reference to the consumption and disposal of energy in collisions. Examples of these applications include such questions as "Why is the enhancement of reaction rate due to reagent vibrational excitation so much smaller when the collision energy is (roughly) selected as compared to when the collision energy has a thermal distribution?" or "What are the optimal conditions for laser pumping of addition reactions?" At the fundamental level, an equivalence was established between the information-theoretic approach and formal collision theory. In particular, the concept of a "sum-rule", central to the predictive formulation of the approach, was given a rigorous dynamical foundation. On the practical side, error bars on the surprisal parameters which reflect experimental uncertainties in the data were provided. In this fashion it is possible to provide a working definition of a "noninformative" constraint: A constraint is noninformative and hence should not be included if the value of zero falls within the error range of its conjugate (Lagrange) parameter. A summary of the main papers follows, where the numbers refer to the list of publications in paragraph 7.

A. Surprisal Analysis.

An algorithm for surprisal analysis and synthesis has been developed [5,14]. Copies of the program plus a user's manual are available for distribution and have been requested by many groups. A performance criterion [22] and a rigorous analysis of the role of experimental uncertainties, leading to error bars on the surprisal parameters [28] have been provided. A guidebook of surprisal analysis including a flow chart has been published [8]. Applications to more complex molecular processes include: unimolecular dissociations [23,29] energy transfer to polyatomic molecules [9,11], laser pumped addition reactions [32], heavy-ion collisions [16,17,19,27] and multiphoton excitation [11]. Several points previously made had to be reiterated [25,20] and a review of the first five years of surprisal analysis has been published [7].

B. Dynamics

The identification of constraints on dynamical grounds has been shown possible, [2,15]. The concept of a "sum-rule," long a mainstay of surprisal synthesis has been derived as a rigorous result. This derivation is the primary practical result of these fundamental

studies. Preliminary applications were to simple models of energy transfer [2] and of reactive collisions [3]. Work on more realistic potential energy surfaces is however required. Reviews of different aspects of this work have been published [12,20]. Recent work [31,35], based on earlier foundations [15] has sought to relate the present point of view to so-called "stochastic reduction procedures" which have recently been studied by several groups.

C. Macroscopic Systems.

A number of practical applications (e.g. [10,11] and several theoretical studies [21,14,31] point out that surprisal analysis has an important role to play in our understanding of systems in molecular disequilibrium. Yet, we still do not know how to identify constraints, from first principles, for such systems. The situation is particularly vexing because we do now know what to do at either of the two limiting cases: At equilibrium the constraints are the ordinary constants of the motion. For reversible evolution (e.g. isolated collisions) the constraints are the time-dependent constants of the motion [14,20]. What are they then in the intermediate situation of irreversible evolution towards equilibrium?

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Low Temperature Fluorine Chemistry of Electronegative Elements

2. PRINCIPAL INVESTIGATOR: Dr. Gleb Mamantov
Department of Chemistry
University of Tennessee
Knoxville, TN 37916

3. INCLUSIVE DATES: 1 December 1976 - 29 February 1980

4. GRANT NUMBER: AFOSR 77-3165

5. COST AND FY SOURCE: \$36,949, FY 1977; \$35,928, FY 1978;
\$38,843, FY 1979

6. SENIOR RESEARCH PERSONNEL:

Dr. R. A. Crocombe
Dr. J. A. de Haseth
Dr. N. R. Smyrl

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Matrix Reactions of Fluorine with Chlorine, Bromine and Iodine,"
E. S. Prochaska, L. Andrews, N. R. Smyrl and G. Mamantov, Inorg. Chem.,
17, 970-977 (1978).

"Vibrational Spectra of the Binary Fluorides of the Main Group Elements
- A Review," N. R. Smyrl and G. Mamantov, Advances in Inorganic
Chemistry and Radiochemistry, 21, H. J. Emeleus and A. G. Sharpe, eds.,
Academic Press, (1978) 231-254.

"Infrared Laser Photochemistry of Matrix-Isolated Molecules,"
R. A. Crocombe, N. R. Smyrl and G. Mamantov, J. Am. Chem. Soc., 100,
6526 (1978).

"Practical Aspects of Rapid Scanning Fourier Transform Time Resolved
Infrared Spectroscopy," A. A. Garrison, R. A. Crocombe, G. Mamantov and
J. A. de Haseth, Appl. Spectrosc., 34, 399-404 (1980).

"Low Temperature Fluorine Chemistry of Electronegative Elements," Gleb
Mamantov, Final Technical Report (1980).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This program was concerned with the synthesis and characterization of fluorine-containing compounds by novel methods. A detailed study of the systems $X_2 + F_2$ where $X = Cl, Br, \text{ or } I$ was carried out, producing evidence for the new species XF_2 , X_2F and X_2F_2 as well as some of the normally unfavored members of the series XF_n ($n=1,3,5$). High resolution infrared spectra of the interhalogen compounds ClF and $BrCl$ were measured for the first time. The uses of an infrared laser to produce new species in matrices via multiphoton dissociation and to open up new synthetic routes in the gas phase have been examined. A new technique of obtaining infrared spectra of shortlived species has been studied and its potential evaluated.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Anisotropic and Electro-optical Effects in Liquid Crystals

2. PRINCIPAL INVESTIGATOR: Dr. J. David Margerum
Exploratory Studies Department
Hughes Research Laboratories
Malibu, CA 90265

3. INCLUSIVE DATES: 1 October 1976 - 30 November 1980

4. CONTRACT NUMBER: F49620-77-C-0017

5. COSTS AND FY SOURCE: \$50,905, FY77; \$54,535, FY78; \$58,228, FY79;
\$64,898, FY80

6. SENIOR RESEARCH PERSONNEL:

Anna M. Lackner
John E. Jensen
Dr. Siu-May Wong
Dr. Hong S. Lim

Scott A. Verzwylt
Dr. Michael Piliavin
Gary P. Myer
Dr. Leroy J. Miller

7. JUNIOR RESEARCH PERSONNEL:

Camille I. VanAst
Deborah S. Smythe
Willish H. Smith

8. PUBLICATIONS:

"Effects of Molecular Length on Nematic Mixtures. I. Anisotropic and Dynamic Scattering Properties of 4-Alkoxyphenyl 4-Alkylbenzoate Mixtures," J. D. Margerum, J. E. Jensen, and A. M. Lackner, Molecular Crystals and Liquid Crystals, in press (1981).

"Effects of Molecular Length on Nematic Mixtures. II. Anisotropic and Dynamic Scattering Properties of 4-Alkoxyphenyl 4-Alkylcyclohexanecarboxylate Mixtures," J. D. Margerum, S.-M. Wong, A. M. Lackner, and J. E. Jensen, Molecular Crystals and Liquid Crystals, in press (1981).

"Variable Grating Mode Liquid Crystal Device for Optical Processing and Computing," B. H. Soffer, J. D. Margerum, A. M. Lackner, D. Boxwell, A. R. Tanguary, Jr., T. C. Strand, A. A. Sawchuk, and P. Chavel, Molecular Crystals and Liquid Crystals, in press (1981).

"Effects of Molecular Length on Nematic Mixtures. III. Anisotropic Properties of 4-Alkylphenyl 4-Alkoxybenzoate Mixtures," J. D. Margerum, S.-M. Wong, A. M. Lackner, J. E. Jensen, and S. A. Verzwylt, in preparation.

"Effects of Molecular Length on Nematic Mixtures. IV. Structure Effects on Viscosity of Ester Mixtures," J. D. Margerum, S.-M Wong, and J. E. Jensen, in preparation.

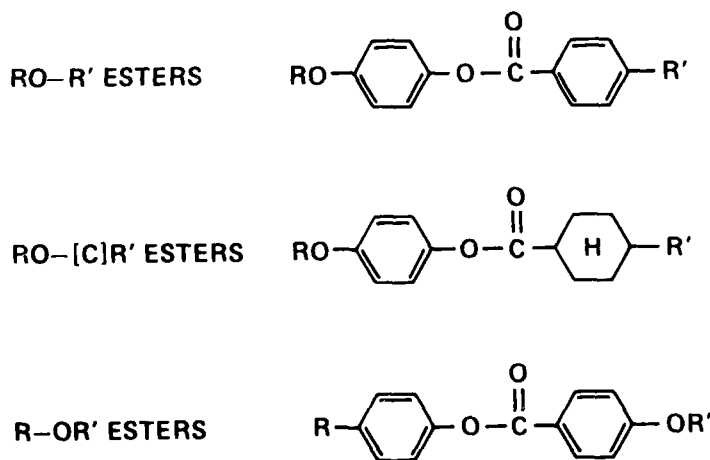
"Factors Affecting the Dynamic Scattering of a Nematic Ester Mixture," J. D. Margerum, A. M. Lackner, H. S. Lim, and J. E. Jensen, in preparation.

"Anisotropic and Electro-optical Effects in Liquid Crystals," J. D. Margerum, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this program was to study the effects of the chemical structure of liquid crystal (LC) components on the anisotropic properties of nematic mixtures, especially in regard to their electro-optical response characteristics. The program was particularly aimed at obtaining a better understanding of the effects of components on the dynamic scattering (DS) mode, which is a LC electro-optical effect being applied in the development of flat panel pictorial matrix displays for airplane cockpits and of electronic reticle devices for tank fire-control systems. A parallel, company-sponsored project provided all of the materials (components, LC mixtures, dopants, cells, etc.) for this program and was also used to extend the viscosity studies to a wider variety of LC chemical structures.

A major approach in this program was to investigate the anisotropic properties of ester LC mixtures as a function of their average molecular length ($\bar{L}$) and their structure. Three series of ester mixtures were studied, with each series containing only one class of LC components that differed only in the length of their R and R' n-alkyl end groups. The following RO-R', RO-[C]R', and R-OR' classes of esters were studied, using mixtures formulated to have similar nematic temperature ranges within each class:



The flow viscosity and the anisotropic values of refractive index, ionic conduction, and dielectric constant were studied in each series; the DS properties were studied in the RO-R' and RO-[C]R' series. In each series the viscosity increased as $\bar{L}$ increased, especially in the longer $\bar{L}$ mixtures due to an increase in their cybotactic nematic characteristics (i.e., short range smectic order). The cybotactic effect was identified by a relatively low value of conductivity anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) at 25°C along with a maximum value of $\sigma_{\parallel}/\sigma_{\perp}$ at a temperature between 25°C and the clearpoint temperature (where $\sigma_{\parallel}/\sigma_{\perp} = 1.0$). The presence of the cyclohexane ring caused particularly strong cybotactic characteristics in the long $\bar{L}$ RO-[C]R' mixtures, which had $\sigma_{\parallel}/\sigma_{\perp} = 0.5$ whereas the short $\bar{L}$ mixtures had $\sigma_{\parallel}/\sigma_{\perp} = 1.6$. The effect of $\bar{L}$ on dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) was different in each series; a surprisingly large effect was observed in the R-OR' series, in which $\Delta\epsilon$ was positive for short $\bar{L}$ but negative for long $\bar{L}$ mixtures, ostensibly due to enhanced molecular pairing in the long $\bar{L}$ mixtures. In general, more favorable electro-optical DS characteristics were found in the shorter $\bar{L}$ mixtures of the RO-R' and RO-[C]R' series. This is because in the shorter length mixtures the conductivity dopants have greater solubility, the threshold voltages of DS are lower due to higher $\sigma_{\parallel}/\sigma_{\perp}$ values, and the response times are faster due to lower viscosities.

Another major area of study was the correlation of flow viscosity with the molecular structure of 18 different classes of ester LCs. Comparative viscosity measurements were made at constant $\bar{L}$ by adding components from a structural class to RO-R' mixtures in such a way that both the $\bar{L}$ of the additives and the $\bar{L}$ of the final mixture were constant. This data was used to calculate approximate class viscosities for each of the 18 structural categories, including the above RO-R', RO-[C]R' and R-OR' classes. The class viscosities increased with structural contributions from aromatic, polar, and polarizable groups; the increases are especially large when multiple polar groups are present. These correlations are valuable in predicting the effects of structural variations on the viscosity of other classes of ester LCs. Also, it was found that the class viscosities can be used to calculate the approximate viscosity of LC ester mixtures within about 10% of their actual value. The pre-calculation of viscosity is very useful in choosing formulations for multi-component ester mixtures in which a low viscosity is desired as well as other properties such as a wide nematic temperature range.

Various factors affecting the anisotropic and DS characteristics of one particular eutectic mixture of LC esters were investigated, including studies on the effects of dopant structure, surface alignment, temperature, cell thickness, and type of electrical activating signal. These studies showed that the differences in the conductivity anisotropy of the dopant had the largest effect on the DS threshold voltage; however, the change of threshold with temperature was more strongly affected by changes in the bend elastic constant. The optical density

of scattering was found to increase linearly with the reciprocal of cell thickness. Thus, thin cells are advantageous not only because the LC response times are proportional to the square of the thickness, but also because thin cells provide higher scattering levels with DS activation. Some systematic studies were started on the relationships between the structure of dopants and their conductivity anisotropy in LCs. Although some correlations were observed, more studies need to be carried out as a wider selection of organic salt structures become available.

The variable grating mode (VGM) electro-optical effect was also studied in various nematic LCs, primarily in regard to potential use in optical processing and computing techniques. It was found that the VGM effects decreased as the $\bar{L}$ of RO-R' ester mixtures increased, probably due to increased negative values of $\Delta\Sigma$. In studies with wedge-shaped cells, it was found that the VGM effect can be obtained in much thicker cells than had previously been considered to be possible based on mechanisms that others have proposed for the effect.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Calculation of the Energetics and Collision Dynamics for Electronic Transitions
2. PRINCIPAL INVESTIGATOR: H. Harvey Michels
United Technologies Research Center
Hartford, CT 06108
3. INCLUSIVE DATES: 1 April 1977 - 31 March 1980
4. CONTRACT NUMBER: F49620-77-C-0064
5. COSTS AND FY SOURCE: \$34,628, FY77; \$59,918, FY78; \$78,256, FY79;
\$34,926, FY80
6. SENIOR RESEARCH PERSONNEL: R. H. Hobbs
7. JUNIOR RESEARCH PERSONNEL: J. B. Addison
8. PUBLICATIONS:

"Electronic Structure of the Noble Gas Dimer Ions," H. H. Michels, R. H. Hobbs and L. A. Wright, International Journal of Quantum Chemistry, 1978 Sanibel Symposium Issue, 12, 257 (1978).

"Configuration Interaction Studies of the HeH^+ Molecular Ion. IV. The Triplet Sigma, Pi and Delta States," T. A. Green, H. H. Michels and J. C. Browne, Journal of Chemical Physics, 69, 101 (1978).

"Electronic Structure of the Noble Gas Dimer Ions. I. Potential Energy Curves and Spectroscopic Constants," H. H. Michels and R. H. Hobbs, Journal of Chemical Physics, 69, 5151 (1978).

"Electronic Structure of the Noble Gas Dimer Ions. II. Absorption Spectrum for the $A\ ^2\Sigma_u^+ \rightarrow D\ ^2\Sigma_g^+$ System," H. H. Michels, R. H. Hobbs, and L. A. Wright, Journal of Chemical Physics, 71, 5053 (1979).

"Electronic Structure of the Noble Gas Dimer Ions. III. Absorption Spectrum for the $A\ ^2\Sigma_u^+ \rightarrow B\ ^2\Pi_g$ System," H. H. Michels and R. H. Hobbs to be published in the Journal of Chemical Physics, 1980.

"Visible Photoabsorption by Noble Gas Trimer Ions," H. H. Michels, R. H. Hobbs, and L. A. Wright, Applied Physics Letters, 35, 153 (1979).

"Electronic Structure and Photoabsorption of the Hg_2^+ Dimer Ions," H. H. Michels, R. H. Hobbs, and J. W. D. Connolly, Chemical Physics Letters, 68, 549 (1979).

"Laser Chemiluminescence of LiCa," D. I. Neumann, D. J. Benard and H. H. Michels. To be published in Chemical Physics Letters, 1980.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The theoretical research conducted under this program was concerned with a study of the energetics of the noble gas halides and noble gas dimer and trimer molecular ions and studies of candidate laser molecules operating on an electronic transition. The emphasis of the study of the noble gas halides was on the definition of potential energy curves, prediction of the radiative lifetimes of electronically excited states, and studies of photon energy loss paths such as photoabsorption and photoionization of the upper excited electronic states. A major effort of the study of the noble gas dimer and trimer ions was the definition of the potential energy curves and prediction of the photoabsorption cross-section for these species.

With the exception of the recent calculations by Wadt, no attempts at systematic studies of noble gas dimer and trimer ions have been reported. Accurate ab initio methods would appear to be practical only for the lighter ions with diminished accuracy for heavier systems such as Xe_2^+ . Recent density functional calculations of noble gas halide molecules (ArF and Ar_2F) have yielded reliable predictions of geometry and chemical binding, provided certain optimization criteria are followed. Such calculations, which should be of more uniform quality than ab initio studies, since numerical molecular orbitals not limited by basis set constraints are employed, constituted the principal effort in the present study. A limited number of ab initio calculations were carried out for Ar_2^+ for comparison purposes. The systems ArF , Ar_2F , Ne_2^+ , Ar_2^+ , Kr_2^+ , Xe_2^+ , and Ar_3^+ were chosen for detailed study.

In addition to our studies of noble gas systems, electronic structure calculations were carried out for MgO , SnO , SnF and $LiCa$. These calculations were performed in support of on-going research programs in the Advanced Laser Concepts (ALC) branch of AFWL. A significant amount of new computer code development was required to up-grade our capabilities to accurately handle large molecules such as SnF . In addition, relativistic corrections were developed for incorporation in our density functional code. The systems studied included the $1,3\Sigma$ and $1,3\Pi$ states of MgO , the $1,3\Sigma$ and $1,3\Pi$ states of SnO , the 2Σ and 2Π states of SnF and the 2Σ and 2Π states of $LiCa$.

Calculations have also been initiated on the MgNa, LiMg, HgTl, Hg_2^+ , and SiF/SiF₂ molecules. The systems studied included the $A^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states for Hg_2^+ , all low-lying 2Σ and 2Π states of MgNa, the 2Σ and 2Π states of HgTl, the 2Σ and 2Π states of LiMg, and the X^1A_1 and A^1B_1 states of SiF₂.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Investigation of Electrochromic Diphthalocyanines
2. PRINCIPAL INVESTIGATOR: Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
Anaheim, CA 92803
3. INCLUSIVE DATES: 1 April 1977 - 31 March 1980
4. CONTRACT NUMBERS: F49620-77-C-0074; F49620-79-C-0104
5. COSTS AND FY SOURCE: \$17,000, FY77; \$35,579, FY78; \$39,414, FY79
\$19,876, FY80
6. SENIOR RESEARCH PERSONNEL:

F. A. Pizzarello
R. V. Galiardi
G. A. Layman
7. PUBLICATIONS:

"Solid State Anion Migration in the Anodic Oxidation of Lutetium Diphthalocyanine," F. A. Pizzarello and M. M. Nicholson, J. Electron. Mat., 9, 231 (1980).

"Galvanostatic Transients in Lutetium Diphthalocyanine Films," M. M. Nicholson and F. A. Pizzarello, J. Electrochem. Soc., 127, 821 (1980).

"Kinetics of Color Changes in Lutetium Diphthalocyanine Oxidation Products Containing Different Anions," F. A. Pizzarello and M. M. Nicholson, Manuscript in preparation for Journal of the Electrochemical Society.

"Thin-Layer Electrochemical Cells Constructed from Precision-Etched Glass Cavities," M. M. Nicholson and R. V. Galiardi, Manuscript planned for Analytical Chemistry.

"Investigation of Electrochromic Diphthalocyanines," M. M. Nicholson, Final Technical Report.
8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Lanthanide diphthalocyanine films on tin oxide electrodes in contact with aqueous electrolytes exhibit a series of color changes on variation of the applied potential. These systems are of special interest because

of their unusual electrochemistry and their potentialities for electrochromic display applications. In this project, the electrochromism of lutetium diphthalocyanine films was investigated by several experimental approaches. The results confirmed that the color changes were due to faradaic reactions rather than temporary field effects. They provided information on the stoichiometry and kinetics of the electrode processes and on the stabilities of color-converted forms of the dye.

The lutetium diphthalocyanine film was initially green. By simple chemical and electrochemical diagnostic experiments, it was found that a blue cathodic product formed with utilization of hydrogen ion. The blue material was converted to green by reaction with oxygen. Anodic reactions could produce more than one red form of the dye, generally without a pH change in the electrolyte. The red materials were strong oxidizing agents. Thin-layer electrochemical measurements confirmed the participation of protons in the cathodic process. The thin-layer cell design, which included a shallow, precisely etched glass cavity, may prove useful in other research.

A complementary solid-state electrochemical investigation of lutetium diphthalocyanine in this laboratory led to the proposal that anodic oxidation occurred by rapid migration of anions from the electrolyte into the solid organic film. This mechanism was independently verified in the present work by radiotracer experiments using chloride and sulfate electrolytes. The results showed, approximately, that two electrons were lost per molecule of diphthalocyanine converted from green to red.

The kinetics of the anodic dye reaction on tin oxide in 1 M KCl was investigated by a galvanostatic transient technique, with simultaneous monitoring of the optical transmission of the film. At current densities of 0.3 to 6 mA/cm², the rate was controlled by an ionic space charge in the red oxidation product. Interpretation of the data by space-charge theory yielded a dielectric constant of approximately 10 for the red material.

Some of the red films gradually reverted to green on standing. The faded films were still convertible to the usual series of colors, however, by reactivation in the electrochemical cell. The rates of these chemically-produced color changes in chloride-containing films on tin oxide in ambient air were measured spectrophotometrically at temperatures from 25 to 60°C. A related, but more detailed, study was made on sapphire-supported films with electrolytes containing different anions. In that case, the red films were produced anodically by propagation of the red/green boundary upward from the liquid surface toward the electronic contact. The fading reactions in moist air followed first-order kinetics with respect to the red dye species.

Three types of behavior were characterized: (a) low-voltage color propagation and relatively fast return from red to green ($k \approx 0.1 \text{ hr}^{-1}$) (OAc^- and F^-); (b) higher-voltage propagation and little or no fading ($k < 0.003 \text{ hr}^{-1}$) (Cl^- , Br^- , and $\text{SO}_4^{=}$); and (c) no color propagation (I^- and OCCO^-).

AFOSk Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: High Resolution Vacuum Ultraviolet Spectroscopy of Small Molecules
2. PRINCIPAL INVESTIGATORS: Dr. W. H. Parkinson
Dr. D. E. Freeman
Dr. K. Yoshino
Harvard College Observatory
60 Garden Street
Cambridge, MA 02138
3. INCLUSIVE DATES: 1 October 1976 - 30 September 1980
4. GRANT NUMBER: F49620-77-C-0010/AFOSR-80-0018
5. COSTS AND FY SOURCE: \$170,896, FY77; \$124,998, FY78; \$90,000, FY79;
\$62,000, FY80
6. SENIOR RESEARCH PERSONNEL: None
7. JUNIOR RESEARCH PERSONNEL: None
8. PUBLICATIONS:

"Vacuum Ultraviolet Absorption Spectra of Binary Rare Gas Mixtures and the Properties of Heteronuclear Rare Gas van der Waals Molecules," D. E. Freeman, K. Yoshino and Y. Tanaka, J. Chem. Phys., **67**, 3462 (1977).

"High Resolution VUV Absorption Spectrum of N_2 , Homogeneous Perturbation between $c'_4(0) \ ^1\Sigma_u^+$ and $b'(1) \ ^1\Sigma_u^+$ Levels," K. Yoshino and Y. Tanaka, J. Mol. Spectros., **66**, 219 (1977).

"Emission Spectrum of Rare Gas Dimers in the Vacuum UV Region. I. Ar_2 ," Y. Tanaka, W. C. Walker and K. Yoshino, J. Chem. Phys., **70**, 380 (1979).

"Emission Spectrum of Rare Gas Dimers in the Vacuum UV Region. II. Rotational Analysis of Band System I of Ar_2 ," D. E. Freeman, K. Yoshino and Y. Tanaka, J. Chem. Phys., **71**, 1780 (1979).

"Absorption Spectrum of Krypton in the Vacuum UV Region," K. Yoshino and Y. Tanaka, J. Opt. Soc. Am., **69**, 159 (1979).

"High Resolution VUV Absorption Spectrum of N_2 , $c'_4 \ ^1\Sigma_u^+ \leftarrow X \ ^1\Sigma_g^+$ Bands," K. Yoshino, D. E. Freeman and Y. Tanaka, J. Mol. Spectros., **75**, 153 (1979).

"High Resolution VUV Absorption Spectrum of N_2 , $c_5^1 \Sigma_u^+$ + $X^1 \Sigma_g^+$ Bands," K. Yoshino and D. E. Freeman (in preparation).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A 6.65 metre vacuum spectrograph operated at a wavelength resolution of 0.0006 nm has been used to study (a) the spectroscopy of rare gas molecules relevant to the development of intense vacuum ultraviolet radiation sources and lasers, and (b) photoabsorption and predissociation processes in molecular nitrogen, which in the 80-100 nm region are important sources of upper atmospheric atomic nitrogen.

Absorption spectra of XeHe, XeNe, XeAr, XeKr, KrHe, KrNe, and KrAr have been photographed and interpreted as arising from transitions from bound ground states to bound or free excited electronic states of these van der Waals molecules; bound excited states have been found for XeKr and XeAr. The emission spectrum of diatomic argon in the 100-150 nm region has been found to consist of four band systems all terminating on the ground electronic state; the only discrete band system, that emitted from the lowest excited state, has been analyzed rotationally and characterized spectroscopically as a triplet state for which the long range potential has been estimated. The absorption spectrum of atomic krypton in the 84-124 nm region has been obtained, and excited Rydberg states with principal quantum number as high as 60 have been assigned; the lowest two ionization energies have been accurately determined.

High resolution absorption spectra of dipole allowed transitions in molecular nitrogen, from the ground state to excited Rydberg and valence states have been rotationally analyzed. Some large anomalies in frequency spacings and relative intensities have been interpreted in terms of strong homogeneous perturbations rather than predissociations.

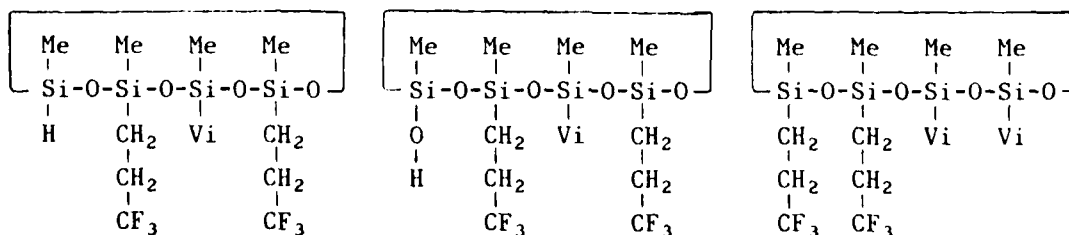
AFOSR Program Manager: William G. Thorpe, Capt, USAF

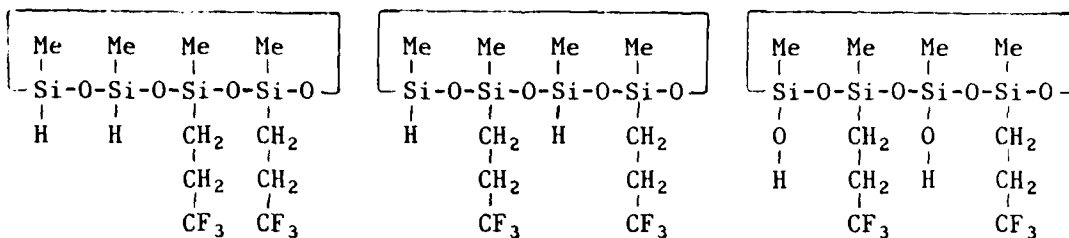
COMPLETED PROJECT SUMMARY

1. TITLE: Cyclic Fluorosilicone Polymers and Copolymers
2. PRINCIPAL INVESTIGATORS: Dr. Ogden Pierce (Died 8-14-79)
Mr. Ken M. Lee
Advanced Research Laboratory
Dow Corning Corporation
Midland, Michigan 48640
3. INCLUSIVE DATES: 1 January 1977 - 29 February 1980
4. CONTRACT NUMBER: F49620-77-C-0012
5. COSTS AND FY SOURCE: \$30,000, FY77; \$42,242, FY78; \$44,757, FY79;
\$11,176, FY80
6. PUBLICATIONS:

"Cyclic Fluorosilicone Polymers and Copolymers," O. R. Pierce and K. M. Lee, Final Technical Report.
7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

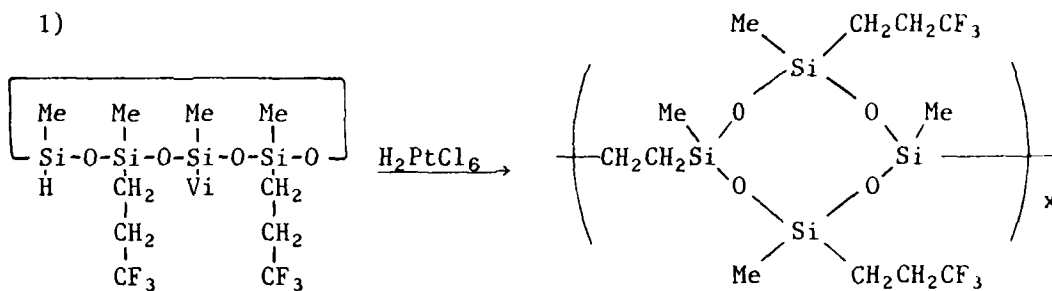
Several reactions were examined as potential routes to reactive cyclic tetrasiloxanes and their precursors. The reactions examined in some detail were cohydrolysis, siloxy-chloride exchange, hydrolysis of $\equiv\text{SiCl}$, $\equiv\text{SiOMe}$ and $\equiv\text{SiH}$ and acetoxy-silanol condensations. Using these reactions several intermediates were prepared and the new compounds were characterized. From the intermediates, six reactive cyclic tetrasiloxanes were prepared and characterized; these are listed below.





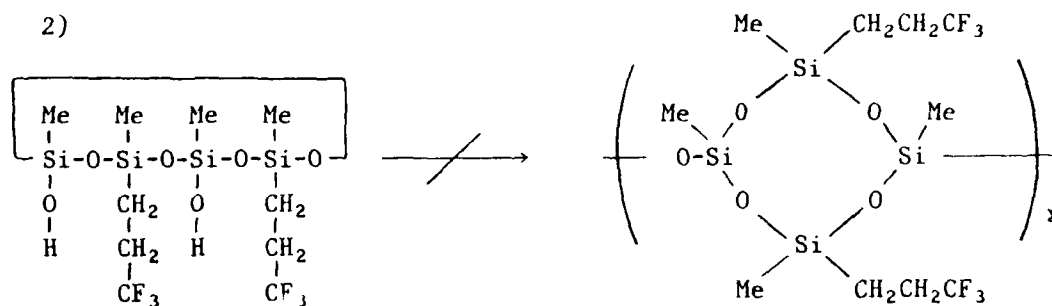
Two of these compounds were studied in polymerization reactions:

1)



Molecular weight of 43,300 was achieved; and

2)



Polymerization was not achieved in this system.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Carbon-Carbon Composite Matrix Decomposition Reactions and Densification
2. PRINCIPAL INVESTIGATOR: Mr. James P. Pope
Material Science Operations
Science Applications, Inc.
Irvine, CA 92215
3. INCLUSIVE DATES: 1 November 1977 to 14 January 1980.
4. CONTRACT NUMBER: F49620-78-C-0002; F49620-79-C-0068
5. COSTS AND FY SOURCE: \$44,763, FY78; \$54,014, FY79; \$15,470, FY80
6. SENIOR RESEARCH PERSONNEL: Dr. David A. Eitman
7. JUNIOR RESEARCH PERSONNEL: None
8. PUBLICATIONS: "Carbon-Carbon Composite Matrix Decomposition Reactions and Densification," James P. Pope, Final Technical Report, Contract F49620-78-C-0002, 11 May 1979.
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Advanced strategic missile systems will employ carbon-carbon structural composite materials for nozzles and nosetips. Performance models which relate the microstructure of the composites to their environmental response are limited since the fundamental relationships between process chemistry, in-process events and microstructure formation have not been defined. The objective of this research was to define the critical chemical phenomena and kinetics occurring in composite matrix decomposition as a function of pressure under simulated fabrication conditions. The intent was to contribute to the establishment of a process science base which would permit tailoring of the carbon-carbon composite processing cycle to optimize carbon yield, obtain desired microstructures for achieving improved thermochemical and thermostructural response, and obtain high quality composites via low pressure processing. The approach included three tasks: (1) Definition of the reaction rates of the decomposition of matrix pitches without the presence of fibers, powders or mechanical constraints through determination of time-temperature-pressure relationships; (2) investigation of matrix decomposition as modified by the presence of active surfaces and mechanical constraints in fluid flow; and (3) analysis of decomposition reactions and solid state products through consideration of microstructure, chemical structure, crystallographic orientation and degree of ordering, fluid dynamics, heat conduction, diffusion and mechanical environment.

This research, part of an AFWAL/ML-AFOSR processing science program in carbon-carbon composites, contributed to research resulting in an analytical model for providing process guidance in terms of carbon-carbon composite preform construction and graphitization temperatures. Pitch matrix decomposition reaction rates were identified and density data at temperature and pressure were obtained which iteratively interacted with process environment model development. Microstructure development after carbonization and graphitization of various carbonization cycles and its relation to densification, decomposition, pressure and temperature dependence, and autoclave can location were systematically studied for the first time.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Computational Study of Nonadiabatic Effects in Atom-Molecule Reactive Scattering
2. PRINCIPAL INVESTIGATOR: Dr. Michael J. Redmon
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201
3. INCLUSIVE DATES: 15 March 1979 - 30 September 1980
4. CONTRACT NUMBER: F49620-79-C-0050
5. COSTS AND FY SOURCE: \$60,000, FY79; \$60,000, FY80
6. SENIOR RESEARCH PERSONNEL:

Dr. Bruce C. Garrett
Dr. Isaiah Shavitt
7. JUNIOR RESEARCH PERSONNEL: None
8. PUBLICATIONS:

"Recent Results from Three-Dimensional Quantum Reactive Scattering Theory," Michael J. Redmon, Int. J. Quantum Chem. Symp., 13, 559 (1979).

"Integral Equations with Reference Potentials," Michael J. Redmon, in Proceedings of the Workshop on Algorithms and Computer Codes for Atomic and Molecular Quantum Scattering Theory, Vol. I, L. Thomas, Ed., NRCC Proceedings No. 5, LBL 9501, Lawrence Berkeley Laboratory, Berkeley, CA 94720 (June 1979).

"Applications of Integral Equations with Reference Potentials to the NRCC Close-Coupling Test Problems (INSCAT)," Michael J. Redmon, in Proceedings of the Workshop on Algorithms and Computer Codes for Atomic and Molecular Quantum Scattering Theory, Vol. II, L. Thomas, Ed., NRCC Proceedings No. 5, LBL-9501, Lawrence Berkeley Laboratory, Berkeley, CA 94720 (July 1, 1980).

"An Analytical Fit to an Accurate ab initio ($^1A_1$) Potential Surface of H_2O ," Michael J. Redmon and G. C. Schatz, Chem. Phys. (in press).

"Ab initio Treatment of Electronically Inelastic $K + H$ Collisions Using a Direct Integration Method for the Solution of the Coupled-Channel Scattering Equations in Electronically Adiabatic Representations," Michael J. Redmon, B. C. Garrett, D. G. Trunlar, and C. F. Melius, J. Chem. Phys. (in press).

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"An Analytical Fit to the Ground State Potential Surface of CO₂,"
Michael J. Redmon and G. C. Schatz, in preparation.

"Computational Study of Nonadiabatic Effects in Atom-Molecule Reactive
Scattering," Michael J. Redmon, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research effort was terminated early due to Dr. Redmon's leaving Battelle, Columbus Laboratories. The purpose of the effort was to develop the computational techniques needed for studying nonadiabatic transitions in atom-diatom molecule collisions. Systematic approaches to fitting potential energy surfaces obtained from ab initio quantum chemistry have been investigated. A practical formalism for accurately treating nonadiabatic electronic couplings was developed and tested in an application to electronic quenching in K plus H collisions. The first 3-D quantum mechanical calculation of the reaction rate for F plus H₂ was carried out. It was possible to compute probabilities at enough values of energy and total angular momentum to obtain total state-to-state cross sections over the range of energies required to compute a thermal rate.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Experimental and Theoretical Studies of Intramolecular and Intermolecular Dynamics
2. PRINCIPAL INVESTIGATOR: Dr. Stuart A. Rice
The James Franck Institute
University of Chicago
Chicago, IL 60637
3. INCLUSIVE DATES: 1 September 1976 - 30 September 1980
4. GRANT/CONTRACT NUMBER: F49620-76-C-0017; AFOSR-80-0004
5. COSTS AND FY SOURCE: \$8,000, FY76; \$91,944, FY77; \$99,973, FY78;
\$107,052, FY79; \$116,447, FY80
6. SENIOR RESEARCH PERSONNEL:
V. Sethuraman
M. Sulkes
C. Jouvét
N. Mikami
7. JUNIOR RESEARCH PERSONNEL:
N. Choporis
P. Radloff
T. Stephenson
J. Tusa
J. McVey
T. Rolfe
8. PUBLICATIONS:
"Large Amplitude Vibrational Motion in a One Dimensional Chain; Coherent State Representation," John Dancz and Stuart A. Rice, J. Chem. Phys., 67, 1418 (1977).
"Spectroscopic Properties of Polyenes III. 1, 3, 5, 7-Octatetraene," R. M. Gavin, Jr., Charles Weisman, Jeffrey K. McVey and Stuart A. Rice, J. Chem. Phys., 68, 522 (1978).
"On Vibrational Population Relaxation in Solution," Joseph N. Kushick and Stuart A. Rice, Chem. Phys. Letters, 52, 208 (1977).
"Internal Energy Transfer in Isolated Molecules: Ergodic and Nonergodic Behavior," Stuart A. Rice, Proceedings of a Symposium on Advances in Laser Chemistry, California Institute of Technology, March 1978. Ed. A. Zewail. Springer Verlag (1978).

"On the Influence of Nonrandom Sequential Coupling on Radiationless Relaxation Processes," M. Muthukumar and Stuart A. Rice, J. Chem. Phys., 69, 1619 (1978).

"On Rotational Effects in Radiationless Processes in Polyatomic Molecules," Frank Novak, Karl Freed and Stuart A. Rice, Radiationless Transitions, ed. S. H. Lin, Academic Press, p. 135 (1980).

"Single Vibronic Level Fluorescence from Aniline," Donald A. Chernoff and Stuart A. Rice, J. Chem. Phys., 70, 2511 (1979).

"Collision Induced Intramolecular Vibrational Energy Transfer in $^{18}\text{O}_2$ Aniline," Donald A. Chernoff and Stuart A. Rice, J. Chem. Phys., 70, 2521 (1979).

"A Numerical Study of Large Amplitude Motion on a Chain of Coupled Nonlinear Oscillators," Timothy J. Rolfe, John Dancz and Stuart A. Rice, J. Chem. Phys., 70, 26 (1979).

"Angular Momentum Constraints in Radiationless Processes: The Symmetric Top Molecule," Frank A. Novak and Stuart A. Rice, J. Chem. Phys. (submitted).

"Low Energy Collisional Relaxation of I_2^* in He: Evidence for Resonance Enhanced Vibrational Deactivation," James Tusa, Mark Sulkes and Stuart A. Rice, J. Chem. Phys., 70, 3136 (1979).

"Dynamics of Radiationless Processes Studied in Pulsed Supersonic Free Jets: Some Naphthalene Lifetimes," Fred M. Behlen, Nohiko Mikami and Stuart A. Rice, Chem. Phys. Letters, 60, 364 (1979).

"Collision Induced Intramolecular Energy Transfer in Electronically Excited Polyatomic Molecules," Advances in Chemical Physics. Photoselective Chemistry, Eds. J. Jortner, R. Levine and S. Rice, John Wiley and Sons, Inc., in press.

"Quantum Effects Intramolecular Energy Transfer: The Role of Observations," R. Kosloff and Stuart A. Rice, Chem. Phys. Lett., 69, 209 (1980).

"The Influence of Rotational Motion on Intersystem Crossing in Isolated Molecules," F. A. Novak and Stuart A. Rice, J. Chem. Phys., 73, 858 (1980).

"A Study of the Rotational State Dependence of Predissociation of a Polyatomic Molecule: The Case of ClO_2 ," S. Michielsen, A. Merer, F. A. Novak, K. F. Freed, Y. Hamada and Stuart A. Rice, J. Chem. Phys., in press.

"Very Low Energy Cross Sections for Collision Induced Relaxation of I_2 Seeded in a Supersonic Free Jet," J. Tusa, M. Sulkes and Stuart A. Rice, Proceedings of the National Academy of Sciences, **77**, 2367 (1980).

"Quasiperiodic and Stochastic Intramolecular Dynamics: The Nature of Intramolecular Energy Transfer," NATO Advanced Study Institute Series, R. G. Wooley, Ed., Plenum Press, New York, 1980.

"Collision Induced Relaxation of an Electronically Excited Molecule: Evidence for Low Energy Resonance Enhanced Vibrational Deactivation," M. Sulkes, J. Tusa and Stuart A. Rice, J. Chem. Phys., **72**, 5733 (1980).

"Comment on the Rotational State Dependence of Indirect Photodissociation of a Polyatomic Molecule," F. Novak and Stuart A. Rice, Proceedings of the National Academy of Sciences, **77**, 3753 (1980).

"The Influence of Quantization on the Onset of Chaos in Hamiltonian Systems: The Kolmogorov Entropy Interpretation," R. Kosloff and Stuart A. Rice, J. Chem. Phys., in press.

"Dynamical Correlation and Chaos in Classical Hamiltonian Systems," R. Kosloff and Stuart A. Rice, J. Chem. Phys., in press.

"Intramolecular Vibrational Energy Transfer in $^1B_2$ Aniline Induced by Collisions with H_2O and CH_3F ," M. Vandersall, D. Chernoff and Stuart A. Rice, J. Chem. Phys., in press.

"Single Vibronic Level Fluorescence from $^1B_{3u}$ Pyrazine: The Role of Fermi Resonance and Duschinski Rotation," D. McDonald and Stuart A. Rice, J. Chem. Phys., in press.

"Collision Induced Intramolecular Vibrational Energy Transfer in $^1B_{3u}$ Pyrazine," D. McDonald and Stuart A. Rice, J. Chem. Phys., in press.

"A Correlation Diagram Model for Interpreting Propensity Rules in Collision Induced Vibrational Relaxation," D. McDonald, J. Chem. Phys., in press.

"An Overview of the Dynamics of Intramolecular Transfer of Vibrational Energy," Advances in Chemical Physics, J. Jortner, R. Levine and Stuart A. Rice, eds., J. Wiley and Sons, Inc., in press.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The goal of this effort was to provide both experimental information and theoretical descriptions which will elucidate the primary processes in unimolecular reactions, the pathways of energy transfer in bimolecular encounters and the relationships of these with physical processes and

chemical reactions, and the nature of the reaction products and energy disposal between them, for given initial states of the reactants.

Extensive studies of collisionally induced intramolecular vibrational relaxation in aniline have been conducted. In the completed work Ar was the collision partner. The data show that the cross section for vibrational relaxation on the excited electronic surface is very large, that the pathway of vibrational relaxation is selective, and that endothermic processes are extremely important in the approach to equilibrium. This work has been augmented by studies of collision induced vibrational relaxation with water and methyl fluoride as partners and by a detailed study of the same processes in collisions between pyrazine and argon. A correlation type theory of the rules governing such processes has been developed. A detailed study of radiationless processes in cold isolated molecules of naphthalene, including the first evidence for a clearly identified promoting mode was completed.

A pulsed supersonic jet molecular beam apparatus was constructed to study the energy dependence of collision induced energy transfer. With this apparatus a new, extremely efficient collision induced vibrational relaxation mechanism was discovered. Thus far a study of collisions between helium, neon and argon atoms and electronically excited iodine molecules has been completed. It is found that extremely low relative kinetic energy collisions have essentially hard sphere cross sections for vibrational relaxation of the iodine molecule. A mechanism for this process based upon orbiting resonances has been proposed. Work now in progress includes extension of the study of very low energy collisions to the case of electronically excited polyatomic molecules and the development of a full quantum mechanical theory of the process.

The theory of the effect of rotational state selection on radiationless processes, both molecule preserving and molecule destroying, has been developed. Contrary to expectation, the role played by conservation of angular momentum so greatly constrains the possible final states that, in first order, initial selection of rotational state has no influence on the rate of the process. This is an important theoretical result, since it permits one to invert experimental observations and state with confidence that when a dependence of rate on initial rotational state is seen, there is a resonance interaction in the manifold of molecular states.

In addition, the behavior of large amplitude motion in molecules and its representation in terms of coherent states and solitary waves has been studied. In this effort the relationship between the onset of stochastic behavior and nonlinear resonances in a model molecule was shown, the relationship between the onset of stochastic behavior and state-selective chemistry was probed, and the concept of Kolmogorov

entropy was extended to the quantum mechanical case where it was used to interpret the nature of chaos in quantum mechanical systems.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Inorganic Reactants for Synthesis of Novel Fluorocarbon Derivatives
2. PRINCIPAL INVESTIGATORS: Dr. Carl J. Schack
Dr. Karl O. Christe
Rocketdyne Division
Rockwell International
Canoga Park, CA 91304
3. INCLUSIVE DATES: 15 March 1978 - 14 March 1980
4. CONTRACT NUMBER: F49620-77-C-0038
5. COSTS AND FY SOURCE: \$26,847, FY77; \$35,093, FY78; \$39,274, FY79;
\$17,922, FY80
6. PUBLICATIONS:

"Reactions of Electropositive Chlorine Compounds with Fluorocarbons,"
C. J. Schack and K. O. Christe, Israel J. Chem., 17, 20 (1978).

"Improved Syntheses of Some Sulfur Fluoride and Oxyfluoride Peroxides,"
C. J. Schack and K. O. Christe, Inorg. and Nuclear Chem. Letters, 14,
293 (1978).

"Fluoroacyl Hypochlorites and Ester Derivatives," C. J. Schack and
K. O. Christe, J. Fluorine Chem., 19, 325 (1978).

"Introduction of Functional Groups into Some Chlorofluorocarbon Ethers,"
C. J. Schack and K. O. Christe, J. Fluorine Chem., 14, 519 (1979).

"Halogen Fluorosulfate Reactions with Fluorocarbons," C. J. Schack and
K. O. Christe, J. Fluorine Chem., to appear July 1980.

"Iodine Fluorosulfate Reactions with Fluorocarbons," C. J. Schack and
K. O. Christe, to be submitted for publication.

"Substitution and Addition Reactions of NF_4BF_4 with Fluorocarbons,"
C. J. Schack and K. O. Christe, to be submitted for publication.

"Inorganic Reactants for Synthesis of Novel Fluorocarbon Derivatives,"
C. J. Schack and K. O. Christe, Final Technical Report.

PATENT APPLICATION DISCLOSURES:

"The Preparation of Fluorocarbon Halides Using Halogen Fluorosulfates," C. J. Schack and K. O. Christe.

"The Synthesis of Fluorocarbon Esters," C. J. Schack and K. O. Christe.

"Introduction of Fluorine into an Aromatic Ring," K. O. Christe and C. J. Schack.

"Fluorocarbon Fluorosulfate Iodides," C. J. Schack.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Several different fluorocarbon fluids containing the SF_5O- and CF_3O- groups have been prepared using fluoroolefins and either SF_5OOSO_2F or CF_3OOSO_2F . In addition the fluorocarbon ethers, $SF_5OC_2F_4OSO_2F$ and $CF_3OC_2F_4OSO_2F$, and several of their derivatives were prepared and characterized. Chlorine fluorosulfate and bromine fluorosulfate were shown to have wide utility in the displacement of halide from fluorocarbon halides (R_fX) resulting in the formation of fluorocarbon fluorosulfates. The R_fSO_3F compounds are readily converted to derivatives such as acid fluorides, acids, etc., and in this way functionality is introduced into relatively inert fluorocarbons. Furthermore both $Cl-$ and $BrSO_3F$ readily react with fluorocarbon acids and derivatives resulting in the loss of CO_2 and the formation of R_fX ($X=Cl, Br$) species. Together, the conversion of R_fCF_2X to $R_fCF_2SO_3F$, followed by hydrolysis of $R_fCF_2SO_3F$ to R_fCO_2M and decarboxylation with XSO_3F to give R_fX , represents a new high yield chain shortening process. New procedures for synthesizing iodine fluorosulfate were developed. Previously unknown olefin addition reactions of ISO_3F were discovered which furnish potentially useful difunctional derivatives. Chlorine nitrate oxidation of iodine in $i-C_3F_7I$ gave a new, thermally stable bis-nitrate compound. The necessity for iso- R_fI in forming these stable bis-adducts was demonstrated. A new method was discovered for the introduction of fluorine into an aromatic ring with retention of aromaticity, using NF_4BF_4 in HF solution. Also when the arene is already highly fluorinated, it was shown that a slower addition of fluorine occurred to give cyclohexadienes and cyclohexenes.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Electron Paramagnetic Resonance Spectroscopy of Vanadium (IV) Complexes and Related Species
2. PRINCIPAL INVESTIGATOR: Professor Kenneth R. Seddon
Inorganic Chemistry Laboratory
Oxford University
Oxford, OX1 3QR, England
3. INCLUSIVE DATES: 1 October 1977 - 31 July 1980
4. GRANT NUMBER: AFOSR-77-3368
5. COSTS AND FY SOURCE: \$1750, FY77
6. SENIOR RESEARCH PERSONNEL: None
7. JUNIOR RESEARCH PERSONNEL: None
8. PUBLICATIONS:

"EPR Spectroscopy of Vanadium Complexes," K. R. Seddon, Final Report: EOARD-TR-80-13.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The general objective was to develop the use of electron paramagnetic resonance (EPR) as an analytical tool in vanadium chemistry. EPR is a much neglected but a potentially very powerful probe into the structure of these paramagnetic species in solution and in the solid state. The initial research indicated the possibility that, within a given series, a species may be identified by means of its isotropic hyperfine splitting constant, A_{iso} and its g_{iso} value. For example, the following dissociation has been detected in toluene solution:



No other spectroscopic technique could have detected this dissociation in dilute solution (ca. $10^{-4}M$), and EPR has not been used in this investigative manner previously in vanadium (IV) chemistry. EPR has proven an invaluable structural tool for relating the structure of a complex in an amorphous or polycrystalline sample to that of the same complex in solution. Solution studies by EPR have previously revealed unsuspected dissociation and displacement phenomena for complexes of the type $[VOX_2L_n]$ ($X = Cl$ or Br , $L =$ mono or bi-dentate ligand), which

means that many literature reports need be reexamined. The results from this research contains several tables of EPR results and spectral data of vanadium complexes, as well as a comprehensive literature survey.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Multicomponent Oxide Systems for Corrosion Protection

2. PRINCIPAL INVESTIGATOR: Dr. Gary W. Stupian
Chemistry and Physics Laboratory
The Aerospace Corporation
Los Angeles, Calif 90007

3. INCLUSIVE DATES: 1 July 1977 - 30 September 1980

4. GRANT NUMBER: AFOSR 77-3334

5. COSTS AND FY SOURCE: \$60,533, FY77; \$65,498, FY78; \$68,827, FY79

6. SENIOR RESEARCH PERSONNEL:

Dr. Paul D. Fleishauer
Dr. Howard A. Katzman
Dr. Russell A. Lipeles
Dr. Frank E. Hanson
Dr. James A. Doi

7. JUNIOR RESEARCH PERSONNEL:

Ted H. Lee
Reinhold Bauer

8. PUBLICATIONS:

"Corrosion - Protective Chromate Coatings on Aluminum," H. A. Katzman, G. M. Malouf, R. Bauer, and G. W. Stupian, Applications of Surface Science, 2, 416-432 (1979).

"The Formation of Corrosion Protective Mixed Aluminum - Titanium Oxide Films from Tetrabutyl Titanate," R. A. Lipeles, G. M. Malouf, P. D. Fleischauer, and G. W. Stupian, submitted to Applications of Surface Science (1980).

G. W. Stupian and P. D. Fleischauer, Final Report: Multicomponent Oxide Systems for Corrosion Protection, ATR-81(7679)-1, The Aerospace Corporation, El Segundo, Calif (1980).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The formation and function of corrosion resistant surface oxide films on aluminum have been investigated during a three-year research effort. "Mixed" oxide coatings should, based on a conceptual model, offer superior corrosion resistance (a mixed oxide is defined as an oxide

system based on more than one cation species). The structures of the mixed oxide coatings studied were characterized using Auger electron spectroscopy, x-ray photoelectron spectroscopy, and ion microprobe mass analysis. Corrosion resistance was assessed by exposing specimens in a salt chamber.

Chromate coating systems, long in use on aluminum, were examined first to provide a standard against which to measure coating performance. Chromate coating formation was explained in terms of the role of hydrogen fluoride (or hydroxyl ion) in the dissolution of the native aluminum oxide layer and through the influence of the slight solubility difference between chromium and aluminum hydroxides on film growth.

New types of mixed oxide coatings deposited from nonaqueous solutions of organometallic compounds were developed. Titanium-aluminum mixed oxide coatings, deposited from solutions of titanium alkoxides in isopropanol, served as a prototype system for much of this work. It was found that the application of certain sulfur compounds in conjunction with titanate coatings resulted in enhanced corrosion resistance, and in one case (AA 6061), the corrosion resistance exceeded that of the chromate coatings. The feasibility of the basic approach taken here has been validated. It remains for future work to effect further improvements in the technique.

AFOSR Program Manager: Lorelei A. Krebs, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Photofragment Momentum Spectroscopy of N_2O^+ and D_2^+ at 334.1 nm
2. PRINCIPAL INVESTIGATOR: Dr. Timothy F. Thomas
Department of Chemistry
University of Missouri-Kansas City
Kansas City, MO 64110
3. INCLUSIVE DATES: 1 June 1979 - 1 June 1980
4. CONTRACT NUMBER: F49620-79-C-0167
5. COSTS AND FY SOURCE: \$9,987, FY 79 (MINI GRANT)
6. PUBLICATION: "Construction and Testing of an Ion Photofragment Momentum Spectrometer," Timothy F. Thomas, Final Technical Report.
7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This work was undertaken in order to determine the distribution of kinetic energies (derived from the distribution of momenta) of fragment ions formed by photodissociation of N_2O^+ and D_2^+ . A Nuclide 12-90-G mass spectrometer was modified to function as a photofragment momentum spectrometer. The conversion required a reconstruction of the ion source and the construction of an ion lens to focus the ion beam. Initial measurements indicate the instrument can now resolve the vibrational structure in the momentum distribution of NO^+ produced by photodissociation of N_2O^+ with a detector slit width of 0.25 mm. At this slit width, an ion current of 5 picoamps of Ar^+ at the detector is achievable. Now that the instrument modification is complete, a study of the N_2O^+ photodissociation reaction can be completed.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of the Correlation of Electrode Kinetics with Molecular Structure
2. PRINCIPAL INVESTIGATOR: Dr. Michael J. Weaver
Department of Chemistry
Michigan State University
East Lansing, MI 48824
3. INCLUSIVE DATES: 1 September 1977 - 30 September 1980
4. GRANT NUMBER: AFOSR-77-3408
5. COSTS AND FY SOURCE: \$45,894, FY78; \$51,000, FY79; \$51,428, FY80
6. SENIOR RESEARCH PERSONNEL:
Professor David Larkin
Dr. Viswanathan Srinivasan
7. JUNIOR RESEARCH PERSONNEL:
Stephen W. Barr
Kendall L. Guyer
Joseph T. Hupp
Yongjoo Kim
Hsue-Yang Liu
Scott M. Nettles
Edward W. Schindler
Paul D. Tyma
Edmund L. Yee
8. PUBLICATIONS:
"The Elucidation of the Reaction Sites for the Electroreduction of Some Co(III) Ammine Complexes at the Mercury-Aqueous Interface. The Effect of Anion Specific Adsorption from Mixed Alkali Fluoride Electrolytes," T. L. Satterberg, M. J. Weaver, J. Phys. Chem., 82, 1784 (1978).
"Co(III) Ammine Electroreduction Reactions as Kinetic Probes of Double-Layer Structure. The Reduction of Fluoropentaamine Cobalt(III) at Varying Ionic Strengths," M. J. Weaver, J. Electroanal. Chem., 93, 231 (1978).
"On the Role of the Bridging Ligand in Electrochemical Inner-Sphere Reactions," M. J. Weaver, Inorg. Chem., 18, 402 (1979).
"Survey of Ligand Effects upon the Reaction Entropies of Some Transition-Metal Redox Couples," E. L. Yee, R. J. Cave, K. L. Guyer, P. D. Tyma, M. J. Weaver, J. Am. Chem. Soc., 101, 1131 (1979).

"Activation Parameters for Simple Electrode Reactions. Application to the Elucidation of Ion-Solvent Interactions in the Transition State for Heterogeneous Electron Transfer," M. J. Weaver, J. Phys. Chem., 83, 1748 (1979).

"Some Recent Approaches to the Study of Heterogeneous Redox Kinetics of Metal Complexes. Comparisons with Homogeneous Redox Processes," M. J. Weaver, Israel J. Chem., 18, 35 (1979).

"Electrode Kinetics and Double-Layer Structure at Solid Electrodes," K. L. Guyer, S. W. Barr, R. J. Cave, M. J. Weaver, in Proc. Third Symposium on Electrode Processes," S. Bruckenstein, J. D. E. McIntyre, B. Miller, E. Yeager (eds), Electrochemical Society (pub), 1980, p. 390.

"A High-Speed Device for Synchronization of Natural-Drop Experiments with a Dropping Mercury Electrode," P. D. Tyma, M. J. Weaver, C. G. Enke, Anal. Chem., 51, 2300 (1979).

"Correlations between Outer-Sphere Self-Exchange Rates and Reaction Entropies for Some Simple Redox Couples," N. Sutin, M. J. Weaver, E. L. Yee, Inorg. Chem., 19, 1096 (1980).

"Activation Parameters for Homogeneous Outer-Sphere Electron-Transfer Reactions. Comparisons between Self-Exchange and Cross-Reactions Using Marcus Theory," M. J. Weaver, E. L. Yee, Inorg. Chem., 19, 1936 (1980).

"On the Functional Dependence upon Ligand Composition of the Reaction Entropies for Some Transition-Metal Redox Couples Containing Mixed Ligands," E. L. Yee, M. J. Weaver, Inorg. Chem., 19, 1077 (1980).

"Correlations between Electrochemical and Homogeneous Redox Reactivity. Quantitative Comparisons of Rate Constants and Activation Parameters for Some Inorganic Outer-Sphere Reactions," M. J. Weaver, J. Phys. Chem., 84, 568 (1980).

"Solvent Isotope Effects upon the Thermodynamics of Some Transition-Metal Redox Couples in Aqueous Media," M. J. Weaver, S. M. Nettles, Inorg. Chem., 19, 1641 (1980).

"Electrochemical Studies of Europium and Ytterbium Cryptate Formation in Aqueous Solution. The Effects of Varying the Metal Oxidation State upon Cryptate Thermodynamics and Kinetics," E. L. Yee, O. A. Gansow, M. J. Weaver, J. Am. Chem. Soc., 102, 2278 (1980).

"The Dependence of the Kinetics of Some Simple Outer-Sphere Electrode Reactions on the Nature of the Electrode Material," S. W. Barr, K. L. Guyer, M. J. Weaver, J. Electroanal. Chem., 111, 41 (1980).

"Further Observations on the Dependence of the Electrochemical Transfer Coefficient on the Electrode Potential," P. D. Tyma, M. J. Weaver, J. Electroanal. Chem., 111, 195 (1980).

"Solvent Isotope Effects upon the Kinetics of Some Simple Electrode Reactions," P. D. Tyma, S. M. Nettles, M. J. Weaver, J. Electroanal. Chem., 114, 53 (1980).

"The Role of the Supporting Electrolyte Cation in the Kinetics of Outer-Sphere Electrochemical Redox Processes Involving Metal Complexes," M. J. Weaver, H. Y. Liu, Y. Kim, Can. J. Chem., in press.

"Studies of the Correlation of Electrode Kinetics with Molecular Structure," M. J. Weaver, Final Technical Report, AFOSR-TR-81-0014.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall objective was to develop an understanding of the relationships between the kinetics and mechanisms of some simple heterogeneous electron-transfer reactions and the molecular structure of the reactant and the electrode-solution interface. Emphasis was placed on studies of transition-metal redox couples involving substitutionally inert complexes in aqueous media at a number of solid metals as well as at mercury electrodes. Either inner- or outer-sphere reaction mechanisms can be induced, depending on the ability of the coordinated ligands to bind to the electrode surface.

A central problem that was addressed concerns understanding the ways by which metal electrodes can catalyze simple electrode reactions by forming chemical bonds with the reacting species, i.e., the extent to which inner-sphere pathways can be favored over the alternative "noncatalytic" outer-sphere route. It was found that the extent of such catalyses for Co(III)/(II) and Cr(III)/(II) redox couples induced by binding the reactants to the electrode surface via bridging ligands is extremely sensitive to the structure of both the ligand and the metal substrate. By combining kinetic and reactant adsorption measurements, the especially large catalyses induced by Cl⁻ and Br⁻ bridging ligands were shown to be due partly to a diminution of the intrinsic reorganization barrier to electron transfer, while the smaller catalyses induced by polyatomic inorganic and organic bridges appear to arise chiefly by enhancements of the reactant concentration at the electrode surface.

The effect of varying the electrode material upon the rates of simple outer-sphere electrode reactions was studied in order to test the theoretical prediction that the nature of the electrode material should not influence the rates beyond electrostatic double-layer effects. Although this prediction was approximately verified for Co(III)/(II) ammine couples, very substantial (up to ca 10⁸-fold) differences in

rate parameters were seen for a number of M(III)/(II) aquo couples between mercury, platinum, gold, and silver electrodes. These rate variations appear to reflect the influence of hydrogen-bonding interactions between the aquo reactants and interfacial water molecules, the structure of the latter being strongly influenced by the nature of the metal substrate. It is proposed that outer-sphere reactions can therefore be usefully divided into "surface structure-insensitive" and "surface structure-sensitive" categories. However, at a given metal surface, the influence of the electrostatic double-layer appears to be broadly in accordance with the predictions of the classical Frumkin model both in the absence and presence of specific ionic adsorption, once the likely noncoincidence of the reaction site and the outer Helmholtz plane is taken into account.

Solvent structural influences upon electron-transfer processes have also been probed by monitoring the dependence of redox kinetics and equilibria upon temperature and to the replacement of H₂O by D₂O solvent. These and other studies illustrate the importance of specific ligand-solvent interactions to the energetics of electron transfer.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Organosilicon Chemistry
2. PRINCIPAL INVESTIGATOR: Dr. William Weber
Department of Chemistry
University of Southern California
Los Angeles, CA 90007
3. INCLUSIVE DATES: 1 October 1976 - 30 September 1979
4. GRANT NUMBER: AFOSR-77-3123
5. COSTS AND FY SOURCE: \$41,961, FY77; \$42,843, FY78; \$45,244, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. Tai Shan Fang
Dr. Hiroshige Okinoshima
Dr. Bruce I. Rosen
7. JUNIOR RESEARCH PERSONNEL:

Shin-Shin Chen	H. S. D. Soysa
James Chihi	Kent P. Steele
Sair Hogopian	Robert Swaim
Bruce I. Rosen	Dongjaw Tzeng
Gowrie N. Soysa	Tai Yin Yang
8. PUBLICATIONS:

"Synthesis of 4,5-Dihydrobenz[b]furans, 4,5-Dihydrobenzo[b]thiophenes, and 4,5-Dihydroindols - Vacuum Pyrolysis - Electrocyclic Reactions," B. I. Rosen and William P. Weber, Tetrahedron Letters, 151 (1977).

"A New Route to Dimethylsilanone [(CH₃)₂Si=O]; Deoxygenation of Dimethylsulfoxide by Dimethylsilylene," H. S. D. Soysa, H. Okinoshima, and William P. Weber, J. Organometal. Chem., 133, C-17 (1977).

"Cyclization via Pyrolysis," William P. Weber and Brice Irwin Rosen, Chemical Technology, 690 (1977).

"Facile Reduction of Sulfoxides by Disilthianes," H. S. D. Soysa and William P. Weber, Tetrahedron Letters, 235 (1978)

- "Photolysis of Aryl Substituted Disilanes in the Presence of DMSO," Hiroshige Okinoshima and William P. Weber, J. Organometal. Chem., 149, 279 (1978).
- "Insertion of Methylphenylsilylene in Cyclic Siloxanes - Effect of Ring Size on Siloxane Reactivity," H. Okinoshima and W. P. Weber, J. Organometal. Chem., 150, C25 (1978).
- "Photolysis of Heptamethyl-2-phenyltrisilane and Octamethyl-2,3-diphenyltetrasilane in the Presence of DMSO," Hiroshige Okinoshima and William P. Weber, J. Organometal. Chem., 155, 165 (1978).
- "Reduction of Sulfoxides by Dichlorocarbene under Phase Transfer Catalysis Conditions," H. S. D. Soysa and William P. Weber, Tetrahedron Letters, 1969 (1978).
- "Pyrolysis of Hexamethylcyclotrisilthiane and Tetramethylcyclo-disilthiane in the Presence of Cyclic Siloxanes. Evidence for the Intermediacy of Dimethylsilathione $[(CH_3)_2Si=S]$," H. S. D. Soysa and William P. Weber, J. Organometal. Chem., 165, C1 (1979).
- "Pyrolysis of 1,1,2,2-Tetramethyl-1,2-Disila-3,6-Dithiacyclohexane - Evidence for Dimethylsilathione $[(CH_3)_2Si=S]$ Intermediate," H. S. D. Soysa, I. N. Jung, and W. P. Weber, J. Organometal. Chem., 171, 177 (1979).
- "Reinvestigation of the Photolysis of Aryl-Substituted Disilanes in the Presence of Dimethylsulfoxide," H. S. Dilanjan Soysa and William P. Weber, J. Organometal. Chem., 173, 269 (1979).
- "Photo-Oxidation of 1,1,1-Trimethyl-2,2,2-Triphenyldisilane by DMSO," Robert E. Swaim and William P. Weber, J. Am. Chem. Soc., 101, 5703 (1979).
- "Insertion of Dimethylsilylene into O-H and N-H Single Bonds," Tai-Yin Yang Gu and William P. Weber, J. Organometal. Chem., in press.
- "Mechanism of the Reactions of Dimethylsilylene with Oxetanes," Tai-Yin Yang Gu and William P. Weber, J. Am. Chem. Soc., submitted.
- "Mass Spectrometry of Aryl-substituted Di- and Tri-Siloxanes," Robert E. Swaim and William P. Weber, J. Organic Mass Spectrometry, submitted.
- "Organosilicon Chemistry," William P. Weber, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Several areas of silicon chemistry have been explored. Two methods to photochemically generate silicon-oxygen doubly bonded intermediates--silanones--in solution have been developed. Dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane deoxygenates dimethylsulfoxide (DMSO) to yield dimethylsilanone and dimethylsulfide (DMS). Photo-oxidation of aryl substituted disilanes by DMSO has been shown to proceed by two major pathways. One involves direct oxidation of the Si-Si single bond of the disilane to yield a disiloxane and DMS. The second results in formation of an aryl substituted monosilane, a silanone reactive intermediate and DMS. The ratio of these two pathways is affected by solvent. The second is maximized in furan. This combined with the high quantum yields for these photo-oxidation reactions permits the efficient generation of silanone intermediates. Insertion of silanone intermediates into Si-O single bonds of siloxanes is not limited to angle strained Si-O bonds as is the case for silylene insertions. These silanone insertion reactions may provide new ways to functionalize silicone polymers.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: High Energy Sources and Materials: High-Temperature Molecules and Molecular Energy Storage
2. PRINCIPAL INVESTIGATOR: Professor William Weltner, Jr.
Department of Chemistry
University of Florida
Gainesville, Florida 32611
3. INCLUSIVE DATES: 1 November 1975 - 31 October 1980
4. GRANT NUMBER: AFOSR 76-2906
5. COSTS AND FY SOURCE: \$74,027, FY76; \$75,000, FY77; \$75,000, FY78;
\$84,000, FY79; No-Cost Extension FY 80
6. SENIOR RESEARCH PERSONNEL:

Dr. W. R. M. Graham	Dr. R. J. Van Zee
Dr. J. M. Brom, Jr.	Dr. A. Dendramis
Dr. R. R. Lembke	Dr. S. V. Bhat
Dr. T. C. DeVore	
7. JUNIOR RESEARCH PERSONNEL:

B. R. Bicknell	J. L. Wilkerson
J. V. Martinez	C. M. Brown
R. F. Ferrante	K. J. Zeringue
M. L. Seely	
8. PUBLICATIONS:

"ESR of Methylene in Neon, Argon, and Krypton Matrices," B. R. Bicknell, W. R. M. Graham and W. Weltner, Jr., J. Chem. Phys., 64, 3319 (1976).

"ESR Spectrum of the BeOH Molecule," J. M. Brom, Jr. and W. Weltner, Jr., J. Chem. Phys. 64, 3894 (1976).

"B Atoms, B₂, and H₂BO Molecules: ESR and Optical Spectra at 4°K," W. R. M. Graham and W. Weltner, Jr., J. Chem. Phys., 65, 1516 (1976).

"ESR of C & 2 - in Various Ion Pairs at 4°K and the Theory of V Centers," J. V. Martinez de Pinillos and W. Weltner, Jr., J. Chem. Phys., 65, 4256 (1976).

"SiCO, SiN₂, and Si(CO)₂ Molecules: Electron Spin Resonance and Optical Spectra at 4°K," R. R. Lembke, R. F. Ferrante, and W. Weltner, Jr., J. Am. Chem. Soc., 99, 416 (1977).

"TiF₂ and TiF₃ Molecules: Electron Spin Resonance Spectra in Rare-Gas Matrices at 4°K," T. C. DeVore and W. Weltner, Jr., J. Am. Chem. Soc., 99, 4700 (1977).

"YbH and YoD Molecules: ESR and Optical Spectroscopy in Argon Matrices at 4°K," R. J. Van Zee, M. L. Seely, and W. Weltner, Jr., J. Chem. Phys., 67, 861 (1977).

"ESR Spectra of the MnO, MnO₂, MnO₃, and MnO₄ Molecules at 4°K," R. F. Ferrante, J. L. Wilkerson, W. R. M. Graham, and W. Weltner, Jr., J. Chem. Phys., 67, 5904 (1977).

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was the characterization of molecular species which are important because of (a) their occurrence in high-temperature environments, as for example in the vapor over refractory solids, and in combustion, flames, and propellant burning; (b) their relevance to clarification and/or extension of the basic theory of molecular properties. The molecules studied were usually highly reactive or metastable and often inaccessible by the usual gas-phase spectroscopic methods. They were therefore trapped in a solid matrix, usually neon or Argon, at 4°K, and investigated by optical and electron-spin-resonance (ESR) spectroscopies. This isolation procedure is known to produce only small perturbations and to yield information pertinent to the gas-phase species. The species studied included boron and bromine atoms, methylene radicals, diatomic boron, beryllium hydroxide, diatomic chlorine anion, carbonyl silene, diazasilene, the first-row transition-metal mono-, di-, and tri-fluorides and their corresponding hydrides and oxides, and a few rare-earth hydrides and fluorides. Vibrational frequencies, electronic transitions, g factors, spin-rotation constants, hyperfine coupling constants, zero-field-splittings, ground-state multiplicities, and perhaps some information about structure, were obtained. The molecules contained from one to seven unpaired electrons.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Gas-Surface Dynamics
2. PRINCIPAL INVESTIGATOR: Dr. Lennard Wharton
Department of Chemistry
University of Chicago
Chicago, Illinois 60637
3. INCLUSIVE DATES: 1 December 1978 - 30 November 1979
4. GRANT NUMBER: AFOSR 77-3186
5. COSTS AND FY SOURCE: \$45,000, FY77; \$50,000, FY78; \$54,987, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. Daniel Auerbach (IBM Research Labs, San Jose, Calif.)
Dr. Kenneth Janda (California Institute of Technology)
Dr. Daniel Winicur (Visiting Scientist, Notre Dame University)
7. JUNIOR RESEARCH PERSONNEL:

Jerry Horst
James Cowin
Jinwa Lee
Charles Becker
8. PUBLICATIONS:

"Energy Accommodation and Reactivity of O₂ on Tungsten," Lennard Wharton, Daniel Auerbach, Charles Becker and James Cowin, Appl. Phys., 14, 141 (1977).

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"Intermolecular Potentials and Energy Exchange Processes Between Alkali Halides and Other Gases as Determined by Scattering Experiments," Lennard Wharton, chapter in a book tentatively entitled Alkali Halide Vapors, edited by Paul Davidovits and D. L. McFadden (Academic Press, N.Y., 1978).

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"Direct Measurement of Velocity Distributions in Argon Beam-Tungsten Surface Scattering," K. C. Janda, J. E. Hurst, C. A. Becker, J. P. Cowin, Daniel J. Auerbach, L. Wharton, J. Chem. Phys. (in press).

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"Oxidation of CO on Pt(111)," C. Becker, (in preparation).

"He Diffraction Study of Surface Structure of H on Pt(111)," J. Lee, (in preparation).

"Ar, Xe Energy Accommodation on Pt(111)," J. Hurst, (in preparation).

"HD Exchanger Reaction on Pt(111) Studied by Laser Induced Desorption and Modulated Molecular Beams," J. Cowin, (in preparation).

"CO Desorption and Adsorption on Pt(111)," D. Minicur, J. Hurst, C. Becker, to be submitted to Surf. Sci.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This was a study of the specialized aspects of fundamental processes of gas-surface dynamics. The studies included a range of adsorbate-substrate chemical and physical combinations. Particular emphasis was directed toward understanding the processes of desorption at especially high rates. An extremely rapid temperature jump was induced by laser radiation heating of a metallic substrate. The ensuing temperature ramp served as a shutter for observing the velocity distribution of the desorbing species by time-of-flight methods. Further studies of gas-surface dynamics were conducted with the aid of a doubly differentially pumped rotatable mass spectrometer detector and highly differentially pumped supersonic and thermal dosing beams. These studies are relevant to effects of high power laser beams on surfaces, in particular the initial products of such situations. The instrumentation and techniques developed provide a better understanding of the causes of susceptibility to laser damage and remedies for it. The studies give fundamental information on processes and reactions that occur at high speeds and high temperatures involving gases and solids. These include evaporation, chemical reactions, and energy exchange. Related studies have included measurement of the velocity and angular distributions of atoms and molecules involved in physical and chemical gas-surface-processes, in which the initiation and control come from high speed mechanical chopping of molecular beams.

Two studies were performed using gas-surface laser desorption, an earlier one desorbing H_2 from W, and a later one, with the improved laser, desorbing H_2 from Pt(111). The later Pt studies have extended our knowledge of the phenomena of H_2 desorption from Pt to such a high temperature and surface coverage that a much more reliable measure of the activation energy of desorption and the pre-exponential frequency factor of this process was determined than could otherwise be obtained under the controlled conditions of UHV, single crystal surface.

The accommodation processes of noble gases and unreacted molecules such as O_2 and N_2 on clean metal surfaces were shown to involve accommodation coefficients that are independent of beam energy and surface temperature over wide ranges. The nature of the direct inelastic scattering channel was determined. The values of these translational accommodation coefficients have been measured, and they have been the subject of considerable theoretical modeling of gas-surface energy exchange, stimulated by the accurate and comprehensive measurements that have been reported by this laboratory.

The study of the oxidation of CO on Pt(111) has revealed that this mechanism involves an activated complex whose energy of activation appears in the translational energy of the products.

Rich patterns of diffraction of He from H on Pt(111) have determined the exact geometry of the H overlayer on Pt(111). The H is bound in the 3-fold site on the Pt(111) in a single domain. The amplitude of the repulsion potential of this surface has been determined by modeling the He scattering with a 2-dimensional repulsion wall model.

The nature of the mechanisms of surface reaction of O₂ and N₂ on W were determined by analysis of the energy and angle of the unreacted O₂ and N₂ molecules. O₂ reacts via direct chemisorption, while N₂ reacts via a molecular precursor mechanism, the efficiency of which diminishes as the surface temperature is raised through re-evaporation and direct inelastic scattering of the N₂.

AFOSR Program Manager: Lorelei A. Krebs, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: X-Ray Photoelectron Spectroscopic Studies of Electrode Surfaces
2. PRINCIPAL INVESTIGATOR: Professor Nicholas Winograd
Chemistry Department
Purdue University
West Lafayette, IN 47907
3. INCLUSIVE DATES: 15 January 1976 - 14 December 1979
4. GRANT NUMBER: AFOSR-76-2974
5. COSTS AND FY SOURCE: \$36,286, FY76; \$75,000, FY77; \$50,000, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. Theo Fleisch
Dr. Kwang Kim
Dr. Vanecia Young
7. JUNIOR RESEARCH PERSONNEL:

Stephen Gaarenstroom
Richard Hewitt
John Brace

Richard Gibbs
John Holland
John Hammond
8. PUBLICATIONS:

"Detection of High Mass Cluster Ions Sputtered from Bi Surfaces,"
A. Shepard, R. W. Hewitt, G. S. Slusser, W. E. Baitinger, N. Winograd,
R. G. Cooks, A. Varon, G. Devant, and W. N. Delgass, Chem. Phys. Lett.,
44, 371, (1976).

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Galvanostatic Oxidation of Pt Electrodes," J. S. Hammond, and
N. Winograd, J. Electroanal. Chem., 78, 55 (1977).

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Ag and Cu on Pt Electrodes," J. S. Hammond and N. Winograd,
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"Stoichiometric Determination of Chlorophyll a Water Aggregates and Photosynthesis. Symbiotic Roles of the Mg Atom and the Ring V Cyclopentanone Group in the Structural and Photochemical Properties of Chlorophyll a Monohydrate and Dihydrate," J. C. Brace, F. K. Fong, D. H. Karweik, V. Koester, A. Shepard, and N. Winograd, J. Am. Chem. Soc., 50, 1286 (1978).

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"Ejection of Molecular Clusters from Ion Bombarded Surfaces," B. J. Garrison, N. Winograd and D. E. Harrison, Jr., J. Vac. Sci. Tech., 16, 789 (1979).

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"Classical Trajectory Calculations of the Energy Distribution of Ejected Atoms from Ion Bombarded Single Crystals," B. J. Garrison, N. Winograd, and D. E. Harrison, Jr., Surface Sci., 87, 101 (1979).

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"Detection of Reversibly Bound Adsorbates by SIMS, CO on Ni(001) and Polycrystalline Iron," T. Fleisch, G. L. Ott, W. N. Delgass, and N. Winograd, Surface Sci., submitted.

"Oxidation of Polycrystalline Indium Studies by XPS and Static SIMS," R. W. Hewitt and N. Winograd, J. Applied Phys., submitted.

"X-Ray Photoelectron Spectroscopic Studies of Electrode Surfaces," N. Winograd, Final Technical Report, AFOSR-TR-80-0420.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The basic objective of this research has emphasized the development of x-ray photoelectron spectroscopy (XPS) in characterizing electrochemical reaction mechanisms. During the last several years, attention has been focused on developing XPS as a mechanistic aid in following electrode

reactions, primarily those whose surfaces can be altered by the formation of oxide layers. In addition, the method has proved valuable in examining the surface chemistry of metal electrodes where monolayers of foreign metal ions can be deposited at underpotential. These studies are particularly relevant to electrocatalysis since trace metals interacting with an electrode surface can drastically alter the electrode characteristics. The idea has been exploited that the information gleaned about surfaces by XPS can be greatly enhanced by coupling this spectroscopy with other types such as secondary ion mass spectrometry (SIMS).

The major advantages of XPS to the study of electrode surfaces are that the depth sensitivity to most metals is quite high with the escape length of the emitted electrons occurring only through 10-10Å of the sample surface. In addition, the measured binding energies are sensitive to the oxidation state of the metal atom. Using specially designed apparatus for transferring the electrode into the vacuum system, the growth of PtO , Pt(OH)_2 and PtO_2 films on platinum oxidized in acidic media were successfully monitored. It was also possible to monitor the thickness of the overlayer by following the intensity of the various peaks.

Of special recent interest is the incorporation of additional surface analysis methods to the XPS spectrometer. The combination of XPS and SIMS seems particularly appropriate since many of the disadvantages of XPS are offset by the additional capability of SIMS. Its ability to detect hydrogen is such an example. The instrument design philosophy is to connect two satellite vacuum systems via a set of magnetically driven transfer devices. This configuration allows each technique to have its own chamber and allows a separate chamber for electrode preparation. This combined approach has been illustrated in numerous applications of the study of metal/oxygen systems.

A final accomplishment in the work is the investigation of high energy ion beams for use in the ion implantation of various substrates aimed at the possibility of creating new materials with unusual properties. Initial studies have been focused on the use of Cu^+ , Ag^+ and Au^+ ion beams directed toward SiO_2 and graphite. For these systems, the XPS measurements reveal the implanted atoms have atomic-like electronic structures similar to the underpotential deposition procedure discussed earlier. The relevance of these investigations to electrochemical studies is preliminary, but this idea has considerable future potential, since ion implantation methods could be used to prepare high purity doped electrodes or to prepare corrosion resistance surfaces by implantation of trace quantities of transition metals.

This work has focused on the development of modern surface analysis methods, particularly XPS and SIMS, for the characterization of metal or

electrochemically modified surfaces. The chemical specificity and surface sensitivity of these methods clearly provides a new dimension to the ability to characterize these systems. It will be particularly interesting in the future to extend these systems to more complex surfaces such as alloys and metals covered with organic films, since the electrochemical properties of these assemblages are only barely known.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Polybenzothiazoles: Synthesis and Characterization

2. PRINCIPAL INVESTIGATOR: Dr. James F. Wolfe
Chemistry Laboratory
SRI, International
Menlo Park, CA 94025

3. INCLUSIVE DATES: 1 September 1978 to 31 August 1980

4. CONTRACT NUMBER: F49620-78-C-0110

5. COSTS AND FY SOURCE: \$4,990, FY78; \$98,776, FY79; \$60,088, FY80

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Step-Growth Propagation of High-Molecular Rigid Rod Polymers," James F. Wolfe, Annual Report, Contract F49620-78-C-0110, 15 Mar 1980.

"Step-Growth Propagation of High-Molecular Weight Rigid Rod Polymers, James F. Wolfe, Final Technical Report, Contract F49620-78-C-0110, 15 December 1980.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to investigate the chemistry and structural requirements of several monomers that form the benzothiazole unit, and to study the effects of various synthesis parameters on the formation of high molecular weight wholly aromatic polymers containing benzothiazole units.

The necessary controls for the reproducible preparation of the rodlike polymer poly {[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]1,4-phenylene}, referred to as PBT, were defined. The polymer was prepared with intrinsic viscosities as high as 30 dl/g. The following factors were found to dramatically affect the attainable molecular weight in the polymerization of PBT; monomer purity, monomer particle size, complete PPA deaeration, complete dehydrohalogenation, heating schedule, sufficient reaction time. Bulk forms with a high degree of fibrillar structure in the direction of shear were prepared from PBT/PPA solution. This system shows great promise for use in high modulus, high strength applications.

The synthesis of two isomeric poly(benzothiazoles) via the self-polycondensation of two isomeric (o-aminomercapto)benzoic acids was investigated. Poly(2,6-benzothiazole) was prepared from 4-amino-3-mercaptobenzoic acid in polyphosphoric acid at concentrations 3 to 10%. Intrinsic viscosities between 3 and 4.6 dL/g in methanesulfonic acid were obtained. The purity of the requisite monomer for poly(2,5-benzothiazole), namely 3-amino-4-mercaptobenzoic acid was not sufficient to obtain high molecular weight polymer. The polymers are candidate matrix resins for molecular composites with the rigid polymer, poly(p-phenylene benzobisthiazole) (PBT).

This research is being conducted within the AFWAL/ML-AFOSR Order Polymers Research Program.

AFOSR Program Manager: Dr. Donald R. Ulrich

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