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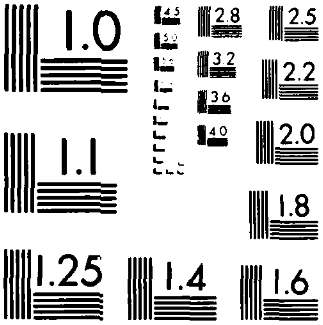

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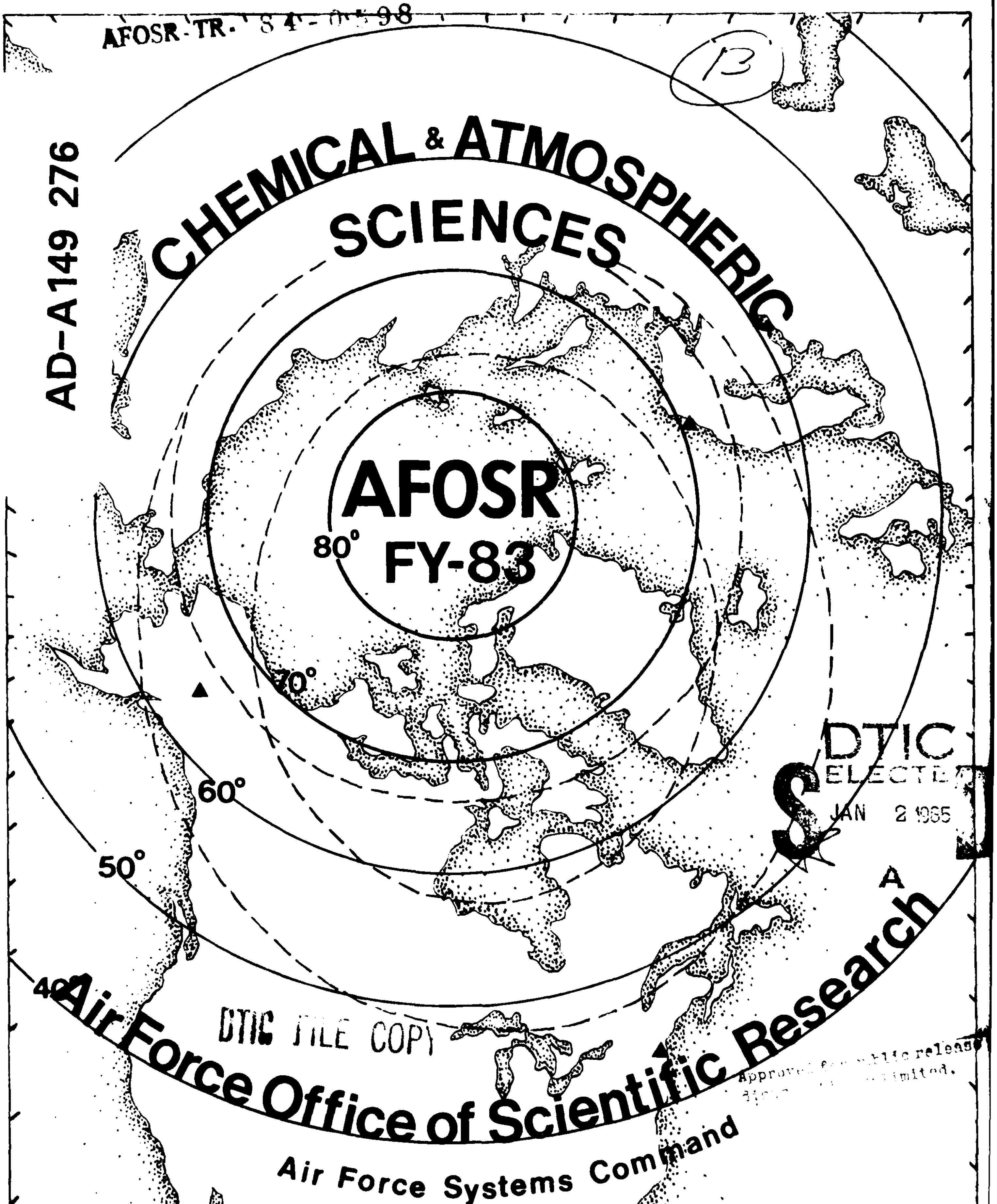
CHEMICAL & ATMOSPHERIC SCIENCES

AFOSR FY-83



Air Force Office of Scientific Research

Air Force Systems Command

USAF 28th edition

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COVER

RADAR MAPPING OF IONOSPHERIC DISTURBANCES

The performance of worldwide communications and surveillance systems is significantly affected by disturbances in the earth's ionosphere. Atmospheric scientists are conducting research to bring to fruition the development of models which predict the future state of the ionosphere and, in particular, ionospheric disturbances. One of the major tools for ionospheric research is the high-power incoherent scatter radar (ICS), but heretofore only single radar site measurements of temporal variations were possible due to the absence of ICS research radar facilities. During parts of 1981 and 1982, the auroral zone of the ionosphere was simultaneously observed from three longitudinally separated radar sites, shown as small triangles on the cover, and the NASA Dynamics Explorer Satellite. Both geographic and magnetic latitudes are depicted in the diagram.

Analysis of the simultaneous measurement data is proceeding with valuable contributions being made to the understanding of the high latitude ionosphere. A particular value of the multiple-site data is its value to determining the performance of ionospheric research models. In particular, a comparison of the performance of a global model to real data has produced very encouraging results, strongly suggesting that a truly predictive ionospheric model may evolve based on input data requirements now being investigated.

This program has moved from the comprehensive and systematic accumulation of data to in-depth analysis. The long-term payoff will be accurate prediction of the global ionospheric variability in electron density which controls the reliability of high frequency radio communication and surveillance systems.

The work was and is being done by a multinational team consisting of SRI, MIT, Utah State University, University of Texas at Dallas, the French organization of CNET/CNRS, and the European EISCAT organization and in cooperation with the National Science Foundation and the National Center for Atmospheric Research.

The cover art was designed after an SRI figure and drawn by Patricia A. Myers.

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Atmospheric Sciences Mesoscale Weather Forecasting Cloud Physics,
Radar Atmospheric Research Upper Atmosphere

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 Science 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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28TH AFOSR
CHEMICAL & ATMOSPHERIC SCIENCES
PROGRAM REVIEW
FY83

LEE E. MYERS, EDITOR
IRIS M. CROSS, MANAGING EDITOR

JUNE 1984

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
DIRECTORATE OF CHEMICAL AND ATMOSPHERIC SCIENCES
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WASHINGTON, D. C. 20332

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EDITORS' FOREWORD

The format of the 28th edition of the Chemical and Atmospheric Sciences Review is essentially the same as the 27th edition's format. We have decided to continue publication of the short descriptions of Air Force in-house laboratory research in basic chemical and atmospheric sciences. This year the funding chart has been shortened to reflect the constant dollar budgets for only the last ten years of Air Force basic chemical research. We have continued to organize the active research programs and completed project summaries by program manager. This will help users of the review locate material most relevant to their interests. We invite your comments and suggestions on methods to improve our Chemical and Atmospheric Sciences Review. A copy of AFSC Form 459 is included inside the front cover for this purpose.

The editors wish to thank all of the Directorate of Chemical and Atmospheric Sciences staff for their assistance and timely submission of material for this tome. Special thanks go to our secretarial staff for the long hours and dedication to completion of this year's review.

Lee E. Myers

Iris M. Cross

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 by defense technology.

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.

DEPARTMENT OF DEFENSE

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

June 1984

TO: FRIENDS OF AFOSR

The preparation and publication of this annual report represents a major investment of time and energy by the Directorate staff. We consider it time well spent and that we have a responsibility to advise the scientific public of our planned areas of research emphasis as well as past successes. We ask for your help in assuring that the limited number of copies of this report reaches the hands of those interested in it. Your prompt return of the enclosed survey card will assure your continued receipt of future editions (if you wish it). If we do not hear from you, we will conclude that your place on the mailing list can be yielded to someone else.

Sincerely,

Donald L Ball

DONALD L. BALL
Director of Chemical and
Atmospheric Sciences

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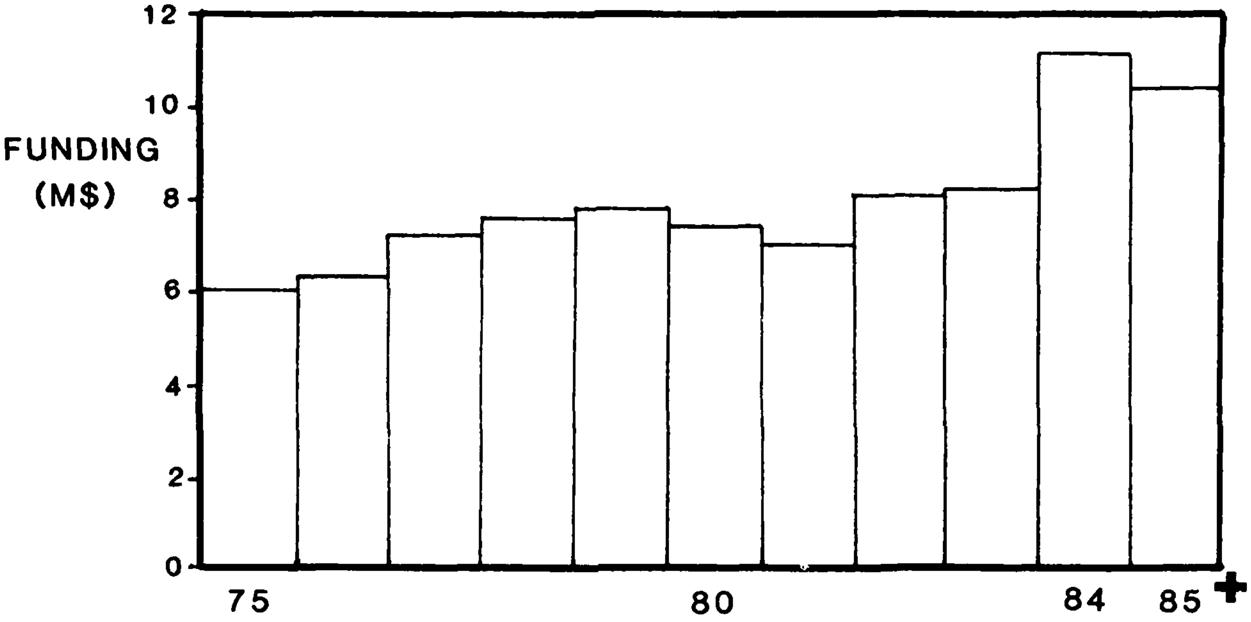
RECENT CHEMISTRY FUNDING

1984 Dollars*



+ 1984 basis year

* projected budget and inflation

FY 83 CHEMISTRY & ATMOSPHERIC SCIENCES PROGRAM STATISTICS

Total number of proposals received	314
Total number of inquiries received	235
New work efforts initiated	86
Renewals	74
Proposals declined	143
Proposals withdrawn	7
Proposals transferred	4
Conferences and Symposia supported	10

CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY 83 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.

1983 Gordon Research Conference on Electrochemistry

Dr. Cruickshank
Santa Barbara, CA
23-28 January 1983

International Conference on Ultrastructure Processing of
Ceramics, Glasses, and Composites

Dr. L. Hench
Gainesville, FL
13-16 February 1984

Symposium on the Chemistry and Physics of Electrocatalysis

Dr. J. McIntyre
Electrochemical Society, Inc.
San Francisco, CA
8-13 May 1983

Conference on Crack Tip Structure and Processes

Dr. R. Thomson
National Bureau of Standards
Gaithersburg, MD
6-8 June 1983

1983 Conference on the Dynamics of Molecular Collisions

Dr. D. Truhlar
Gull Lake, MI
26 June - 1 July 1983

International Meeting on Nitrations

Dr. D. Ross
SRI International, Inc.
Menlo Park, CA
27-29 July 1983

1983 Gordon Conference on the Dynamics of Gas-Surface Interactions

Dr. J. Yates
Plymouth, New Hampshire
1-5 August 1983

2nd International Symposium on Halide Glasses

Dr. C. Moynihan
Troy, NY
2-5 August 1983

The Sixth International Summer Institute in Surface Science
(ISISS 1983)

Dr. R. Vanselow
Milwaukee, WI
22-26 August 1983

11th International Conference on Organometallic Chemistry

Dr. E. Ashby
Callaway Gardens, Pine Mountain, GA
10-14 October 1983

ACTIVE RESEARCH EFFORTS

As of 1 October 1983

CHEMICAL TECHNIQUES - DENTON W. ELLIOTT

Surface Processes and Trace Analysis Using Solid Electrodes AFOSR-83-0004	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, NY 14214
Evaluation of Chemical and Atmospheric Sciences Research Relevant to Current and Projected U.S. Air Force Interests F49620-81-C-0085	Joseph E. Earley Department of Chemistry Georgetown University Washington, DC 20057
New Materials for Electrochemical Cells AFOSR-83-0052	John B. Goodenough Peter G. Dickens Inorganic Chemistry Laboratory Oxford University Oxford, UK OX1 3QR
Synthesis Structure and Reactivity of Molecules Attached to Electrode Surfaces AFOSR-81-0149	Arthur T. Hubbard Department of Chemistry University of California, Santa Barbara Santa Barbara, CA 93106
Electrochemistry and Electrochemical Methodology in Molten Salts AFOSR-81-0007	Robert A. Osteryoung Janet G. Osteryoung Department of Chemistry State University of New York Buffalo, NY 14214
Fast Protonic Conducting Solid Electrolytes AFOSR-82-0221	Mark A. Ratner Donald H. Whitmore Department of Chemistry Northwestern University Evanston, IL 60201
Innovative Detection Separation and Sampling Techniques for Trace Analysis by Gas Chromatography AFOSR-84-0093	Robert E. Sievers Department of Chemistry University of Colorado Boulder, CO 80309

Molecular Structural Basis of Electrode Kinetics AFOSR-83-0011	Michael Weaver Department of Chemistry Purdue University West Lafayette, IN 47907
Analytical Gas Phase Spectrometry and Combustion Diagnostics F49620-84-C-0002	James D. Winefordner Department of Chemistry University of Florida Gainesville, FL 32611
Secondary Ion Mass Spectrometry Studies of Solids and Surfaces AFOSR-82-0057	Nicholas Winograd Department of Chemistry Pennsylvania State University University Park, PA 16802

SURFACE CHEMISTRY - CAPTAIN LEE E. MYERS

Picosecond Laser Studies of Energy Transfer in Molecules on Surfaces AFOSR-ISSA-83-00057	Richard R. Cavanagh John C. Stephenson Molecular Spectroscopy Division National Bureau of Standards Washington, DC 20234
Investigation of Surface Phenomena in Termionic Energy Conversion AFOSR-83-0105	Paul R. Davis Lynwood W. Swanson Dept of Appl Phy & Elec Sc Oregon Graduate Center Beaverton, OR 97006
Modulated Molecular Beam Investigation of the Reactions of Fluorine and Oxygen with Silicon Surfaces AFOSR-83-0115	Thomas Engel Department of Chemistry University of Washington Seattle, WA 98195
High Resolution Electron Energy Loss Studies of Chemisorbed Species on Aluminum and Titanium AFOSR-83-0131	James L. Erskine John M. White Department of Physics University of Texas Austin, TX 78712
Theoretical Studies of Laser-Induced Molecular Rate Processes: Topics in Line Broadening and Spectroscopy AFOSR-82-0046	Thomas F. George Department of Chemistry University of Rochester Rochester, NY 14627
Structure of Solid Surfaces in Wear Situations AFOSR-81-0005	James L. Lauer Department of Mechanical Engineering Rensselaer Polytechnic Institute Troy, NY 12181
Threshold Electron Studies of Gas-Surface Interactions AFOSR-83-0260	P. Terrence Murray University of Dayton Research Institute 300 College Park Avenue Dayton, OH 45469
Theoretical Investigation of Homogeneous and Heterogeneous Reactions in the Chemical Vapor Deposition of Silicon from Silane AFOSR-82-0311	Lionel M. Raff Department of Chemistry Oklahoma State University Stillwater, OK 74078

Surface Generation of Electronically Excited States of O_2 F49620-82-K-0025	T. G. Slanger Molecular Physics Laboratory SRI International 333 Ravenswood Avenue Menlo Park, CA 94025
Program to Explore and Evaluate the Influence of Surface Structural Defects on the Chemical Properties of Solid Surfaces AFOSR-83-0302	Peter C. Stair Department of Chemistry Northwestern University Evanston, IL 60201
Secondary Ion Mass Spectrometry Studies of Solids and Surfaces AFOSR-82-0057	Nicholas Winograd Department of Chemistry Pennsylvania State University University Park, PA 16802
Chemistry of Non-Equilibrium Film Deposition F49620-81-C-0074	Francis J. Wodarczyk Rockwell International Science Center Thousand Oaks, CA 91360
Structure of Molecular Adsorbates on Surfaces AFOSR-82-0133	John T. Yates, Jr. Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260

CHEMICAL STRUCTURES - DR. DONALD R. ULRICH

Microdesigning of Lightweight/ High Strength Ceramic Materials AFOSR-83-0375	Ilhan A. Aksay Dept of Mining Metallurgical University of Washington Seattle, WA 98195
Large Molecule Diffusion and Interfacial Effects in Oriented Polymers AFOSR-82-0290	R. Edward Barker, Jr. Kenneth R. Lawless Department of Materials Science University of Virginia Charlottesville, VA 22901
Light Scattering Studies of Molecular Dynamics in Molecular Crystals, Liquid Crystals, and Polymers for Applications in Chemical Defense AFOSR-82-0122	Elliot R. Bernstein Department of Chemistry Colorado State University Fort Collins, CO 80521
Basic Research on Processing of Ceramics for Space Structures AFOSR-83-0192	H. K. Bowen R. L. Pober Materials Processing MIT Cambridge, MA 02139
Pulsed Microwave Characterization of Conducting Polymers AFOSR-82-0184	Larry R. Dalton Department of Chemistry University of Southern California Los Angeles, CA 90007
Physical and Morphological Properties of Polymers AFOSR-82-0009	Paul J. Flory Department of Chemistry Stanford University Stanford, CA 94305
BeF2 Based Glasses For Bulk Optical and Waveguide Applications F49620-83-C-0090	John R. Gannon Corning Glass Works Exploratory Research Department Corning, NY 14831
Improvement and Optimization of Internal Damping in Fiber Reinforced Composite Materials AFOSR-83-0156	Ronald F. Gibson Dept of Mechanical Engineering University of Idaho Moscow, ID 83843
Microstructural Engineering of Lightweight Ceramic Structures F49620-83-C-0078	David Green Department of Engineering Rockwell International Thousand Oaks, CA 91360

Ultrastructure Processing Research on Advanced Ceramics and Composites F49620-83-C-0072	Larry L. Hench Department of Materials Science University of Florida Gainesville, FL 32611
NMR Study of Disordered Materials Under Extreme Conditions of Pressure and Temperature AFOSR-81-0010	Jiri Jonas Department of Chemistry University of Illinois Urbana, IL 61801
Ultrastructure Processing of Macromolecular Materials F49620-83-K-00006	Frank E. Karasz Polymer Science & Engineering University of Massachusetts Amherst, MA 01003
Fundamental Studies of Time-Dependent Response and Fracture of Cross-Linked Polymers F49620-83-C-0032	Frank N. Kelley Maurice Morton Institute of Polymer Science University of Akron Akron, OH 44325
New Materials for Spacecraft Stability and Damping - A Feasibility Study AFOSR-83-0221	John D. Mackenzie Dept of Mat Science & Engrg School of Engrg & Applied Sc University of California Los Angeles, CA 90024
Preparation & Properties of Halide Glasses and Glass-Polymer Composites AFOSR-84-0022	John D. Mackenzie Dept of Mat Science & Engrg School of Engrg & Applied Sc University of California Los Angeles, CA 90024
High-Performance Polymeric Materials AFOSR-83-0027	James E. Mark Department of Chemistry University of Cincinnati Cincinnati, OH 45221
Aromatic Polyester-Polysiloxane Block CoPolymers: Multiphase Transparent Damping Materials AFOSR-83-0201	James E. McGrath Department of Chemistry Virginia Polytechnic Institute and State University 301 Burruss Hall Blacksburg, VA 24061
Ultra Low Thermal Expansion Ceramics AFOSR-83-0291	H. A. McKinstry Materials Research Laboratory Pennsylvania State University Philadelphia, PA

Surface Chemistry and Structural Effects in the Stress Corrosion of Glass and Ceramic Materials AFOSR-82-0013	Carlo G. Pantano Department of Materials Pennsylvania State University University Park, PA 16802
Molecular Mechanics of Polymeric Interactions in Relation to Chemical Defense AFOSR-82-0118	Paras N. Prasad Department of Chemistry State University of New York Buffalo, NY 14260
Development of Spacecraft Materials and Structures Fundamentals F49620-83-C-0101	Svante Prochazka Stephen L. Dole Ceramics Br, Inorganic Mat Lab General Electric Co Schenectady, NY 12301
Exploitation of the Sol-Gel Process in Preparation of New Ceramics AFOSR-83-0212	Rustum Roy Pennsylvania State University Materials Research Laboratory University Park, PA 16802
Improvement and Optimization of Internal Damping in Fiber Reinforced Composite Materials AFOSR-83-0154	C. T. Sun Dept of Engineering Sciences University of Florida Gainesville, FL 32611
Microstructure of Amorphous and Semi-Crystalline Polymers AFOSR-81-0011	Donald R. Uhlmann J. B. Vander Sande Department of Materials Science & Engineering Massachusetts Institute of Technology Cambridge, MA 02139
Ordered Polymers for Space Applications F49620-83-K-0036	James F. Wolfe David B. Cotts Polymer Sciences Dept SRI International Menlo Park, CA 94025
Laser Beam Technology Promoting High Speed and Selective Plating Processes AFOSR-82-0236	J. Zahavi Technion-Israel Inst of Technology Israel Institute of Metals Haifa, IS 32 000
A Study on High Technology Ceramics in Japan AFOSR-ISSA-83-00049	Klaus M. Zwilsky Executive Director National Academy of Science Washington, D. C. 20418

MOLECULAR DYNAMICS - CAPTAIN LEE E. MYERS

Rates of Intramolecular Conversions Over Barriers AFOSR-80-0046	Simon H. Bauer Department of Chemistry Cornell University Ithaca, NY 14853
Energy Disposal in Ion-Molecule Reactions AFOSR-82-0035	Michael T. Bowers Department of Chemistry University of California Santa Barbara, CA 93106
Study in Molecular Lasers AFOSR-81-0028	George Burns Department of Chemistry University of Toronto Toronto, Ontario, Canada M5S 1A1
Physical Chemistry of Energetic Nitrides AFOSR-84-0031	R. D. Coombe Department of Chemistry University of Denver Denver, CO 80208
Ion Photofragment Spectroscopy: Structure and Dissociation of Molecular Ion F49620-81-K-0006	Philip C. Cosby James R. Peterson Molecular Physics Laboratory SRI International Menlo Park, CA 94025
Vibrational Relaxation Rates and Pathways in Highly Excited Molecules AFOSR-82-0244	F. Fleming Crim Department of Chemistry University of Wisconsin Madison, WI 53706
Gas-Phase Photoelectron Spectroscopy of Metals and Metal Oxides of Importance in the Upper Atmosphere AFOSR-83-0283	John M. Dyke Department of Chemistry The University of Southampton Highfield Southampton, SO9 5NH, UK
Rotational and Vibrational Spectra of Molecular Clusters F49620-83-C-0007	Thomas R. Dyke Department of Chemistry University of Oregon Eugene, OR 97403
Collisional Energy Exchange in Polyatomic Molecules F49620-84-C 0038	John B. Fenn Department of Engineering and Applied Science Yale University New Haven, CT 06520

Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties F49620-83-C-0010	Robert W. Field James L. Kinsey Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
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Laser-Induced Kinetics: An Experimental and Theoretical Program for the Study of Elementary Chemical Processes F49620-K-83-0001	David M. Golden Michel J. Rossi Physical Sciences Division SRI International Menlo Park, CA 94025
Spectroscopy and Energy Transfer Kinetics of Excited State of the Interhalogens: Laser Induced Fluorescence Studies of Metastable AFOSR-83-0173	Michael Heaven Department of Chemistry Illinois Institute of Technology Chicago, IL 60616
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Measurement of Rate Constants of Elementary Gas Reactions of Importance to Upper Atmosphere and Combustion Systems AFOSR-80-0207	Frederick Kaufman Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260
Computer Modeling of Pulsed Chemical Lasers AFOSR-80-0003	Ronald L. Kerber Electrical & Mechanical Engineering Department Michigan State University East Lansing, MI 48824

Theoretical and Experimental Studies in Reactive Scattering AFOSR-82-0341	Aron Kuppermann Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, CA 91125
State-Resolved Dynamics of Ion-Molecule Reactions in a Flowing Afterglow F49620-83-C-0013	Stephen R. Leone G. Barney Ellison Veronica M. Bierbaum Department of Chemistry University of Colorado Boulder, CO 80309
Analysis and Prediction of Experimental Results for Elementary Molecular Processes AFOSR-81-0030	Raphael D. Levine James L. Kinsey Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
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Energetic and Collision Dynamics of Electronic Transition Laser Systems F49620-81-C-0097	H. Michels Robert H. Hobbs United Technologies Research Center East Hartford, CT 06108
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Nanosecond IR Spectroscopy and Vibrational Enhancement of Chemical Reactions AFOSR-82-0031	G. Pimentel Department of Chemistry University of California at Berkeley Berkeley, CA 94720

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Experimental and Theoretical Studies of Molecular Dynamics F49620-83-C-0002	Stuart A. Rice Department of Chemistry University of Chicago Chicago, IL 60637
Theory and Experiments on Chemical Dynamics and Instabilities AFOSR-81-0125	John Ross Department of Chemistry Stanford University Stanford, CA 94305
Reactions of Laser-Generated Free Radicals at Semi-Conductor Surfaces AFOSR-83-0007	Jeffrey I. Steinfeld Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
Spectroscopic Studies of the Halogens AFOSR-83-0110	Joel B. Tellinghuisen Department of Chemistry Vanderbilt University Nashville, TN 37235
Photoionization Investigation of Iodine Molecules and Clusters in A Supersonic Molecular Beam AFOSR-83 0183	Edward A. Walters Department of Chemistry University of New Mexico Albuquerque, NM 87131
Dynamics of Fragmentation of Electronically Energetic Species Produced by Short-Pulsed UV Excitation of Molecules In the Gas Phase AFOSR-84-0019	Richard G. Weiss Department of Chemistry Georgetown University Washington, DC 20057
Studies of Energy Storage and Transfer AFOSR-82-0037	John Wiesenfeld Department of Chemistry Cornell University Ithaca, NY 14853
Laser Kinetic Spectroscopy of Unimolecular and Bimolecular Processes in the Gas Phase AFOSR-83-0022	Curt Wittig Hanna Reisler Dept. of Electrical Engineering Univ. of Southern California Los Angeles, CA 90087-1141
State Identification of Reaction Products AFOSR-81-0053	Richard N. Zare Department of Chemistry Stanford University Stanford, CA 94305

CHEMICAL REACTIVITY AND SYNTHESIS - DR. ANTHONY J. MATUSZKO

Distibines, New One-Dimensional Materials AFOSR-81-0099	Arthur J. Ashe, III Department of Chemistry University of Michigan Ann Arbor, MI 48109
Synthesis and Chemistry of Polynitrolkanes and Polynitroolefins F49620-83-K-0028	Clifford D. Bedford Robert J. Schmitt Chemistry Laboratory SRI International Menlo Park, CA 94025
New Approaches to the Synthesis of Novel Organosilanes AFOSR-80-0239	Philip Boudjouk Department of Chemistry North Dakota State University Fargo, ND 58105
New Approaches to Functionalized Fluorocarbons AFOSR-80-0259	Donald J. Burton Department of Chemistry University of Iowa Iowa City, IA 52242
A New Approach to Highly Fluorinated Lubricants AFOSR-82-0084	R. D. Chambers Department of Chemistry University of Durham Durham, England DH1 3LE
Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials F49620-83-C-0024	Michael J. S. Dewar Department of Chemistry University of Texas Austin, TX 78712
Picosecond Laser Studies of Chemical Intermediates AFOSR-84-0013	Kenneth B. Eisenthal Department of Chemistry Columbia University New York, NY 10027
Quantum-Theoretical Studies of Nerve Agents and Vesicant Compounds AFOSR-82-0100	Carl S. Ewig John R. Van Wazer Wolf D. Dettbarn Department of Chemistry Vanderbilt University Nashville, TN 37235
Electrolytic Preparation of Novel Azidodinitro Compounds F49620-83-C-0036	Milton B. Frankel Chemical Processing Rockwell International Canoga Park, CA 91304

Ground and Excited State Reactions of Phosphonofluoridic Acids and Esters and Their Isomers AFOSR-82-0190	Mark S. Gordon Department of Chemistry North Dakota State University Fargo, ND 58105
Effect of Toluene on the Solubility of Biohazardous Volatile Synthetic Organic Compounds AFOSR-83-0175	Ervin Hindin Civil & Env. Engineering Washington State University Pullman, WA 99164-2912
Polysilylated Unsaturated Molecules AFOSR-83-0244	Paul R. Jones Department of Chemistry North Texas State University Denton, TX 76203-5068
Structural and Synthetic Organosilicon Chemistry AFOSR-81-0185	Michael E. Jung Department of Chemistry University of California, Los Angeles Los Angeles, CA 90024
Synthesis of a Series of Acetylene Terminated Sulfone Oligomers: Structure Property Relationships AFOSR-83-0123	James J. Kane Department of Chemistry Wright State University Dayton, OH 45435
Polyphosphorus Compounds Containing Phosphorus-Nitrogen Bonds AFOSR-81-0051	R. Bruce King Chemistry Department University of Georgia Athens, GA 30602
New Experimental Challenges in Elemental Fluorine Chemistry AFOSR-82-0197	Richard J. Lagow Department of Chemistry University of Texas Austin, TX 78712
Structure and Reactivity of Perfluorinated Annulenes and Their Relatives AFOSR-83-0047	David M. Lemal Department of Chemistry Dartmouth College Hanover, NJ 03755
Investigation of Deviations from Ideality in the Two Liquid Phase Region of Systems of Medium Molecular Weight Hydrocarbon Mixtures AFOSR-83-0036	William G. MacIntyre C. W. Su Virginia Institute of Marine Science College of William and Mary Gloucester Point, VA 23062

Fabricable Polymers for Use Under Extreme Conditions AFOSR-82-0007	Carl S. Marvel Department of Chemistry University of Arizona Tucson, AZ 85721
Mechanisms and Kinetics of Diphthalocyanine Electrode Processes F49620-83-C-0088	M. M. Nicholson Electronics Research Division Rockwell International Corp Anaheim, CA 92803
Synthesis of Novel Nitrogen and Phosphorus Heterocycles F49620-82-C-0021	Kay L. Paciorek Chemical & Materials Research Ultrasystems, Inc. Irvine, CA 92664
The Chemistry of Precursors to Silicon-Carbide AFOSR-83-0209	Morey A. Ring H. Edward O'Neal Department of Chemistry San Diego State University San Diego, CA 92182
Basic Research in Novel Inorganic Reagents and Fluorocarbon Chemistry F49620-81-C-0020	C. J. Schack Rocketdyne Division Rockwell International Canoga Park, CA 91304
Organosilicon Compounds and Organosilicon Polymer Intermediates AFOSR-83-0003	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
Synthesis of Difluoraminoxy-, Difluoramino- or Fluorodiazonium-Containing Materials AFOSR-82-0247	Jean'ne M. Shreeve Department of Chemistry University of Idaho Moscow, ID 83843
Properties of Reactive Species Generated at High Temperatures and Their Low Temperature Reactions to Form Novel Substances AFOSR-82-0195	Philip S. Skell Department of Chemistry Pennsylvania State University University Park, PA 16802
Compounds Containing Heteronuclear Metal-Metal Bonds AFOSR-82-0070	F.G.A. Stone Department of Inorganic Chemistry University of Bristol Bristol, BS8 1TS, UK

Theoretical Study of Pentavalent Phosphorus AFOSR-82-0114	Andrew Streitwieser, Jr. Department of Chemistry University of California Berkeley, CA 94720
Spectroscopic Studies of the Halogens AFOSR-83-0110	Joel B. Tellinghuisen Department of Chemistry Vanderbilt University Nashville, TN 37235
Synthesis and Chemistry of Energetic Metallotetraazadienes AFOSR-83-0121	William C. Trogler Chemistry Department Northwestern University Evanston, IL 60201
Structural and Dynamics Studies of Materials Possessing High Energy Content AFOSR-84-0040	Nicholas J. Turro Department of Chemistry Columbia University New York, NY 10027
Chemistry of New Silicon Containing Polymers and Triply Bonded Silicon Intermediates AFOSR-82-0333	William P. Weber Department of Chemistry University of Southern California Los Angeles, CA 90007
Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials AFOSR-83-C-0044	Robert C. West Department of Chemistry University of Wisconsin Madison, WI 53706

ATMOSPHERIC SCIENCES - LT COL TED S. CRESS

MIIHRAS: Analysis Phase F49620-83-K-0005	Odile de la Beaujardiere Radio Physics Laboratory SRI International 333 Ravenswood Avenue Menlo Park, CA 94025
Behavior of the Atmosphere in the Desert Planetary Boundary Layer AFOSR-84-0036	Louis Berkofsky Meteorology Department Ben Gurion University of the Negev Beer-Sheva, Israel
The Growth Potential of Corona Discharges From Aircraft Flying In Precipitation AFOSR-83-0083	John A. Bicknell Institute of Science & Technology P.O. Box 88 University of Manchester Manchester M60 1QO England
Analysis and Prediction of Mid-Latitude Mesoscale Convective Precipitation Systems AFOSR-83-0064	T. N. Carlson Department of Meteorology Pennsylvania State University University Park, PA 16802
Nonlinear Internal Gravity-Wave Propagation, Saturation, and Absorption in the Atmosphere F49620-83-C-0061	Timothy J. Dunkerton Staff Scientist Physical Dynamics, Inc. Bellevue, WA 98009
Analyze Frontal-Passage Data From the Sousy-VHF-Radar AFOSR-83-0100	Donald T. Farley School of Electrical Engineering Cornell University Ithaca, NY 14853
Dynamic-Chemical Coupling in the Mesosphere and Lower Thermosphere AFOSR-81-0090	Jeffrey M. Forbes Space Data Analysis Laboratory Boston College Newton, MA 02159
Studies of the Auroral Zone Ionosphere Using the Mithras Data Base AFOSR-83-00002	John C. Foster Massachusetts Institute of Tech Haystack Observatory Westford, MA 01886

High Time Resolution Studies of the Auroral Ionosphere AFOSR-82-0093	John C. Foster Center for Atmospheric & Space Sciences Utah State University Logan, UT 84322
A Numerical and Observational Investigation of Gravity-Wave/ Mean Flow Interactions in the Atmosphere AFOSR-82-0125	David Fritts Geophysical Institute University of Alaska Fairbanks, AK 99701
A Scientific Planning Meeting on the Study of Gravity Waves and Turbulence in the Middle Atmosphere AFOSR-83-0216	David Fritts Geophysical Institute University of Alaska Fairbanks, AK 99701
Stochastic Theory of Multiple Light Scattering AFOSR-MIPR-83-00048	D. T. Gillespie Naval Weapons Center China Lake, CA 93555
Techniques & Procedures For Meteorological Measurements Support of Electrooptical Systems AFOSR-MIPR-83-00060	Andreas Goroch Naval Environmental Prediction Research Facility Department of the Navy Monterey, CA 93940
High Frequency Radar Studies on the Very High Latitute Ionosphere AFOSR-ISSA-83-00039	Raymond A. Greenwald Johns Hopkins University Applied Physics Laboratory Laurel, MD 20707
Atmospheric Structure Variations AFOSR-84-0045	Gerald V. Groves Dept of Physics & Astronomy University College London, UK WC1E 6BT
Upper Atmospheric Dynamics AFOSR-ISSA-82-00053	Gonzolo Hernandez National Oceanic and Atmospheric Administration Aeronomy Laboratory Boulder, CO 80303
Studies of Extratropical Cyclonic Storms; The CYCLES Project AFOSR-ISSA-83-00004	Peter V. Hobbs Department of Atmospheric Sciences University of Washington Seattle, WA 98195

A Theoretical Framework for Examining Geographical Variability in the Microphysical Mechanisms of Precipitation Development AFOSR-82-0179	David B. Johnson Illinois State Water Survey P.O. Box 5050, Station A Champaign, IL 61820
Construction of University of Missouri-Rolla's Full Scale Cloud Simulation Chamber F49620-80-C-0090	James J. Kassner, Jr. D. R. White Department of Physics University of Missouri-Rolla Rolla, MO 65401
The Stability of Atmospheric Fields Induced By Localized Topography and Heat Sources AFOSR-83-0069	Lee-Or Merkine Department of Mathematics Technion-Israel Institute of Tech Haifa, Israel
Ionic Reactions in the Earth's Upper Atmosphere AFOSR-83-0177	Thomas M. Miller Department of Physics & Astronomy University of Oklahoma Norman, OK 73019
A Study of the Effects of Triggered Lightning AFOSR-82-0206	Charles B. Moore Langmuir Laboratory New Mexico Institute of Mining and Technology Socorro, NM 87801
Vertical Wind Speeds Observed by the Poker Flat, Alaska, MST F49620-82-C-0029	G. Nastrom Department of Meteorology Control Data Corporation Minneapolis, MN 55440
Effects of Mountain Ranges on Mesoscale Systems Development AFOSR-82-0162	Elmar Reiter Teizi Henmi Department of Atmospheric Sciences Colorado State University Fort Collins, CO 80523
High Time Resolution Thermospheric Temperature and Wind Studies in the Arctic AFOSR-80-0240	Gerald J. Romick Geophysical Institute University of Alaska Fairbanks, AK 99701
Comparison of Ionospheric Model Predictions With MITHRAS Observations AFOSR-84-0029	R. W. Schunk Center for Atmospheric and Space Sciences Utah State University Logan, UT 84321

High Time-Resolution Thermospheric Temperature and Wind Studies in the Arctic AFOSR-80-0240	G.G. Sivjee Geophysical Institute University of Alaska Fairbanks, AK 99701
Infrared Airglow Clutter F49620-83-C-0122	James C. Ulwick Utah State University Space Dynamics University Logan, Utah 84322
High-Latitude Ionospheric Irregularities F49620-83-K-0025	James F. Vickrey SRI International Radio Physics Laboratory Menlo Park, CA 94025

AIR FORCE LABORATORY CHEMICAL SCIENCES

RESEARCH PROJECTS

1. TITLE: Physical Chemistry and Electrochemistry

2. PRINCIPAL INVESTIGATOR: Capt John L. Williams
Frank J. Seiler Research Laboratory
Air Force Academy, CO 80840

3. ABSTRACT OF OBJECTIVES:

Provide scientific basis for the development of high current density and high energy density electrochemical power supplies.

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1. TITLE: Energetic Materials Chemistry Research

2. PRINCIPAL INVESTIGATOR: Dr. John S. Wilkes
Frank J. Seiler Research Laboratory
Air Force Academy, CO 80840

3. ABSTRACT OF OBJECTIVES:

Discover new energetic materials for solid propellant formulations to enhance missile payload and range extension capabilities. Understand the thermochemical and photochemical decomposition mechanisms of explosives. Discover new low-hydrogen content energetic materials.

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1. TITLE: Surface Phenomena

2. PRINCIPAL INVESTIGATOR: Dr. Trice W. Haas
Air Force Wright Aeronautical Laboratories
Materials Laboratory
Wright-Patterson AFB OH 45433

3. ABSTRACT OF OBJECTIVES:

Elucidate the basic chemical and physical factors affecting the control, activation, lifetime, and poisoning of various types of low work function cathodes (oxide, dispenser, matrix, etc.) for use in spaceborne traveling wave tubes. Determine chemical and physical factors which affect and control epitaxial film growth of such semiconductors as Si and GaAs on a variety of substrates. Characterize properties of various metals and alloys grown on semiconductor substrates by such deposition technologies as laser beam vaporization and ion beam sputtering.

1. TITLE: Synthesis and Mechanism of Propellant Ingredients

2. PRINCIPAL INVESTIGATOR: Major Scott Shackelford
Air Force Rocket Propulsion Laboratory
Edwards AFB, CA 93523

3. ABSTRACT OF OBJECTIVES:

Synthesize or modify new tough, cureable, high energy polymer binder candidates for smokeless propellants, high solid loaded formulations and/or high performance hybrid fuels with vastly improved mechanical, physical, and chemical compatibility characteristics including a thermochemical stability greater than 200°C and a glass transition temperature as low as -55°C. Synthesize nonenergetic and energetic copolymers of different molecular weight distribution ranges for subsequent curing into monomodal, bimodal and polymodal binder networks. Investigation of Mark's generalized new multimodal concept for improved stress/strain properties as applicable for propellant binder systems. Investigate chemical syntheses designed to define specific new chemical synthetic transformations, to achieve novel chemical structures, to improve overall synthetic routes to known candidate propellant ingredients, to produce new target compounds, and to provide on-going syntheses of novel model compounds required for investigations in complementary in-house chemical research programs. Determine the detailed initial and rate-controlling thermochemical mechanisms of propellant ingredient decomposition reactions as applicable to precombustion conditions and to establish systematic relationships between key initially controlling steady-state decomposition mechanisms and molecular structure as applied to chemical stability, compatibility, and decomposition rate modification. In-situ elucidation of the ingredient rate-determining bond rupture and mechanism responsible for controlling the global propellant burn rate process. Determine the degree of kinetic versus thermodynamic control in propellant ingredient burning processes and in selected propellant formulations. Elucidate important chemical interactions between specific formulated propellant ingredients.

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1. TITLE: Electronic Transition Chemical Laser Concepts

2. PRINCIPAL INVESTIGATOR: Dr. Steve Davis
Air Force Weapons Laboratory
Kirtland AFB NM 87117

3. ABSTRACT OF OBJECTIVES:

Identify and explore new candidates for development of efficient, high-energy, electronic transition, gas phase chemical lasers.

1. TITLE: Polymer Research

2. PRINCIPAL INVESTIGATOR: Dr. Richard L. Van Deusen
Air Force Wright Aeronautical Laboratories
Materials Laboratory
Wright-Patterson AFB OH 45433

3. ABSTRACT OF OBJECTIVES:

Provide fundamental knowledge about the synthesis and characterization of polymeric materials. Provide new base materials and knowledge of their behavior and composition for future development of new improved nonmetallic structural materials for advanced aircraft systems. Provide characterization of newly emerging polymeric materials with respect to physical, mechanical and engineering properties for ultimate correlation with molecular and supermolecular structures to supplement the science base for nonmetallic materials.

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1. TITLE: Fuels Chemistry

2. PRINCIPAL INVESTIGATOR: Dr. Ronald D. Butler
Air Force Wright Aeronautical Laboratories
Aero-Propulsion Laboratory
Wright-Patterson AFB OH 45433

3. ABSTRACT OF OBJECTIVES:

Develop superior high-efficiency techniques for the liquid chromatographic separation of complex hydrocarbon mixtures by chemical classes for further analysis. Develop superior high-resolution gas chromatographic instrumentation and techniques for the detailed analysis of complex hydrocarbon mixtures. Survey the effects of certain trace elements on the operational performance of aircraft fuels; optimize instrumental techniques for accurately determining a broad range of elements at the sub-ppm level. Develop and demonstrate high-resolution ^{1}H and ^{13}C nuclear magnetic resonance spectrometric techniques for the determination of the bulk chemical properties of hydrocarbon fuels. Develop and apply chemometric techniques for the understanding and prediction of fuel operational characteristics from analytical data.

1. TITLE: Electrochemistry

2. PRINCIPAL INVESTIGATOR: Dr. David H. Fritts
Air Force Wright Aeronautical Laboratories
Aero-Propulsion Laboratory
Wright-Patterson AFB OH 45433

3. ABSTRACT OF OBJECTIVES:

Elucidate the life limiting mechanisms at nickel electrodes associated with mechanical alteration. Determine the means by which cadmium migration causes cell failures. Investigate self-discharge mechanisms discharge rate capability, and passivation while enhancing the safety of primary high energy density batteries. Evaluate low temperature molten salt electrolytes and ambient temperature non-aqueous electrolytes for potential application in high energy density rechargeable batteries. Study the electrochemistry associated with very high current discharge (for short time periods) delivered by either primary or rechargeable batteries. In the case of secondary cells, discharge currents would be greater than fifty times the normal rated load so that thermal control will also be investigated. Explore the electrochemical aspects of lithium rechargeability in combination with various potential cathodes.

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1. TITLE: Laser Kinetics

2. PRINCIPAL INVESTIGATOR: Dr. Leroy E. Wilson
Air Force Weapons Laboratory
Kirtland AFB NM 87117

3. ABSTRACT OF OBJECTIVES:

Theoretically and experimentally determine the physical chemistry parameters of rotational energy transfer rate, quenching rate, V-V exchange, and line broadening parameters of an optically pumped transfer cell. Experimentally determine the HF/DF high vibration state relaxation rate constants using double resonant techniques and develop new experimental and theoretical techniques for determining state to state reaction rates. Model energy transfer kinetics, including rotational non-equilibrium effects. Experimentally and analytically determine limiting processes when radiative times become comparable to kinetic times. Experimentally determine limiting processes in high gain lasers, such as superfluorescence, supersaturation, and parasitic oscillations. Measure the effect of anomalous dispersion on the output beam quality of a high energy chemical laser during power broadening.

AIR FORCE LABORATORY ATMOSPHERIC SCIENCES

RESEARCH PROJECTS

Air Force Geophysics Laboratory
Hanscom AFB, MA 01731

1. TITLE: Molecular and Aerosol Properties of the Atmosphere

2. PRINCIPAL INVESTIGATOR: Dr. George A. Vanasse

3. ABSTRACT OF OBJECTIVES:

Obtain laboratory high-resolution, ambient and high-temperature data of atmospheric constituents, and perform balloon-borne measurements of stratospheric emission using a high resolution cryogenic interferometer. Conduct research leading to the development of more sensitive techniques for improving the accuracy of spectral and remote sensing measurements. The high-resolution data will be used to obtain improved molecular parameters for use in the theoretical spectroscopy effort of the task, and also for updating the transmission/emission codes. Develop techniques to compute molecular absorption/emission line widths and shapes, and compare results with laboratory and field measurements. Develop an understanding of the intermolecular forces and statistics of molecular collision processes; and also new methods for calculating atmospheric spectra from a set of known absorption line parameters and line shapes. Develop models of the optical properties of aerosols in order to calculate such parameters as beam attenuation, angular scattering intensities, polarization, path radiance and contrast transmission. Also perform experimental and theoretical studies in order to correlate aerosol particle refractive index, size distribution, and concentration with meteorological and environmental conditions.

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1. TITLE: Upper Atmosphere Composition

2. PRINCIPAL INVESTIGATOR: Dr. William Swider

3. ABSTRACT OF OBJECTIVES:

Measure the ionospheric species present in the atmospheric D- and E-regions during solar-disturbed periods to determine upper atmospheric physical-chemical processes important to LF/VLF/HF communications. Develop models of ion/electron structure, physical-chemical processes and transport mechanisms in order to describe the twilight and daytime disturbed high-latitude ionosphere. Measure composition with high spatial resolution to provide understanding of the physical-chemistry and transport processes in the creation of ionospheric irregularities/scintillations in the equatorial, mid-latitude, and polar cap regions.

1. TITLE: Infrared Atmospheric Processes

2. PRINCIPAL INVESTIGATOR: Dr. R. A. Armstrong

3. ABSTRACT OF OBJECTIVES:

Study and define the processes that control infrared emissions in auroral and nuclear-disturbed atmospheres. Determine the spectral, spatial and temporal character of airglow infrared emissions with and without solar illumination. Investigate and measure vibrational excitation cross sections for high velocity collisions of major rocket plume species with atmospheric species. The results are ultimately used in plume analysis and prediction.

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1. TITLE: Local Ionospheric Processes

2. PRINCIPAL INVESTIGATOR: Dr. J. R. Jasperse

3. ABSTRACT OF OBJECTIVES:

Develop quantitative methods for specifying the electron density profile from the analysis of particle, optical and electromagnetic wave data. Develop an understanding of the onset of plasma turbulence in the ionosphere and how the properties of the turbulent regions can be specified by remote measurements. Develop an understanding of how changes in the magnetosphere affect the state of the high-latitude ionosphere.

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1. TITLE: Atmospheric Dynamic Models

2. PRINCIPAL INVESTIGATOR: Dr. Chien-hsiung Yang

3. ABSTRACT OF OBJECTIVES:

Formulate a dynamic-numerical model of the moist atmosphere on a global scale to serve as a research vehicle to understand the dynamics and physics of the atmosphere. Understand and model medium (meso) scale dynamics and the interactions between this scale and both the larger and the smaller scale processes.

1. TITLE: Advanced Weather Satellite Techniques

2. PRINCIPAL INVESTIGATOR: Dr. K. R. Hardy

3. ABSTRACT OF OBJECTIVES:

Develop and test theories and techniques for the retrieval of meteorological information from satellite observations and devise techniques for the incorporation of satellite data into numerical weather prediction models.

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1. TITLE: Global Ionospheric Dynamics

2. PRINCIPAL INVESTIGATOR: Dr. H. Carlson

3. ABSTRACT OF OBJECTIVES:

Determine the dominant physical processes driving temporal and spatial ionospheric variability over scales of concern to Air Force systems.

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1. TITLE: Upper Atmosphere Chemistry

2. PRINCIPAL INVESTIGATOR: Dr. John Paulson
Air Force Geophysics Laboratory
Hanscom AFB, MA 01731

3. ABSTRACT OF OBJECTIVES:

Measure rate coefficients for reactions between atmospheric ion species and neutral molecules as a function of energy and temperature. Measure the optical emission produced in such reactions. Study photoabsorption processes in atmospheric neutrals and ions. Study the collisional and radiative quenching reactions for photoexcited species. Measure rate coefficients for electron attachment, ion-electron recombination, and positive ion-negative ion mutual neutralization.

CHEMICAL TECHNIQUES

Denton W. Elliott

The two areas of specific interest sponsored under this task include electrochemistry and detection. There has been some shift of emphasis in the electrochemistry program. Whereto before the focus was almost entirely on batteries, it now includes the electrochemical aspects related to environmental resistant materials as well as electromagnetic materials. Some of the research is directed to structure determination, orientation of molecules on surfaces, and to the reactivity of surface molecular species which form when metal surfaces are treated with chemical compounds. On the detection side, new methods and instrumentation are stressed, with additional emphasis on the environmental aspects. The exploration of new diagnostic techniques, such as laser excited atomic fluorescence (LEAF) in an inductively coupled plasma (ICP) cell for ultra-low single element measurement, shows increasing promise.

At the University of Florida, Professor Jim Winefordner and his group have come up with a novel approach in their studies of flames, in which two inductively coupled plasmas are used in an atomic fluorescence system. One ICP is used as the excitation source and the second ICP is used as the atomization cell.

The inductively coupled plasma (ICP) has long been used as an effective vaporization, atomization, excitation, and ionization (VAEI) cell for emission spectrometry. Many physical parameters of the ICP have been investigated. However, in emission, inherently complex spectra are produced, resulting in the need of a high-resolution monochromator to isolate the analytical lines of interest.

Xenon arc lamps, electrodeless discharge lamps (EDLs), boosted hallow cathode lamps (HCLs), ICP emission, and dye lasers have all been previously used as excitation sources for flame atomic fluorescence spectrometry (AFS). However, in flames, chemical and ionization interferences along with quenching effects of fluorescence by flame gas molecules are a major concern. The use of the ICP as an atomization cell for AFS should be beneficial due to its high volatilization and quantum efficiency.

The first use of the ICP as an excitation source for flame AFS was reported by Hussein and Nickless. Relatively poor detection limits were obtained. Since then, improvements in the sample introduction and the plasma stability have resulted in the increasing use of the ICP as an excitation source for flame AFS. Epstein et al. have shown that the advantage of the ICP as compared to other AFS sources is its flexibility with respect to the available intense atomic and ionic line radiation. Changing from one element to the next is simply done by aspirating a different solution into the source ICP.

Omenetto et al. have examined ICP emission profiles by using the resonance monochromator method. In this method, a low concentration of analyte is aspirated into a flame and increasing concentrations of the analyte are aspirated into the ICP. The resulting fluorescence from the flame is monitored, allowing certain limiting characteristics of the ICP emission profile to be inferred.

The properties of high intensity, long-term stability, narrow line width, and freedom from self-reversal all contribute to the ICP being an excellent excitation source for AFS. Also, due to the narrow line width of spectral lines in the ICP, spectral interferences are insignificant.

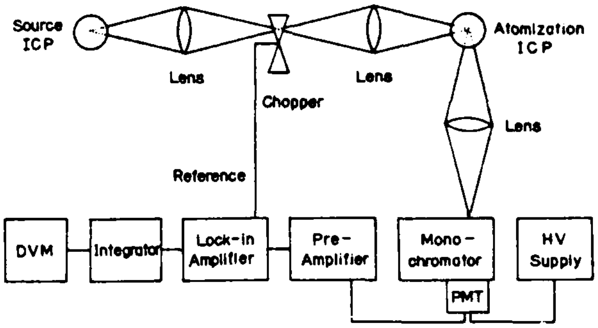


Figure 1. Block diagram of the ICP-ICP-AFS system.

In this work of Winefordner's group, the utilization of the ICP as an excitation source for atomic and ionic fluorescence in a second ICP was investigated (ICP-ICP-AFS) Fig 1. Emission, excitation and fluorescence analytical curves of growth were obtained and, from these, further information about the line profile of the ICP was revealed. For the conventional emission curve of growth, the emission from the source ICP was plotted vs. concentration. For the excitation curve of growth, a fixed, low concentration of the analyte was aspirated into the atomization ICP, while increasing concentrations were introduced to the source ICP.

Thirdly, the fluorescence analytical curve of growth was obtained by aspirating a fixed high concentration (20 mg mL^{-1}) into the source ICP while increasing concentrations of the analyte were introduced to the atomization ICP. Vertical distributions of atomic and ionic species densities were obtained and detection limits for 16 elements are compared to other ICP techniques. Further, a few examples of chemical and spectral interferences were examined. Finally, the noise sources limiting the measurements were investigated.

Limits of Detection. As shown in Table I, limits of detection for many of the elements investigated are within 1 order of magnitude for the best reported values using the ICP as an excitation source for flame AFS. Also presented are some detection limits obtained by laser-ICP-AFS and HCL-ICP-AFS.

Table I. Limits of Detection

species	ex λ/fl λ,[a] nm	limits of detection, ng mL^{-1}			
		ICP-ICP-AFS	ICP-flame-AFS[c]	laser-excited ICP-AFS[d]	– HCL-ICP-AFS[e]
Al I	309.278	8000	1000		
	394.401/396.152			5	
Ca I	422.673	60	4	100	0.08
Ca II	393.366	2		1	
Co I	240.725	40	11		5
Co II	228.616	300			
Cr I	357.869	900	2		10
Cr II	205.552	2000			
Cu I	324.754	30	2		1
Fe I	248.327	1300	6		10
Fe II	259.940	100			
Mn I	279.482				0.3
	279.827	150	2		
Mn II	257.610	9			
Mo I	313.259				30
	386.411	1500		100	
Mo II	202.030	12000			
Na I	588.995	100			0.5
Nd II	430.358	N.D.[b]			
Ni I	232.003	380			10
Ni II	231.604	100			
Sm II	363.429	30000			
Tb II	350.917	N.D.[b]			
V I	411.178	8000	400		90
V II	309.311	1000			
	390.326/290.882			10000	
Yb I	398.799	150			
Yb II	369.419	30			
Zn I	213.856	6	0.5		0.5
Zn II	206.200	600			

[a] Excitation λ/fluorescence λ, if different from excitation wavelength. [b] Not detectable. [c] Reported by Epstein et al. (*6*). [d] Reported by Kosinski et al. (*11*). [e] Reported by Demers and Allemand (*13*).

For additional information see Analytical Chemistry, Vol. 55, No. 4, 691, April 1983.

An item of interest in the electrochemistry area was cited by Professor Ted Kuwana and his group at Ohio State University in their studies on "Electrocatalysis of Oxygen Using Water Soluble Metal Porphyrins and Chemically Modified Porphyrin Electrodes." It was during the process of immobilizing iron or cobalt porphyrins onto polymer/glassy carbon (GC) electrodes that they discovered that metal could be electrodeposited into the polymeric matrix as dispersed micro particles. These particles were randomly dispersed throughout the polymer with a gaussian size distribution. Preliminary results indicated that the quantity and the particle size of the metal in the polymer could be controlled by the electrochemical method of deposition. Thus, large surface areas of the metal could be achieved with low loading levels. For example, H_2 could be electrogenerated at or near reversible potentials with as little as 10 ug/cm^2 (geometric area of electrode) of Pt. The polymer used was polyvinylacetic acid (PVAA) with an estimated thickness of 100 nm or less. Oxygen reduction was also catalyzed by the Pt particles and the pH dependence of the potential and the exchange current density (I_0) were similar to those determined at smooth Pt. The I_0 calculation assumed that the total surface area, assuming spherically shaped particles, was electroactive.

The Pt particles dispersed in PVAA/GC were not removed by ultrasonic cleaning for periods up to 15 minutes. However, Pt particles deposited directly on the GC surface without polymer, the particles were readily removed by the ultrasonic treatment. The entrainment of the particles in the polymer apparently prevented particle aggregation.

Preliminary experiments have indicated that other metals such as Pd, Ni, Cd, and Ag could be similarly deposited into PVAA/GC. It should also be possible to disperse multilayer metals or alloys as particles into a variety of polymers on conducting and semiconducting substrates. This novel method of dispersing micro-particles in polymeric films coated on electrodes could be most attractive for a variety of redox applications including photocatalysis.

SURFACE CHEMISTRY

Captain Lee E. Myers

Fiscal Year 1983 was a period of maturing for the surface chemistry program at AFOSR. During the year the close out of the research areas of lubrication and adhesion was completed and the remaining research areas, surface reactions and thin films, grew to a level which will remain constant for the next couple of years. The surface reactions and thin film programs shared equally the dollar investment made during FY 83. I feel the present program represents a well balanced starting point from which to build an outstanding surface science effort at AFOSR. The year saw the procurement of five new experimental programs in diverse areas of surface chemistry. Two scientific conferences were supported in addition to the annual contractors' meeting. This brought the program up to a total of fourteen research projects with an investment of $1,243,000 for FY 83. This will probably be a stable level of effort for the next two or three years. Stability is expected due to impending management personnel changes, weak fiscal forcasts for FY 84 and FY 85, and the lack of currently planned surface "initiative" programs. Modest growth may still be expected.

Future program changes are unclear. I expect the present program to move towards a mix of research topics which more clearly support an Air Force technology need of the future. Possible areas of emphasis include condensed phase interfaces, laser/surface effects, cluster chemical activity, and space environmental interactions. Regardless of the direction in which the program moves, the emphasis will remain on the microscopic, atomic and molecular, interpretation of surface phenomena.

My final topic of discussion is the success of our annual Molecular Dynamics and Surface Chemistry Contractors' Meeting held at Hanscom AFB, 25-27 October 1983. Approximately 90 registrants heard 24 presentations by molecular dynamic and surface chemistry contractors and Air Force laboratory personnel. The overall opinion voiced by the reviewers present at the meeting was favorable to both of the research programs and the quality of the work presented at the conference. The FY 84 meeting will take place at Kirtland AFB and will have some minor changes in format, including a compilation of abstracts which will be available to attendees.

FISCAL YEAR 1983 INITIATIVE ON SPACECRAFT MATERIALS AND STRUCTURES

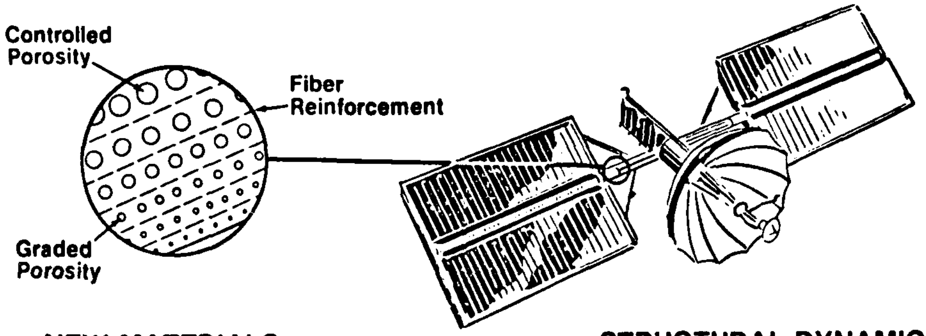
Dr. Donald R. Ulrich

Introduction

A major multidisciplinary FY 83 initiative program was started to address: (1) passive damping requirements for the precise geometric and dimensional control of large space structures (Figure 1), and (2) aeroshell structure requirements for reusable demand launch vehicles or military transatmospheric vehicles. Under the overall management of the Directorate of Chemical and Atmospheric Sciences, which is conducting the materials research, the research is interfacing with structural dynamics and control science research in the Directorates of Aerospace Sciences and Mathematical and Information Sciences, respectively. The approach is unique. Lightweight ceramic structures, prepared by chemical processing methods, and viscoelastic polymer damping materials comprise the thrust of this effort rather than the more conventional metal-matrix, carbon-carbon and polymeric matrix composites approaches.

GOALS

- New Materials for Space Stability & Enhanced Damping
- Structural & Control Concepts for Precision Performance



NEW MATERIALS

- Low Density Composites
- Vibrational Damping
- Dimensional Stability
- Environmental Resistance
- In Situ Space Joining

STRUCTURAL DYNAMICS

- Active Control Concepts
- Orbital Transfer Dynamics
- Damping Enhancement
- Nonlinear Dynamic Modeling
- Assembly/Deployment Mechanics

Figure 1

Statement of Problem - Large Precision Space Structures

The dimensional tolerances of large precision structures for high energy and surveillance electro-optical and electromagnetic systems will commonly approach 1/50 wavelength. These precision tolerances must be maintained during system orbital operations and the tolerances must be regained rapidly after any orbital maneuver. Severe vibration control requirements are associated with both jitter levels and settling time. Passive damping has been identified as a key element in meeting these control requirements. In conjunction with active control, a plethora of very low frequency, closely spaced vibration modes must be accommodated. These will inevitably result from the size and weight efficiencies envisioned for Large Precision Structural Systems(LPSS). For example, in the analysis of the vibration of a column element there are two modes of vibration. The extensional at material frequencies less than 1 Hz is a global motion; the flexural at a natural frequency of 10-100 Hz will continue after damping of the global motion. Flexural fatigue will result if there is no damping in the column itself. Structural damping significantly enhances the performance of active modal control systems by improving error tolerance and decreasing the levels of distrubances.

In the case of LPSS, damping due to nonlinear mechanisms is reduced by design. The damping mechanisms associated with viscosity (air pumping, boundary losses) and acoustic radiation loss are eliminated because of the space environment. This leaves only a small amount of unavoidable joint loss and material damping as the primary damping mechanisms. Most damping, however, is in the material, e.g. composite materials damping.

There have been many studies over the past years on the suitability of materials, construction and design approaches for LPSS. These studies have not included the intentional introduction of passive damping into the system. This introduces the problem - viscoelastic damping materials and damping composite materials for reliable performance of LPSS in the space environment have not been developed or optimized. Passive damping material technology itself has been neglected. There has been some work on high temperature engine enamel R&D. There has been a small amount of empirically based development for the higher frequencies for space (100-10,000 Hz).

However, the unique requirements for space application have not been addressed. Specifically there has been very little work or data base established for stable materials over the frequency and temperature ranges of 0.1 to 200 Hz and from -170°C to 100°C. Passive damping materials technology - the dynamics of low frequency modes and dynamic behavior is not available to make damping a design criteria.

State-of-the-art damping capabilities and requirements are shown in Figure 2. The interdisciplinary nature of precision space structures is shown in Figure 3.

DAMPING MATERIALS AND METHODS CAPABILITIES AND REQUIREMENTS

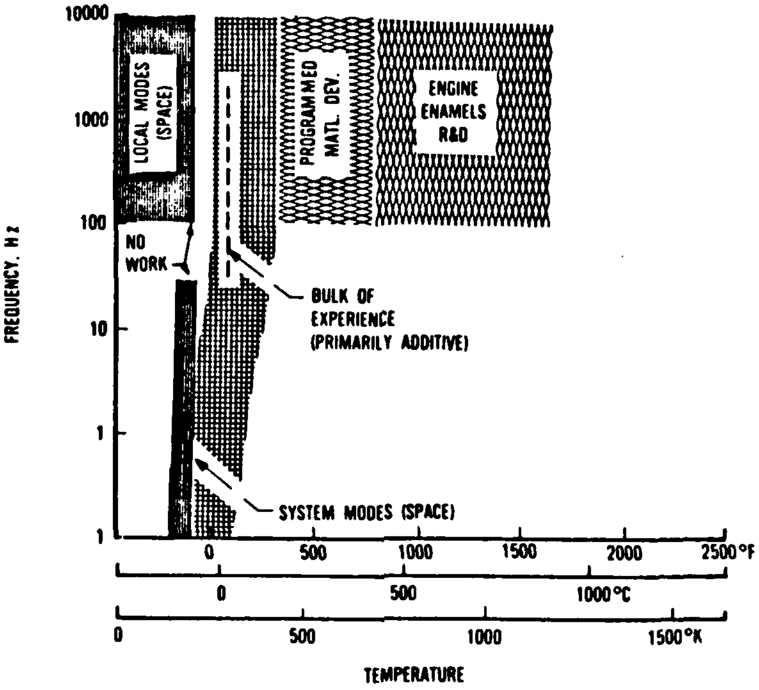


Figure 2

INTERDISCIPLINARY NATURE OF PRECISION SPACE STRUCTURE

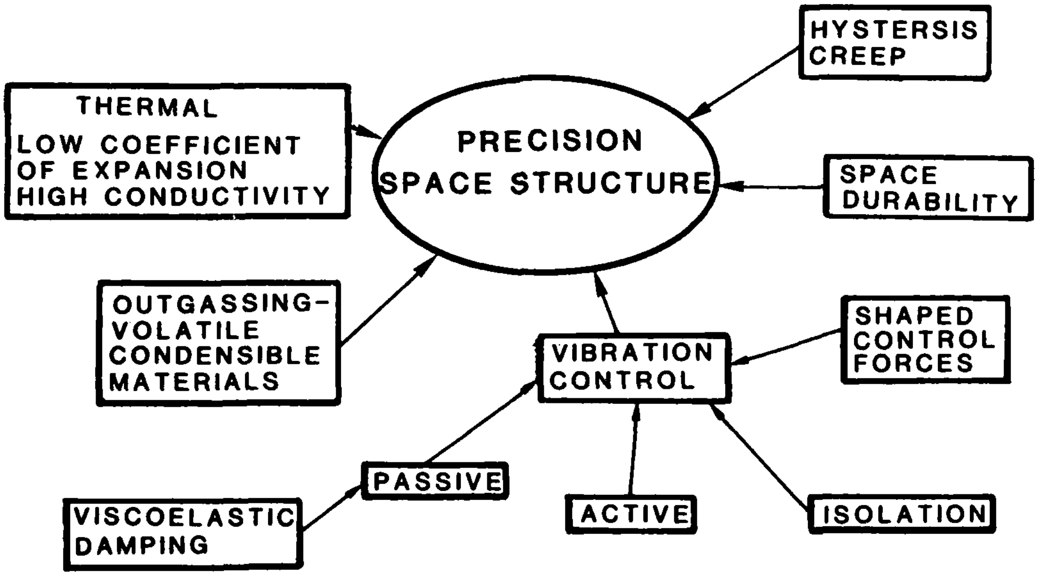


Figure 3

Statement of the Problem - Reusable Demand Launch Vehicles

Generic orbital technology requires materials with some strength which are light, are capable of withstanding high temperatures for extended periods of time, can endure cyclic extremes and high temperature stresses, have excellent durability under all weather conditions, have tailorable thermal properties, and are structurally reliable.

Approaches and Supporting Work Units

Three approaches were defined and selected to meet the advanced materials requirements for large precision space structures and reuseable demand launch vehicles. These are: (1) viscoelastic damping polymers, (2) lightweight ceramic structures, and (3) organometallic sources for lightweight ceramics.

Viscoelastic Damping Polymers

A joint workshop was held during January 1982 by AFOSR and the Air Force Wright Aeronautical Laboratory/Materials Laboratory to identify and prioritize the properties of importance in the space environment for polymeric damping structures. The results are listed below.

Spacecraft Materials Properties

Driver: Space Environment

Prioritized Properties:

1 - Low Density
  - Low Outgassing

2 - Tailored Dielectric Properties (Spacecraft Charging)

3 - Inherent Viscoelasticity
  (Vibration Damping, Complex Mechanical Properties)

4 - High Inherent Stiffness
  - Low Thermal Expansion
  - Reasonable Thermal Conductivity

5 - Resistance to Radiation

Based on these results, the following research was initiated to establish the fundamentals of low frequency damping and dimensional stability in polymeric materials and composites.

Aromatic Polyester-Polysiloxane Block Copolymers: Multiphase Transparent Damping Materials - Dr. James E. McGrath, Virginia Polytechnic Institute and State University, AFOSR-83-0201

The objective is to demonstrate the synthesis of transparent multiphase block copolymers that would demonstrate multiple glass transition temperatures and hence multiple damping characteristics over a wide temperature and frequency range. (Polymeric materials typically show a maximum in damping near and only near the glass temperature.) Moreover, by precisely defining the structure, it should be possible to prepare transparent coating materials which will permit additional systems development to proceed. Since candidate materials should display low creep, low density, low outgassing characteristics and adequate mechanical properties in addition to surviving long-term exposure in space, multiphase segmented copolymers derived from aromatic polyesters (arylates) and soft polydimethylsiloxane segments were selected as the initial materials for study.

Improvement and Optimization of Internal Damping in Fiber Reinforced Composite Materials - Dr. Ronald F. Gibson, University of Idaho, AFOSR-83-0156, and Dr. C. T. Sun, University of Florida, AFOSR-83-0154

The vibration damping properties of polymer matrix, fiber-reinforced composite materials may be improved and possibly optimized by using short fibers rather than continuous fibers. This research constitutes a systematic analytical and experimental study of the effects of fiber aspect ratio, fiber spacing, fiber orientation, and the complex viscoelastic moduli of matrix and fiber materials on the complex moduli of short-fiber-reinforced composites. Complex modulus notation is simply a convenient way of expressing the elastic and dissipative properties of a vibrating structure or material in one complex number, the real part being the elastic storage modulus and the imaginary part being the loss modulus. Continuous, discontinuous and hybrid continuous/discontinuous fiber composites are also being studied.

Fundamental Studies of Time-Dependent Response and Fracture of Cross-Linked Polymers - Dr. Frank M. Kelley and Dr. Maurice Norton, University of Akron, F49620-83-C-0032

This study is concerned with the synthesis, preparation and characterization of cross-linked space stable polymers, and their time-dependent fracture behavior. Emphasis is given to well-defined polymer network structures of two types: (1) end-linked terminally functional liquid polymers having nearly uniform or deliberately distributed initial chain lengths, and (2) model inhomogeneous glassy networks in which the extent and distribution of cross-linked nodules may be precisely controlled. A variety of microstructural variables are being introduced in these special materials in order to provide a quantitative basis for their influence on time-dependent fracture behavior, as well as a correlation with small deformation viscoelastic response. The non-equilibrium state of glassy-thermosetting polymers are being examined in detail. Embrittling phenomena which lead to changes in dynamic response, dimensional stability and fracture toughness is being studied, with particular emphasis on conditions prevalent in the space environment.

Lightweight Ceramic Structures

The investigation of ceramic structures for space structures is a very new idea and at the leading edge of chemical, material and structure science and technology. Low density and porosity are considered disadvantages within the realm of traditional ceramic wisdom. However, using the license of basic research to investigate new high risk, high payoff areas, AFOSR has ventured into the positive aspect of lightweight structures with microdesigned porosity to provide new concepts in cryogenic and high temperature ceramics for large precision space structures as well as reusable demand launch vehicles.

Several unique concepts based on chemical processing are described to produce tailored and oriented porous structures concurrent with tailored microstructures. This work has initiated a national interest in and momentum in lightweight ceramics. Research efforts supporting this approach are described.

Ultrastructure Processing Research of Advanced Ceramics and Composites - Dr. Larry L. Hench and Dr. David Clark, University of Florida, F49620-83-C-0072

Ultrastructure processing as used in this program refers to the manipulation and control of surface and interfaces for the purpose of attaining a new generation of high performance materials with predictable properties and environmental insensitivity or control. The primary end use application of ultrastructure processing in the initiative is for in-space manufacture of a new generation of composite lightweight assembled structures for space (CLASS) materials specifically designed for large scale space structures.

Three parallel chemistry based approaches to produce the ultrastructure processed CLASS materials are being pursued. Primary emphasis is devoted to the science and application of sol-gel processing. The rationale for this heavy emphasis on sol-gel processing is the low thermal requirements to produce materials in this way. Consequently, in-space energy requirements for fabrication of large scale structural components are minimized. In addition, it is possible that the energy for mixing of precursor solutions and extrusion or casting of gels into components can be obtained simply by storing the chemicals under elevated pressure. Transport of tanks of pressurized liquids via the space shuttle maximizes the packing density of transport, an important economic feature, and it is conceivable that the shipping tanks can be designed for use as modular components in a large scale space structure after emptying and cleaning. Recycling of all chemicals other than those used in the structure may be possible in order to minimize transport.

An important material characteristic of sol-gel derived materials is the very large (30-70%) percentage of microporosity in the materials after drying. Consequently a wide range of physical properties can be achieved with materials of the same chemical composition by varying the volume fraction, size distribution, and connectivity of the microporosity. Microporosity gradients are possible and impregnation of microporous structures to produce a wide range of composite materials is also possible. Preparation of sol-gel derived materials with reinforcing whiskers, fibers, or weaves is also possible resulting in an even wider range of properties.

Consequently, one of the operating hypotheses is that understanding the chemistry of sol-gel derived materials will make it possible to achieve unique combinations of physical properties to fulfill large scale space structure design objectives with the capability of manufacturing the materials in-space.

The second approach is based on "micromorphology processing" based on the chemistry of powder synthesis and control at the molecular level. The third approach is based in part upon the discovery of Professor West and his colleagues at the University of Wisconsin that silane precursors can be thermally decompressed to form silicon carbide and other ceramics.

Exploitation of the Sol-Gel Process in Preparation of New Ceramics - Dr. Rustum Roy, Pennsylvania State University, AFOSR-83-0212

The research is aimed at understanding and exploiting the inherent properties of the gel to yield new spacecraft structural materials in three novel ways. The first will seek to create diphasic ceramic xerogels with the maximum amount of stored energy by utilizing high heats of reaction between two pre-selected compositions. In effect it will be determined whether a whole new class of tailor-made "ceramothermic" reactions (analogous to aluminothermic reactions) can be made to occur. The second innovation will develop the microwave processing of gels even to melting. (This is not connected with the microwave processing of ceramics in which there is much current interest.) Exploiting the optimum water content and nanostructure of the gel [combined (as needed) with a second lossy phase] make possible the manipulation of microwave heating for this unique subset of ceramics. The third novel approach will involve the study of "hydrothermal" reaction of gels as the minimum energy route to ceramic consolidation.

Ultra Low Thermal Expansion Ceramics - Dr. H. A. McKinstry, Pennsylvania State University, AFOSR-83-0291

A new structural family of low thermal expansion ceramics which crystallize in the sodium zirconium phosphate (NZP) structure is being studied for space structures. The extremely wide variety of elements which can crystallize in this structure form provides the basis for controlling the anisotropy and magnitude of the thermal expansion by chemical substitution. This should lead to tailor-made materials each with exceptionally high dimensional stability over a temperature range of 200°C. A rigid ion model of this structure will be developed that should prove useful in the prediction of which ionic substitutions should be made to attain the desired anisotropy and magnitude of thermal expansion.

Doping of this material to provide conducting phases for adequate dissipation of electrical charge build up should be possible without appreciably affecting the thermal expansion characteristics of the material. This goal will be of direct interest to the problem of spacecraft charging.

Other structural families will also be considered in order to build up understanding of low coefficient of expansion materials. In particular, the complex perovskites offer an interesting additional property which may provide a means for counteracting mechnaical movement of space structures by electrical coupling through the piezoelectric response of the material.

Composites of these materials will be processed utilizing the sol-gel technique developed by Professor Roy under AFOSR-83-0212.

New Materials for Spacecraft Stability and Damping - A Feasibility Study - Dr. John D. MacKenzie, University of California, Los Angeles, AFOSR-83-0221

Precision space structures require engineering materials with uncommon properties to perform under exacting circumstances. In this program the feasibility of some new materials, new fabrication techniques, and new concepts to develop new composites for use as various components of a spacecraft will be studied. New materials include low expansion glasses and ceramics based on copper aluminosilcates and impregnated porous glass; new processing methods include the use of the sol-gel method to fabricate low expansion matrices at low temperatures; new concepts include the use of hollow fibers to control thermal and mechanical properties and to contain organic polymers to prevent outgassing. Recommendations will be made concerning the potentials of these new materials and new composites and needed research and development.

Basic Research on Processing of Ceramics for Space Structures - Dr. H. K. Bowen and Dr. R. L. Pober, Massachusetts Institute of Technology, AFOSR-83-0192

Composite ceramic structures with controlled composition and microstructure are needed as lightweight and high temperature materials for space structures. This technology does not exist and will require research on processing. Processing ceramic powders (crystalline or amorphous; single phase or polyphase) into useful products and components requires the manipulation of greater than 10^{12} particles/component. Inhomogeneities in the packing of particles prior to the densification process is the major source of property limiting flaws. The proposed research combines fundamental understanding of particulate formation and surface chemistry with the development of theoretical models for processing, including critical experiments with model ceramics (glass, glass-ceramics, ceramics, ceramic composites) to test the generalizations for controlling the presintered structure and sintered microstructure. The research involves novel chemical preparative concepts with colloid and ceramic science in order to provide reproducible and reliable microstructures: controlled size and distribution or pores and other minor phases; contolled composition for thermal, dielectric and mechanical characteristics.

Microstructural Engineering of Lightweight Ceramics Structures - Dr. David Green, Rockwell International, F49620-83-C-0078

In this research, a micromechanical model to describe mechanical behavior of cellular ceramics, for example, the relationships between toughness, density, elastic constants, strength and the microstructural geometry will be developed. Predictions of the model will be compared with properties of materials fabricated from hollow glass spheres. The process of spray roasting will be studied so that ceramic powders can be formed as uniform cenospheres and ceramic materials with cellular microstructures fabricated. The microstructural development will be observed and possible strength-controlling flaws identified. The mechanical properties of real systems will be compared with those predicted by the micromechanical model.

Microdesigning of Lightweight/High Strength Cermaic Materials - Dr. I. A. Aksay, University of Washington, AFOSR-83-0375

Colloidal suspensions provide this required control mechanism over particle-particle interactions in powder-processed systems. The first major goal of this research is to perform an in-depth investigation which will primarily emphasize the development of porous, lightweight structural materials through colloidal consolidation techniques. Studies will be directed toward identifying the optimal geometrical arrangement of porosity required to retain high strength with emphasis initially on mullite systems. The second major goal of the proposed work is to conduct research on the development of lightweight/high strength structural materials which are based on intrinsically low density materials. Initially this work will be based on the development of B_4C and SiC cermet systems since both of these systems have the potential of satisfying not only the high strength but also the low density requirements. In particular, B_4C based ceramics may offer distinct advantages over many other materials for space ceramic armor, since after diamond and boron nitride, B_4C is the next hardest material.

Development of Spacecraft Materials and Structures Fundamentals - Dr. Svante Prochazka and Dr. Stephen L. Dole, General Electric Research and Development Center, F49620-83-C-0101

This research program addresses the development of fundamental information useful for the design and fabrication of large aspect ratio, electrically insulating space craft members for long term operation in the -200°C to +200°C temperature range. The ceramic boron carbide has been selected as the prime candidate material for the structural component of such spacecraft members on the basis that this material offers an extremely high stiffness-to-weight ratio. Approaches for the provision of the necessary oscillation damping to such a member are being investigated as are materials, tests and procedures for the incorporation of high damping factor within a structural member such as boron carbide.

Microstructural Investigation of Ceramic Composites - Dr. D. C. Larson, Illinois Institute of Technology, AFOSR-PD-83-0005

There is not an established science base for controlling the processing and the surface chemistry of ceramic materials to achieve the interfacial stability between the phases of composites and microstructures for superior space structure properties and environment stability. The purpose of this research is to permit a more fundamental understanding of the microstructure and fracture process in ceramic matrix composites and their relationship to optical, electrical and mechanical properties. High resolution scanning and transmission electron microscopy techniques and associated microanalytical techniques will be employed to investigate the relationship of microstructure to fracture processes, and degradation mechanisms in emerging ceramic-ceramic composite materials. Such materials include transformation-toughened zirconia, as well as whisker-, particle- and fiber-reinforced glass and polycrystalline ceramic matrices, and chemically processed matrix materials.

Organometallic Sources for Lightweight Ceramics
(Chemical Synthesis and Reactivity)

A major chemical approach to achieving lightweight space structures is the processing of lightweight ceramic structures from polymers which have been synthesized through organosilicon chemistry. The organosilicon chemistry research program was initiated at AFOSR with the work in the 1950's of Dr. Robert West, University of Wisconsin. The fruits of this program, pioneered and developed by Dr. Anthony Matuszko, now are being brought to bear on the chemical preparation of ultrastructural ceramics being developed by AFOSR, one focus of which is the spacecraft structures thrust. The following research is supporting this approach.

Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials - Dr. Robert West, University of Wisconsin, F49620-83-C-0044

Optimum silane polymers for conversion to silicon carbide are being addressed. Dr. West is interfacing his research with that of Dr. Hench at the University of Florida (F49620-83-C-0072).

Organosilicon Compounds and Organosilicon Polymer Intermediates - Dr. Dietmar Seyferth, Massachusetts Institute of Technology, AFOSR-83-0003

This research addresses the chemistry and synthesis of organosilane monomeric precursors to silicon carbide and silicon nitride. Dr. Seyferth is interfacing his research with of Dr. Bowen at MIT (AFOSR-83-0192)

Chemistry of New Silicon Containing Polymers and Triply Bonded Silicon Intermediates - Dr. William Weber, University of S. California, AFOSR-82-0333

This program addresses the synthesis of polysilane and polysiloxane precursors to silicon carbide.

The Chemistry of Precursors to Silicon Carbide - Dr. Morey A. Ring and Dr. H. Edward O'Neal, San Diego State University, AFOSR-83-0209

The kinetics and mechanisms of organosilane decomposition to ceramics are being established.

ADVANCES IN MATERIALS CHEMISTRY

Dr. Donald R. Ulrich

SOLUTION CERAMICS

AFOSR sponsored research in the chemical processing of ceramics has pioneered the development of the science and application of solution ceramics processing. The primary approach has been via metal organic sol-gel chemistry, which allows the fabrication of homogeneous, high temperature performance glass, ceramics and composites at considerably lower temperatures (300° - 1000° C) than those required by the conventional fabrication procedures (1300° - 2000°). This significant temperature advantage is illustrated in the thermal-compositional processing diagram for silicate glasses (Figure 1). The homogeneity of these new materials arises from the atomic scale mixing which is an intrinsic characteristic of the low temperature solution approach. In addition new, controlled metastable structures and expanded composition ranges can be achieved which are not attainable with conventional approaches. The processing is compatible with conventional ceramic fabrication methods.

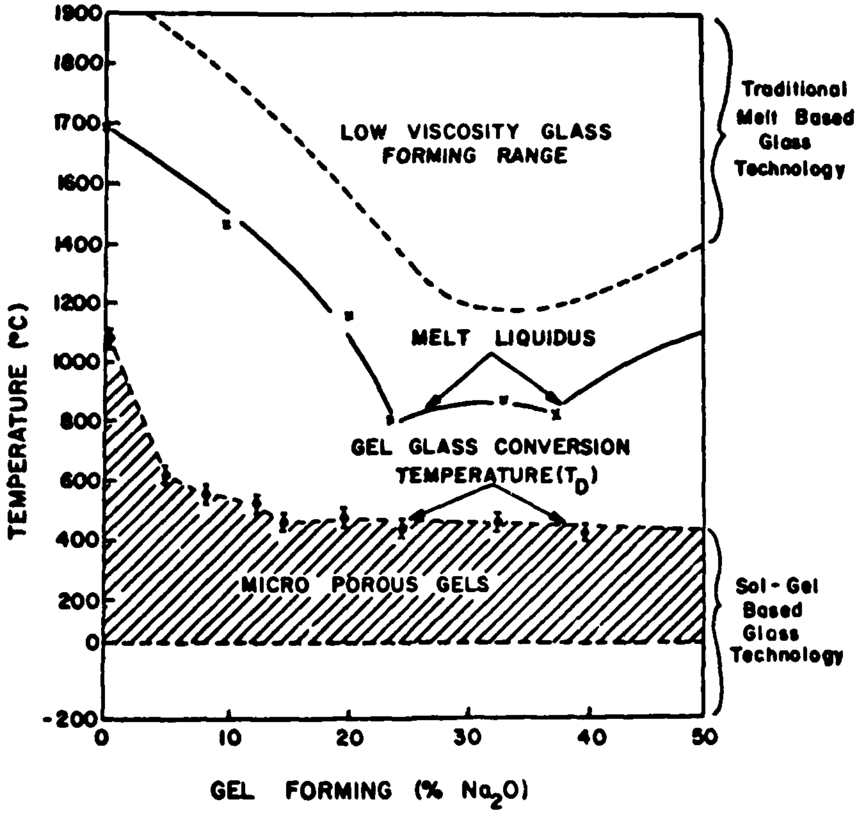


Figure 1

The sol-gel process, shown in Figure 2, consists of mixing, in liquid form, a variety of organometallic solutions which are then caused to form a gel whose composition contains the desired components for the final glass or ceramic object. A series of subsequent drying, decomposition and densification steps removes the organic sol and consolidates the gelled structure into a solid object. A sol is a dispersion of colloids in liquid, a colloid being particles which are 10-1000 Angstrons in size. A gel is a rigid sol or polymer network with a great deal of posorosity. The process can be carried out in a mold to achieve desired shapes. There are many variations, such as the use of inorganic starting materials, and the inclusion of numerous additives at various stages of the process for better control of either the processing steps or the final properties of the material. In some processes, suspensions are also used as starting sols.

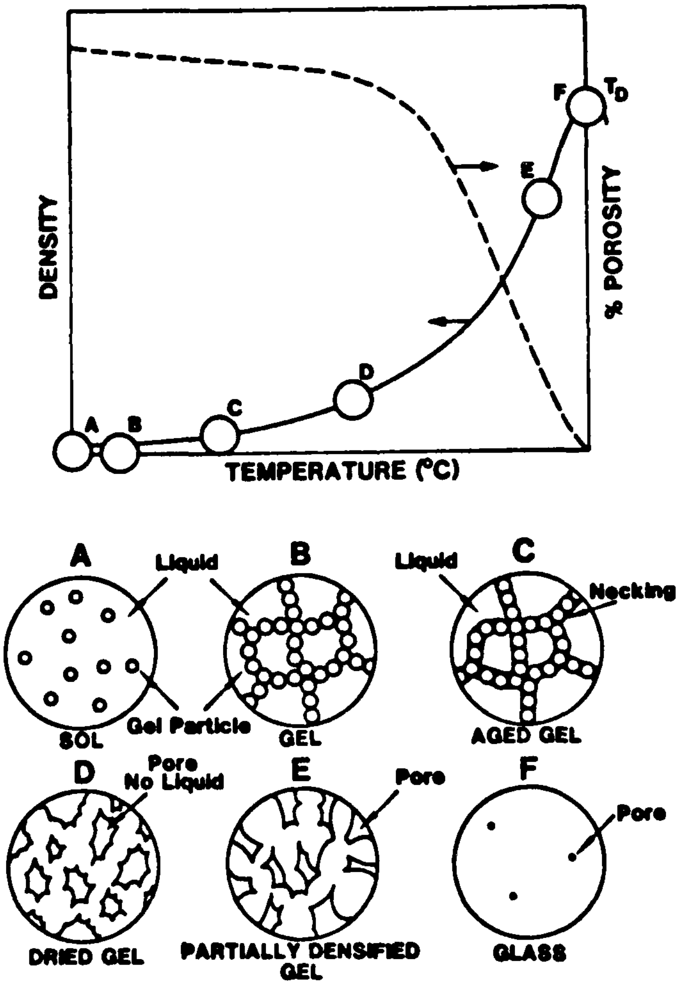


Figure 2

A major basic discovery has eliminated the cracking problem associated with drying shrinkage. The use of drying control chemical additives (DCCA's) makes the development of a versatile and rapid metal organic sol-gel technology feasible for large scale production. The mechanism of stress development during drying has been investigated in detail, and special additives were developed which sucessfully avoid the cracking problem during rapid drying. By understanding the controlling mechanisms during drying and consolidation, a variety of materials and conditions, including rapid processing requirements can be accommodated. A series of DCCA's, in particular, formamide and oxalic acid, and their use in making 100% SiO_2, alkali-silicates, alkali-boro-silicates, and SiO_2 composites via sol-gel processing have been investigated. Patents have been applied for the DCCA concept and its optimization.

Production times of prototype 4" diameter optical components have been achieved within a 24 to 40 hour precessing schedule. Figure 3 shows a collection of prototype silica optical components all made within a 1-2 day processing schedule. These components were made with a total of a 1.0 man-day effort.

This research has been transitioned into a major DARPA/RADC contract for large scale, lightweight mirror single stage production for the Rapid Optics Fabrication Technology Program.

An important material characteristic of sol-gel derived materials is the very large (30-70%) percentage of microporosity in the materials after drying. Consequently, a wide range of physical properties can be achieved with materials of the same chemical composition by varying the volume fraction, size distribution, and connectivity of the microporosity. Microporosity gradients are possible amd impregnation of microporous structures to produce a wide range of composite materials is also possible. Preparation of sol-gel derived materials with reinforcing whiskers, fibers, or weaves is also possible resulting in an even wider range of properties. These advanced concepts are being applied to a new generation of composite lightweight assembled structures for space materials specifically designed for precision large scale structures, and to new ceramic-ceramic composites for turbine engine hot sections. These processes have also been patented.

This research was conducted at the University of Florida in the Multi-Investigation Research Program (MIRP) under the leadership of Dr. Larry L. Hench.

ADVANCES IN ORDERED POLYMERS

The AFOSR/AFWAL/ML Ordered Polymers Program has resulted in the new liquid crystalline, rigid chain polymer polybenzothiazole (PBT). As a result of

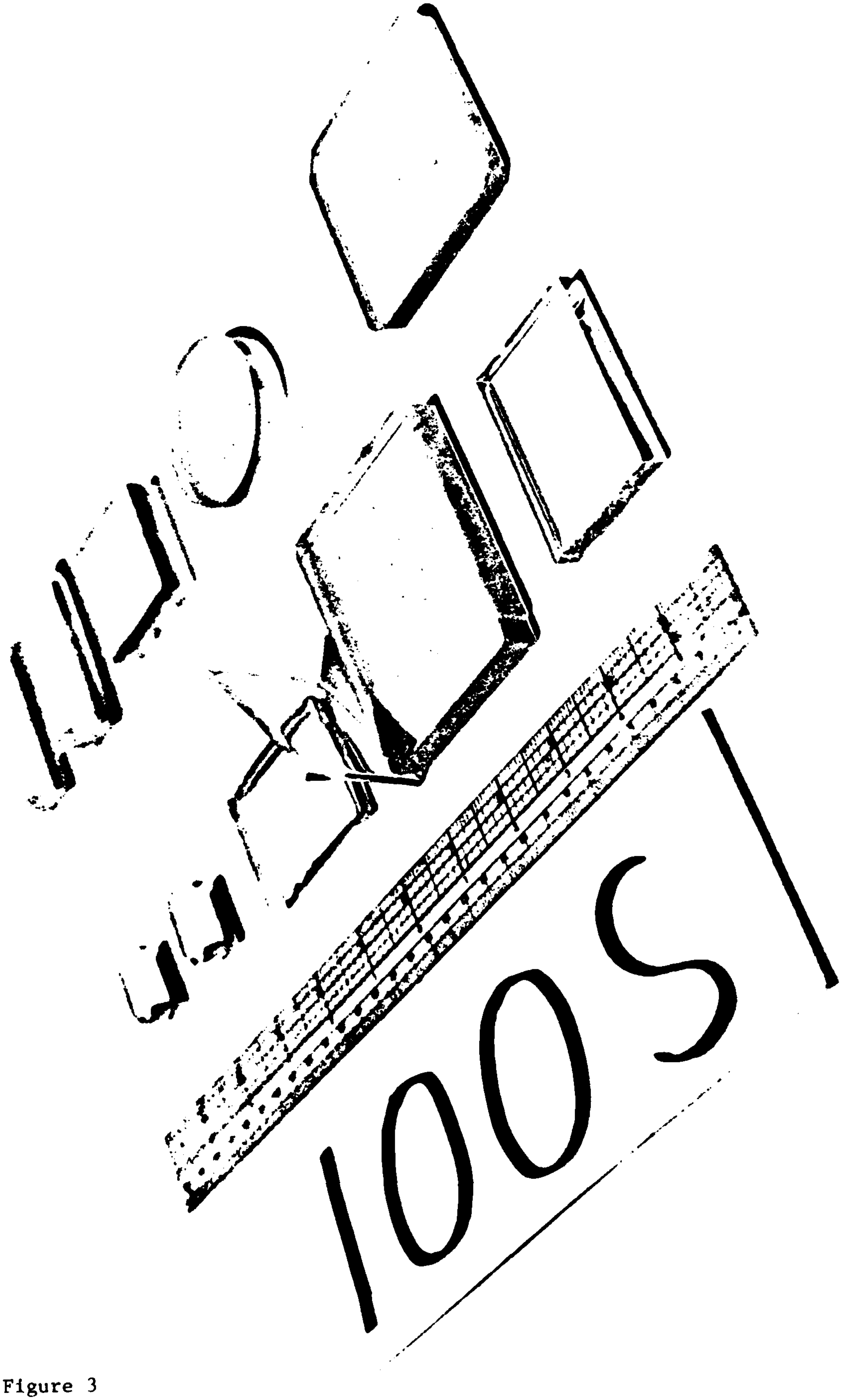


Figure 3

the rigid molecular alignment (other polymers have flexible or semiflexible alignments), PBT has superior strength, ultra high stiffness and excellent thermal stability and environmental resistance in comparison with other materials (Figure 4).

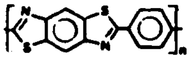
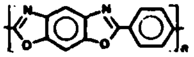
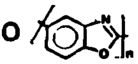
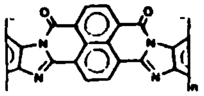
		MODULUS	TENSILE STRENGTH	COMPR STRENGTH
PBT		60msi	600ksi	0.4 (rel. to graphite)
PBO		87	600	0.49
AB-PBO		30	650	0.66
BBL		?	?	?
"Kevlar"		28	450	0.45
Graphite		42	200	1.0

Figure 4

A recent major accomplishment is a new polymerization synthetic method that allows the chemist to polymerize at very high concentrations, has broad applicability to a wide range of polymers, and has made production on a large scale feasible. New scientific understanding of the requirements of polyphosphoric acid for improved control polymerization variables such as reaction times and dehydrochlorination times has resulted in the ability to polymerize a range of new polymers from liquid crystalline solutions with tailored rigid and extended chain structures and enhanced properties (Figures 4 and 5). These include polybenzoxazole (PBO), the liquid crystalline, flexible chain forms of PBO and PBT, AB-PBO and AB-PBT, and the high temperature ladder polymer benzimidazobenzophenanthrolin (BBL).

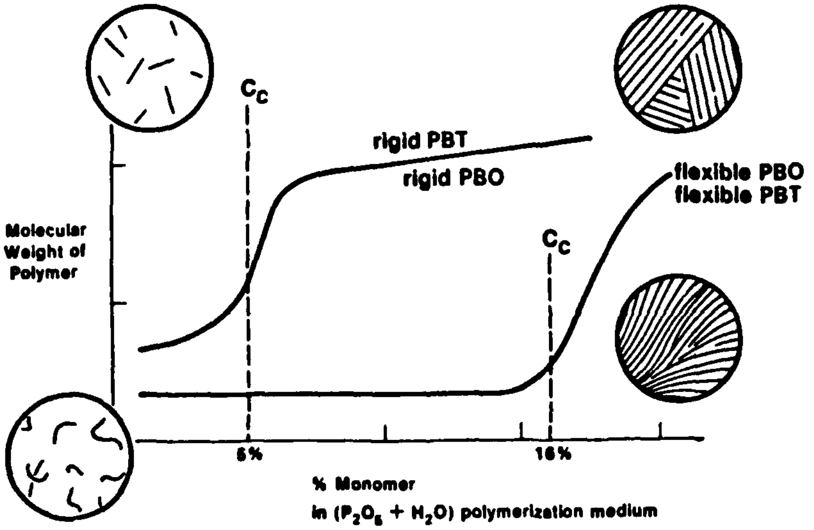
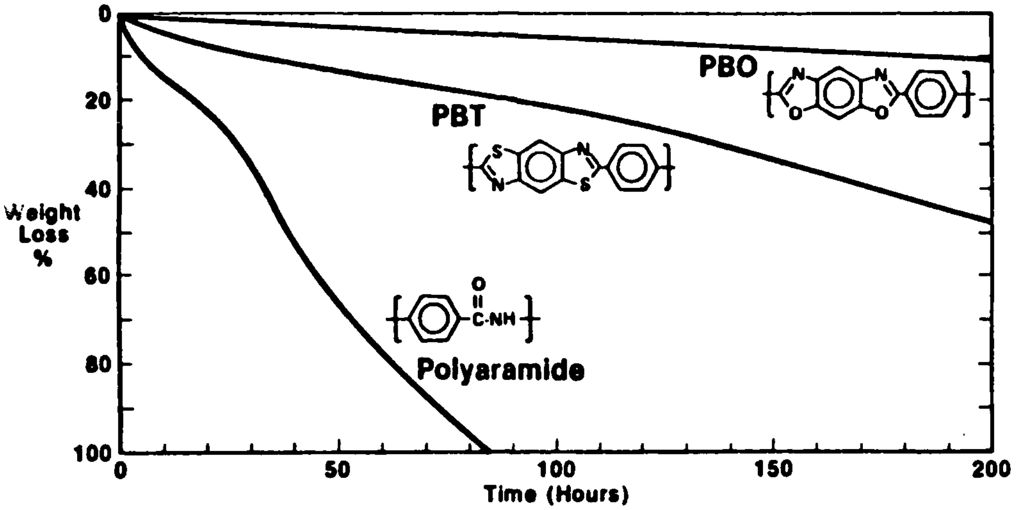


Figure 5

As examples of the outstanding properties (Figures 5 and 6), PBO has achieved the theoretically predicted stiffness of 87 MSI modulus and thermal stability exceeding PBT. The BBL is the first liquid crystalline conducting polymer and is the first conducting polymer to have associated outstanding mechanical property and thermal attributes (300° C conducting polymers).



Isothermal Aging in Circulating Air at 700° F

Figure 6

The status of the Ordered Polymer Program is summarized in Figure 7. Patents have been applied for worldwide. There are promising opportunities for commercialization. Transitioning for a multitude of applications is in progress. The Ordered Polymer Program is the basis for the FY 84 Optical Signal Processing Initiative based on liquid crystalline polymers which promise to demonstrate speeds in the sub-pico-second range. It is the focus of a new Interservice Laser Counter-Measures Program.

Summary

Ordered Polymers

- **AFOSR-AFWAL Corporate Research Program**
  - **27 AF, Academic, and Industry Investigators**
- **Revolutionary New Polymers**
  - **Structural Properties Far Exceed High Performance Polymers**
  - **Nonlinear Optical Behavior**
  - **Unique Transport Properties**
- **Major Polymerization Break Through**
  - **Applicable to Broad Range of Polymers**
  - **Patent Applications In U.S., Japan, Western Europe**
- **Transition**
  - **Prime PBT In Fiber Scale-Up Development**
  - **Laminates & Molecular Composites to 6.2**
  - **Interservice Laser Countermeasure Program**
  - **Optical Signal Processing Initiative**

Figure 7

The Ordered Polymers Program is managed as a corporate Air Force program by Dr. Donald R. Ulrich, AFOSR, and Dr. T. E. Helminiak, AFWAL/ML. Major breakthroughs described have been made in all aspects of the program - synthesis, processing, characterization, and scale-up - by a large number of investigators. Dr. James Wolfe of SRI International is the inventor of the new synthesis process. Dr. Fred Arnold successfully synthesized liquid crystallene BBL at AFWAL/ML.

CHEMICALLY STABLE INFRARED GLASSES

Since 1976, AFOSR/NC has been supporting research in halide glass systems which would open approaches to infrared transmitting optical fibers as well as new infrared domes, lenses and mirrors. The current materials, oxide glasses, are limited by their optical cutoffs in the near infrared. AFOSR research has pioneered the development of chemically stable, low loss glass systems which are based on fluorides, chlorides and bromides. Newly developed systems (Figure 8) offer high transmission out to 20 microns in the infrared region of the electromagnetic spectrum (Figure 9).

TYPICAL HALIDE GLASS SYSTEMS

FLUORIDES

$XF_4 - BaF_2 - MF_y$ X = Zr, Hf
MF_y = LaF_3, NdF_3, ThF_4, UF_4

$LnF_3 - BaF_2 - MF_2$ Ln = Any rare earth
M = Zn, Mn

$PbF_2 - XF_2 - MF_3$ X = Mn, Zn, Fe, Co, Ni, Cu
M = V, Cr, Ga

CHLORIDES

$NaCl - KCl - ThCl_4$

$RCl - BaCl_2 - CdCl_2$ R = Na, K

$AgCl - PbCl_2 - CdCl_2$

$KCl - BiCl_3$

BROMIDES

$AgBr - PbBr_2 - CdBr_2$

$RBr - ZnBr_2$ R = Na, K, Rb, Cs

Figure 8

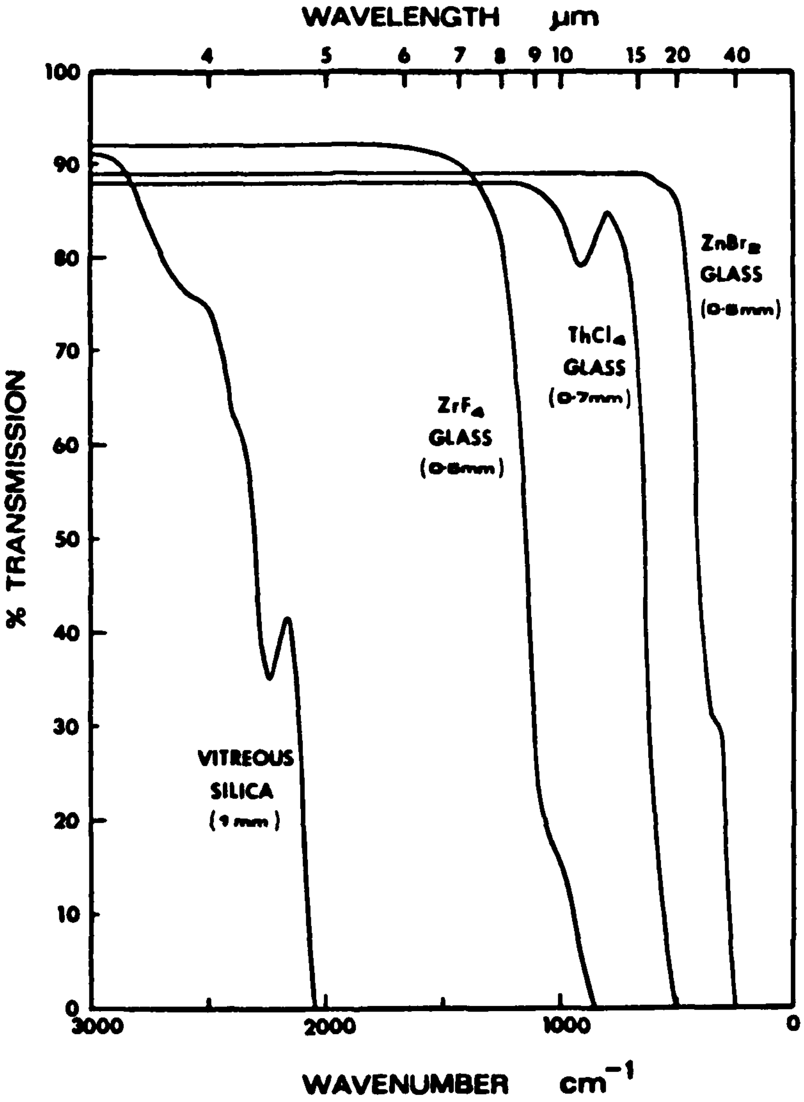


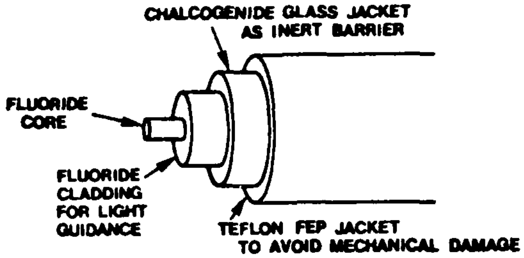
Figure 9

Purification techniques based on distillation of the raw materials and new procedures for glass formation, annealing, and fiber drawing in inert environments have been developed. These have resulted in glass fibers which have transition metal ion and oxygen contents below the limits of detection.

A second major recent accomplishment has been the development of a jacketing system which is impermeable to water and protects the fibers from stress corrosion. Stress corrosion, the reaction of water with glass surface defects, results in loss of strength and failure of the fibers. Current organic cladding systems such as Teflon and silicones are susceptible to water penetration and loss of strength (Figure 10). A inert impermeable chalcogenide glass system has been developed which is impermeable, compatible with fiber properties and fabrication (Figure 11), and prevents the loss of strength (Figure 10).

SOME CRITERIA FOR SELECTING JACKET MATERIALS

- Chemically durable
- Impermeable to corrosive agents e.g. water
- Mechanical strength
- Matched thermal properties e.g. expansion
- Good adhesion at interface
- Fabrication rate compatible with fiber drawing speed



EXPERIMENTAL FIBER STRUCTURE DEVELOPED AT UCLA

Figure 10

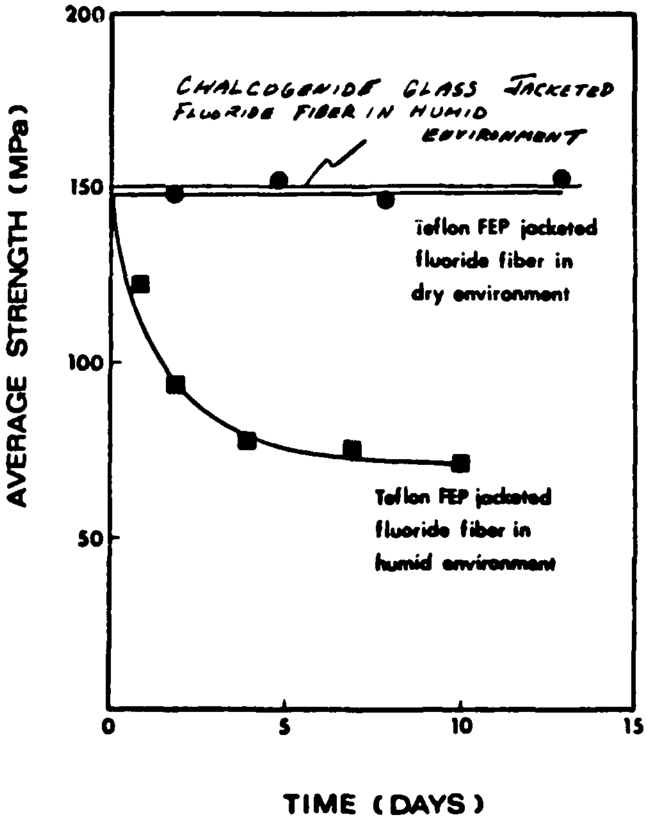


Figure 11

A patent has been applied for. These chalcogenide jacketed halide glasses are undergoing evaluation by Defense Contractors and Laboratories for use in specific new systems.

These advancements were achieved by Dr. John D. Mackenzie of the University of California, Los Angeles.

MOLECULAR DYNAMICS

Captain Lee E. Myers

Management instability characterized FY 83 for the molecular dynamics program at AFOSR. We began the year with the program in the capable hands of Major William G. Thorpe. Mid-year, Bill left AFOSR to attend the Air Force Command and Staff College in Montgomery, AL. At that time I took over management of the molecular dynamics program as an interim manager for Dr. Barry S. Feldman. Barry joined this directorate at the end of FY 83 and managed the molecular dynamics program for three months. After three months, Barry took a permanent position at the Naval Research Laboratories, once again placing management of the molecular dynamics program with me. A permanent civilian program manager is now expected to be chosen by the end of 1984. The result of these management changes has been a general slowdown of activity in the molecular dynamics program. Both the total dollar investment and program content have remained generally stable. This can be expected to change upon arrival of a new civilian program manager.

Although it is impossible for me to forecast the interests and preferences of a new program manager, some general comments can be made regarding the current research areas and possible future trends. The current program is keyed to two general areas of interest, reflecting the interests of the laboratories with which we most frequently interact. The first is chemical lasers, the second atmospheric chemistry. Recent changes at the Air Force Weapons Laboratory have clouded somewhat the relative levels of interest in specific chemical laser systems. Regardless, the AFOSR molecular dynamics program will continue to emphasize, as it has in the past, new chemical laser concepts. This program was augmented during FY 84 by a short wavelength laser initiative which was partially managed by this directorate. I expect this program to continue as a major portion of the molecular dynamics program in the foreseeable future. Our second major funding area is atmospheric chemistry. This program has remained constant in interest, ion-molecule reactions of atmospheric species, and investment level. No significant changes are planned for this program in the near term. There are two smaller areas of interest also funded by the molecular dynamics program, interactive dynamics and energetic materials. Interactive dynamics emphasizes energy flow within reacting systems. Energetic materials keys on the initial steps of thermal decomposition of energetic materials - fuels, explosives, and propellants. Whereas the interactive dynamics program has been an area of active support for AFOSR chemistry for many years, energetic materials is a new area of support. I expect the interactive dynamics subtask to be maintained at the present funding level but the future of the energetic materials area will depend heavily upon the choice of our new program manager. The energetic materials program is at present very small.

CHEMICAL REACTIVITY AND SYNTHESIS: SOME RECENT ACHIEVEMENTS

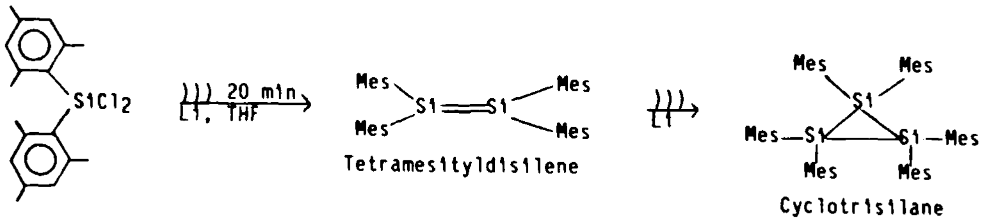
Dr. Anthony J. Matuszko

A basic research proposal for a three or four year program of work should be a well thought out, scientifically sound plan of attack. However, if everything worked out 100% as planned, the research would probably not be worth funding as basic research. Although this is not always true, significant discoveries are often made which were not anticipated when the research proposal was written or when the program was started. This may be referred to as serendipitous or accidental discovery. In this year's review, I should like to report on two such discoveries from the AFOSR program of sponsored research which have received considerable attention from the news media and from the industrial community and should find important uses in the Air Force. The first involves the application of ultrasound to synthesis, and the second utilizes magnetic field effects to influence polymer synthesis.

Synthesis with Ultrasound

At North Dakota State University, Professor Philip Boudjouk found that ultrasonic energy greatly accelerates a wide variety of reactions, especially reactions that involve metals. Although ultrasound equipment has been in use for a number of years in such areas as the cleaning of laboratory glassware, non-destructive testing of materials, medical testing, etc., not much was done in applying ultrasound to synthesis.

Boudjouk originally started using ultrasound in his study of organosilicon reactions. Soon after Professor West and others reported the first synthesis of disilenes on another AFOSR program (Science, 214, 1343-1344, 1981), Boudjouk reported the synthesis of disilenes in approximately 90% crude yield under milder conditions using ultrasound (J. Am. Chem. Soc., 104, 4992, 1982). Further work on this reaction showed that, when allowed to go to completion, (the disilene is very reactive towards Li) high yields (60%) of very pure cyclotrisilane is obtained. This is the best route to this novel, very highly strained ring system.

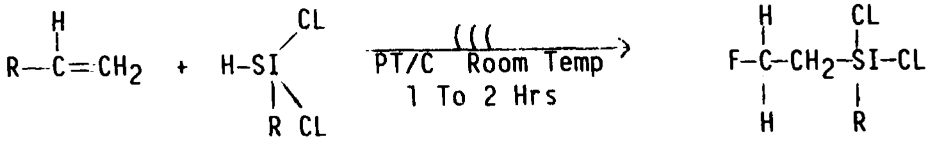


In studying more than a dozen different organic reactions, Boudjouk and his co-workers found that ultrasound not only shortens reaction times at room temperatures but also permits reactions to be conducted under mild conditions (30° -40°C and atmospheric pressure) which normally require more vigorous conditions. In addition to the obvious benefit of running reactions at lower temperatures and pressures, it was found that very often yields were significantly higher and product distribution simpler than when the same reactions were run at high temperatures and/or high pressures.

When high intensity sound waves pass through a liquid they cause tiny bubbles to form. The bubbles collapse creating local hot spots. As with shock initiated reactions and flash photolysis the process takes place in a very short period of time (a few nanoseconds) and for that period of time rather high temperatures and high pressures are achieved.

Reactions which have been tried and found to benefit from ultrasonic stimulation include hydrosilation, coupling of organic halides, hydrogenation of unsaturates, Reformatsky reaction, reduction of aryl halides, etc. The use of ultrasound in the hydrosilation reaction is an illustration:

HYDROSILATION



(Normally Temps > 90°C are required)   (70-90% Yield)

Since Boudjouk first presented his initial results at the National American Chemical Society meeting in the spring of 1982, he has gotten numerous inquiries about the work from other scientists and from industrial people. The research has been written up in Science News, Science Digest, and Nation's Business. The work was highlighted in one of the twenty articles describing accomplishments in chemistry in the American Chemical Society's 1984 edition of What's Happening in Chemistry. In the meantime, Boudjouk and his research group continue their study of ultrasonically stimulated chemical synthesis as part of a broader program of chemical research.

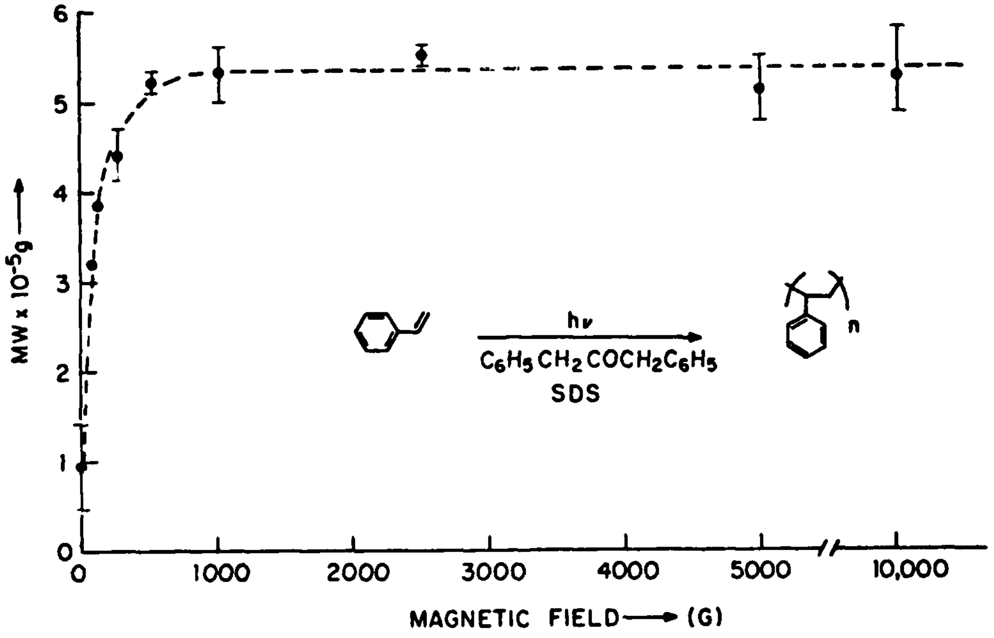
Magnetic Field Effects in Polymer Synthesis

Professor Nicholas Turro of Columbia University is a leading researcher in organic photochemistry. He has for several years collaborated with another AFOSR Investigator at Columbia, Professor Kenneth Eisenthal, in combining organic photochemistry basic research with laser flash spectroscopy to study mechanistic processes in organic reactions which occur in the time frame of milliseconds (10^{-3} sec) to picoseconds (10^{-12} sec). However, the many accomplishments of this work will have to be covered in a future article.

How did an organic photochemist get involved with magnetic field effects in polymer synthesis? Professor Turro was experimenting with the photoinduced emulsion polymerization of styrene in order to understand the basis initiation and propagation steps in the polymerization. The styrene monomer is emulsified with water by the addition of detergent in the presence of small quantities of dibenzyl ketone as a photoinitiator. The reaction mixture is stirred and polymerization is started photochemically by shining light on the mixture. The polymerization went three times faster and gave polystyrene with a molecular weight three times greater if the reaction vessel was stirred magnetically rather than mechanically.

The initial results were first reported in a communication to the Journal of American Chemical Society (J. Am. Chem. Soc., 102, 7391-7393, 1980). Chemical & Engineering News soon followed with a feature article. The London Times, New York Times, Industrial Chemical News, and others followed with news stories and considerable industrial interest evolved.

After making these extraordinary exploratory observations, Turro and his research group continued a systematic study of the magnetically influenced polymerizations. Included in the study were styrene, methyl methacrylate and acrylic acid polymerizations. A plot of magnetic field vs. molecular weight for polystyrene is shown below. A comprehensive account of the results together with Turro's explanation of the magnetic effect was recently published (J. Am. Chem. Soc., 105, 1572-1577, 1983; Ind. Eng. Chem. Prod. Res. Dev., 22, 272-276, 1983). A patent has been granted and will be issued shortly.



Magnetic field dependence of the average molecular weight of polystyrene produced by emulsion polymerization photoinitiated by dibenzyl ketone.

This magnetic field effect may be utilized in manipulating the rate of polymerization, average molecular weight, molecular weight distribution, and structure of polymers. The demonstrated effects have potential application in a range of areas from the bulk production of polymers to the production of printed circuits for computer chips. The ability to manipulate polymerization parameters with weak magnetic fields is practical because of the ease of generation and application of weak fields. The theory of magnetic field effects on polymerization can be applied to a number of reactions involving initiation of chain reactions.

A number of applications of these phenomena may find use in areas far afield from polymerization, i.e., combustion processes. The latter involve complex chain processes and may be subject to efficiency inhancement and control via applied magnetic fields. Another potential area for use is the design of photoresists for integrated circuits. Many photoresists employ polymerization methods to build complex prestructures needed to obtain the high density circuitry for the manufacture of computer chips. Magnetic fields may be useful in the control of polymerization and may often provide a means of producing novel chip architecture.

ATMOSPHERIC SCIENCES

Lieutenant Colonel Ted S. Cress

Major James I. Metcalf
(USAF Reserve)

As the single manager of Air Force basic research, AFOSR supports an extramural atmospheric research program and an in-house research program at Air Force laboratories. The in-house and contractual basic research at Air Force Geophysics Laboratory (AFGL) dominates the overall atmospheric science basic research program and is oriented toward the support of exploratory development efforts in the laboratory. The extramural program sponsored directly by AFOSR is more widely ranging and higher risk, seeking to produce the fundamental knowledge that will support problem-solving efforts in the future. Close coordination between AFOSR and AFGL insures that the respective efforts are complementary and avoid duplication.

The purpose of the AFOSR atmospheric sciences basic research program is to stimulate and support innovative research that will ultimately lead to a more thorough understanding of the fundamental physical processes of the atmosphere. The scope of the program includes phenomena at scales from molecular to global and from the earth's surface to the outer limits of the atmosphere. This domain includes nearly all of the geophysical processes influencing the use and performance of current and proposed Air Force systems, including space-based communications and surveillance systems. Environmental effects on space-based systems, e.g., drag, electrostatic charging, and surface chemistry, are generally addressed in other AFOSR program areas. Magnetospheric processes are included in this program only to the extent that they affect the behavior of the ionosphere.

The atmospheric sciences program is comprised of two traditional research areas: tropospheric meteorology and the upper atmosphere (including the ionosphere). In each of these areas most of the funding is concentrated in a few areas of special emphasis. This approach to the allocation of funds, together with our encouragement of collaborative efforts among principal investigators, is intended to maximize the likelihood of major advances in the selected areas. In FY 83 the meteorology program continued to emphasize mesoscale processes, cloud physics, and atmospheric dynamics, while the upper atmosphere program emphasized a large cooperative analytical effort aimed at understanding the global character of auroral zone variability. The following sections describe research in the two primary areas and provide examples of recent accomplishments, major thrusts of ongoing efforts, and possible future directions of the program.

Meteorology

Research in mesoscale meteorology is aimed at the development of improved models for predicting atmospheric phenomena. The present uncertainties of such predictions are due, at least in part, to the imperfect representation of such processes as convection, radiation, and the exchange of heat and moisture with the earth's surface through the planetary boundary layer. Significant progress has been made by Dr. Elmar Reiter of Colorado State University both in the measurement of exchange processes at the surface and in the representation of these processes in a mesoscale model. Dr. Reiter and his colleagues developed instrumentation to measure the surface flux of latent and sensible heat, with the goal of obtaining measurements of these quantities in high terrain. The CSU research is aimed at determining the role of high terrain, such as the plateau regions of the U.S. and China, in the development of mesoscale and synoptic weather systems.

Research by Dr. Toby Carlson at the Pennsylvania State University is investigating the roles of surface wind divergence, moisture distribution, and vertical temperature structure on the development of mesoscale convective complexes. Soon to support the long-standing Penn State involvement in mesoscale modeling will be a network of three VHF radars now being constructed at Pennsylvania State under the Department of Defense University Research Instrumentation Program. These will provide measurements of the vector velocity and its spatial gradients with high resolution in time and height for incorporation into model simulations. The importance of mesoscale weather in military operations indicates that this area will continue to receive emphasis at AFOSR. The National STORM Program plan illustrates the broader importance of mesoscale meteorology and can be expected to provide a foundation upon which more specific AFOSR sponsored research will be based in the years ahead.

Efforts in cloud physics include water drop nucleation, precipitation development in clouds, optical and infrared scattering and transmission in clouds, and electrification. Closely related areas of interest include aerosol physics and the effects of aerosols and water vapor on visual/infrared propagation. The two cloud simulation chambers being built at the University of Missouri under the leadership of Dr. James Kassner with Tri-Service support are nearing completion. The small chamber is now undergoing operational tests, and the 3-meter chamber is expected to be ready for operational testing by late summer 1984. These chambers will provide an unprecedented capability for research in a wide variety of fundamental problems of cloud physics as well as a highly flexible capability for the development of cloud and aerosol sensors and for the investigation of signal propagation phenomena in aerosols and clouds. The phenomenology of lightning is being investigated through a joint research effort with the AF Flight Dynamics Laboratory and the Naval Research Laboratory. A key element of this research is the suspected triggering of lightning by aircraft. This and related efforts at the University of Manchester in England may be expected to yield essential knowledge related to the mitigation of lightning hazards to aircraft.

Research in atmospheric dynamics encompasses the planetary boundary layer, the transport of momentum and energy by gravity waves, and the dynamics of synoptic-scale weather systems. Progress in the latter two areas has been greatly facilitated by the use of high-power VHF and UHF radars. (Known as mesosphere-stratosphere-troposphere (MST) radars, these are also being used for research in the dynamics of the upper atmosphere.) Among the current research efforts utilizing these radars are those of Dr. Donald Farley at Cornell University and Dr. Daniel Keyser at NASA Goddard Space Flight Center, both of which involve the use of MST radars in the study of air mass frontal dynamics. Dr. Farley's research is primarily an observational study of frontal passages over a radar site, while Dr. Keyser's is primarily a one-dimensional numerical investigation which addresses,, among other topics, the use of high-resolution vector wind profiles derived from radars in the initialization of the numerical model. The value of VHF and UHF radars in the study of a wide variety of atmospheric dynamical processes virtually assures that research based on these observations will continue as an important part of the AFOSR program.

Upper Atmosphere

The primary emphases of the upper atmospheric research program are the temporal and spatial morphology of ionospheric structure, particularly electron density irregularities and gradients, and the dynamics of the upper atmosphere. The issues involved in this research are global in character and include auroral zone phenomenology, equatorial F-region irregularities, dynamics of the neutral components, distribution of chemical species, solar influences on the neutral atmosphere, ionospheric disturbances, deliberate and inadvertent ionospheric modification, and the modeling of ionosphere-magnetosphere interactions. Current research is strongly oriented toward understanding the spatial and temporal variability of the high-latitude ionosphere. Other research efforts include neutral winds and temperature in the equatorial F-region, interferometric measurement of winds in the high-latitude thermosphere, and theoretical studies of tidal motions in the upper atmosphere.

Analysis and interpretation of data acquired in the Magnetosphere-Ionosphere-Thermosphere Radar Studies (MITHRAS) observational phase continue to dominate the upper atmosphere program. The measurements were made between May 1981 and June 1982 by three incoherent scatter radars: Chatanika (Alaska), Millstone Hill (Massachusetts), and the European Incoherent Scatter (EISCAT) radar in Norway. Other measurements included in the analysis are from the NASA Dynamics Explorer (DE) satellite, the Scandinavian Twin Auroral Radar Experiment (STARE), and the worldwide magnetometer network. Participating scientists being supported by AFOSR include Dr. Odile de la Beaujardiere at SRI International, Dr. John C. Foster at Massachusetts Institute of Technology, and Dr Robert W. Schunk at Utah State University. Other participants are at the University of Texas at Dallas, Stanford University, the National Center for Atmospheric Research, and the Centre National d'Etudes de Telecommunications (CNET) in France. The EISCAT Scientific Association includes representatives of research organizations in France, Finland, West Germany, Norway, Sweden, and the United Kingdom. A significant result to emerge from this effort has been the capability of modeling time sequences of ionospheric structure observed simultaneously by two or three radars (Observations by a single radar may be modeled with the simplifying assumption of interchangeability of time and longitude). The MITHRAS effort will lead to greater understanding of the temporal and spatial variations of the upper atmosphere. Specific topics being addressed in the analysis include ion convection, discrete and diffuse aurorae, the midlatitude trough, field-aligned currents, and neutral winds.

In a distinctly different investigation AFOSR, NOAA, AFGL, Utah State University and the University of Alaska cooperated in a rocket radar experiment to confirm the performance and capability of the MST radar above 70km and, at the same time, investigate the early summer "turbulence" observed by the radar near 90km. The field program involved three rocket salvos (14, 15, 17 June 1983). The data from the radar and rocket sensors is currently being analyzed and results should be forthcoming in the near future.

The need to compare model calculations with experimental data and the difficulties and costs of obtaining and interpreting upper atmospheric data dictate that advances in knowledge will be closely tied to observational capabilities. Current and planned instrumentation capabilities include the line of incoherent scatter radars between Sondre Stromfjord, Greenland, and Jicamarca, Peru; the NASA Upper Atmosphere Research Satellite (UARS), and the continuing opportunities afforded by the Space Shuttle. Another possibility is the use of ultraviolet remote sensing for ionospheric dynamics research. As in the past, theory and observations will continue to support each other, as each poses problems or establishes requirements for the other. The results of the research sponsored by AFOSR may be expected to improve understanding of the environment in which aerospace systems operate and of the effects of Air Force operations on the environment.

RESEARCH EFFORTS COMPLETED IN FY 83

CHEMICAL TECHNIQUES - DENTON W. ELLIOTT

Molten Salt Electrochemical System AFOSR-80-0173	Roger K. Bunting Department of Chemistry Illinois State University Normal-Bloomington, IL 61761
Electrosorption of Organic Molecules AFOSR-80-0262	Robert de Levie Department of Chemistry Georgetown University Washington, DC 20057
High Energy Density Non-Aqueous Battery System AFOSR-82-0111	Vijay K. Gupta Department of Chemistry Central State University Wilberforce, OH 45384
Electrocatalysis of Oxygen Using Water Soluble Metal Porphryrins and Chemically Modified Porphyrin Electrodes AFOSR-78-3672	Theodore Kuwana Department of Chemistry Ohio State University Columbus, OH 43212
Innovative Detection, Separation, and Sampling Techniques for Trace Analysis by Gas Chromatography AFOSR-80-0011	Robert E. Sievers Department of Chemistry University of Colorado Boulder, CO 80309
Correlation of Electrode Kinetics with Surface Structure AFOSR-80-0271	Michael J. Weaver Department of Chemistry Michigan State University East Lansing, MI 48824
Atomic and Molecular Gas Phase Spectrometry F49620-80-C-0005	James D. Winefordner Department of Chemistry University of Florida Gainesville, FL 32611

COMPLETED PROJECT SUMMARY

1. TITLE: Molten Salt Electrochemical Systems

2. PRINCIPAL INVESTIGATOR: Professor Roger K. Bunting
Department of Chemistry
Illinois State University
Normal, IL 61761

3. INCLUSIVE DATES: 1 June 1980 - 31 March 1983

4. GRANT NUMBER: AFOSR-80-0173

5. COSTS AND FY SOURCE: $10,000, FY 80; $25,261, FY 81

6. SENIOR RESEARCH PERSONNEL: Professor D. X. West

7. JUNIOR RESEARCH PERSONNEL:

T. J. Parsons	R. B. Ashman

8. PUBLICATIONS:

"Spectroscopic Investigation of the Tetrachlorocobaltate(II), -nickelate(II) and -cuprate(II) Salts of 2-, 3-, and 4-Acetylpyridinium Cations," D. X. West, T. J. Parsons, and R. K. Bunting, Inorg. Chim. Acta., submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to investigate the physical and electrochemical properties of new molten salt systems which have properties suitable as electrolytes in secondary battery systems. Tetrachloroaluminate and tetrafluoroborate molten systems were explored, along with the fluoroarsenates and closochloroborate salts. Their thermal stabilities were examined. The unexpected thermal behavior of the $NaAlCl_4$-KBF_4 mixtures prompted a more thorough investigation of the thermal properties of KBF_4 alone. This investigation revealed that there is a solid state phase change in KBF_4 at a temperature of 286° C. The remaining alkali metal tetrafluoroborates were also examined. Except for $LiBF_4$ each of the salts gave an endothermic peak (reversible) on the Perkin-Elmer DSC corresponding to the orthorhombic to cubic transition. The enthalpies of these transitions have not been previously reported. The infrared spectra of three tetrachlorocobaltate salts were obtained as reflectance spectra. Each salt shows intense absorption near 300 cm^{-1}, which is assigned to a Co-Cl vibration of tetrahedral Co(II) species.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Electrosorption of Organic Molecules

2. PRINCIPAL INVESTIGATOR: Dr. Robert de Levie
Department of Chemistry
Georgetown University
Washington, DC 20057

3. INCLUSIVE DATES: 1 September 1980 - 30 September 1983

4. GRANT NUMBER: AFOSR-80-0262

5. COSTS AND FY SOURCE: $80,138, FY 80; $90,407, FY 82; $101,226, FY 83

6. SENIOR RESEARCH PERSONNEL:

Dr. M. M. Jones	Dr. F. Plucinski

7. JUNIOR RESEARCH PERSONNEL:

R. J. Atwell	J. Smuda
C. C. Chang	M. Saffarian
M. Krishnan	R. Sridharan
P. Lashmet	T. Tran

8. PUBLICATIONS:

"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., 117, 167 (1981).

"The Structure of Charged Interfaces," R. de Levie, Sensors and Actuators, 1, 97 (1981).

"Some Aspects of Modern Electrochemical Instrumentation," R. de Levie, Trans. SAEST, 109 (1981).

"On the Mutual Interactions of Adsorbed Molecules and Ions: Sucrose and Chloride in the Ternary System H_2O + Sucrose + NaCl at the Mercury-Water Interface," M. Krishnan and R. de Levie, J. Electronanal. Chem., 131, 97 (1982).

"Stochastic Effects in the Formation of Condensed Thymine Films at the Water-Mercury Interface," R. Sridharan and R. de Levie, *J. Phys. Chem.*, *86*, 4489 (1982).

"Hadamard Transform Alternating Current Polarography," C. C. Chang and R. de Levie, *Anal. Chem.*, *55*, 356 (1983).

"Closoborane Anion Adsorbs onto Lipid Bilayer Membranes and Affects Ion Transport," R. J. Atwell and R. de Levie, *J. Electroanal. Chem.*, *148*, 305 (1983).

"On One-Dimensional Nucleation and Growth of "Living" Polymers I: Homogeneous Nucleation," M. P. Firestone, S. K. Rangarajan, and R. de Levie, *J. Theoret. Biol.*, in press.

"On One-Dimensional Nucleation and Growth of "Living" Polymers II: Growth at Constant Monomer Concentration," S. K. Rangarjan and R. de Levie, *J. Theoret. Biol.*, in press.

"Electrochemical Observations of Single Molecular Events," R. de Levie, *Advances in Electrochemistry and Electrochemical Engineering*, H. Gerischer and C. W. Tobias, Eds., (Wiley), in press.

"On the Statistics of Electrochemical Nucleation: Application of the Non-Homogeneous Poisson Distribution," R. Sridharan and R. de Levie, *J. Electroanal. Chem.*, submitted.

"A Simple Separation of Faradaic and Charging Polarographic Currents," R. J. Atwell and R. de Levie, in preparation.

"The Kinetics of Formation of Thymine Films at the Mercury-Water Interface I: Deterministic Observations," R. Sridharan and R. de Levie, in preparation.

"The Kinetics of Formation of Thymine Films at the Mercury-Water Interface II: Stochastic Observations," R. Sridharan and R. de Levie, in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Objective. The original objective of this project was, first, to study the effect of adsorbed ions on the electrosorption of organic molecules, and vice versa and, second, to study the kinetics of formation of condensed films.

Study of the mutal effects of adsorbed ions and molecules. Numerous reports in the literature had suggested that there was a strong effect of specifically adsorbed anions on the simultaneous adsorption of organic molecules and, likewise, or organic electrosorption on the specific adsorption of anions. Such conclusions had often been reached by fitting measured adsorption data to presumed adsorption isotherms, followed by an interpretation of the fitted parameters. This method clearly depends on the validity of the assumed isotherm about which, unfortunately, there is a significant lack of consensus. The presence or absence of such mutual interactions without making any model assumptions was investigated. The choice of systems to study was limited by the following considerations:

a. There should be a significant range of potentials over which adsorption of both ions and organic molecules should occur simultaneously. Since ion adsorption is most pronounced at highly charged interfaces, whereas adsorption of neutral molecules is maximal in the region of zero electrode charge, such a requirement of sufficient adsorption overlap restricts the choice to strongly adsorbed ions and molecules.

b. The system should be one for which the thermodynamic activities of the mixtures are known, so that the interfacial effects can clearly be distinguished from those due to bulk interactions.

Only few systems satisfy both requirements. It was decided that the coadsorption of NaCl and sucrose would be the one. A large number of surface tension data (approximately 30,000) were collected with the computer-controlled, high-precision instrument. The result was surprising: after correction for the considerable mutual interactions in the bulk solution, and upon comparing data at constant electrode charge density (which already incorporates some effects of ionic and organic adsorption), no significant mutual effects could be detected. This despite the fact that chloride ions and sucrose molecules are considerably more crowded on the interface than they are in the bulk solution. The tentative interpretation of this result is that the mutual effects of NaCl and sucrose are most likely to be indirect, through their influence on the water structure. Since the structure of interfacial water is likely to be determined largely by the electric field, the influence of adsorbed ions and molecules on that structure, and hence their mutual interaction, may well be much weaker than that in solution.

Study of the kinetics of formation of condensed films. When this project began, a number of intriguing observations had been reported, showing that condensed monolayer films could be formed from a variety of organic molecules and under quite a range of circumstances. In many cases, their rate of formation had been reported to be quite slow, so that the kinetics of their formation should be experimentally accessible.

This laboratory first established that the formation of these films could be described in terms of conventional models for nucleation and growth of two-dimensional layers. Such models, however, allow only a semi-quantitative description, because they do not provide a way to differentiate between the rate parameters for nucleation and those for growth, even though these can be expected to have quite different functional behaviors.

It was realized that, in order to make progress beyond this point, a radically new approach was needed, which would allow one to observe individual nucleation events. Guided by the earlier work with bilayer membranes, where such observations are sometimes possible when the membrane area is made sufficiently small, the same approach was tried, and was successful. On a sufficiently small electrode, one is now able to observe individual nucleation events and, separately, the kinetics of growth of single nuclei.

Since individual nucleation events are stochastic, i.e., randomly distributed around some mean value, a large number of observations needs to be recorded in order to extract from these the rate parameters of nucleation. The necessary automated equipment was designed and built. The required data analysis methods for such a stochastic analysis was developed. The principal findings so far can be summarized as follows:

a. The formation of condensed films of thymine and of guanine at the interface between mercury and aqueous electrolyte solutions is a nucleated process.

b. Such nucleation can be observed as a stochastic process, by making the electrode surface sufficiently small. In our case, an electrode area of approximately 0.04 mm^2 was used.

c. Nucleation in both cases follows non-steady-state kinetics; the corresponding statistics are those of a non-homogeneous Poisson distributon.

d. The rate of nucleation is a strong function of potential. The specific law involved has yet to be determined.

e. From the nucleation statistics, one can obtain an estimate of the stoichiometry of the critical nucleus. The numbers so obtained, of the order of 10, also depend on potential.

f. Growth of single nuclei can be observed directly. Such growth can be described quantitatively by a simple model of isotropic growth.

g. The resolution of the growth data is insufficient to decide whether the condensed film is a two-dimensional liquid or solid, i.e., whether its shape is principally determined by considerations of edge energy or those of molecular packing.

h. The dissolution of a condensed film follows simple first-order order kinetics, and does not seem to involve nucleation.

j. With thymine, additional condensed phases are observed at lower temperatures. It is likely that these are also monolayer films, but with different molecular orientations, governed largely by interactions of the dipole moment with the electric field of the double layer.

k. The region of stability of the condensed phases observed depends strongly on both potential and concentration, as expected. However, it also depends on the nature and concentration of the electrolyte used, although the precise nature of that dependence has not yet been clarified.

Clearly, the possibility to observe, separately, the kinetics of nucleation and growth, and to study their functional dependencies, is opening a rich new field of observations in an area of general importance in many scientific disciplines. The type of detailed information on the kinetics of nucleation and growth which can now be obtained is available in only very few cases. The electrochemical context is very helpful, because the two-dimensional nature of the phenomenon allows precise control of experimental conditions as well as efficient buffering of interfacial concentrations while, at the same time, sensitive detection is facilitated.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: High Energy Density Non-Aqueous Battery Systems

2. PRINCIPAL INVESTIGATOR: Dr. Vijay K. Gupta
Department of Chemistry
Central State University
Wilberforce, OH 45384

3. INCLUSIVE DATES: 1 April 1982 - 31 March 1983

4. GRANT NUMBER: AFOSR-82-0111 (Mini-Grant)

5. COSTS AND FY SOURCE: $9,999, FY 82

6. PUBLICATIONS:

"High Energy Density Non-Aqueous Battery System," V. K. Gupta, Final Scientific Report.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The corrosion of the calcium anode in the calcium thionyl chloride cell has been a persistant problem which has kept this otherwise attractive couple from use in commercial batteries. This report includes the work on corrosion studies of calcium/calcium-lithium alloys in thionyl chloride electrolyte systems as a function of $LiAlCl_4$ concentration, time, and temperature, and investigations of cells with anodes made from calcium/calcium-lithium alloys. The results of corrosion studies indicate the following: (1) the corrosion of calcium and calcium-lithium alloys is a significant problem; (2) the corrosion phenomena is very sensitive to air and moisture; (3) the corrosion occurs during storage and more rapidly at 55° C; (4) in pure thionyl chloride the alloys appear to be more resistant to corrosion than pure calcium metal; (5) in electrolyte solutions ($LiAlCl_4$ in thionyl chloride, concentration range 0.6 M to 1.8 M) the calcium metal seems to be more resistant to corrosion than the alloys, and 1.2 M electrolye seems to be suitable for batteries; and (6) the corrosion film formed on the surface appears to be mechanically unstable since it periodically becomes loose with time and comes off. The results indicate that some degree of synergism does exist but that the surface film is not sufficiently stable to protect the anode from continuous corrosion. It is concluded that the stability problem is one of a mechanical shedding of the film which occurs independent of lithium content in the alloy. Also, it is felt that a change in the electrolyte salt is the most promising approach to calcium corrosion problem.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Electrocatalysis of Oxygen Using Water Soluble Metal Porphyrins and Chemically Modified Porphyrin Electrodes

2. PRINCIPAL INVESTIGATOR: Professor Theodore Kuwana
Department of Chemistry
Ohio State University
Columbus, OH 43212

3. INCLUSIVE DATES: 1 September 1978 - 31 March 1983

4. GRANT NUMBER: AFOSR-78-3672

5. COSTS AND FY SOURCE: $54,164, FY 78; $64,114, FY 79; $72,039, FY 81
$49,991, FY 82

6. SENIOR RESEARCH PERSONNEL:

Dr. A. Bettelheim
Dr. D. DiMarco
Dr. D. Karweik
Dr. S. Weng
Dr. J. Zak

7. JUNIOR RESEARCH PERSONNEL:

J.-H.R. Chan
P. Forshey
W.-H. Kao
C. W. Miller
M. D. Porter
T. Harbaugh
K. Lyons
L. Marshall
R. Trask
L. Siperko

8. PUBLICATIONS:

"Rotating Ring-Disc Analysis of Iron Tetro-(N-methylpyridyl)porphyrin in Electrocatalysis of Oxygen," A. Bettelheim and T. Kuwana, *Anal. Chem.*, *51*, 2257 (1979).

"Electrocatalysis of Oxygen Reduction, Part III. Selective Reduction to Hydrogen Peroxide Reduction or Water Using Polymeric Attachment of Metalloporphyrins," A. Bettelheim, R.J.H. Chan, and T. Kuwana, *J. Electroanal. Chem.*, *110*, 93 (1980).

"Electrochemical and Spectral Speciation at Iron Tetrakis(N-methyl-4-pyridyl)porphyrin in Aqueous Media," P. A. Forshey and T. Kuwana, *Inorg. Chem.*, 20, 693 (1981).

"Scanning Electron Microscopic and X-Ray Photoelectron Spectroscopic Examination of Tokai Glassy Carbon Surfaces Subjected to Radio Frequency Plasmas," C. W. Miller, D. H. Karweik, and T. Kuwana, *Anal. Chem.*, *53*, 2319 (1981).

"A Versatile Sample Isolation, Chemical Modification and Introduction System Designed for Physical Electronics Model 548 Electron Spectrometer," C. W. Miller, J. R. Fagan, D. H. Karweik, and T. Kuwana, Appl. Surf. Science, 9, 214 (1981).

"Radio Frequency Plasma Introduction of Surface Functionalities onto Carbon and Surface Characterization by X-Ray Photoelectron Spectroscopy," C. W. Miller, D. H. Karweik, and T. Kuwana, Recent Advances in Analytical Spectroscopy, K. Fuwa, Ed., (Pergamon Press, New York), pp. 233-247 (1982).

"Electrocatalytic Reduction of Molecular Oxygen Using Water-Soluble and Immobilized Iron and Cobalt Porphyrins," P. Forshey, T. Kuwana, N. Kobayashi, and T. Osa, Advances in Chemistry, Series No. 201, K. Kadish, Ed., (American Chemical Society Publ., Washington, DC), pp. 601-614 (1982).

"A Simulation of the Cyclic Voltammetric Characteristics of a Second Order EC Catalytic Mechanism," D. DiMarco, P. Forshey, and T. Kuwana, ACS Symposia Series No. 192, Chemically Modified Surfaces in Catalysis and Electrocatalysis, J. S. Miller, Ed., (American Chemical Society Publ., Washington, DC), pp. 71-97 (1982).

"Prospects in the Analysis of Chemically Modified Electrodes," D. H. Karweik, C. W. Miller, M. D. Porter, and T. Kuwana, ACS Symposium Series No. 199, Industrial Applications of Surface Analysis, L. A. Casper and C. J. Powell, Eds., (Americal Chemical Society Publ., Washington, DC), pp 89-119 (1982).

"Electrochemistry of Oxygen Reduction. 4. Oxygen to Water Conversion by Iron(II) Tetrakis(M-methyl-4-pyridyl)porphyrin via Hydrogen Peroxide," P. Forshey and T. Kuwana, Inorg. Chem., 22, 699 (1983).

"The Detection Capabilities of Fourier Transform External Reflection and Photoacoustic Spectroscopy for Electrode Supported Films," M. D. Porter, D. H. Karweik, T. Kuwana, W. B. Theis, and G. B. Morris, Appl. Spec., accepted.

"Thin-Layer Electrochemical Cell Optimized for Long Optical Pathlength Observation of Solution Species," J. Zak, M. D. Porter, and T. Kuwana, Anal. Chem., accepted.

"Electrocatalysis by Electrodeposited Spherical Pt Micro-Particles Dispersed in a Polymeric Film Electrode," W-H. Kao and T. Kuwana, J. Amer. Chem. Soc., accepted.

"Glassy Carbon and Graphite Holey Electrodes for Long Pathlength, Thin-Layer Spectroelectrochemistry," M. D. Porter and T. Kuwana, Anal. Chem., submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Primary effort was devoted to the study of oxygen reduction using water-soluble iron and cobalt porphyrins, namely, iron and cobalt tetrakis [N-methyl-4-pyridyl]porphyrin. These prophyrins with the metal in the +3 oxidation state can be electrochemically reduced to the divalent state which then reacted with oxygen. In the case of the iron containing porphyrin, oxygen was reduced at a bimolecular rate of ca. 1×10^7 l/m/s to hydrogen peroxide which was then reduced rapidly to water. A mechanistic scheme was postulated for the reduction and using experimentally determined parameters, current-potential curves were simulated. Good agreement between the experimental and computer calculated current-potential curves supported the proposed scheme. Cross-correlation between optical, electrochemical and magnetic circular dichroism results have provided axial ligation, dimerization and spin state information of the ferric and ferrous tetrakis[N-methyl-4-pyridyl]porphyrins. Glassy or graphitic carbon electrodes were rendered catalytic by the incorporation of iron porphyrin derivatives, e.g. iron tetra-(oamino-phenyl)porphyrin and iron tetra-[N-(2-hydroxyethyl) pyridyl]porphyrinΣ in thin polymeric films adhering to the carbon. The extent of oxygen reduction to hydrogen peroxide and water depended on the amount of iron porphyin.

In the case of the water-soluble cobalt tetrakis[N-methyl-4-pyridyl]porphyrin, it irreversibly adsorbed onto the glassy carbon surface and produced hydrogen peroxide as the main product with nearly a 100 percent current efficiency. It was found that the electron transfer rate between the adsorbed cobalt porphyrin and that in solution could be accelerated by the presence of thiocyanate ion.

It was also deemed important to prepare in a predictable manner the surface of carbon electrodes and to be able to determine the physical and chemical nature of the surface. Radio frequency plasma was one method of introducing surface functional groups with the functionality dependent on the nature of the reactive gas. Surface topography of the carbon electrodes was determined by scanning electron microscopy, and surface elemental and functional group analysis was by x-ray photoelectron and auger spectroscopy. Optical methods (FTIR reflectance, uv-vis spectroelectrochemistry) were also explored as part of our effort to analyze functional and molecular species on carbon surfaces.

Finally, it was discovered that metals could be electrodeposited as dispersed micro particles into a thin polymeric matrix of polyvinylacetic acid adhering on a glassy carbon surface. These microparticles were randomly dispersed through the polymer with a gaussian size distribution. Large surface areas of the metal could be achieved with low loading levels. The electrocatalytic generation of hydrogen and reduction of oxygen were studied.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Innovative Detection, Separation, and Sampling Techniques for Trace Analysis by Gas Chromatography

2. PRINCIPAL INVESTIGATOR: Professor Robert E. Sievers
Department of Chemistry
Campus Box 215
University of Colorado
Boulder, CO 80309

3. INCLUSIVE DATES: 1 October 1979 - 30 September 1983

4. GRANT NUMBER: AFOSR-80-0011

5. COSTS AND FY SOURCE: $60,155, FY 80; $85,000, FY 81; $100,000, FY 82
$110,000, FY 83

6. SENIOR RESEARCH PERSONNEL:

Dr. R. M. Barkley
Dr. K. C. Brooks
Dr. C. A. Koval
Dr. R. W. Siergiej
Dr. S. Singhawangcha

7. JUNIOR RESEARCH PERSONNEL:

M. K. Conditt
J. DeAngelis
J. N. Gillis
R. C. Greaves
S. D. Harvey
S. B. Hawthorne
A. J. Hills
R. S. Hutte
B. A. Medeiros
S. A. Nyarady
M. P. Phillips
J. E. Picker
K. W. Sigvardson
S. W. Stiller
E. J. Williams
M. A. Wizner

8. PUBLICATIONS:

"Gas Chromatography Combined with Mass Spectrometry in Studies of Complex Mixtures of Tris(β-diketonato)chromium(III) Geometrical Isomers with Fused Silica Capillary Columns," R. E. Sievers and K. C. Brooks, *Int. J. of Mass Spectr. and Ion Physics*, *47*, 527 (1983).

"Trennung der Geometischen Isomere von Cr-β-Diketonaten mit Reversed-Phase HPLC," B. Wenclawiak und R. E. Sievers, *Fresenius Z. Anal. Chem.*, *314*, 682 (1983).

"Selective Electron Capture Sensitization of Water, Phenols, Amines and Aromatic and Heterocyclic Compounds," M. A. Wizner, S. Singhawangcha, R. M. Barkley, and R. E. Sievers, *J. Chromatogr.*, *239*, 145 (1982).

"Selective Electron Capture Sensitization," M. P. Phillips, P. D. Golden, F. C. Fehsenfeld, and R. E. Sievers, Electron Capture - Theory and Practice in Chromatography," (Elsevier Publishing Co) 1981.

"Applications of Selective Complexation by a Europium(III) Coordination Polymer Sorbent for the Pre-fractionation of Volatile Compounds," J. E. Picker and R. E. Sievers, J. Chromatogr., 217 275 (1981).

"Lanthanide Metal Chelates as Selective Complexing Sorbents for Gas Chromatography," J. E. Picker and R. E. Sievers, J. Chromatogr., 203, 29 (1981).

"Vinyl Chloride Detection at Sub-ppb Levels Using a Chemically Sensitized Electron Capture Detector," P. D. Golden, F. C. Fehsenfeld, W. C. Kuster, M. P. Phillips, and R. E. Sievers, Anal. Chem., 52, 1751 (1980).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objectives of the research originally proposed under the grant are presented below.

a. Continuation of the development and study of selective electron capture sensitization (SECS) as a means to perform highly sensitive measurements of compounds that generally are not amenable to electron capture detection.

b. Pre-analysis separation of complex mixtures using a serial sorbent sample collection system.

c. Studies of chromatographic columns using lanthanide metal chelates including chiral chelates as a means to separate optical isomers.

d. Studies of microwave heating in chromatographic systems.

The following summarizes the results and conclusions of this research.

Selective Electron Capture Sensitization (SECS)

Progress has been made in understanding and eliminating response peculiarities observed with a N_2O-SECS system. Several problems associated with SECS are eliminated by carefully purifying the gases employed in the system. Various gas purifying schemes have been used and a suitable purifying agent has been found that results in reproducible behavior of the system.

Various classes of organic compounds have been studied using SECS. Sizable signal enhancements have been recorded for acetonitrile, acrylonitrile, acrolein, and various amines, phenols, and polycyclic aromatic hydrocarbons. The technique was used to aid in the identification of phenolic compounds in a complex wastewater fraction. A method for the trace analysis of vinyl chloride has also been developed using SECS.

Large differences in response have been found for closely related isomers of amines. These differences could be exploited to positively identify isomers which cannot be identified by other techniques such as mass spectroscopy.

The SECS technique is now being used routinely by other groups. Scientists at the NOAA Aeronomy Laboratory, Boulder, Colorado, collaborators on the initial development of SECS, use the technique to monitor CO concentrations in ambient air. The group has helped Dr. Randolph Ware, a geophysicist colleague at the Cooperative Institute for Research for Environmental Sciences at the University of Colorado to use SECS to monitor H_2 concentrations in soil gases along earthquake fault zones.

Selective Sorbents

A novel bis(β-diketone), H_2dihed, [p-di(4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl)benzene] has been synthesized. This compound has the ability to form coordination polymers with the lanthanides. The polymers retain the excellent Lewis acidity characteristics of previously synthesized fluorinated tris(β-diketonates), yet are extremely non-volatile and consequently more suitable for use as stationary phases in gas chromatography. When incorporated into a pre-analytical column, the polymers were shown to be effective in separating oxygenated compounds from hydrocarbons and chlorinated hydrocarbons, based upon complexation between the nucleophilic oxygen and the coordinatively unsaturated lanthanide.

The pre-column sorbent was applied to the separation of complex-forming from non-complex-forming solutes in the analysis of volatile organic compounds in wastewater effluent, a fragrance essence, tobacco smoke, urine and gasoline. In each case a separation into two fractions was accomplished, producing simplified chromatograms. The net result has facilitated identification of organic compounds by mass spectral and retention time matching techniques. Based on these tests with a variety of sample types containing highly complex mixtures, it can be concluded that this is a highly promising analytica strategy.

Lanthanide β-diketonates have been successfully bonded to styrene-divinylbenzene copolymers. This sorbent has been characterized and used in the analyses of oxygenated species in the atmosphere. Preliminary experiments have also been performed using N,N-ethylenebis (salicylideniminato)cobalt(II), CO(salen), coated on glass beads. This compound shows selectivity for the retention of Lewis bases containing nitrogen such as pyridine and methylpyridines.

The development of a selective sorbent for olefinic compounds has not been successful. Neither Rh(facam)$(CO)_2$, where facam is trifluoroacetyl-d-camphorate, nor Ag(hfa), where hfa is 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, retained any of the olefins passed over a bed of the complex that had been dissolved in a liquid phase and coated on a solid support. Many Pd complexes have also been studied. Although olefins can be retarded in the GC analysis, the interaction does not appear to be strong enough to quantitatively trap target compounds for later desorption and analysis. During the course of this study, however, an improved procedure has been discovered for the synthesis of di(o-phenylenebisdimethylarsine)-palladium(II)dichloride and dichloro-o-phenylenebisdimethylarsine-palladium(II).

Chromatography with Metal Chelates

A mixture of synthesized mixed-ligand Cr(III) complexes was studied by GC/MS. The misture was made from an equimolar solution of Cr(III), Hhfa (1,1,1,5,5,5-hexafluoro-2,4-pentanedione), Htfa (1,1,1-trifluoro-2,4-pentanedione), and Hfod (2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione). Of the 25 possible products, 24 were resolved using a fused silica capillary GC column. Mass spectrometric detection led to facile assignment of identities of the complexes and yielded information concerning gas phase stabilities.

A number of metal chelates with a new ligand, 2,2,7-trimethyloctane-3,5-dione, Htod, have been investigated for their use in gas and liquid chromatographic separations of transition metals. $Cr(tod)_3$ shows extraordinary stability in gas chromatographic columns at temperatures high enough to produce reasonably rapid elution. $Cr(tod)_3$ and $Co(tod)_3$ form geometrical isomers which can be separated on a reversed-phase analytical HPLC column using acetonitrile and water as eluents. $Ni(tod)_2$ MeOH,•$VO(tod)_2$, and $Hg(tod)_2$ have been synthesized and the properties of these new compounds studied. These metal chelates and the isomers of the more stereochemically rigid complexes have been characterized by thermal gravimetric analysis, mass spectrometry, and in the case of the diamagnetic $Co(tod)_3$, by nuclear magnetic resonance spectrometry. Additionally, the separation of all the geometrical isomers in a mixture of $Cr(tfa)_3$, $Cr(fod)_3$, and $Cr(tod)_3$ was acccomplshed in a single HPLC experiment.

The symmetrical hexadentate ligand, 1,1,1-tris-(2-oxo-9,9,9-trifluoro-6,8-nonanedione)ethane (H_3tfne), has been synthesized. The synthesis of the Co(II), Co(III), Fe(III), Eu(III) and Yb(III) complexes with H_3tfne have been investigated, but characterization of the complexes have proven difficult.

The use of chiral lanthanide metal chelates in gas chromatographic stationary phases has resulted in limited success. A stationary phase containing $Eu(III)(facam)_3$ was able to partially resolve the isomers of epoxypropane.

Microwave Heating in Chromatographic Systems

Several attempts were made to use selective microwave heating in chromatographic systems, with limited success. The first involved the selective heating of a microwave-absorbing liquid phase (TCEP) coated on Chromosorb W. Some changes were seen in the separation of six test compounds, but it has been difficult to regulate and predict the effects of microwave radiation on other chromatographic separations.

AFOSR Program Manager: Denton W. Elliott

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 October 1980 - 30 January 1983

4. GRANT NUMBER: AFOSR-80-0271

5. COSTS AND FY SOURCE: $69,591, FY 81; $80,878, FY 82

6. SENIOR RESEARCH PERSONNEL:

Dr. S. Farquharson
Dr. T.T.-T. Li
Prof. D. Larkin
Dr. V. Srinivasan

7. JUNIOR RESEARCH PERSONNEL:

S. Barr
K. Guyer
H.-Y. Liu
M. Wilson
J. K. Farmer
J. Hupp
E. Schindler

8. PUBLICATIONS:

"Electrochemical Reactions," M. J. Weaver, *Inorganic Reactions and Methods*, J. J. Zuckerman, Ed., (Verlag Chemie), in press.

"The Influence of Lead Underpotential Deposition on the Capacitance of the Silver-Aqueous Interface," J. T. Hupp, D. Larkin, H. Y. Liu, and M. J. Weaver, *J. Electroanal. Chem.*, *131*, 299 (1982).

"The Reduction Kinetics of Pentaamminecobalt(III) Complexes Containing 4,4'-Bipyridine and Related Ligands at Mercury, Platinum and Gold Electrodes," V. Srinivasan, S. W. Barr, and M. J. Weaver, *Inorg. Chem.*, *21*, 3154 (1982).

"Inner-Sphere Reactivity at Solid Metal Surfaces: Adsorbed Transition-Metal Reactants at Silver, Platinum, and Gold Electrodes," K. L. Guyer, S. W. Barr, and M. J. Weaver, *Electrocatalysis 1981*, P. N. Ross, Ed., (Electrochemical Society, Pennington, NJ), pp. 377 (1982).

"Some Comparisons between the Energetics of Electrochemical and Homogeneous Electron-Transfer Reactions," M. J. Weaver and J. T. Hupp, *Mechanistic Aspects of Inorganic Reactions*, D. B. Rorabacher and J. F. Endicott, Eds., *ACS Symp. Ser.*, *198*, 181 (1982).

"Determination of Specific Adsorption of Some Simple Anions at a Polycrystalline Silver-Aqueous Interface using Differential Capacitance and Kinetic Probe Techniques," D. Larkin, K. L. Guyer, J. T. Hupp, and M. J. Weaver, *J. Electroanal. Chem.*, *138*, 401 (1982).

"Electrochemical Reactivity at Solid Electrodes: Rate Parameters for Adsorbed Transition-Metal Reactants at the Silver-Aqueous Interface," K. L. Guyer and M. J. Weaver, *J. Am. Chem. Soc.*, submitted.

"Electrochemical Reactivity at Solid Electrodes: Relative Energetics of Some Inner- and Outer-Sphere Pathways at Platinum- and Gold-Aqueous Interfaces," S. W. Barr and M. J. Weaver, *J. Am. Chem. Soc.*, submitted.

"The Significance of Electrochemical Activation Parameters for Surface-Attached Reactants," J. T. Hupp and M. J. Weaver, *J. Electroanal. Chem.*, *145*, 43 (1983).

"A Parallel Simulation Scheme for the Rapid Accurate Calculation of Nonideal Electrochemical Transients," W. E. Schindler, Jr. and M. J. Weaver, *Anal. Chim. Acta*, *147*, 347 (1983).

"Electrochemical and Homogeneous Exchange Kinetics for Transition-Metal Aquo Couples: Anomolous Behavior of Hexaaquo Iron(III)/(II)," J. T. Hupp and M. J. Weaver, *Inorg. Chem.*, in press.

"Surface-Enhanced Raman Spectroscopy of Electrochemically Characterized Interfaces Potential Dependence of Raman Spectra for Thiocyanate at Silver Electrodes," M. J. Weaver, F. Barz, J. G. Gordon II, and M. R. Philpott, *Surf. Sci.*, *125*, 409 (1983).

"Effect of Laser Illumination during Oxidation-Reduction Cycles upon Surface-Enhanced Raman Scattering from Silver Electrodes," F. Barz, J. G. Gordon II, M. R. Philpott, and M. J. Weaver, *Chem. Phys. Lett.*, *91*, 291 (1982).

"Time Dependence of Surface-Enhanced Raman Scattering During and After Oxidation-Reduction Cycles," M. R. Philpott, F. Barz, J. G. Gordon II, and M. J. Weaver, *J. Electroanal. Chem.*, in press.

"Comparisons between Theoretical and Experimental Deuterium Isotope Effects for Some Outer-Sphere Electrochemical Reactions," M. J. Weaver and T. T.-T. Li, *J. Phys. Chem.*, *87*, 1153 (1983).

"Specific Adsorption of Halide and Pseudohalide Ions at Electrochemically Roughened Versus Smooth Silver-Aqueous Interfaces," J. T. Hupp, D. Larkin, and M. J. Weaver, *Surf. Sci.*, *125*, 429 (1983).

"The Influence of Experimental Nonidealities on the Determination of Rapid Electrochemical Rate Constants using Large-Amplitude Potential Steps," P. D. Tyma, E. W. Schindler, Jr., and M. J. Weaver, *Anal. Chem.*, submitted.

"The Frequency Factor for Outer-Sphere Electrochemical Reactions," J. T. Hupp, and M. J. Weaver, *J. Electroanal. Chem.*, in press.

"Dependence of Electrocatalysis for Oxygen Reduction by Adsorbed Dicobalt Cofacial Porphyrins upon Catalyst Structure," H. Y. Liu, M. J. Weaver, C-B. Wang, and C. K. Chang, *J. Electroanal. Chem.*, *145*, 439 (1983).

"The Nonadiabaticity Question for Europium(III)/(II): Outer-Sphere Reactivities of Eu(III)/(II) Cryptates," E. L. Yee, J. T. Hupp, and M. J. Weaver, *Inorg. Chem.*, in press.

"Observation of a Reversible Adsorbed Redox Couple Using Surface-Enhanced Raman Scattering: Pentaammine Pyridineosmium(III)/(II) at Silver Electrodes," S. Farquharson, M. J. Weaver, P. A. Lay, R. H. Magnuson, and H. Taube, *J. Am. Chem. Soc.*, *105*, 3350 (1983).

"Entropic Driving Force Effects upon Preexponential Factors for Intramolecular Electron Transfer: Implications for the Assessment of Nonadiabaticity," J. T. Hupp and M. J. Weaver, *Inorg. Chem.*, submitted.

"Surface-Enhanced Raman Spectroscopy of Electrochemically Characterized Interfaces. Relations between Raman Scattering Intensity and Surface Coverage for Simple Anionic Adsorbates," M. J. Weaver, J.T. Hupp, F. Barz, J. G. Gordon II, and M. R. Philpott, *J. Electroanal. Chem.*, in press.

"Electron-Transfer Kinetics of Redox Centers Anchored to Metal Surfaces: Weak- versus Strong-Overlap Reaction Pathways," S. W. Barr, K. L. Guyer, T. T.-T. Li, H. Y. Liu, and M. J. Weaver, *The Chemistry and Physics of Electrocatalysis*, J.D.E. McIntyre, M. J. Weaver, and E. Yeager, Eds., (The Electrochemical Society, Pennington, NJ), in press.

"Redox Thermodynamics of Surface-Bound Reactants. Illustrative Behavior of Cobalt(III)/(II) Macrobicyclic 'Cage' Complexes", J. T. Hupp, P. A. Lay, H. Y. Liu, W.H.F. Petri, A. M. Sargeson, and M. J. Weaver, *J. Electroanal. Chem.*, submitted.

"Utilities of Surface Reaction Entropies for Examining Reactant-Solvent Interactions at Electrochemical Interfaces. Ferricinium-Ferrocene Attached to Platinum Electrodes," J. T. Hupp, and M. J. Weaver, *J. Electrochem. Soc.*, submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective was to develop an understanding of the connections between the kinetics and mechanisms of heterogeneous electron-transfer reactions at metal-electrolyte interfaces and the molecular structure of the reactant and the interfacial region. Attention was focussed on transition-metal redox couples, especially Co(III)/(II), Cr(III)/(II), and Ru(III)/(II) containing adsorbing inorganic and organic ligands at a number of electrocatalytic solid surfaces, especially silver, platinum, and gold, as well as at mercury electrodes. By combining electrochemical kinetic and reactant adsorption thermodynamic measurements, along with *in situ* vibrational spectroscopic studies using Surface-Enhanced Raman Scattering (SERS), the various catalytic influences exerted by the metal interface upon the energetics of electrode reactions have been probed in detail.

A summary of accomplishments includes the following. The electron-transfer kinetics of a number of Co(III)/(II) and Cr(III)/(II) couples attached to mercury, silver, platinum, and gold surfaces via simple inorganic bridging groups has been monitored in order to ascertain how the energetics of electron transfer depend upon the chemical nature of the electrode surface and the structure of the bridging ligands. Comparisons were made with the kinetics of corresponding outer-sphere reactions in both electrochemical and homogeneous reaction environments. These comparisons indicate that the elementary barrier to heterogeneous electron transfer can be significantly lowered by surface attachment, although the catalyses thus induced are somewhat smaller than often found for homogeneous ligand-bridged processes.

Concurrent with these experimental studies, kinetic formalisms were developed to aid the comparison between experiment and contemporary theoretical models, and to facilitate the analysis of electrochemical kinetic data in a parallel fashion to the sophisticated treatments recently developed for homogeneous electron-transfer processes.

An important new development in the research program has been to utilize SERS to provide molecular-level information on the structure of adsorbates, especially those engaging in electron-transfer reactions. Initial studies have focussed on establishing quantitative relationships between the nature and intensity of the SERS spectra and the interfacial composition of silver-aqueous interfaces determined independently by electrochemical means. These studies have included the quantitative determination of electrode coverage-potential data for a number of structurally simple adsorbed anions and the direct comparison with corresponding SERS intensity-potential for these adsorbates. This group recently reported the first observation of a simple adsorbed redox couple, $Os(NH_3)_5$ pyridine(III)/(II), using SERS. These studies are providing hitherto unavailable information on the nature of adsorbate-surface bonding in structurally well-defined electrochemical systems.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Atomic and Molecular Gas Phase Spectrometry

2. PRINCIPAL INVESTIGATOR: Professor J. D. Winefordner
Department of Chemistry
University of Flordia
Gainesville, FL 32611

3. INCLUSIVE DATES: 1 October 1979 - 30 September 1983

4. CONTRACT NUMBER: F49620-80-C-0005

5. COSTS AND FY SOURCE: $219,903, FY 80; $221,009, FY 81; $192,480, FY 82
$215,576, FY 83

6. SENIOR RESEARCH PERSONNEL:

Dr. M. Blackburn
Dr. J. Bradshaw
Dr. K. Fujiwara
Dr. O. Genc
Dr. S. Hanamura
Dr. I. Kantor
Dr. K. Liu
Dr. G. Long
Dr. J. McHard
Dr. K. Ohta
Dr. N. Omenetto
Dr. R. Smith
Dr. D. Stojanovic
Dr. H. Uchida
Dr. C. van Dijk
Dr. E. Voigtman
Dr. P. Walters
Dr. R. Ward
Dr. G. Zizak

7. JUNIOR RESEARCH PERSONNEL:

E. Akomer
S. Bayer
D. Bolton
J. Bower
J. Bradshaw
M. Elder
L. Hirschy
J. Horvath
E. Inman, Jr.
H. Jurgensen
H. Karnes
J. Kerkhoff
M. Kosinski
R. Krupa
E. Lai
J. Lanauze
S. McCall
S. Y. Su
A. Wang
J. Ward
P. Wittman
T. Wynn

8. PUBLICATIONS:

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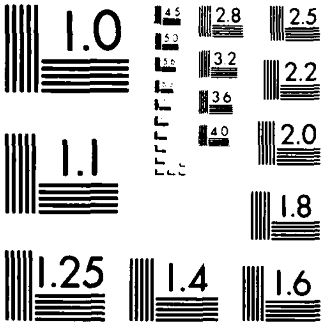
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"A Review and Tutorial Discussion of Noise and Signal-To-Noise Ratios in Analytical Spectrometry-III., Multiplicative Noises," C.Th.J. Alkemade, W. Snelleman, G. D. Boutilier, and J. D. Winefordner, Spectrochim. Acta B, 35, 261 (1980).

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"Laser Excited Atomic Fluorescence with Graphite Filament Atomization," P. Wittman and J. D. Winefordner, Canad. J. Spectrosc., in press.

"Laser Excited Atomic Fluorescence Technique for Temperature Measurements in Flames: A Summarizing Table," G. Zizak, N. Omenetto, and J. D. Winefordner, Spectrochim. Acta B, submitted.

"A Single Electrode Atmospheric Pressure Microwave Discharge System for Elemental Analysis," S. Hanamura, B. W. Smith, and J. D. Winefordner, Canad. J. Spectrosc., in press.

"Spatially Resolved Concentration Studies of Ground State Atoms in a Flame: Saturated Absorption Spectroscopic Methods," P. E. Walters, J. Lanauze, and J. D. Winefordner, Spectrochim. Acta B, in press.

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"Comparison of Nebulizer-Burner System For Laser Excited Atomic Fluorescence Spectrometry," J. J. Horvath, J. D. Bradshaw, J. N. Bower, M. S. Epstein, and J. D. Winefordner, Anal. Chem., 53, 6 (1981).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The major goals of this research have been to develop diagnostical spectroscopic methods for measuring spatial/temporal temperatures of combustion flames and plasmas and to develop sensitive, selective, precise, reliable, rapid spectrometric methods of trace analysis of elements present in jet engine libricating oils, metallurgical samples, biological materials, and automobile and other engine exhausts. The diagnostical approaches have been based upon the measurement of pulsed laser excited fluorescence of seeds, such as In, Tl, Pb, etc., introduced into the flames, plasmas, or hot gases or in the case of flames, the measurement of natural flame species as OH. Because of the excellent fluorescence signal to noise ratios, it has been possible to measure temperatures of combustion flames for volumes smaller than 1 mm^3 and for single laser pulses of a few nanoseconds. The technique with the most promise for use in combustion flames and in reactors is based upon thermally assisted fluorescence of an externally introduced seed as Tl or In or of an internal species as OH. By exciting the species with a dye laser and measuring the fluorescence from energy levels thermally excited from the laser excited state, the flame (plasma) temperature can be readily measured (±10^{o}C) for a volume <1 mm^3 and for a single laser pulse.

Other diagnostical studies during the past four years have included: an evaluation of the spatial and spectral characteristics of the EIMAC (CERMAX) xenon point arc source; study of the reaction sequences and quantitative changes of alkaline earth phosphates in the presence of lanthanum salts; derivation of the rate equations describing the temporal behavior of 3-level atoms excited by a pulsed dye laser and extension of the theory to thermally assisted levels; evaluation of the significance of detection limits defined by IUPAC, measurement of the collisional redistribution of radiatively-excited levels of Na, Tl and Ga atoms in acetylene flames using pulsed laser excited fluorescence; development of an extended model for saturation in 2-level and 3-level atoms or molecules, including the temporal dependence; measurement of spatial and temporal characteristics of Na in a low pressure Ar or Ne glow discharge as studied by laser excited fluorescence; measurement of atom diffusion coefficients at high temperatures using an atomic absorption method; definition of the saturation spectral irradiance as applied to 2-level and 3-level energy systems and measurement of saturation for several atoms by laser excited fluorescence; experimental evaluation of diffracted stimulated emission as a poor analytical tool; measurement of volatilization characteristics of magnesium compounds in graphite furnaces and in combustion flames, measurement of the spectral noise distribution in acetylene/air, acetylene/N_2O and other analytically important flames and in the inductively coupled plasma; a tutorial discussion of additive and multiplicative noises in analytical spectrometry; measurement of quantum efficiencies and lifetimes of atoms in the inductively coupled plasma; and measurement of atom spatial profiles in flames and plasmas using either laser excited atomic fluorescence or a new saturated absorption method.

All analytical studies have been directed towards improvement of detection limits, selectivity and reliability of measurement of atoms and towards the ultimate goal of single atom detection in real samples. The approaches used have consisted of either dye laser of conventional source excitation of atoms in flames, plasmas or furnaces and detection of atomic fluorescence. Pulsed N_2-pumped or excimer pumped dye laser excitation of atomic species in acetlyene flames, graphite furnaces, and inductively coupled plasmas have led to detection limits in the pg/mL range for many elements. The dye laser approach is unfortunately sufficiently complex and expensive to negate its general analytical use but is still useful for selected analyses where other analytical techniques are not satisfactory either due to poor detection power or more likely due to poor spectral selectivity.

Other analytical studies have included: evaluation of nebulizer-burner systems for atomic spectroscopy; analysis of trace elements in jet engine lubricating oils, in orange juice, in biological materials, and in environmental samples; development of a chemiluminescence method based upon O_3 oxidation of metal hydrides and of a chemiluminescence method based upon metastable N_2- the O_3 oxidation process is used to measure As, Bi, Sb, Te and Se and the metastable N_2 excitation is used to measure polycyclic aromatic hydrocarbons in gases in gas chromatographic effluents; development of an inductively coupled plasma (ICP) source with either an ICP or a flame atomizer and atomic fluorescence detection method - this approach is useful for single or multi-element detection and has detection limits as good as or better than conventional flame atomic absorption spectroscopy; development of a continuum source atomic absorption flame spectrometer with resonance flame detection and a molybdenum tube atomizer atomic absorption system - the latter system has been used to detect trace elements in sea water; and the speciation of metal species in agricultural, biological and environmental samples by thermal gas evolution and microwave excited emission - this approach allows the determination of the empirical formulae of compounds, such as mercury compounds in animal tissue. The above analytical approaches have been highly successful in terms of analytical figures of merit. However the approach to single species detection with no interferences is still far from a reality.

Program Manager: Denton W. Elliott

RESEARCH EFFORTS COMPLETED IN FY 83

SURFACE CHEMISTRY - CAPTAIN LEE E. MYERS

Reactions of Organic Molecules on Metal Surfaces AFOSR-82-0302	Jay B. Benziger Department of Chemical Engineering Princeton University Princeton, NJ 08544
Molecular Order and Solidification Processes in Organic Liquids and Solutions AFOSR-80-0166	J. W. Brasch R. J. Jakobsen Battelle Memorial Institute Columbus Laboratories 505 King Avenue Columbus, OH 43201
High Resolution Electron Energy Loss Studies of Chemisorbed Species on Aluminum and Titanium AFOSR-80-0154	J. L. Erskine Department of Physics J. M. White Department of Chemistry University of Texas Austin, TX 78712
Time-Temperature Studies of High Temperature *Deterioration* Phenomena in Lubricant Systems: Synthetic Ester Lubricants F49620-80-C-0061	S. Korcek Fuel and Lubricants Department Ford Motor Company Dearborn, MI 48121
The Role of Coupling Agents in Metal-Polymer Adhesion F49620-79-C-0085	C. S. P. Sung N. H. Sung Department of Materials Science & Engineering Massachusetts Institute of Technology Cambridge, MA 02139

COMPLETED PROJECT SUMMARY

1. TITLE: A Mechanistic Study of Nitromethane Decomposition on Ni Catalysts

2. PRINCIPAL INVESTIGATOR: Dr. Jay B. Benziger
Department of Chemical Engineering
Princeton University
Princeton, NJ 08544

3. INCLUSIVE DATES: 1 February 1982 - 1 January 1983

4. GRANT NUMBER: AFOSR-82-0099 (Mini Grant)

5. COSTS AND FY SOURCE: $9,646, FY 82

6. JUNIOR RESEARCH PERSONNEL:

R. E. Preston J. E. Strong

7. PUBLICATIONS:

"Decomposition of Nitromethane over NiO and Cr2O3 Catalysts," J. B. Benziger, Combustion Science and Technology, 29, 195 (1982).

"A Mechanistic Study of Nitromethane on Ni Catalysts," J. B. Benziger, Applications of Surface Science, submitted.

"Design Criteria for Ignition in Monopropellant Engines," J. B. Benziger and J. E. Strong, Journal of Spacecraft and Rockets, submitted.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this work was to examine the feasibility of using a nitromethane based monopropellant. The initial work was performed at the AFRPL and focused on measuring reaction kinetics for nitromethane decomposition. Because of the high adiabatic decomposition temperature for nitromethane (in excess of 2000 K) oxide catalysts were chosen for the initial investigation. The results from this study indicated that nitromethane could be used as a monopropellant but the catalyst bed would require preheating to temperatures near 450 K to assure lightoff. Additionally it was found that the nitromethane caused catalyst deactivation due to coking.

In a study on well defined Ni single crystal surfaces it was found that the rate of nitromethane decomposition was limited by scission of the N-O bonds. These bonds were weakened by adsorption to the surface and it was found that the stronger the adsorption bonds the more facile was the decomposition of nitromethane. These results indicated that more active catalysts should be available. The problem of catalyst deactivation was found to be due to secondary reactions and should be eliminated by addition of an oxidant rich material to the nitromethane, such as nitroform or tetranitromethane.

As part of this study, a model was developed to indicate the important design parameters for nitromethane monopropellants. It was found that the inlet feed temperature and bed preheat temperature are the most important parameters affecting the response time. The model calculations showed that there is an optimal bed preheat temperature giving the fastest response for a given catalyst bed size and nitromethane feed temperature. This optimal temperature results in the lightoff point to be at the exit of the reactor bed.

AFOSR Program Manager: Capt Lee E. Myers

COMPLETED PROJECT SUMMARY

1. TITLE: Molecular Order and Solidification Processes in Organic Liquids and Solutions

2. PRINCIPAL INVESTIGATORS: Dr. J. W. Brasch
Dr. R. J. Jakobsen
Battelle Memorial Institute
Columbus Laboratories
505 King Avenue
Columbis, OH 43201

3. INCLUSIVE DATES: 1 May 1980 - 30 April 1983

4. GRANT NUMBER: AFOSR-80-0166

5. COSTS AND FY SOURCE: $48,303, FY 80; $53,338, FY 81; $56,340, FY 82

6. SENIOR RESEARCH PERSONNEL: Dr. E. J. Drauglis

7. JUNIOR RESEARCH PERSONNEL: C. J. Riggle

8. PUBLICATIONS:

"A Combination Microscope-Beam Condenser Accessory For FT-IR Spectrometer Systems," J. W. Brasch, R. J. Jakobsen, and C. J. Riggle, Applied Spectroscopy, submitted.

"FT-IR Studies of Organic Acid Adsorption and Reaction on Metal Surfaces," R. J. Jakobsen, J. W. Brasch, and C. J. Riggle, Applied Spectroscopy, submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

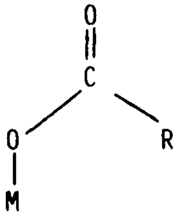
The purpose of this program was to study the behavior of lubricants that are subjected to high temperatures and pressures such as in ball bearing applications. Solutions of organic acids in hydrocarbons were selected as prototype lubricants and a diamond anvil high pressure cell was used for the observations (microscopic, FT-IR, Raman).

a. Short and Long Range Order Studies - Past studies have indicated the possibility of aggregation of acid molecules at high, but constant pressure. In order to check this observation, equipment modifications were needed to precisely measure pressures and to rapidly obtain both pressure measurements and infrared spectra. Accordingly, a combination microscope and beam condenser stage for the high pressure cell was constructed. This allowed us to rapidly align the cell and obtain spectra. Also a monochromater and laser were assembled into a system capable of making ruby chip fluorescence measurements. In this technique a tiny ruby chip is placed in the pressure cell, excited with a laser, and the fluorescence measured. The frequences of the ruby fluorescence can be exactly related to the pressure, in the cell. With this equipment we determined that at high pressure acid aggregation was occurring as evidenced by a low frequency shift of the acid carbonyl frequency, but the pressure measurements indicated that the pressure was slightly increasing, probably due to gasket extrusion. Thus the increased hydrogen bonding or aggregation was a result of this slight pressure increase. Long range order in acids, hydrocarbons, and acid-hydrocarbon solutions while under pressure was tested by means of polarized infrared spectra. No changes in the dichroic ratio were detected indicating no evidence of long range order.

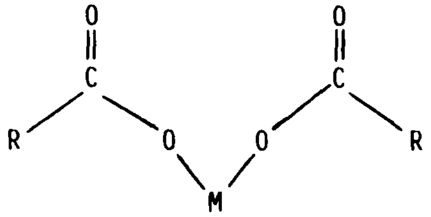
b. Kinetic and Reaction Mechanism Studies - When film lubricants, such as in ball bearing applications, are in contact with metal, these metals can interact with organic acids to form organic salts. It has been postulated that these metal salts actually provide the lubrication in such systems. Past work in our laboratory has demonstrated that such salts will form when acid-hydrocarbon solutions are in contact with metal. However, in this past work with mono-carboxylic acids, no clear evidence of monomer carbonyl infrared bands was observed. Thus the mechanism of reaction appeared to be cyclic dimer acid reacting directly to form acid salt. However, this left open questions about possible intermediate reactions and the observed multiple carboxylate (COO-1) frequencies, which indicate different types of organic salts or different types of acid to metal bonding. In the last phase of this project, numerous temperature studies were carried out in the diamond anvil cell with solutions of lauric acid-dodecane and with the diamond anvils coated with a thin film of iron. With the significant increase in sensitivity from our instrumental developments, these studies showed a small amount of monomer formation at elevated temperatures (as evidenced by a 1767 cm^{-1} corbonyl ban compared to the cyclic dimer carbonyl band at 1717 cm^{-1}). Only after monomer appeared did salt formation commence and then the rate of salt formation appeared to be proportional to the rate of monomer formation, indicating that the salt was formed from the monomer.

In addition, four distinct carboxylate frequencies were observed to form under various experimental conditions. From the rates of formation, the rates of loss of carbonyl, and the observed frequencies, four separate structures have been deduced for the acid salts as indicated below:

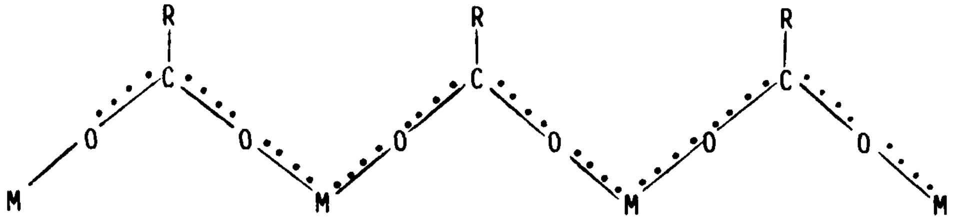
(1)



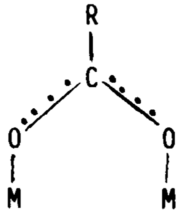
(2)



(3)



(4)



AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: High Resolution Electron Energy Loss Studies of Chemisorbed Species on Aluminum and Titanium

2. PRINCIPAL INVESTIGATORS:

Dr. J. L. Erskine Department of Physics University of Texas Austin, TX 78712	Dr. J. M. White Department of Chemistry University of Texas Austin, TX 78712

3. INCLUSIVE DATES: 1 April 1980 - 31 March 1983

4. GRANT NUMBER: AFOSR-80-0154

5. COSTS AND FY SOURCE: $85,877, FY 80; $55,598, FY 81; $64,944, FY 82

6. SENIOR RESEARCH PERSONNEL: Dr. B. M. Davies

7. JUNIOR RESEARCH PERSONNEL: R. L. Strong

8. PUBLICATIONS:

"High Resolution Electron Energy Loss Spectroscopy Study of the Oxidation of Al(111)," J. L. Erskine and R. L. Strong, Phys. Rev., B25, 5547 (1982).

"Surface-Site Determination Using Electron Energy Loss Spectroscopy and Lattice Dynamical Models," R. L. Strong, B. Firey, F. W. de Wette, and J. L. Erskine, Phys. Rev., B26, 3483 (1982).

"Absorbate Structure Modeling Based on Electron Energy Loss Spectroscopy and Lattice Dynamical Calculations: Application to O/Al(111)," R. L. Strong, B. Firey, F. W. de Wette, and J. L. Erskine, J. Electron Spectroscopy Rel. Phenom., 29, 187 (1983).

"Azimuthal Dependence of Impact Scattering in Electron Energy Loss Spectroscopy," B. M. Davies and J. L. Erskine, J. Electron Spectroscopy Rel. Phenom., 29, 323 (1983).

"Off-Specular EELS Studies of Adsorbates on Ni(100)," R. L. Strong and J. L. Erskine, Bull. American Phys. Soc., 27, 374 (1982).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project utilizes high resolution electron energy loss spectroscopy (EELS) to investigate molecular level chemical processes at metal surfaces. The fundamental principle which forms the basis for this spectroscopy is very simple: Vibrational energies of matter, in particular, solids and species adsorbed on surfaces, are quantized. Therefore, energy exchange involving vibrational levels occurs in quantized units. Electron energy loss spectroscopy determines these quantized vibrational levels by measuring the energy difference (either loss or gain) between electrons incident and scattered at a surface.

The objective of the current research project was to utilize EELS in conjunction with other standard surface science probes including low energy electron diffraction (LEED) and Auger electron spectroscopy to investigate chemical processes which occur at surfaces of metals having important technological applications. Metals falling into this category and which have therefore been chosen for this work include aluminum and titanium. Other metals including nickel and tungsten have also been investigated. In addition to probing chemical processes of surfaces, this project has also attempted to expand the analytical capability of EELS spectroscopy by utilizing lattice dynamical calculations to aid in the interpretation of EELS spectra and by investigating fundamental properties of the scattering mechanisms which form the basis for EELS. Specific accomplishments of the project include the following:

a. The Initial Stage of Oxide Formation on Al(111) - Surface processes which occur during the initial stage of oxidation of aluminum have been investigated using a variety of techniques and appear to be rather complicated. This fact was clear when we began our EELS investigation of O/Al(111). Our EELS study of O/Al(111) established clearly for the first time that the initial stage of oxide formation on aluminum involved simultaneous formation of underlayers and overlayers. This result helped explain many of the difficulties encountered in previous studies.

b. Application of EELS to Underlayer Atoms - The observation of vibrational loss peaks due to subsurface atoms demonstrated the first application of EELS to diffusion processes near surfaces. We have shown that the dipole scattering mechanism clearly describes scattering from subsurface atoms and that lattice dynamical calculations can be utilized to verify loss peak assignments to subsurface atoms.

c. Application of Lattice Dynamical Models to EELS - In order to understand our EELS spectra for O/Al(111) in more detail and to verify the peak assignments, we carried out extensive lattice dynamical calculations for various configurations of oxygen overlayers and underlayers at Al(111) surfaces. These calculations demonstrated clearly the important role the substrate lattice dynamics play in EELS spectra for metal/adsorbate complexes having substrate atoms with mass comparable to the adsorbed species. These calculations verified peak assignments (surface and subsurface modes) for O/Al(111) and permitted an accurate estimate of the preferred high symmetry sites for surface and subsurface atoms.

d. Application of EELS and Lattice Dynamical Calculations to Ordered Overlayers - We have investigated c(2x2) and p(2x2) overlayers of oxygen atoms on the Ni(100) surface to determine if EELS loss features including both dipole losses and impact losses can be used to gain insight into the local structure. Conflicting structure models for these two systems have been recently proposed. One model assumes a pseudo bridge bond configuration for c(2x2) oxygen, and a second model suggests that c(2x2) and p(2x2) oxygen atoms lie at significantly different distances above the substrate. We have shown that lattice dynamical calculations utilizing EELS data can eliminate the model which assumes two heights for c(2x2) and p(2x2) oxygen, and that comparison of the EELS spectra for different ordered chemisorbed layers can yield insight into the differences in chemical bonds of the two configurations.

e. Impact Scattering Studies - Several distinct scattering regimes can be identified in electron scattering from vibrational modes at surfaces. Dipole scattering typically dominate spectra obtained using specular scattering geometry where $\Delta q_{\parallel}=0$. When the scattering angle is significantly different from the incident angle, or out of plane scattering is studied, $\Delta q_{\parallel}=0$ and the dipole scattering mechanism is ineffective. A second mechanism called impact scattering begins to play an important role in the inelastic losses which occur. The same mechanism accounts for the thermal diffuse scattering in LEED.

Impact scattering has some extremely important potential applications in surface studies because of selection rules (associated with the scattering processes) which have direct relationships to the mode symmetries and hence the local site symmetry. We have conducted several experiments aimed at observing the effects predicted by the symmetry relationships. The experiment involved studying the azimuthal dependence of EELS spectra from H on W(110). This surface has two inequivalent mirror planes (in contrast to the two equivalent mirror planes for W(100)). One therefore expects to observe a different behavior in the scattering cross-section as a function of azimuthal angle for these two surfaces.

Our experiment did not establish conclusively the adsorption site of H/W(110) or verify explicitly the selection rules. The experiment did produce a striking azimuthal pattern and did definitely show that impact scattering and dipole scattering are qualitatively different in terms of azimuthal dependence of the scattering cross-section. Additional work on this problem is clearly in order, and we are continuing this investigation.

AFOSR Program Manager: Capt Lee E. Myers

COMPLETED PROJECT SUMMARY

1. TITLE: Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants

2. PRINCIPAL INVESTIGATOR: Dr. Stefan Korcek
Fuels and Lubricants Department
Research Staff
Ford Motor Company
Dearborn, MI 48121

3. INCLUSIVE DATES: 1 May 1980 - 30 April 1983

4. CONTRACT NUMBER: F49620-80-C-0061

5. COSTS AND FY SOURCE: $30,685, FY 80; $75,988, FY 81; $81,180, FY 82; $48,918, FY 83

6. SENIOR RESEARCH PERSONNEL:

Mr. R. K. Jensen	Dr. L. R. Mahoney
Dr. P. A. Willermet	Dr. M. Zinbo

7. JUNIOR RESEARCH PERSONNEL: S. K. Kandah

8. PUBLICATIONS:

"Effects of Structure on the Thermoxidative Stability of Synthetic Ester Lubricants: Theory and Predictive Method Development," L. R. Mahoney, S. Korcek, J. M. Norbeck, and R. K. Jensen, Preprints, Div. Petrol. Chem., ACS, 27, No. 2, 350 (1982).

"Wear Asymmetry - A Comparison of the Wear Volumes of the Rotating and Stationary Balls in the Four-Ball Machine," P. A. Willermet and S. K. Kandah, ASLE Transactions, 26, 2, 173 (1983).

"HPLC Determination of Hydroperoxidic Products Formed in the Autoxidation of n-Hexadecane at Elevated Temperatures," R. K. Jensen, M. Zinbo, and S. Korcek, J. Chromatogr. Sci., 21, 394 (1983).

"Oxidation and Inhibition of Pentaerythritol Esters," S. Korcek, R. K. Jensen, L. R. Mahoney, and M. Zinbo, Proc. 4th Int. Colloquium on Synthetic Lubricants and Operational Fluids, (Technische Akademie Esslingen, W. Germany) January 1984.

"Effects of Oxygen Pressure on Liquid Phase Autoxidation of n-Hexadecane at 160 to 190°C," R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, J. Am. Chem. Soc., in preparation.

"Formation, Isomerization, and Cyclization Reactions of Hydroperoxyalkyl Radicals in n-Hexadecane Autoxidation at 160 to 190°C," R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, J. Am. Chem. Soc., in preparation.

"Liquid Phase Autoxidation of Organic Compounds at Elevated Temperatures. 3. Rate of Radical Formation in n-Hexadecane Autoxidation at 120 to 180°C," R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, J. Am. Chem. Soc., in preparation.

"Inhibition of the Autoxidation of n-Hexadecane by 2,6-di-tert-butyl 4-methyl-phenol at Elevated Temperatures," R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, Oxid. Commun., in preparation.

"Reactions of Alkylperoxycyclohexadienones during Autoxidation Inhibited by Hindred Phenols at Elevated Temperatures," R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, Int. J. Chem. Kinet., in preparation.

"The Effects of Autoxidation on Wear in a System Lubricated with n-Hexadecane," P. A. Willermet, S. Kandah, and R. K. Jensen, ASLE Transactions.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to obtain basic information on lubricant deterioration and wear phenomena occurring in oxidative environments at elevated temperatures.

Application of a stirred flow reactor technique in our previous studies led to elucidation of the kinetics and mechanisms of the autoxidation of the synthetic ester lubricant, pentaerythrityl tetraheptanoate (PETH), and of a model hydrocarbon lubricant, n-hexadecane (HD), at elevated temperatures (120-200°C) and an oxygen pressure of ∿110 kPa. The present research is an extension of that work to studies of the kinetics and mechanisms of autoxidation at reduced oxygen pressures including atmospheric conditions.

The kinetics and mechanisms of liquid phase autoxidation of HD have been investigated at 160 to 190°C and at oxygen pressures from 4 to 120 kPa. Results of these investigations showed that the intromolecular α,γ and α,δ hydrogen abstraction reactions of peroxy radicals, reactions 4 (Figure 1), are highly reversible and that intermediate hydroperoxyalkyl radicals, HOOR•, formed from these abstractions, besides oxygen addition reaction 2 and reverse intramolecular hydrogen abstraction (isomerization) reaction -4, undergo cyclization reaction 10 leading to formation of cyclic ether products. A general reaction scheme consistent with our present and previous results of autoxidation at elevated temperatures is in Figure 1. This scheme is applicable to autoxidation of any system containing alkyl chains with carbon number greater than four. Absolute rate constants for formation, isomerization, and cyclization of hydroperoxylakyl radicals, reactions 4,-4, and 10, have been determined for the first time for

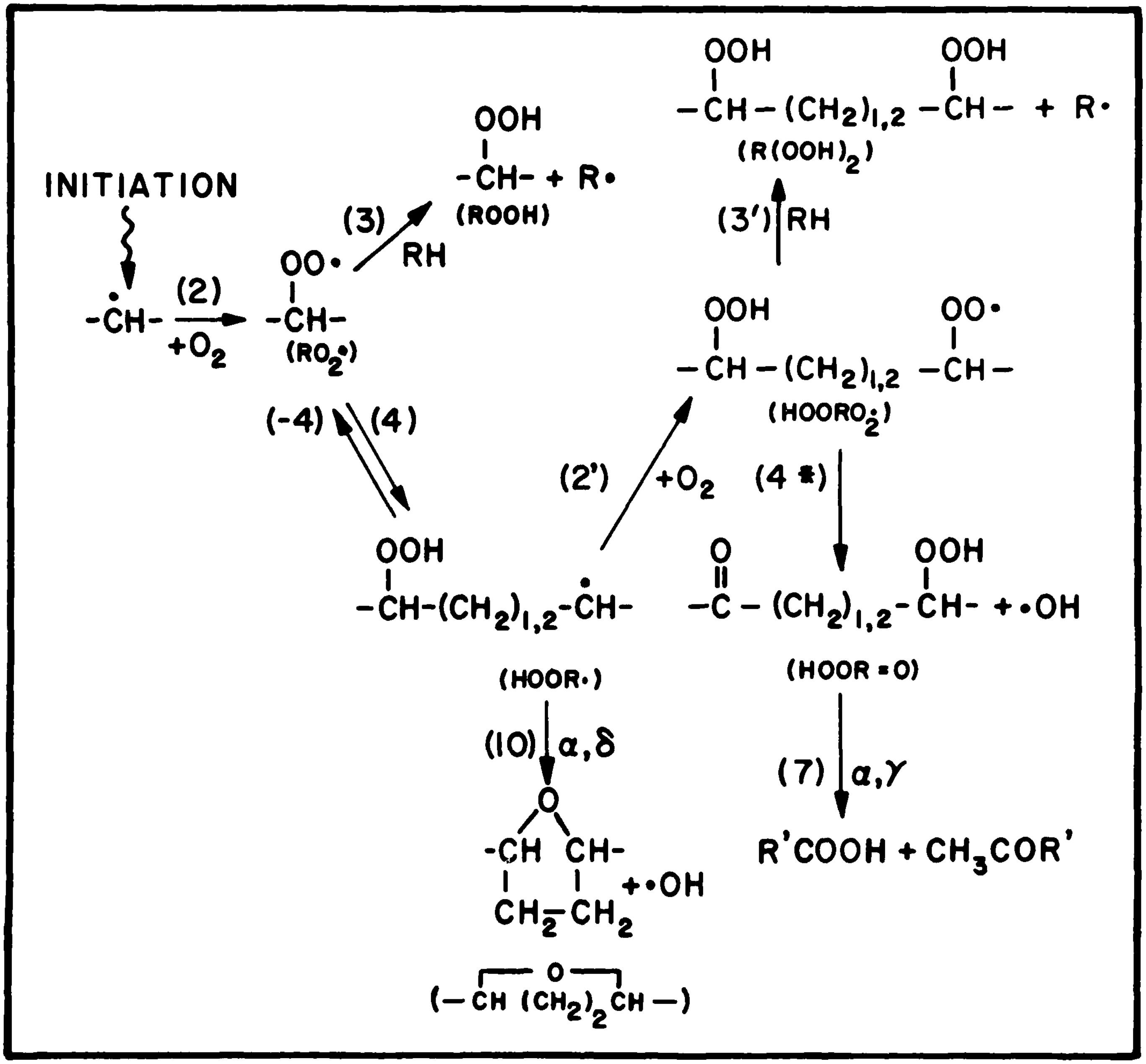


Figure 1. Reaction scheme for the liquid-phase autoxidation of organic substrates at elevated temperatures

liquid-phase autoxidation and the corresponding Arrhenius parameters have been derived. Their values are in general agreement with those previously determined or estimated in gas phase combustion studies. Results of kinetic analysis of cleavage product formation are consistent with two modes of their formation in the entire range of oxygen pressures studied. The first mode involves decomposition of α,γ-hydroperoxyketone species and the second reactions of alkoxy radicals.

Determination of absolute rate constants required knowledge of the rate of initiation, R_i, at each experimental condition. Three approaches were used for that purpose: determination of R_i from the rate of formation of termination products, from the length of the inhibition period caused by addition of an antioxidant, and from the initial rate of antioxidant consumption. Correlation of results obtained indicates that stoichiometric factors, n, for 2,6-di-tert-butyl-4-methylphenol, MPH, and 4,4'-methylene-bis(2,6-di-tert-butylphenol) at elevated temperatures are much lower than those determined as low temperatures (1.0-1.2 and 2.0-2.6 vs. 2 and 4, respectively) while n for N-phenyl-α-naphthylamine does not appear to change with temperature. In the case of MPH this was confirmed by the independent kinetic and mechanistic investigations.

Kinetic and mechanistic studies of inhibition reactions of MPH, and reactions of various MPH derived intermediates under autoxidation conditions at elevated temperatures revealed that the presence of hydroperoxides affects inhibition mechanisms. In the presence of excess hydroperoxides, conditions typical for our stirred flow reactor experiments, the most important reaction of MPH derived phenoxy radicals is that with alkylperoxy radicals leading to formation of the corresponding 4-alkylperoxy-2,5-cyclohexadienone, QOOR. At low hydroperoxide concentrations, conditions typical for inhibition in technological systems, the disproportionation reaction of phenoxy radicals leading to regeneration of MPH and formation of the corresponding quinonemethide also plays an important role. In both cases, however, QOOR is a major source of free radicals which effectively reduces n for MPH at elevated temperatures. In order to assess this reduction quantitatively, the decomposition reactions of a series of QOOR with R = $(CH_3)_3C$-, tetralyl-, and 1-,2-, and 5-$C_{16}H_{33}$- have been investigated in the presence of MPH. Kinetic analyses of the results yielded values of rate constants for radical and non-radical decomposition of QOOR which were used to estimate n for MPH as equal to 1.2 at 160°C.

A method for prediction of the effects of structure on the thermoxidative stability of synthetic ester lubricants, pentaerythrityl tetraalkanoates, in the presence of an antioxidant has been developed. Kinetic equations for the inhibited oxidation of these lubricants have been derived using the above proposed reaction scheme. Numerical solutions of these equations yielded the values of the relative inhibition periods as a function of antioxidant stoichiometric factor and relative reactivities of peroxyradicals in intra- and intermolecular hydrogen abstraction reactions with substrate and antioxidant. The inhibition periods calculated by this method have been found to be in excellent agreement with the experimental values obtained for $\underline{n}$-C_5 through $\underline{n}$-C_8 pentaerythrityl tetraalkanoates containing 1 weight percent N-phenyl-α-naphthylamine at 232°C.

Laboratory studies of wear behavior were carried out with PETH, HD and a synthetic hydrocarbon, SHC, in the presence and absence of oxidation products using a Four-Ball Apparatus. In PETH, the presence of oxidation products increased wear while in SHC a reduction in wear was observed. With PETH, higher wear was observed on the rotating ball than on the three stationary balls above a critical test speed. With SHC, the direction of this wear asymmetry was reversed. With HD, wear kinetics and asymmetry were significantly affected by the type and distribution of oxidation products. Results with model oxidation products added into HD suggest that carboxylic acids and difunctional hydroperoxides are effective in reducing the stationary ball wear while monohydroperoxides do not appear to affect it over the range of conditions employed in these experiments.

AFOSR Program Manager: Capt Lee E. Myers

COMPLETED PROJECT SUMMARY

1. TITLE: Role of Coupling Agents in Metal-Polymer Adhesion

2. PRINCIPAL INVESTIGATORS:

Professor C.S.P. Sung
Dept. of Materials Science
and Engineering
Massachusetts Institute of
Technology
Cambridge, MA 02138

Professor N. H. Sung
Dept. of Chemical Engineering
Tufts University
Medford, MA 02155

3. INCLUSIVE DATES: 1 May 1979 - 30 December 1982

4. CONTRACT NUMBER: F49620-79-C-0085

5. COSTS AND FY SOURCE: $35,000, FY 80; $120,381, FY 81; $121,162, FY 82;

6. SENIOR RESEARCH PERSONNEL:

Dr. I. J. Chin
Dr. A. Kaul

7. JUNIOR RESEARCH PERSONNEL:

S. H. Lee
E. Chen
W. Mui
S. Ni
T. Ying

8. PUBLICATIONS:

"Elucidation of the Structure of the Silane Film at Metal-Polymer Interface," C.S.P. Sung, S. H. Lee, and N. H. Sung, ACS Polymer Preprints, 40-1, 733 (1979).

"Role of Coupling Agents in Metal-Polymer Adhesion, I. The Structure of the Silane Film at Metal-Polymer Interface," C.S.P. Sung, S. H. Lee, and N. H. Sung, Proceedings of the International Conference on Adhesion and Adsorption of Polymers, L. H. Lee, Ed., (Plenum Press), p.p. 757 (1980).

"IR Studies of Organo Silanes and Titanates Adsorbed on Single Crystalline Aluminum Oxide and Glass Fibers," N. H. Sung, S. Ni, and C.S.P. Sung, ACS Org. Coatings and Plastics Chem., 42-1, 743 (1980).

"Role of Organo Silanes and Organo Titanates in Promotion of Adhesion Strength of Aluminum Oxide-Polyethylene Joint," N. H. Sung, A. Kaul, S. Ni, C.S.P. Sung, and I. J. Chin, 36th Annual Technical Conference, Reinforced Plastics/Composites Institute, Society of Plastics Industries, Section 2-B, (1981) and in Adhesion Aspects of Polymeric Coatings, K. L. Mittal, Ed., (Plenum Press), p.p. 379 (1981).

"Mechanism of Adhesion Promotion through Organo-Silanes in α Al_2O_3/ Polyethylene Joints," A. Kaul, N. H. Sung, I. Chin, and C.S.P. Sung, Proceedings of 37th Annual Technical Conference, Reinforced Plastics/Composites Institute, Soc. Plastics Industries, Sec. 2-E, (1982).

"Mechanistic Studies of Adhesion Promotion by γ-Aminopropyl Triethoxy Silane in α-Al_2O_3/ Polyethylene Joint," N. H. Sung and A. Kaul, Polym. Eng. and Sci., 22, 637 (1982).

"Durability and Failure Analyses of a Silane Treated α-Al_2O_3/ Polyethylene Joint in Wet Environment," A. Kaul, N. H. Sung, I. Chin and C.S.P. Sung, Polym. Eng. and Sci., (1983), submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of the research was to elucidate the mechanism of adhesion promotion by an organosilane adhesion promoter in polymer/metal joint where other mechanisms than direct coupling are likely to be important. We chose γ-aminopropyl triethoxy silane (γ-APS) as the adhesion promoter and (unoxidized) polyethylene as the polymer because chemical reaction between them is unlikely. As for the model metal substrate, we chose single crystalline alumina (α-Al_2O_3) for experimental advantages.

By combining several advanced techniques such as FT-IR, ESCA, ellipsometry SEM and x-ray fluorescence energy dispersive analysis (SEM-EDX), we characterized the structure of the deposited bulk silane, interfacial reactions and the failure locus and mode of the joints. Thus obtained structural information was correlated with the property of the joint by measuring 180° peel strength of the α-Al_2O_3/silane/polyethylene joint.

Dry joint strength of such a joint can be markedly improved by the application of γ-APS on α-AL_2O_3, which forms a multimolecular polysiloxane film. There was a strong experimental evidence for the limited interdiffusion between γ-APS silane film and polyethylene at the silane/polyethylene interface and we proposed this interdiffusion to be an important mechanism for adhesion promotion of the joint in dry environment. Drying the silane at an elevated temperature prior to joint formation reduces joint strength and also changes the failure mode from cohesive failure through polyethylene to a mixed mode near the silane/polyethylene interface. It was found that this trend was due to the reduced interdiffusion since dried silane is more fully cured glassy matrix.

The durability of the joints in wet environment is found to depend also on the γ-APS thickness and dehydration condition but not in a same way as the dry joint strength. Relatively thin γ-APS treatment on α-Al_2O_3 appear to provide more durable joint than thicker γ-APS treatment resulting in an optimal thickness in the range of 0.3 ∿ 1% γ-APS concentration level. Dehydration of γ-APS lead to more durable joint with an optimal condition found between 1 ∿ 2 days of dehydration at 100°C in vacuum.

Regardless of the γ-APS thickness and dehydration history, the failure in the debonded area seem to occur by the hydrolysis of γ-APS near α Al_2O_3 side and by the deformation of polyethylene (cohesive failure) in the peeled area. The debonded area increases from the edges toward the central area of the joint with exposure time. After redrying, the debonded area recovers little strength but in the bonded central areas, the strength is largely recovered, characterized by cohesive failure through polyethylene. Diffusion of water in γ-APS near α Al_2O_3 side rater than PE side can explain at least qualitatively most of the observed trend.

AFOSR Program Manager: Capt Lee E. Myers

RESEARCH EFFORTS COMPLETED IN FY 83

CHEMICAL STRUCTURES - DR. DONALD R. ULRICH

Impact Initiated Damage in Laminated Composites F49620-80-C-0050	V. Sharma Avva Dept. of Mechanical Engrg N. Carolina A&T St. Univ. Greensboro, NC 27411
Transport Properties and Structure of Extended Chain Polymers AFOSR-80-0014	R. E. Barker K. R. Lawless Department of Materials Science University of Virginia Charlottesville, VA 22901
Structural Electronic Relationships in Polymeric Solids AFOSR-80-0038	Glenn A. Crosby Department of Chemistry Washington State University Pullman, WA 99164-4630
TICA Study of High-Temperature Thermoplastics AFOSR-82-0301	Joel R. Fried Chemical & Nuclear Engineering University of Cincinnati Cincinnati, OH 45221
Ultrastructure Processing and Environmental Stability of Advanced Structural and Electronic Materials F49620-80-C-0047	L. L. Hench Dept. of Materials Sci. & Engrg University of Florida Gainesville, FL 32611
An Approach to Molecular Composites AFOSR-79-0080	William R. Krigbaum Jack Preston Department of Chemistry Duke University Durham, NC 27706
Theoretical Studies of Relatively Rigid Polymer Chains AFOSR-78-3683	J. E. Mark Dept. of Chemistry & Polymer Rsrch University of Cincinnati Cincinnati, OH 45221
Defect Chemistry of Crystalline Inorganic Materials AFOSR-78-3505	Donald M. Smyth Materials Research Center Lehigh University Bethlehem, PA 18015
Synthesis of Liquid Crystalline, Extended Chain Polymer Compositions in Poly(phosphoric acid) F49620-81-K-0003	James F. Wolfe Polymer Sciences Department SRI International Menlo Park, CA 94025

COMPLETED PROJECT SUMMARY

1. TITLE: Impact-Initiated Damage in Laminated Composites

2. PRINCIPAL INVESTIGATOR: Dr. V. Sharma Avva
Department of Chemistry
North Carolina A&T State University
Greensboro, NC

3. INCLUSIVE DATES: 1 October 1979 - 31 March 1982

4. CONTRACT NUMBER: F49620-80-C-0050

5. COSTS AND FY SOURCE: $53,419, FY 80; $52,016, FY 81

6. PUBLICATION:

"Impact-Initiated Damage in Laminated Composites", V. Sharma Avva, Final Technical Report, 1982.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Graphite/epoxy composite material was used to study the effect of projectile impact on the strength carrying ability of a 16-ply laminate. The orientation and the stacking sequence of the laminate was determined. The impacting projectile was an aluminum sphere, 1.54 cm (0.5 in.) in diameter. Forward velocities of the projectile (up to about 107 m/s, 350 ft/sec) were used with an air gun to cause impact damage to the laminates.

The residual strength studies were performed on impact-damaged laminates subjected to static tensile and compressive loads. The following summarizes the work accomplished. A method was established to measure the rebound velocity of the projectile using a stroboscope and a graphic polaroid camera. A special fixture was designed to support the compression-loaded laminates against column-type buckling failures. Established a residual strength curve as a function of impact energy in both the tension- and the compression-loaded laminates. Evaluated the scatter in establishing the residual strength curve at three different projectile velocities. Assessed the effect of pre-load on the residual strength at three different velocities. Verified the validity of the theoretically predicted residual strength values experimentally both in the tension- and the compression-loaded laminates.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Transport Properties and Structure of Extended Chain Polymers

2. PRINCIPAL INVESTIGATORS: Prof. R. E. Barker, Jr.
Prof. K. R. Lawless
Department of Materials Science
University of Virginia
Charlottesville, VA 22901

3. INCLUSIVE DATES: 1 October 1979 - 31 March 1983

4. GRANT NUMBER: AFOSR-80-0014

5. COSTS AND FY SOURCE: $73,672, FY 80; $94,434, FY 81; $112,088, FY 82

6. JUNIOR RESEARCH PERSONNEL: D. Y. Chen
T. J. Adams
W.-S. Huang

7. PUBLICATIONS:

"Studies of the Effects of Moisture Sorption on Electrical Conduction in Ion Doped Polymers," J. A. Hawk, D. Y. Chen, and R. E. Barker, Jr., Virginia Journal of Science, 34, 181 (1983).

"Transient Dielectric Properties of Polymer-Diluent Systems," C-C. Huang and R. E. Barker, Jr., Virginia Journal of Science, 34, 180 (1983).

"Overview of the Status of Experimental and Theoretical Research on the Electrical Conductivity of Extended Chain Aromatic Heterocyclic Polymers," presented at the U.S. Air Force (AFWAL/MLBC) Meeting on Transport Properties of Rigid Rod Polymers, 9 February 1983, Dayton, OH.

"Diffusion in Polymers: Theory and Experiment," R. E. Barker, Jr., Polymer Physics Seminar, National Bureau of Standards, 17 February 1983, Gaithersburg, MD.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The broad objective of the work was to relate charge, heat, and mass transport in the Air Force's extended chain polymers (especially poly-para-phenylene benzobisthiazole PBT) to other electrical, thermal, mechanical and microstructural properties of the polymers and also to compare these very unusual highly anisotropic Air Force materials with other materials when it is scientifically relevant or when potential applications may be involved. Special techniques were developed for making transport-property determinations on samples in the form of thin fibers and small area films.

A very promising area of the research relates to an anisotropic version of the Barber-Sharbaugh weak electrolyte model for ionic conduction in polymers. Theoretically and experimentally there is substantial overlap with the work on diffusion and solubility. A new technique which they call the "diffusion controlled-differential current" (DCDC) method evolved from experiments related to the weak electrolyte model. This DCDC-technique looks promising as a new analytical tool. A technique developed by the investigator, X-ray dispersive analysis (XREDA) was employed for the determination of diffusion of mercury in amalgams. This technique can also be used to determine concentration profiles for diffusants so that well defined geometrics can be calculated from time dependence of the profiles. Two types of minature cells were developed in the study of PBT transport properties.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Structural Electronic Relationships in Polymeric Solids

2. PRINCIPAL INVESTIGATOR: Dr. Glenn A. Crosby
Department of Chemistry
Washington State University
Pullman, WA 99164-4630

3. INCLUSIVE DATES: 1 October 1979 - 28 February 1983

4. GRANT NUMBER: AFOSR-80-0038

5. COST AND FY SOURCE: $93,613, FY 80; $80,124, FY 81; $74,041, FY 82

6. JUNIOR RESEARCH PERSONNEL:

T. L. Cremers
J. L. Crosby
W. A. Fordyce
R. G. Highland
B. R. McGuire
W. L. Parker
M. L. Stone

7. PUBLICATIONS:

"Charge-Transfer Excited States of Osmium(II) Complexes: I. Assignment of the Visible Absorption Bands," B. J. Pankuch, D. E. Lacky, and G. A. Crosby, J. Phys. Chem. 84, 2061 (1980).

"Charge-Transfer Excited States of Osmium(II) Complexes: II. Quantum Yield and Decay Time Measurements," D. E. Lacky, B. J. Pankuch, and G. A. Crosby, J. Phys. Chem. 84, 2068 (1980).

"Solvent Effects on the Luminescing Excited States of Iridium(III) Complexes," T. L. Cremers and G. A. Crosby, Chem. Phys. Lett., 73, 541 (1980).

"Structure of Bix(4-toluenethiolate-1,10-phenanthroline)zinc(II)," T. L. Cremers, D. R. Bloomquist, R. D. Willett, and G. A. Crosby, Acta Crystallogr. Sect. B, 36, 3097 (1980).

"Multiple State Emission from Rhodium(I) and Iridium(I) Complexes," W. A. Fordyce, H. Rau, M. L. Stone, and G. A. Crosby, Chem. Phys. Lett., 77, 405 (1980).

"Charge-Transfer Luminescence from Ruthenium(II) Complexes Containing Tridentate Ligands," M. L. Stone and G. A. Crosby, Chem. Phys. Lett., 79, 169 (1981).

"Excited States of Mixed Ligand Chelates of Ruthenium(II): Quantum Yield and Decay Time Measurements," W. H. Elfring, Jr. and G. A. Crosby, J. Am. Chem. Soc., 103, 2683 (1981)."

"Electronic Spectroscopy of a Diplatinum(II) Octaphosphite Complex," W. A. Fordyce, J. G. Brummer, and G. A. Crosby, J. Am. Chem. Soc., 103, 7061 (1981).

"Emission Spectra, Decay Times, and Polarization Ratios of Ruthenium(II) Complexes Containing Tridentate Ligands," S. F. Agnew, M. L. Stone, and G. A. Crosby, Chem. Phys. Lett., 85, 57 (1982).

"Electronic Spectroscopy of Diphosphine- and Diarsine-Bridged Rhodium(I) Dimers," W. A. Fordyce and G. A. Crosby, J. Am. Chem. Soc., 104, 985 (1982).

"Electronic Spectroscopy of N-Heterocyclic Complexes of Rhodium (I) and Iridium(I)," W. A. Fordyce and G. A. Crosby, Inorg. Chem., 21, 1023 (1982).

"Electrochemistry of N-Heterocyclic Complexes of Rhodium(I) and Iridium(I)," W. A. Fordyce, K. H. Pool, and G. A. Crosby, Inorg. Chem., 21, 1027 (1982).

"Electronic Spectroscopy of Diphosphine and Diarsine Complexes of Rhodium(I) and Iridium(I)," W. A. Fordyce and G. A. Crosby, Inorg. Chem., 21, 1455 (1982).

"Structure, Bonding, and Excited States of Coordination Complexes," G. A. Crosby. J. Chem. Ed., 60, 791 (1983).

"Structural Electronic Relationships in Polymeric Solids," G. A. Crosby, Final Technical Report, AFOSR-80-0038

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective was to quantify the excited states of metal complexes so that their ultimate roles in photophysical, photochemical, and chemical processes could be assessed. The long term goal was to arrive at a degree of sophistication such that materials with desired electrooptical properties could be designed at a molecular level and synthesized.

A comprehensive study of osmium(II) $(5d)^6$ complexes of D_3 symmetry containing N-heterocyclic ligands was completed. A new series of complexes containing $(nd)^{10}$ $(n = 3,4)$ filled shell metal ions was synthesized and studied spectroscopically, revealing a new type of low-lying excited state. The structure of a typical example of this class of substance was determined by crystallography.

A major accomplishment was the development of a multiple-state model for the lowest excited states of $(nd)^8$ complexes. Compounds of ruthenium(II) with N-heterocyclic ligands of both D_{2d} and D_3 symmetry were also extensively investigated. The low-lying excited states of bimetallic $(nd)^8$ complexes were quantified. Iridium(I) and rhodium(I) complexes were also studied electrochemically. A charge-transfer intensity model was developed and applied to copper (I) and ruthenium(II) complexes of D_{2d} symmetry.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: TICA Study of High-Temperature Thermoplastics

2. PRINCIPAL INVESTIGATOR: Dr. Joel R. Fried
Chemical and Nuclear Engineering
University of Cincinnati
Cincinnati, OH 45221

3. INCLUSIVE DATES: 25 August 1982 - 24 August 1983

4. GRANT NUMBER: AFOSR-82 0301

5. COSTS AND FY SOURCE: $9,997, FY 82 (Mini Grant)

6. JUNIOR RESEARCH PERSONNEL: A. Letton

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Relaxation spectra for highly filled thermoplastic composites have been obtained by use of torsion impregnated cloth analysis (TICA) and a fourth order finite element numerical analysis. Cloths used to make TICA samples included heat cleaned E- and S-glass, an aromatic polyamide (Kevlar), and a phenoxy finished graphite. The principal thermoplastic studied was bisphenol-A polysulfone (PSF). Comparison of spectra for filled and unfilled PSF indicates that polymer-filler interactions result in substantial broadening of the relaxation time distribution although there is little change in the WLF shift parameters, glass transition temperature (Tg), or apparent Arrhenius activation energy for the glass transition. In addition, the dynamic mechanical TICA loss spectra suggest the presence of a weak relaxational process occurring above Tg. This process sometimes has been associated with a liquid-liquid transition whose origins remain controversial.

In addition to composite measurements, the dynamic torsion spectra of neat PSF bars subject to different thermal histories have been obtained. Results confirm the presence of two secondary relaxations below Tg which occurs near 198°C (loss modulus peak at 10 rad/sec). These are a strong γ peak near -100°C and a weak β peak near 60°C. Apparent Arrhenius activation energies determined over a frequency range from 0.1 to 100 rad/sec are 67 ± 35 and 10.7 ± 1.1 kcal/mol, respectively. These compare to 220 ± 55 kcal/mol measured for the glass transition. Annealing or slow cooling results in a suppression of the β peak and intensification of the high temperature side of the γ peak which appears to correlate with a small decrease in impact strength. Preliminary quantum mechanical calcualtions (CNDO/2 geometry optimized) suggest that the γ relaxation may represent contributions from methyl group rotations and swivel motions of isopropylidene and diphenyl sulfone moieties while more energetic diphenyl ether swivels may be associated with the β relaxation. No effect of thermal conditioning in the region of the liquid-liquid transition has been observed.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Ultrastructure Processing and Environmental Stability of Advanced Structural and Electronic Materials

2. PRINCIPAL INVESTIGATOR: Dr. L. L. Hench
Department of Materials Science and Engineering
University of Florida
Gainesville, FL 32611

3. INCLUSIVE DATES: 1 March 1980 - 31 March 1983

4. CONTRACT NUMBER: F49620-80-C-0047

5. COSTS AND FY SOURCE: $117,634, FY 80; $96,860, FY 81; $309,728, FY 82; $155,000, FY 83

6. SENIOR RESEARCH PERSONNEL:

Dr. D. E. Clark	Dr. C. van Vliet
Dr. C. Bosman	Dr. P. H. Holloway
Dr. G. Y. Onoda	Dr. C. L. Beatty

7. PUBLICATIONS:

"Treatment of Glass Surfaces for Polymer-Glass Composites," C. T. Lee, D. E. Clark, K. Shih and C. L. Beatty, presented at the 7th Annual Conference on Composites and Advanced Materials, 16-19 January 1983, Cocoa Beach, FL.

"Phase Transformations in Sol-Gel Derived Aluminas," D. E. Clark and J. J. Lannutti, presented at the International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, 13-17 February 1983, Gainesville, FL, L. L. Hench and D. R. Ulrich, Eds., (J. Wiley & Sons, 1983).

"Static Aqueous Corrosion of Soda-Disilicate Glass (33N) in Simulated Geologic Environments," Y. Chao, M. Taie and D. E. Clark, presented at Annual Meeting of the American Ceramic Society, 5 May 1983, Cincinnati, OH.

"Weathering of Binary Alkali Silicate Glasses and Glass-Ceramics," Y. Chao and D. E. Clark, Ceramic Engineering and Science Proceedings, 3, 458 (1982).

"Surface Analysis of Glasses," L. L. Hench and D. E. Clark, Industrial Applications of Surface Analysis, L. A. Casper and C. J. Powell, Eds, ACS Symposium Series, ISSN 009-6156, 199, p.p. 203 (1982).

"Surface Behavior of Gel-Derived Glasses," L. L. Hench, M. Prassas, and J. Phalippou, Ceramic Engineering and Science Proceedings, 3, 477 (1982).

"Low Temperature Oxidation of SiC," B. O. Yavuz and L. L. Hench, <u>Ceramic Science and Engineering Proceedings</u>, <u>3</u>, 596 (1982).

"Glass Surfaces - 1982," L. L. Hench, <u>Proceedings of International Conference on Physics of Amorphous Solids</u>, J. Zarzycki, Ed., Montpellier, France (1982).

"Preparation of xNa_2O-(1-x)SiO_2 Gels for the Gel-Glass Process. Part I: Atmospheric Effect on the Structural Evolution of the Gels," M. Prassas, L. L. Hench, J. Phalippou and J. Zarzycki, <u>J. Non-Cryst. Solids</u>, <u>48</u>, 79 (1982).

"Preparation of xNa_2O-(1-x)SiO_2 Gels for the Gel-Glass Process. Part II: The Gel-Glass Conversion," M. Prassas, J. Phalippou, and L. L. Hench, <u>J. Non-Cryst. Solids</u>, in press.

"Physical Chemical Factors in Sol-Gel Processing," M. Prassas and L. L. Hench, <u>Ultrastructure Processing of Ceramics, Glasses and Composites</u>, L. L. Hench and D. R. Ulrich, Eds., (J. Wiley & Sons, 1983).

"Processing and Environmental Behavior of a 20 Mol % Na_2O - 80 Mol % (20N) SiO_2 Gel-Glass," L. L. Hench, S. Wallace, S. H. Wang and M. Prassas, presented at 7th Annual Conference on Composites and Advanced Ceramic Materials, 16-19 January 1983, Cocoa Beach, FL.

"Aqueous Durability of Lithium Disilicate Glass-Ceramics," W. J. McCracken, D. E. Clark, and L. L. Hench, <u>Bull. Am. Ceram. Soc.</u>, <u>61</u> 1218 (1982).

"Physical Parameters for Characterizing Agglomerates," G. Y. Onoda and R. T. DeHoff, presented at the Annual Meeting of the American Ceramic Society, 5 May 1982, Cincinnati, OH.

"Role of Effective Stress in Extrusion," M. A. Janney and G. Y. Onoda, presented at the Annual Meeting of the American Ceramic Society, 5 May 1982, Cincinnati, OH.

"Application of Specific Volume Diagrams to Ceramic Processing," G. Y. Onoda, presented at the Annual Meeting of the American Ceramic Society, 5 May 1982, Cincinnati, OH.

"Surface Chemistry of Oxides in Water," G. Y. Onoda, presented at the International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, February 1983, Gainesville, FL.

"Application of Soil Mechanics Concepts to Ceramic Particulate Processing," <u>Advances in Powder Technology</u>, G. Chin, Ed., American Society for Metals, (1982).

"Specific Volume Diagrams for Ceramic Processing," G. Y. Onoda, <u>J. American Ceramic Society</u>, to be published.

"Surface Chemistry in Water," G. Y. Onoda and J. A. Casey, Ultrastructure Processing of Ceramics, Glasses and Composites, L. L. Hench and D. R. Ulrich, Eds., (J. Wiley & Sons, 1983).

"Si_3N_4 and SiC from Organometallic Precursors," C. L. Beatty, Ultrastructure Processing of Ceramics, Glasses and Composites, L. L. Hench and D. R. Ulrich, Eds., (J. Wiley & Sons, 1983).

"Compatibility of a Random Copolymer with Each Homopolymer," K. Fujioka, N. Noethiger, C. L. Beatty, A. Kugemoto and Y. Baba, presented at the ACS/AIChE Joint Meeting on Polymer Compatibility, 14 November 1982, submitted for publication in monograph of meeting.

"Surface Structure and Properties of R. F. Plasma Polymerized Hexamethyl Disilazane," S. K. Varshney and C. L. Beatty, Organic Coatings and Applied Polymer Sci., 47, (1982).

"Compatibility of Polystyrene-Polystyrene-co-n-butyl methacrylate, Poly(n-butyl methacrylate)-Poly(styrene-co-n-butyl methacrylate) and Poly(styrene-co-n-butyl methacrylate)-Poly(styrene-co-n-butyl methacrylate) Systems," K. Fijioka, N. Noethiger, Y. Baba and C. L. Beatty, National Technical Conference, Society of Plastics Engineers, Symposium on Polymer Alloys, Blends and Composites, 25 Oct 1982.

"Characterization of Polysilastyrene," K. S. Shih, C. L. Beatty, and R. West, presented at the High Polymer Div., Am. Phys. Soc. Meeting, 21-25 March 1983, Los Angeles, CA.

"Pyrolysis of Polysilastyrene Thin Films as Studied by XPS and IR," K. Shih, T. Saitta, C. L. Beatty, C. D. Batich and R. West, presented at the High Polymer Div., Am. Phys. Soc. Meeting, 21-25 March 1983, Los Angeles, CA.

"Integranular Segregation of Boron in Sintered Silicon Carbide," W. D. Carter, P. H. Holloway, C. White and R. Clausing, J. Amer. Ceram. Soc., submitted.

"Mechanisms of Electron Stimulated Desorption from Soda-Silica Glass Surfaces," Y.-X Wang, F. Ohuchi and P. H. Holloway, Surf. Interface Anal., submitted.

"Electron Beam Effects during Analysis of Glass Surfaces," P. H. Holloway, presented at Max Planck Institute fur Metallsforschung, 24 May 1982, Stuttgart, Germany.

"Mechanism of ESD from Glass Surfaces," P. H. Holloway, Florida Chapter of American Vacuum Society 12th Annual Symposium, 16 February 1983, Clearwater Beach, FL.

"Electron Stimulated Desorption: Application and Mechanisms," P. H. Holloway, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 10 March 1983, Atlantic City, NJ.

"Electron Beam Effects During Glass Analysis," P. H. Holloway, National Bureau of Standards, 7 March 1983, Gaithersburg, MD.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Ultrastructure processing refers to the manipulation and control of surfaces and interfaces to attain a new generation of high performance materials with predictable properties and environmental insensitivity. Problem areas that may benefit from the use of ultrastructure processing include behavior of particulate and glass-ceramics, fatigue of brittle materials, grain boundary attack of ceramics, effects of energetic particle beams, lifetime of non-oxide ceramics, electronic behavior of high band gap semiconductors, multiphase electronic components. These primary approaches were pursued:

a. Environmental-Surface Studies - Aqueous corrosion mechanisms, and formation of protective surface layers on silicate glasses were reviewed. A type IIIB glass surface was proposed. The mechanisms of hydrothermal attach of two phase lithia-silicate glass-ceramics were identified and related to the volume fraction of crystal and glassy phase. Lifetime prediction diagrams for the lithia silicate glass-ceramics were developed using data from dynamic fatigue and crack growth. Quantitation of analysis of various types of water in glass was developed. Protonic conduction in phosphate glasses was established and thermo and photocoloring of phosphate glasses were produced. A general theory for electron beam interaction with alkali-silicate glasses was extended showing that the sodium, oxygen, and silicon ions desorb with inter-atomic and intra-atomic de-excitations. Fourier Transform infrared reflection spectroscopy (FTIRRS) was used to identify a mixed Si-O-C intermediate phase formed during low temperature oxidation of polycrystalline and single crystal SiC. Scanning Auger electron spectroscopy showed that boron does not segregate to or precipitate at alpha-beta-SiC phase boundaries. Anisotropic noise measurements showed a nonuniform distribution of mobile carriers along the c-axis direction of SiC single crystal establishing the effects of polytypism boundaries on sub-minibands.

b. Chemical Tranformation Processing - Gel-derived monolithic alkali-silicate glasses from 15 to 40 percent sodium oxide were produced at temperatures as low as 480-520 degrees C by use of organometallic sol-gel technology. FTIRRS and XRD were used to develop gel-glass processing diagrams. General principles for producing gel derived glasses at low temperature were developed. Vapor phase chemical reactions were used to produce SiC spherical submicron powders and RF plasma polymerization produced SiC coatings. SiC fibers were made by pyrolysis of polysilastyrene precursors.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: An Approach to Molecular Composites

2. PRINCIPAL INVESTIGATORS: Dr. William R. Krigbaum
Dr. Jack Preston
Department of Chemistry
Duke University
Durham, NC 27706

3. INCLUSIVE DATES: 1 April 1979 - 31 December 1982

4. GRANT NUMBER: AFOSR-79-0080

5. COSTS AND FY SOURCE: $69,178, FY 79; $47,944, FY 81; $58,553, FY 82

6. SENIOR RESEARCH PERSONNEL: Dr. A. Ciferri
Dr. F. Salaris

7. PUBLICATIONS:

"Aromatic Polyamides Forming Cholesteric Phases," W. R. Krigbaum, F. Salaris, A. Ciferri, and J. Preston, J. Polym. Sci., Polym. Lett. Ed. 17, 601 (1979).

"Preparation of Polyamides via the Phosphorylation Reaction. Poly-4,4'-benzanilides," J. Asrar, J. Preston and W. R. Krigbaum, J. Polym. Sci. Polym Chem. Ed., 20, 79 (1982).

"Thermotropic Homopolyesters. I. The Preparation and Properties of Polymers Based on 4,4'-Dihydroxybiphenyl," J. Asrar, H. Toriumi, J. Watanabe, W. R. Krigbaum, and A. Ciferri, J. Polym. Sci. Polym. Phys. Ed., 21, 1119 (1983).

"A Polyester Forming a Thermotropic Cholesteric Phase," W. R. Krigbaum, A. Ciferri, J. Asrar, H. Toriumi, and J. Preston, Mol. Cryst. Liq. Cryst., 76, 79 (1981).

"Thermotropic Homopolyesters. IV. Study of Fiber Formation," D. Acierno, F. P. La Manta, G. Polizotti, A. Ciferri, W. R. Krigbaum, and R. Kotek, J. Polym. Sci. Polym. Phys. Ed., 21, 2027 (1983).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An objective was to demonstrate that a nematogen can be made to exhibit a cholesteric phase by the incorporation of chiral centers into the polymer chain. The Yamazaki reaction was used to introduce 3 mole percent of chiral L-valine into poly(p-benzamide). This was shown to form a lyotropic cholesteric phase by circular dichroism and the induced circular dichroism of an archiral dye. A disadvantage of the use of lyotropic

mesomorphism was that few solvents were available and the production costs were high. The early lattice model treatment of Flory indicated that a highly extended molecular conformation was essential to the formation of this type of mesophase. It has been demonstrated that the melting point depression of a crystalline polymer by this type of mesophase will be quite small unless the polymer-solvent interaction is very favorable. This implies that the polymer solubility will only be sufficient for the formation of a lyotropic mesophase for those few polymer-solvent systems in which the interactions were very favorable. It was found that the Yamazaki phosphorylation reaction could be made to yield aromatic polyamides of higher inherent viscosity by using a monomer having pre-formed amide linkages. It is believed that this occurs due to reduction in the byproducts of the polymerization. Thermotropic mesophases offer the potential of a less expensive route to high modulus fibers and films. Theory indicates that thermotropic nematogens must be less highly chain extended than loytropic nematogens, and the anisotropic interactions are needed to stabilize the mesophase. However, existing theory offers little guidance concerning how the chemical structure of the reporting unit will affect the range of stability of the mesophase, or whether the mesophase will be smectic or nematic. It was suggested that polymers exhibiting thermotropic mesomorphism could be prepared in incorporating a rigid and a flexible segment in the repeating unit. It was ascertained that incorporation of chiral units would transform a nematogenic polymer into one forming a thermotropic cholersteric phase. The properties of three semi-flexible polymers were investigated. These three polymers were spun, and the fiber properties were poor. Two explanations can be offered. It was found that the entropy change for the nematic-isotropic transition is small compared to that for the crystal-nematic transition. This indicates that these molecules do not adopt a rodlike conformation in a thermotropic nematic phase. Secondly, for polymers of this type, the degree of crystallinity of nematogens is notably poorer than that of smectogens. While the cause of this difference is currently unknown, the spinning results strongly suggest that good mechanical properties are related to highly extended chain conformation, and not simply to spinning from the nematic phase.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Theoretical Studies of Relatively Rigid Polymer Chains

2. PRINCIPAL INVESTIGATOR: Professor J. E. Mark
Department of Chemistry and
Polymer Research
The University of Cincinnati
Cincinnati, OH 45221

3. INCLUSIVE DATES: 1 August 1978 - 31 October 1982

4. GRANT NUMBER: AFOSR-78-3683

5. COSTS AND FY SOURCE: $40,000, FY 78; $48,058, FY 79; $55,245, FY 80
$63,106, FY 81

6. SENIOR RESEARCH PERSONNEL:

Dr. W. J. Welsh
Dr. J. L. Thiel
Dr. J. L. Ackerman
Dr. D. Bhaumik
Dr. H. H. Jaffe

7. JUNIOR RESEARCH PERSONNEL: K. Nayak

8. PUBLICATIONS:

"Phenylene Group Rotations and Nonplanar Conformations in Some *Cis* and *Trans* Polybenzobisoxazoles and Polybenzobisthiazoles," W. J. Welsh, D. Bhaumik, and J. E. Mark, *Macromolecules*, *14*, 947 (1981).

"Interchain Interactions in Some Benzobisoxazole and Benzobisthiazole Rigid-Rod Polymers," D. Bhaumik, W. J. Welsh, H. H. Jaffe, and J. E. Mark, *Macromolecules*, *14* 951 (1981).

"Polarizabilities of Some Benzobisoxazole and Benzobisthiazole Rigid-Rod Polymers," D. Bhaumik, H. H. Jaffe, and J. E. Mark, *Macromolecules*, *14*, 1125 (1981).

"The Flexibility of Various Molecular Swivels Used to Control the Rigidity and Tractability of Aromatic Heterocyclic Polymers," W. J. Welsh, D. Bhaumik, and J. E. Mark, *J. Macromol. Sci. - Phys.*, *18*, 59 (1981).

"The Flexibility of Biphenyl and Related Species Utilizable as Molecular Swivels in Rodlike Polymers. A CNDO/2 Analysis," W. J. Welsh, H. H. Jaffe, J. E. Mark, and N. Kondo, *Makromol. Chemie*, *183*, 801 (1982).

"Calculated Polarizabilities for Some Aliphatic and Aromatic Molecules," D. Bhaumik, H. H. Jaffe, and J. E. Mark, *J. Mol. Structure, THEOCHEM*, *87*, 81 (1982).

"CNDO/2 Analyses of the Order of Protonation of Rodlike Polybenzobisoxazoles (PBO)," W. J. Welsh and J. E. Mark, Polym. Bulletin, 8, 21 (1982).

"CNDO Studies on Nonplanar Conformations in Some Cis and Trans Polybenzobisoxazoles and Polybenzobisthiazoles," W. J. Welsh and J. E. Mark, J. Mat. Sci., accepted.

"Effects of Protonation on the Conformational Characteristics and Geometry of the Rodlike Benzobisoxazole (PBO) Polymers: A CNDO/2 Study," W. J. Welsh and J. E. Mark, Polym. Eng. Sci., accepted.

"Calculations of the Electronic Band Structures for Some Rigid Benzobisoxazole and Benzobisthiazole Polymers," D. Bhaumik and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., submitted.

"A Theoretical Investigation of Chain Packing and Electronic Band Structure of the Rigid-Rod Polymer Trans-Poly(p-Phenylene Benzobisthiazole) in the Crystalline State," D. Bhaumik and J. E. Mark, in preparation.

"Theoretical Investigation of Rigid-Rod Polymers," W. J. Welsh, D. Bhaumik, and J. E. Mark, in preparation.

"Random-Coil Configurations of the Polyformals [$CH_2O(CH_2)_y$]. V. Dipole Moments, Unperturbed Dimensions, Optical Anisotropies, and Molar Kerr Constants for 1,3-Dioxolane Polymers Containing Structural Irregularities," E. Riande, E. Saiz, and J. E. Mark, Macromolecules, 13, 448 (1980).

"Crystalline State Configurations of Alkylene Sulfide Polymers," W. J. Welsh, J. E. Mark, and E. Riande, Polymer J., 12, 467 (1980).

"Calculated Intermolecular Energies Relevant to the Unusually High Melting Point of Poly(Ethylene Sulfide)," D. Bhaumik and J. E. Mark, Macromolecules, 14, 162 (1981).

"Unperturbed Dimensions of Some Aryloxy Polyphosphazenes," A. L. Andrady and J. E. Mark, Eur. Polym. J., 17, 323 (1981).

"Random-Coil Configurations of the Polyformals CH_2-O-(CH_2)$_y$-O- VI. Dipole Moments of the Stereochemically Variable Polymer Prepared from 4-Methyl-1,3-dioxolane," E. Riande, M. Garcia, and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., 19, 1739 (1981).

"Configurational Characteristics of the Polysulfides. I. Dipole Moments of Poly(Pentamethylene Sulfide)," E. Riande, J. Guzman, W. J. Welsh, and J. E. Mark, Makromol. Chemie, 183, 2555 (1982).

"Configurational Characteristics of the Polysulfides. II. Dipole Moments and Gauche Effects in Poly(1,3-Dithiocane)," W. J. Welsh, J. E. Mark, J. Guzman, and E. Riande, Makromol. Chemie, 183, 2565 (1982).

"Configurational Characteristics of the Polysulfides. III. Dipole Moments of Poly(Trimethylene Sulfide) and Comparisons Between Some Polysulfides and the Corresponding Polyoxides," J. Guzman, E. Riande, W. J. Welsh, and J. E. Mark, Makromol. Chemie, 183, 2573 (1982).

"CNDO/2 Molecular Orbital Calculations on the Antifolate DAMP and Some Related Species: Structural Geometries, Ring Distortions, Charge Distributions, and Conformational Characteristics," W. J. Welsh, V. Cody, J. E. Mark, and S. F. Zakrzewski, J. Med. Chem., submitted.

CNDO/2 Molecular Orbital Calculations on the Antifolate DAMP and Some of its Analogues," W. J. Welsh, J. E. Mark, V. Cody, and S. F. Zakrzewski, Proceedings of the Seventh International Symposium on Pteridines and Folic Acid Derivatives, (W. de Gruyter Pub. Co., Berlin, Germany, 1983).

"Theoretical Investigation of Conformational Isomerism in the Alicyclic-Aromatic Molecule 2-(4-Morpholinothio)Benzothiazole," D. Bhaumik and J. E. Mark, in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

One primary goal was to use semi-empirical and quantum-mechanical methods to obtain information on the physical properties of rigid-rod benzobisoxazole (PBO) and benzobisthiazole (PBT) polymers which are of importance to the Air Force because of their high mechanical strength and excellent thermal stability. Such calculations involve energy calculations on both intramolecular (conformational) effects and interchain interactions for the polymers in both the unprotonated and protonated states. Of particular interest is the extent to which the various ring structures in the chains deviate from coplanarity, and how these deviations affect the ordering of the chains in the crystalline state. A related feature is the protonation of these chains, which occurs in the strongly acidic media used as solvents, and its effect on structure and deviations from coplanarity.

A second area of importance is the nature and magnitudes of the interchain interactions, and how they relate to the excellent mechanical properties of these materials. Also of great interest are the effects of oxygen, sulfur, and wholly aromatic "swivels" on the processability of these materials, the ordering of the chains, and the mechanical strength of the resulting films or fibers.

Intramolecular (conformational) energy calculations using semi-empirical molecular mechanics techniques were carried out on PBO and PBT repeat units in order to characterize deviations from coplanarity. The results indicated that PBO should be planar, in agreement with experimental results on model compounds. The PBT was correctly predicted to be nonplanar but its degree of nonplanarity was overestimated. Inclusion of intermolecular interactions improved agreement between theory and experiment. These intermolecular interaction energies were very large, suggesting that the failure mechanism in these materials might generally be bond breakage rather than bond slippage. Predicted densities and details of chain packing were in good agreement with experimental results.

Similar techniques were used to calculate the intramolecular energies of various molecular "swivels", which are inserted into the rodlike chains to impart flexibility, in order to characterize their flexibilizing ability. Wholly aromatic swivels were found to excel in this regard, particularly those containing ring nitrogen atoms adjacent to the rotatable bond. Three theoretical approaches were used to calculate the repeat unit polarizabilities of the polymers. Two of these gave comparable values of the polarizabilities, and corresponding values of the anisotropic ratio qualitatively agreed with experiment. The third method seriously underestimated the polarizabilities for PBO and PBT and for the n-alkanes but gave good agreement with experiment for benzene and biphenyl.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Defect Chemistry of Crystalline Inorganic Materials

2. PRINCIPAL INVESTIGATOR: Dr. Donald M. Smyth
Materials Research Center
Lehigh University
Bethlehem, PA 18015

3. INCLUSIVE DATES: 1 December 1977 - 31 October 1982

4. GRANT NUMBER: AFOSR-78 3505

5. COSTS AND FY SOURCE: \$49,130, FY 78; \$73,040, FY 79; \$45,385, FY 80; \$71,993, FY 81

6. SENIOR RESEARCH PERSONNEL:

Dr. Y. Limb
Dr. Y. Ho Han
Dr. K. W. Cheng

7. PUBLICATIONS:

"Composition and Electrical Properties in $LiNbO_3$, Y. Limb, K. W. Cheng, and D. M. Smyth, Ferroelectrics, 38, 813 (1981).

"Defects and Transport in $LiNbO_3$," D. M. Smyth, Proceedings of the 1983 IEEE International Symposium on Applications of Ferroelectrics.

"Evaluation of Crystals of Lithium Niobate Doped with MgO and TiO_2 for Wave Guide Applications," R. J. Holmes, Y. S. Kim, D. Smyth, and C. D. Brandle, Jr., Proceedings of the 1983 IEEE International Symposium on Applications of Ferroelectrics.

"The Chemistry of $LiNbO_3$ as an Optoelectronic Material," D. M. Smyth, to appear in the Proceedings of the SPIE Los Angeles '84 Technical Symposium.

"Diffusion of Ti into $LiNbO_3$ Crystals of Different Compositions at 1050°C," R. J. Holmes and D. M. Smyth, J. Appl. Phys., submitted.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this program was to establish defect models for compounds whose applicability depends on the types and amounts of ionic and electronic defects. Attention was focused on $LiNbO_3$, and electrooptic material of interest for surface acoustic wave devices, light wave guides, electrooptic modulation, and phase-matched optical second harmonic generation. The main experimental approach was the measurement of the equilibrium electrical conductivity of $LiNbO_3$ single crystals as a function of temperature (900-100°C), oxygen partial pressure (10^{-15} - 10^5 Pa or 10^{20} - 1 atm), Li/Nb ratio (0.92-1.00), and impurity additions (up to 8.9 mole % MgO and 5.7 mole % TiO_2).

Previous discussions of the defect chemistry of $LiNbO_3$ have been based on the assumption that oxygen vacancies are the major product of reduction. This is inconsistent, however, with the earlier determination that the density of $LiNbO_3$ increases with loss of Li_2O, indicating that niobium-excess defects are formed rather than oxygen vacancies. In fact, the density also increases with reduction and a self-consistent defect model is proposed that involves only lithium vacancies, electrons, and niobium located on lithium sites. Oxygen vacancies are not a major defect species in this compound.

The insensitivity of the equilibrium conductivity of $LiNbO_3$ to changes in the Li/Nb ratio, and to additions of aliovalent impurities in the percent range, indicates that the concentration of major defects is unaffected by these compositional changes. This suggests that $LiNbO_3$ has a very high degree of intrinsic disorder. The $LiNbO_3$ structure is approximately a hexagonal-close-packed oxygen sublattice with the cations in 2/3 of the available octahedral sites. The cation sequence in the linear strings of face-sharing octahedra is -Li-Nb-V-Li-Nb-V-, where V represents an empty octahedral site. The structure of $FeTiO_3$, ilmenite, is the same except that the cation sequence is -Fe-Ti-V-Ti-Fe-V-. It is proposed that there is little energetic difference between these two sequences and that $LiNbO_3$ has substantial disorder (1-10%) in the cation sequence. This corresponds to fragments of the ilmenite structure scattered throughout the $LiNbO_3$ lattice. This intrinsic disorder is the major source of defects except at the most Li_2O-deficient or highly reduced compositions.

Our results indicate that the electrons created by reduction of $LiNbO_3$ are all contributing to conduction at temperatures $\overline{>}$ 900°C. Other published results show that below about 500°C the electrons are increasingly trapped with an activation energy of 24 kJ/mol (0.25 eV). It is proposed that the trapping centers are the niobium-excess defects, which represent a local excess of positive charge. In the congruently-melting composition typical of almost all single crystals (48.6 mol % Li_2O) there are more than enough niobium defects to surve as single electron traps for all of the electrons generated by even extensive reduction.

The change in defect concentrations resulting from reduction causes an increase in the Li_2O activity. For a crystal already at the Li_2O-rich phase boundary, reduction causes a turbidity due to phase separation. While the equilibrium conductivity of $LiNbO_3$ reaches equilibrium values rapidly and reversibly for oxygen partial pressures above 10^{-5} Pa (10^{-10} atm), for more extensive reduction the equilibration is extremely slow and poorly reversible for all values of Li/Nb. It is proposed for these cases that the reduction is sufficient to drive the Li_2O activity to the Li_2O-rich phase boundary with subsequent phase separation, regardless of the initial Li/Nb ratio.

This research project stimulated an investigation of the diffusion kinetics of titanium into $LiNbO_3$, in the form of the doctoral dissertation of R. J. Holmes, Member of the Technical Staff at Bell Laboratories. Contrary to previous reports, the diffusion is isotropic. The diffusion constant increases slightly as the Li/Nb ratio decreases, from 0.41×10^{-12} cm^2/sec for the Li_2O rich composition (50.0 mol % Li_2O), to 0.89×10^{-12} cm^2/sec for the congruent composition (48.6 mol % Li_2O), to 2.62×10^{-12} cm^2/sec for the Li_2O-deficient composition (48.1 mol % Li_2O), all at 1050°C. With this weak compositional dependence, it is possible to obtain more rapid diffusion in the ferroelectric phase at the Li_2O-rich composition because of its higher Curie temperature.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis of Liquid Crystalline, Extended Chain Polymer
Compositions in Poly(phosphoric acid)

2. PRINCIPAL INVESTIGATOR: Dr. James F. Wolfe
Polymer Sciences Department
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

3. INCLUSIVE DATES: 15 November 1980 - 14 November 1982

4. CONTRACT NUMBER: F49620-81-K 0003

5. COST AND FY SOURCE: \$138,996, FY 81; \$217,844, FY 82; \$10,820, FY 83

6. SENIOR RESEARCH PERSONNEL: Dr. P. D. Sybert

7. JUNIOR RESEARCH PERSONNEL:

B. Wilson
J. Sybert
B. Loo
D. MacBlane
D. Osborn
J. Hardee
E. Sevilla

8. PUBLICATIONS:

"Rigid Rod Polymers. 2. Synthesis and Thermal Properties of Para-Aromatic Polymers with 2,6-Benzobisthiazole Units in the Main Chain," J. F. Wolfe, B. H. Loo, and F. E. Arnold, *Macromolecules*, *14*, 915 (1981).

"Synthesis of Rigid Rod Polymers. Improved Synthesis Method for Poly(*p*-phenylene benzobisthiazole)," J. F. Wolfe and P. D. Sybert, Interim Annual Report, Contract F49620-81-K-0003, January 1982.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Initial objectives were to improve the synthesis procedure for the rigid rod polymer poly(*p*-phenylenebenzobisthiazole) by studying the various paramters of PPA polycondensations.

A general synthesis procedure was developed for preparing liquid-crystalline compositions that contain poly(phosphoric acid) and aromatic, heterocyclic, extended chain homopolymers, random copolymers, or block copolymers. The polymers are characterized by rigid or semirigid molecular structures having benzobisthiazole, benzobisoxazole, benzothiazole, benzoxazole, or benzimidazole units in the main chain. Copolymers were prepared that contain such main chain units as *trans*-1,4-cyclohexylene, 4,4'-biphenylene, 1,8-octylene, and *m*-phenylene.

The reaction mixtures obtained by this synthesis procedure can be used directly to prepare high strength fibers and films of these polymers, because of the high polymer concentrations (as high as 21 wt%), high polymer molecular weight, and liquid crystalline characteristics. Liquid crystalline behavior in PPA of high molecular weight poly(p-phenylene-2,6-benzo[1,2-d:5,4-d']bisoxazole) (PBO) was demonstrated for the first time. Liquid crystalline behavior (in any solvent) of the homopolymers poly(2,6-benzothiazole) (2,6-ABPBT) and poly(2,5-benzoxazole) (2,5-ABPBO) was demonstrated for the first time.

AFOSR Program Manager: Dr. Donald R. Ulrich

RESEARCH EFFORTS COMPLETED IN FY 83

MOLECULAR DYNAMICS - CAPTAIN LEE E. MYERS

Chemiluminescence and Laser Induced Fluorescence of Boron Atom Reactions AFOSR 80-0061	Paul Davidovits Department of Chemistry Boston College Chestnut Hill, MA 02167
A Molecular Orbital Study of Atmospherically Imported Cluster Species AFOSR-82-0198	Carol A. Deakyne Department of Chemistry College of the Holy Cross Worcester, MA 01610
Collisional Energy Exchange in Polyatomic Molecules F49620-80-C-0026	John B. Fenn Subbarao B. Ryali Department of Chemical Engineering Yale University New Haven, CT 06520
Spectroscopic Studies of the Products of the Reactions of Excited Noble-Gas Atoms AFOSR-79-0089	Michael F. Golde Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260
A Theoretical Study of The Energetics and Dynamics of High Energy Inelastic Collision Processes F49620-80-C-0017	Dudley Herschbach Department of Chemistry Harvard University Cambridge, MA 02138
Energy Disposal in Electronically Excited Halogen Atoms and Oxygen AFOSR 78-3513	Paul L. Houston Department of Chemistry Cornell University Ithaca, NY 14853
Spectroscopic Determination of Intermolecular Potentials of Gas Laser Components and of Major Atmospheric Constituents AFOSR-82-0036	William Klemperer Department of Chemistry Harvard University Cambridge, MA 02138
Nonlinear Interactions Between the Pumping Kinetics, Fluid Dynamics and Optical Resonator of cw Fluid Flow Lasers AFOSR-80-0133	L. H. Sentman Aeronautical & Astronautical Engineering Department M. H. Nayfeh Physics Department University of Illinois Urbana, IL 61801
Theoretical Studies of Excited State Energy Transfer, and Radiative Properties of Transient Species, Using MCSCF/CI Methods AFOSR 79-0073	David R. Yarkony Department of Chemistry The Johns Hopkins University Baltimore, MD 21218

COMPLETED PROJECT SUMMARY

1. TITLE: Chemiluminescence and Laser Induced Fluorescence of Boron Atom Reactions

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

3. INCLUSIVE DATES: 1 December 1979 - 30 June 1983

4. GRANT NUMBER: AFOSR 80-0061

5. COSTS AND FY SOURCE: $60,000, FY 80; $61,234, FY 81; $67,663, FY 82

6. SENIOR RESEARCH PERSONNEL:

Dr. M. Bullitt
Dr. R. Rao

7. JUNIOR RESEARCH PERSONNEL:

T. DiGiuseppe
S. M. Hosseini
M. B. Tabacco
J. Gardner
R. D. Estes
J. J. DeHaven
C. Stanton

8. PUBLICATIONS:

"Rate Constants for the Reaction of Boron Atoms with O_2, SO_2, N_2O and CO_2," U. C. Sridharan, T. G. DiGiuseppe, D. L. McFadden, and P. Davidovits, J. Chem. Phys., 70, 5422 (1979).

"Boron Atom Reactions II: Rate Constants with O_2, SO_2, CO_2 and N_2O," T. G. DiGiuseppe and P. Davidovits, J. Chem. Phys., 74, 3287 (1981).

"Studies of Chemiluminescence in Boron Atom Reactions with O_2, SO_2, N_2O and H_2O_2," J. DeHaven, M. T. O'Connor, and P. Davidovits, J. Chem. Phys., 75, 1746 (1981).

"Studies of Chemiluminescence in Boron Atom Reactions with Epoxides," S. M. Hosseini, J. DeHaven, and P. Davidovits, Chem. Phys. Letters, 86, 495 (1982).

"Boron Atom Reactions III: Rate Constants with H_2O, H_2O_2 and the Alcohols," T. G. DiGiuseppe, R. D. Estes, and P. Davidovits, J. Phys. Chem., 86, 260 (1982).

"Boron Atom Reactions IV: Rate Constants with Epoxides," R. Estes, M. B. Tabacco, T. G. DiGiuseppe, and P. Davidovits, Chem. Phys. Letters, 86 491 (1982).

"Boron Atom Reactions with the Epoxides: Vibrational Distributions in the Product BO(A^2) State," M. K. Bullitt, R. R. Paladugu, J. DeHaven, and P. Davidovits, J. Phys. Chem, to be published.

"Boron Atom Reactions V: Rate Constants and Reaction Model For the Epoxides," M. B. Tabacco, C. Stanton, and P. Davidovits, in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of the work sponsored by this grant was to study the highly exoergic gas phase reactions of boron atoms. The main goal of these studies is to obtain a basic understanding of exoergic reactions of non-metal atoms. These types of reactions play a fundamental role in fields such as combustion, plasma chemistry, laser induced chemistry and chemical lasers. We have developed experimental techniques for studying boron atom reactions. A flow apparatus was built to measure the total cross section for the reaction of boron atoms with a wide range of reactive molecules. A single collision beam apparatus was constructed to study electronically excited molecules produced in the boron atom reactions. We have obtained a dye laser system and have built a flow apparatus to perform LIF studies with the products of boron atom reactions.

We have completed rate and chemiluminescence studies of boron atom reactions with a large number of oxygen containing molecules. These reactants include simple molecules such as O_2, SO_2, N_2O, CO_2, H_2O, H_2O_2, NO_2, OCS, the alcohols, thiols, ethers and epoxides. The results of the experiments show several surprising and interesting patterns. Using MNDO computer calculations we have developed a model which explains qualitatively our results as well as the results obtained with the group four atoms in other laboratories. The model suggests that the reactivity of non-metal atoms is determined primarily by the local charge distribution within the reactant molecule.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: A Molecular Orbital Study of Atmospherically Imported Cluster Species

2. PRINCIPAL INVESTIGATOR: Dr. Carol A. Deakyne
Department of Chemistry
College of the Holy Cross
Worcester, MA 01610

3. INCLUSIVE DATES: 15 June 1982 - 14 June 1983

4. GRANT NUMBER: AFOSR-82-0198

5. COSTS AND FY SOURCE: $9,640, FY 82 (Mini Grant)

6. PUBLICATIONS:

"A Molecular Orbital Study of Atmospherically Important Species," C. A. Deakyne, Final Technical Report, (1983).

"The Role of Diffuse Functions in the Structure of $H_3O_2^-$," C. A. Deakyne, J. Chem. Phys., to be submitted.

"The Structure of HNO_3^-," C. A. Deakyne, J. Chem. Phys., to be submitted.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The theoretical research conducted under this program was concerned with a study of the structures, total energies, and charge distributions of a series of atmospherically important species. These included OH, OH^-, NH, NH^-, H_2O, NH_2, NH_2^-, OOH, OOH^-, $OH^-{\bullet}H_2O$, NO_2, NO_2^-, HNO_3, HNO_3^-, and $H_2NO_4^-$. The calculations were carried out ab initio primarily at the MP2/6-31+G** and MP2/4-31+G basis set levels. The total energies obtained were used to compute energy changes for several reactions involving the above species and electron affinities for OH, NH, NH_2, OOH, $OH{\bullet}H_2O$, NO_2, and HNO_3. The theoretical bond lengths, bond angles, electron affinities, and reaction energies are in reasonable agreement with their experimental values, particularly for the MP2/6-31+G** results.

An analysis was performed of the effect of diffuse functions, polarization functions, and electron correlation on the above molecular and thermodynamic properties. It was found that reasonable geometries are obtained without adding diffuse functions to the basis set and reasonable energetics are obtained without adding polarization functions.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Collisional Energy Exchange in Polyatomic Molecules

2. PRINCIPAL INVESTIGATORS: Dr. John B. Fenn
Dr. Subbarao B. Ryali
Department of Chemical Engineering
Yale University
P.O. Box 2159 YS
New Haven, CT 06520

3. INCLUSIVE DATES: 1 October 1979 - 30 September 1982

4. CONTRACT NUMBER: F49620-80-C-0026

5. COSTS AND FY SOURCE: $53,700, FY 80; $72,874, FY 81; $80,736, FY 82

6. SENIOR RESEARCH PERSONNEL:

Dr. G. L. Haller
Dr. B. L. Halpern
Dr. S. D. Shen
Dr. S. P. Venkateshan
Dr. D. Sethi

7. JUNIOR RESEARCH PERSONNEL:

D. A. Mantell
Y. F. Maa
M. Kori

8. PUBLICATIONS:

"Flowfield Calculations in Nonequilibrium Free Jets by the Method of Characteristics," M. Labowsky, S. B. Ryali, J. B. Fenn, and D. R. Miller, Rarefied Gas Dynamics, S. S. Fisher, Ed., Prog. in Astro. and Aero., 74, 695 (1981).

"Collisional Excitation of CO_2 by N_2, O_2, and Ar," S. B. Ryali, J. B. Fenn, C. E. Kolb, and J. A. Silver, J. Chem. Phys., 76, 5878 (1982).

"Rotational Energy Distribution in CO_2 Vibrationally Excited by Collision with N_2," S. P. Venkateshan, S. B. Ryali, and J. B. Fenn, Chem. Phys. Lett., 92, 606 (1982).

"Terminal Distributions of Rotational Energy in Free Jets of CO_2 by Infrared Emission Spectrometry, S. P. Venkateshan, S. B. Ryali, and J. B. Fenn, J. Chem. Phys., 77, 2599 (1982).

"Distribution of Internal Energy in CO and CO_2 Scattered by a Hot Platinum Surface," D. A. Mantell, S. B. Ryali, G. L. Haller, and J. B. Fenn, J. Chem. Phys., 78, 4250 (1983).

"Distribution of Internal Energy in NO Vibrationally Excited by a Hot Platinum Surface," D. A. Mantell, Y.-F. Maa, G. L. Haller, and J. B. Fenn, J. Chem. Phys., 78, 6338 (1983).

"The Exciting Oxidation of CO on Pt," D. A. Mantell, S. B. Ryali, B. L. Halpern, G. L. Haller, and J. B. Fenn, Chem. Phys. Lett., 81, 185 (1981).

"The Dynamics of CO Oxidation on Pt Deduced from Translational, Rotational and Vibrational Excitation in Product CO_2," D. A. Mantell, S. B. Ryali, G. L. Haller, and J. B. Fenn, Surface Science, submitted.

"Time Resolved Infrared Emission Studies of CO_2 Formed by CO Oxidation on Pt and Pd," D. A. Mantell, S. B. Ryali, and G. L. Haller, Chem. Phys. Lett., accepted.

"Vibrational Energy Distribution of CO in the Oxidation of C on Pt," M. Kori and B. L. Halpern, Chem. Phys. Lett., 98, 32 (1983).

"Surface Catalyzed Production of N_2O from the Reaction of N Atoms and O_2 on Platinum," E. J. Murphy, J. B. Fenn, and B. L. Halpern, J. Catal., 74, 434 (1981).

"Collision Kinetics in Gas Dynamics," J. B. Fenn, Applied Atomic Collision Physics, Vol 5, E. W. McDaniel, Ed., (Academic Press, New York), p.p. 349 (1982).

"Order from Chaos with Molecular Beams," J. B. Fenn, Proc. Indian Acad. Sci. (Chem. Sci.), 89, 309 (1979).

"Where Are We Going With Molecular Beams," J. B. Fenn, Proc. 13th Rarefied Gas Dynamics Symposium, in press.

"Clusters as a Source of Error In Molecular Beam Scattering Experiments," H. L. Tien, S. B. Ryali, P. J. Gale, and J. B. Fenn, Chem. Phys. Lett., 93, 213 (1982).

"Further Reflections on the Role of a Mass Flux Guage in the Calibration of Mass Spectrometers for Dimers," J. B. Fenn and N. Lee, Rev. Sci. Instr., 53, 1494 (1982).

"On the Time Required to Reach Fully Developed Flow," J. B. Fenn and K. J. Saenger, J. Chem. Phys., submitted.

"Research Is Engineering," J. B. Fenn, Chem. Eng. Educ., 190 (Fall 1982).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Our objective has been to understand the details of energy exchange during encounters between polyatomic molecules in the gas phase and between such molecules and surfaces. In particular, we have been interested in the distribution of rotational and vibrational energy consequent to inelastic and reactive collisions. Information on these distributions is obtained by infrared radiometry and Fourier Transform Infrared Spectrometry (FTIS). The collisions that we study occur: (a) during expansion of supersonic free jets in vacuo; (b) when two such jets intersect each other as uncollimated molecular beams; and (c) when one such jet is incident upon a surface. Following are some key results:

1. Terminal distributions of rotational energy in free jets of CO and CO_2 show a non-Boltzmann distribution that can be characterized by a two-temperature model and explained in terms of a competition between rotation-rotation and rotation-translation transfers.

2. Spectra CO_2 molecules vibrationally excited by collisions with N_2 molecules at velocities up to 5 km/sec indicate a similar two-temperature distribution. A possible explanation is that the collision that excites vibration results in only a small amount of rotational excitation giving rise to the low temperature population. A second collision between vibrationally excited CO_2 and N_2 results in more rotational excitation that gives rise to the high temperature population.

3. There is substantial variation in excitation behavior when molecules are incident on a hot metal surface. Results with CO_2 show a probability of about 0.2 that the asymmetric stretch mode is excited. The rotational distribution of the vibrationally excited molecules is Boltzmann and corresponds to an accommodation of between 0.4 and 0.6. On the other hand, about 40% of the CO molecules reach complete vibrational accommodation with the surface and show a non-Boltzmann distribution of rotational energy corresponding to an overall rotational accommodation about the same as for CO_2.

4. Spectra of nascent CO and CO_2 molecules formed respectively by catalytic oxidation of C and CO on a platinum surface indicate internal "temperatures" substantially higher than the surface temperature. An energy balance indicates that only about 1/3 of the available reaction energy is absorbed by the surface. The remainder goes into excess translational, rotational and vibrational energy in the product molecules.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Spectroscopic Studies of the Products of the Reactions of Excited Noble-Gas Atoms

2. PRINCIPAL INVESTIGATOR: Dr. Michael F. Golde
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

3. INCLUSIVE DATES: 15 March 1979 - 14 May 1983

4. GRANT NUMBER: AFOSR-79-0089

5. COSTS AND FY SOURCE: \$54,287, FY 79; \$46,470, FY 80; \$51,139, FY 81
\$60,998, FY 82

6. SENIOR RESEARCH PERSONNEL: Dr. H. Ogura

7. JUNIOR RESEARCH PERSONNEL:

J. Balamuta	Y. S. Ho
A. M. Moyle	R. A. Poletti

8. PUBLICATIONS:

"Comparison of Reactivity of Ar($^3P_0$) and Ar($^3P_2$) Metastable Species I. Rate Constants for Quenching by Kr and CO," M. F. Golde and R. A. Poletti, Chem. Phys. Lett., 80, 18 (1981).

"Comparison of Reactivity of Ar($^3P_0$) and Ar($^3P_2$) Metastable Species II. Products of Quenching by Some Halogen-containing Species," M. F. Golde and R. A. Poletti, Chem. Phys. Lett., 80, 23 (1981).

"Quenching of Metastable AR, Kr, and Xe Atoms by Ocygen-containing Compounds: A resonance Fluorescence Study of Reaction Products," J. Balamuta and M. F. Golde, J. Chem. Phys., 76, 2430 (1982).

"Chemiionization Reactions of Metastable Ar($^3P_{0,2}$) Atoms," M. F. Golde, Y.-S. Ho, and H. Ogura, J. Chem. Phys., 76, 3535 (1982).

"Formation of Electronically-Excited Oxygen Atoms in the Reactions of Ar($^3P_{0,2}$) and Xe($^3P_2$) Atmos with O_2," J. Balamuta and M. F. Golde, J. Phys. Chem., 86, 2765 (1982).

"Product Distributions in the Reactions of Excited Noble-Gas Atoms with Hydrogen-Containing Compounds," J. Balamuta, M. F. Golde, and Y-S. Ho, J. Chem. Phys., in press.

"Chemiionization in Reactions of State-Selected Ar($^3P_2$) and Ar($^3P_0$) Excited Atoms with Small Molecules," M. F. Golde, Y.-S. Ho and H. Ogura, J. Chem. Phys., in preparation.

"Product Distributions in the Reactions of Excited Noble-Gas Atoms with Chlorine-Containing Compounds," J. Balamuta, M. F. Golde and A. M. Moyle, J. Chem. Phys., in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Energy transfer from electronically-excited species is of importance in many fields, such as atmospheric chemistry and visible/UV lasers. Although many rate constants for electronic quenching have been measured, much less is known about the products of such processes and thus mechanisms of energy transfer are very poorly understood. This project sought to identify the major channels in the highly-efficient quenching of metastable ($^3P_{0,2}$) states of Ar, Kr and Xe by molecular reagents and to obtain absolute branching fractions for all observed channels. The discharge flow technique was used, with emission spectroscopy to detect electronically-excited products, saturation ion-current measurements to monitor the total yield of chemiionization, and atomic resonance fluorescence (H, O and Cl atoms) to allow detection for the first time of 'dark channels', in which the energy-rich acceptor molecule dissociates into non-emitting fragments. Several experiments were also performed on state-selected Ar($^3P_0$) and ($^3P_2$) metastables. The reagents included small O- and H-containing molecules, such as O_2, CO_2, N_2O, NO_2, H_2O, CH_3OH, CH_4 and CH_2O, and several chlorine- and bromine- containing compounds, including the halomethanes.

The principal finding was that the 'dark' dissociation channel is usually the dominant mode of reaction. In contrast, branching fractions for chemiionization (when energetically accessible) are typically 0.1-0.4 and the cross-sections for noble-gas halide excimer formation are smaller than those for the analogous reactions of ground state alkali atoms. For the dissociation channel, the molecules studied exhibited the following general behavior.

a. Terminal bonds of the molecules are broken readily, central bonds of larger molecules, such as CH_3OH and C_2H_6, much less readily.

b. Molecular elimination of H_2 is concluded to be negligible in several reactions, particularly those of Xe*, in sharp contrast to the vacuum UV photochemistry of CH_4, C_2H_6, NH_3 and CH_2O.

c. The available energy is used efficiently to break more than one bond of the molecule, resulting in the release commonly of more than one atom per reactive event.

d. Dissociation channels often occur only weakly near threshold and branching fractions increase only slowly with metastable energy. As a corollary, in reactions with related compounds, the atom yield increases as the threshold energy is lowered. In contrast, the saturation ion-current data are consistent with a sharp onset of Penning ionization near threshold.

The high quenching efficiency and dominance of dissociation and ionization channels are associated with the availability of accessible acceptor states of the quenching molecule, as revealed by its absorption spectrum. It is proposed that these efficient reactions occur by energy transfer at relatively long range with no major prior distortion of the quenching molecule.

It is expected that this model should be directly applicable to the reactions of certain other excited species, which exhibit a similar correlation of quenching rate constants with the availability of acceptor states at the appropriate energy.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: A Theoretical Study of the Energetics and Dynamics of High Energy Inelastic Collison Processes

2. PRINCIPAL INVESTIGATOR: Professor Dudley Herschbach
Department of Chemistry
Harvard University
Cambridge, MA 02138

3. INCLUSIVE DATES: 1 January 1980 - 14 May 1983

4. CONTRACT NUMBER: F49620-80-C-0017

5. COSTS AND FY SOURCE: $60,000, FY 80; $79,832, FY 81; $65,725, FY 82
$40,899, FY 83

6. SENIOR RESEARCH PERSONNEL: Dr. J. W. Duff
Dr. C. E. Kolb (Aerodyne Research Inc.)
Dr. M. B. Faist (Radian Corporation)

7. PUBLICATIONS:

"Diatomics-in-Molecules Approximation for Rydberg States of H_3," S. Raynor and D. R. Herschbach, J. Phys. Chem., 86, 1214 (1982).

"Angular Correlations in Chemical Reactions. Statistical Theory for Four-Vector Correlations," J. D. Barnwell, J. G. Loeser, and D. R. Herschbach, J. Phys. Chem., 87, 2781 (1983).

"The Rotating Rod Model: Opacity, Excitation, Deflection and Angular Distribution Functions from Collinear Reaction Probabilities," W. Agmon, Chem. Phys., 61, 189 (1981).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall objective of this research program was to develop theoretical methods for improving the prediction of potential energy surfaces relevant to high energy inelastic collision processes. A "diamotics-in-molecules" approximation for constructing potential energy surfaces of excited electronic states of the prototypical triatomic hydrogen system was developed. A new approximation method was devised to estimate cross sections for inelastic or reactive collision processes from a "rotating rigid rod" model. These semiempirical approaches were complimented by a comprehensive statistical theory for vector properties of collisions, including all angular distributions describing the orientations of the initial and final relative velocity vectors and/or the reactant and product rotational angular momentum vectors.

A satisfactory theoretical treatment has been achieved which accounts for "ballistic energy transfer." This denotes extremely efficient inelastic transfer of translational to rovibrational energy observed in hyperthermal collisions of rare gas atoms with alkali halide molecules. A very detailed analysis was carried out for the Ar-Cs-F system, by constructing a potential energy surface by the diatomics-in-molecules method and computing quasiclassical collision trajectories for a wide range of conditions. The results are in excellent agreement with experiment. Thus they serve to account for ballistic energy transfer, a mechanism which had eluded theoretical explanation for over ten years.

A potential energy surface has been constructed for the H + CO system by combining results from ab-initio calculations with spectroscopic data on the HCO radical. Trajectory calculations employing this surface were carried out to compare with the exceptionally good experimental results recently obtained for hyperthermal inelastic collisions of H + CO. Excellent agreement was found for the data on translational-to-vibrational energy transfer. Agreement with the data on vibrational-to-rotational transfer is also good in an average sense. However, the calculations failed to predict a pronounced bimodal structure observed in the energy transfer, and this appears to be due to inaccuracy in an important region of the surface.

A new and novel "dimensional interpolation" approach to accurate electronic structure calculations has also been discovered. This indicates that calculations for the rather simple limiting cases corresponding to one-dimension ($D = 1$) and infinite dimension ($D = \infty$) will allow interpolation in terms of $1/D$ to provide quite high accuracy. So far the method has been tested only for two electron systems.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Energy Disposal in Electronically Excited Halogen Atoms and Oxygen

2. PRINCIPAL INVESTIGATOR: Dr. Paul L. Houston
Department of Chemistry
Cornell University
Ithaca, NY 14853

3. INCLUSIVE DATES: 1 November 1977 - 31 October 1982

4. GRANT NUMBER: AFOSR 78-3513

5. COSTS AND FY SOURCE: \$33,660, FY 78; \$38,473, FY 79; \$60,259, FY 80
\$63,952, FY 81; \$102,814, FY 82

6. SENIOR RESEARCH PERSONNEL:

Dr. G. Hall
Dr. E. Wurzberg
Dr. R. Aviles
Dr. G. Zhen-nan
Dr. W. Marinelli

7. JUNIOR RESEARCH PERSONNEL:

A. J. Grimley
A. T. Young
David F. Muller

8. PUBLICATIONS:

"Electronic to Vibrational Energy Transfer from Excited Halogen Atoms," P. L. Houston and A. J. Grimley, in *Electronic Transition Lasers II*, Wilson, Suchard, and Steinfeld, Eds., (MIT Press) pp. 257 (1977).

"Electronic to Vibrational Energy Transfer from $I(5^2P_{1/2})$: I. HCl, HBr, and NO," A. J. Grimley and P. L. Houston, *J. Chem. Phys.*, *68*, 3366 (1978).

"The Possibility of Laser Pumping via Energy Transfer from or Reactive Collisions with $I(^2P_{1/2})$," P. L. Houston, in *High-Power Lasers and Applications*, K.-L. Kompa and H. Walther, Eds., (Springer-Verlag) pp. 81 (1978).

"Electronic to Vibrational Energy Transfer from $I(5^2P_{1/2})$: II. H_2O, HDO, and D_2O," A. J. Grimley and P. L. Houston, *J. Chem. Phys.*, *69*, 2339 (1978).

"Hydrogen Abstraction by Fluorine Atoms: F + HX and F + DX (X = I, Br, Cl)," E. Wurzberg, A. J. Grimley, and P. L. Houston, *Chem. Phys. Lett.*, *57*, 373 (1978).

"Infrared Multiphoton Dissociation of CF_3Br," E. Wurzberg, L. J. Kovalenko, and P. L. Houston, *Chem. Phys.*, *35*, 317 (1978).

"Laser Studies of Atom-Molecule Reactions," P. L. Houston, *Proc. Soc. Photo opt. Instr. Eng.*, *158*, 23 (1978).

"Electronic to Vibrational Energy Transfer from $I(5^2P_{1/2})$: III. H_2, HD, and D_2," A. J. Grimley and P. L. Houston, *J. Chem. Phys.*, *70*, 4724 (1979).

"Electronic to Vibrational Energy Transfer from $Br(4^2P_{1/2})$ to H_2, HD, and D_2," A. J. Grimley and P. L. Houston, *J. Chem. Phys.*, *70*, 5184 (1979).

"Electronic to Vibrational Energy Transfer from Excited Halogen Atoms," P. L. Houston, in *Photoselective Chemistry*, Part 2, J. Jortner, Ed., 381 (1981).

"Initiation of Atom-Molecule Reactions by Infrared Multiphoton Dissociation," P. L. Houston, in *Photoselective Chemistry*, Part 1, J. Jortner, Ed., 625 (1981).

"The Photochemistry of Nitrosyl Halides: The $X + NOX \rightarrow X_2 + NO(v)$ Reaction (X=Cl, BR)," A. J. Grimley and P. L. Houston, *J. Chem. Phys.*, *72*, 1471 (1980).

"The Temperature Dependence of Absolute Rate Constants for the $F + H_2$ and $F + D_2$ Reactions," E. Wurzberg and P. L. Houston, *J. Chem. Phys.*, *72*, 4811 (1980).

"The Temperature Dependence of Hydrogen Abstraction Reactions: F + HCl, F + HBr, F + DBr, and F + HI," E. Wurzberg and P. L. Houston, *J. Chem. Phys.*, *72*, 5915 (1980).

"Quenching of Laser Excited $O_2(b^1\Sigma_g^+)$ by CO_2, H_2O, and I_2," R. G. Aviles, D. F. Muller, and P. L. Houston, *Appl. Phys. Lett.*, *37*, 358 (1980).

"Direct Observation of I_2 Collisional Dissociation by $O_2(b^1\Sigma_g^+)$," D. F. Muller, R. H. Young, P. L. Houston, and J. R. Wiesenfeld, *Appl. Phys. Lett.*, *38*, 404 (1981).

"Direct Observation of Electronic-to-Vibrational Energy Transfer from $O_2(^1\Sigma)$ to CO_2 (ν_3)," D. F. Muller and P. L. Houston, *J. Phys. Chem.*, *85*, 3563 (1981).

"The $I(^2P_{1/2}) + O_2 \leftrightarrow I(^2P_{3/2}) + O_2(^1\Delta)$ Equilibrium," A. T. Young and P. L. Houston, *J. Chem. Phys.*, *78*, 2317 (1983).

"Electronic-to-Vibrational Energy Transfer from I*($5^2P_{1/2}$) to I_2 ($25<v<43$)," G. E. Hall, W. J. Marinelli, and P. L. Houston, J. Phys. Chem., 87, 2153 (1983).

"The Collisional Quenching of Electronically Excited Iodine Atoms by Molecular Oxygen," A. T. Young, Doctoral Thesis, Cornell University, 1982.

"Studies of Electronic-to-Vibrational Energy Transfer from Excited Iodine and Bromine Atoms," A. J. Grimley, Doctoral Thesis, Cornell University, 1979.

"Quenching Studies of Laser Excited O_2," D. F. Muller, Doctoral Thesis, Cornell University, 1981.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Electronic-to-Vibrational Energy Transfer

The objective of this part of the research project was to assess the importance of electronic-to-vibrational transfer. The $5^2P_{1/2}$ state of the iodine atom ($E=7603$ cm^{-1}), was of particular interest as the electronic donor because of the possibility that more than one quantum of vibrational energy might be excited. During the first few years of the project we completed studies of the transfer from I($^2P_{1/2}$) to the vibrational modes of HCl, HBr, and NO as well as to H_2O, HDO, and D_2O. These studies demonstrated that, for example, every deactivation of excited iodine by H_2O results in the excitation of two stretching quanta of H_2O vibration. Since these investigations were made by comparing the electronic fluorescence signals to the vibrational fluorescence signals, one disadvantage was that our technique could not be used directly to study the collision partners H_2, and HD, and D_2 (which do not exhibit vibrational fluorescence). These collision partners were of particular interest since their vibrational excitation by energy transfer from Br($4^2P_{1/2}$) and I($5^2P_{1/2}$) had been calculated using a semiclassical theory. Our method of using a trace amount of CO or CO_2 to detect electronic-to vibrational energy transfer through subsequent vibrational-to-vibrational energy transfer to the trace additive allowed us to show that theory and experiment were in qualitative agreement. A striking result of our experiments is that, contrary to prior belief, there is little correlation between the rate of electronic-to-vibrational energy transfer and the efficiency of that transfer; a large fraction of the energy of excitation in the halogen atom is deposited into the collision partner's vibrational degrees of freedom irrespective of the rate at which it is transferred. This result has serious implications for the theory of such energy transfer and is in qualitative agreement with at least three possible theoretical approaches.

Atom-Molecule Reactions

A second objective of our research program was to measure the rates of reaction for halogen atoms, particularly fluorine, with hydrogen-containing species. During our investigations under a different grant, it was found that multiphoton dissociation provided a convenient means for production of transient concentrations of small molecules and atoms. Reaction rates of these transient species could be monitored by observing the appearance rate of excited product species. Thus, the multiphoton dissociation technique was used to initiate fluorine atom reactions with several simple hydrogen containing molecules. For example, multiphoton dissociation of SF_6 in mixtures with H_2 produced an HF infrared fluorescence signal whose rise time was used to determine the rate constant for the $F + H_2$ reaction. This technique was employed to determine the temperature dependence of the rate constants for the reactions of F with H_2, D_2, HCl, HBr, DBr, and HI. In addition, we measured several room-temperature rate constants for hydrogen abstraction by fluorine. Our results for these apparently simple reactions have been quite surprising. For example, the activation energy for the $F + H_2$ reaction is much smaller than that typically used for model potential energy surfaces. In addition, the F + HX reactions (X = Cl,Br,I) give markedly non-linear Arrhenius plots, apparently because the low temperature reaction proceeds through an F-X-H complex while the high temperature reaction involves direct interaction in the F-H-X configuration. Another class of atom-molecule reaction investigated in our group is the system $X + NOX \rightarrow X_2 + NO(v)$, where X = Br or Cl. The transient concentration of X in this case was provided by single-photon rather than multiphoton dissociation of NOX, but the detection scheme was the same: infrared fluorescence from the excited No product was monitored. The results of this investigation provided rate constants for each of the two reactions and demonstrated that the NO product of the Br + NOBr reaction was vibrationally inverted. This reaction is unusual in that it is one of a very few atom-molecule reactions in which the exoergicity does not go predominantly into the newly formed bond.

The Chemical Oxygen-Iodine Laser

The chemical oxygen-iodine laser has been identified by AFWL as a favorable system for further development. However, the chemical dynamics of this laser are poorly understood. Inversion between the spin-orbit levels of iodine is thought to be produced by the following mechanism:

$$O_2(^1\Delta) + O_2(^1\Delta) \rightarrow O_2(^1\Sigma) + O_2(^3\Sigma) \tag{1}$$

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

$$O_2(^1\Delta) + I \rightleftharpoons O_2(^3\Sigma) + I^* \tag{3}$$

$$I^* + O_2(^1\Delta) \rightarrow I + O_2(^1\Sigma) \tag{4}$$

where $I = I(^2P_{1/2})$ and $I^* = I(^2P_{3/2})$. It has been our research objective during the past few years to examine this mechanism in detail, to measure the relevant rate constants, and to determine the branching ratios for alternative steps in the kinetic scheme. Our efforts have focused primarily on steps (2) and (3) of the proposed mechanism.

1. The $I(^2P_{1/2}) + O_2 - I(^2P_{3/2}) + O_2(^1\Delta)$ Equilibrium - The equilibirum between excited iodine atoms and oxygen has been examined by monitoring the time dependent $I^*[\equiv I(^2P_{1/2})]$ concentration following creation of this species by pulsed laser photolysis of iodine-containing precursors. A double exponential decay is observed which relfects a fast approach to equilibrium followed by a slower relaxation of the equilbrated mixture. Data obtained with the I* precursors HI and CH_3I show that the rate constant for the reaction $I^* + O_2 \rightarrow I + O_2$ is insignificant compared to that for the reaction $I^* + O_2 \rightarrow I + O_2(^1\Delta)$. Data obtained from the precursors $i\text{-}C_3F_7I$, $n\text{-}C_3F_7I$, C_2H_5I, and CF_3I suggest that $O_2(^1\Delta)$ is rapidly relaxed by the precursor itself, by the precursor radical, or by some product formed in a reaction between the precursor radical and oxygen.

2. Dissociation of I_2 by $O_2(^1\Sigma)$ - Two studies have shown that it is extremely unlikely that step (2) of the kinetic scheme can be responsible for the dissociation of I_2.

a. The total quenching rates of $O_2(b^1\Sigma^+)$ by CO_2, H_2O, I_2 have been determined to be $(4.53 \pm 0.19) \times 10^{-13}$ cm^3 $molec^{-1}$ sec^{-1}, $(6.71 \times 0.53) \times 10$ 10^{-12} cm^3 $molec^{-1}$ sec^{-1}, and $(2.04 + 0.28) \times 10^{-11}$ cm^3 $molec^{-1}$ sec^{-1}, respectively. A pulsed, Raman-shifted dye laser was used to excite a single rotational line of $O_2(^1\Sigma, v'=0)$, while subsequent $^1\Sigma \rightarrow {^3\Sigma}$ fluorescence was monitored by a photon counting technique to determine the deactivation rate as a function of the partial pressure of quenching gas. Rate constants for deactivation of $O_2(^1\Sigma)$ by CO_2 and H_2O were found to quench $O_2(^1\ )$ an order of magnitude more slowly than reported in the literature. The lower total quenching constant for I_2 suggests that the reaction $O_2(^1\Sigma) + I_2 \rightarrow O_2(^3\Sigma) + 2I$ might not be solely responsible for dissociation of I_2 in the chemical oxygen-iodine laser.

b. Collisional dissociation of I_2 by $O_2(^1\Sigma)$ has been directly observed by monitoring the appearance rate and amplitude of transient $I(5^2P_{3/2})$ absorption on the $6\ ^2P_{3/2}\text{-}5\ ^2P_{3/2}$ resonance line at 178 nm. A pulsed, Raman-shifted dye laser was used to excite a single rotational line of $O_2(^1\Sigma, v'=0)$ near 763 nm. Radiation at this wavelength also dissociated some I_2 via absorption to the continuum region of the $I_2(A\ ^3\Pi_{1u})$ state. The variation in the appearance rate of the iodine atom signal with I_2 pressure leads to a rate constant for total deactivation of $O_2(^1\Sigma)$ by I_2 of $k = 4 \times 10^{-11}$ cm^3 $molec^{-1}$ sec^{-1}. Comparison of the amplitude of the I-atom absorption signal induced by $O_2(^1\Sigma)$ dissociation of I_2 to that resulting from direct I_2 photodissociation leads the conclusion that the branching ratio for $O_2(^1\Sigma) + I_2 \rightarrow O_2 + 2I$ vs. all other pathways is less than 0.2. Thus the rate constant for the specific process listed in step (2) of the kinetic scheme is less than 8×10^{-12} cm^3 $molec^{-1}$ sec^{-1}.

3. Electronic-to-Vibrational Energy Transfer from $I^*(5\ ^2P_{1/2})$ to $I_2(25<v<43)$ - Electronic-to-vibrational energy transfer from $I^*(5\ ^2P_{1/2})$ to $I_2(25<v<43)$ has been observed. I* was created by pulsed

laser photolysis of either I_2/Ar mixtures at 475 nm or CF_3I/I_2/Ar mixtures at 266 nm, while the resulting vibrational distribution of I_2 was monitored by laser induced fluorescence on the $I_2(B \leftarrow X)$ transition. The experimental results are consistent with an a-symmetrically shaped nascent I_2 product distribution peaked near v=40 with half-maximum points at v=41 and v=35. Roughly 2% of the I* deactivations result in I_2(v 40). The rate constants for vibrational relaxation of I^2 (v=40) by argon, helium, and I_2 at room temperature are $(7.3 \pm 0.3) \times 10^5$ sec^{-1} Torr^{-1}, $(1.0 \pm 0.2) \times 10^6$ sec^{-1} Torr^{-1}, and $(1.8 \pm 0.4) \times 10^6$ sec^{-1} Torr^{-1}, respectively. These results have important implications for the mechanism of I_2 dissociation in the chemical oxygen/iodine laser. A chain branching mechanism consisting of the steps $I^* + I_2 \rightarrow I + I_2(20<v<40)$, $I_2(20<v<40) + O_2(^1\Delta) \rightarrow 2I + O_2$, and $O_2(^1\Delta) + I \rightarrow O_2 + I^*$ may be responsible for the dissociation.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Spectroscopic Determination of Intermolecular Potentials of Gas Laser Components and of Major Atmospheric Constituents

2. PRINCIPAL INVESTIGATOR: Dr. William Klemperer
Department of Chemistry
Harvard University
Cambridge, MA 02138

3. INCLUSIVE DATES: 1 November 1981 - 31 October 1982

4. GRANT NUMBER: AFOSR-82-0036

5. COSTS AND FY SOURCE: $96,000, FY 82

6. PUBLICATION:

"The Microwave Spectrum and Molecular Structure of CO_2-HCl," R. S. Altman, M. D. Marshall and W. Klemperer, J. Chem. Phys., 77, 4344 (1982).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In this period we have completed the detailed structural study of a number of complexes of carbon dioxide. The structure of molecular complexes of carbon dioxide may be of considerable importance in developing a better complete understanding of energy transfer processes in the important carbon dioxide laser and especially in our understanding of the earth's (and other planetary) atmosphere.

Earlier studies performed under the support of AFOSR produced structural results for the CO_2 HF complex. This together with the study of SCO HF and N_2O HF showed a problem of considerable complexity. The structures of CO_2 HF and SCO HF are linear hydrogen bonded structures with atomic arrangement written. The structure N_2O HF, a species isoelectronic to CO_2 HF, has a highly nonlinear arrangement. The prediction of the geometry of CO_2 complexes is clearly likely to be complicated.

In pursuing the detailed structure of carbon dioxide complexes the system CO_2 HCl (J. Chem. Phys., 77, 4344 (1982)) has been shown to be similar to CO_2 HF. We have recently completed the study of the system HCN CO_2. Although HCN is well known to form hydrogen bonds, the structure of this system is not hydrogen bonded.

Of great general interest is the complex of CO_2 and H_2O. The importance of this species in the earth's atmosphere is not clear presently. The results at the present stage of research are the rotational constants and electric dipole moment components.

The primary uncertainty presently is the knowledge of the barrier hindering the internal rotation about the C-O axis.

Earlier research emphasized complexes of HF. The present research which initiates studies of complexes with H_2O shows that the structural and dynamical behavior of these two species HF and H_2O can be quite different. In this sense our early optimism that studies of HF binding would likely be adequate for understanding H_2O binding is certainly unwarranted. It is clear that the H_2O systems require much spectroscopic research to place them in a securely understood position.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Nonlinear Interactions between the Pumping Kinetics, Fluid Dynamics and Optical Resonator of cw Fluid Flow Lasers

2. PRINCIPAL INVESTIGATORS: Dr. L. H. Sentman
Aeronautical and Astronautical
Engineering Department
Dr. M. H. Nayfeh
Physics Department
University of Illinois
Urbana, IL 61801

3. INCLUSIVE DATES: 1 February 1980 - 31 August 1983

4. GRANT NUMBER: AFOSR-80-0133

5. COSTS AND FY SOURCE: $87,817, FY 80; $88, 636, FY 81; $91,047, FY 82; $67,898, FY 83

6. JUNIOR RESEARCH PERSONNEL:

K. Herrick
K. King
G. Marinos
W. Mosebach
P. Renzoni
P. Schmidt
S. Townsend
G. Tsioulos

7. PUBLICATIONS:

"Theoretical and Experimental Study of cw HF Chemical Laser Performance," L. H. Sentman, M. H. Nayfeh, W. O. Mosebach, P. Renzoni, K. Herrick, K. King, P. Schmidt, and S. Townsend, Proceedings of the 4th International Symposium on Gas Flow and Chemical Lasers, Stresa, Italy, Plenum Publishing Corporation, NY, in press.

"A Theoretical and Experimental Study of cw Chemical Laser Performance," L. H. Sentman, W. O. Mosebach and P. Renzoni, AAE 81-8, UILU Eng. 81-0508, Aeronautical and Astronautical Engineering Dept., University of Illinois, Urbana, IL, (1981).

"MNOR03: An Efficient Rotational Nonequilibrium cw HF Chemical Laser Model," L. H. Sentman and P. Schmidt, AAE 83-1, UILU Eng. 83-0501, Aeronautical and Astronautical Engineering Dept., University of Illinois, Urbana, IL, (1983).

"Effects of the HF Rate Package and the Optical Resonator on cw HF Chemical Laser Performance," L. H. Sentman, P. F. Schmidt and G. M. Marinos, AAE 83-6, UILU Eng. 83-0506, Aeronautical and Astronautical Engineering Dept., University of Illinois, Urbana, IL, (1983).

"The Effects of Cavity Losses on the Performance of a Subsonic cw HF Chemical Laser," L. H. Sentman, P. Renzoni, S. Townsend, M. H. Nayfeh, and K. King, AAE 83-7, UILU Eng. 83-0507, Aeronautical and Astronautical Engineering Dept., University of Illinois, Urbana, IL, (1983).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The theoretical and experimental studies directed toward measuring the amplitude and frequency of the time dependent oscillations in power which have been predicted to occur in cw HF chemical lasers that employ an unstable resonator to extract power are summarized. The MNORO model was generalized to include rotational nonequilibrium in the HF(0) level as well as in HF(1) and HF(2). To obtain the correct power split between vibrational bands, it was necessary to add to the MNORO kinetics model the backward rate for the cold pumping reaction to HF(3), the HF-H_2 and HF-HF VV reactions and the deactivation of HF by the DF which is formed in the combustor.

A stable resonator model was coupled to the MNORO3 kinetics model to provide a theoretical model (MNORO3SR) for a laser employing a stable resonator. Six of the eight criteria for convergence were satisfied for the Helios CL II test case while two of the eight criteria indicated the solution had not converged. The spectra predicted with the stable resonator model were in better agreement with the data (which was taken with a stable resonator) than were the spectra predicted with the Fabry-Perot model. A study of the effect of the mixing rate showed that the power spectral distribution is significantly affected by the mixing rate. This implies that for situations in which the fluid dynamics of the mixing process are so complicated that they are represented by a very approximate model, the determination of the mixing parameters cannot be considered fixed until a rotational nonequilibrium calculation for the resonator for which the data were taken has shown agreement with the measured spectra.

A physical optics model was coupled to the MNORO3 kinetics model to provide a theoretical model (MNORO3UR) for a laser employing a confocal, unstable resonator. All seven of the convergence criteria were satisfied for the Helios CL II test case. The physical optics-kinetics calculations showed that the time-dependent oscillations which may occur on lines whose saturated gain does not fill the resonator are Fresnel number dependent. For a Fresnel number of 1.5, the time-dependent oscillations did not occur, while, for Fresnel numbers of 18.57 and 9.457, the time-dependent oscillations did occur. For all cases in which the time-dependent oscillations occurred, the period was mostly 40ns with some lines varying between 33 and 40 or 40 and 47 ns.

The comparison between the laser performance predicted using the new and the old HF rate packages showed that the new rate package gives 43% more total power compared to the old rate package, with over half of this difference in the 2→1 vibrational band, and gives a mode length 99% greater than the old rate package. These differences are the result of the omission of the multiquantum deactivation reactions by HF and F and the collisional decomposition of HF(3) by H from the new rate package. The removal of power from the upper vibrational bands is accomplished by the single quantum and the DF deactivation reactions in the new rate package whereas in the old rate package, the removal of power from the upper vibrational bands is accomplished by the collisional decomposition of HF(V), $v \geq 3$ by H atoms. The MNORO3 rotational nonequilibrium calculations showed that the new rate package gives 35% more total power and 30% longer mode width than the old rate package. However, the spectra given by both rate packages agree well with each other and with the data for the CL XI.

The multi-line performance (power and power spectral distribution) of the Helios CL II cw HF chemical laser was measured as a function of the SF_6 and H_2 flow rates, cavity losses, pressure and resonator type. The very good agreement of the Fabry-Perot, stable resonator and unstable resonator laser models with the data as the flow rates, cavity losses and pressure change verified the models. The major result of this research program was the measurement of the amplitude, frequency and Fresnel number dependence of the time-dependent oscillations which occur on lines whose saturated gain does not fill the unstable resonator. The data showed that the oscillations do not occur for Fresnel numbers below 1.5 and that their amplitudes increase as the fraction of the resonator filled by the oscillating lines decreased. The measured periods were mostly 40 ns with some lines varying between 33 and 50 ns. The amplitude modulation varied from 12% to 80%. In addition, in some cases there was a 7 ns oscillation superimposed on the 40 ns oscillation, which, based on the mirror spacing, is probably a mode beating. The a priori prediction of these characteristics of the time-dependent oscillations by the MNORO3UR computer model was in good agreement with the data.

Several other new results were also obtained. The first data from a cw laser for a near resonant energy transfer from $v=3$, $J=3,4$ to $v=2$, $J=14$ with a subsequent rotational cascade to $v=2$, $J=11$ were obtained. In addition, the stable resonator data indicated that the polarization introduced by the Brewster windows affects the power spectral distribution. Preliminary data with a new He injector indicated that under certain conditions, it was possible to obtain a 60% incrase in laser performance.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Theoretical Studies of Excited State Energy Transfer, and Radiative Properties of Transient Species, Using MCSCF/CI Methods

2. PRINCIPAL INVESTIGATOR: Dr. David R. Yarkony
Department of Chemistry
The Johns Hopkins University
Baltimore, MD 21218

3. INCLUSIVE DATES: 1 April 1979 - 31 December 1982

4. GRANT NUMBER: AFOSR 79 0073

5. COSTS AND FY SOURCE: $30,000, FY 79; $40,000, FY 80; $45,000, FY 81
$10,000, FY 82

6. SENIOR RESEARCH PERSONNEL:

Dr. C. W. Bauschlicher, Jr.   Dr. B. H. Lengsfield

7. JUNIOR RESEARCH PERSONNEL: R. N. Diffenderfer

8. PUBLICATIONS:

"MCSCF Wavefunctions for Excited States of Polar Molecules: Application to BeO," C. W. Bauschlicher, Jr. and D. R. Yarkony, J. Chem. Phys., 72, 1138 (1980).

"SCF and MCSCF Wavefunctions for MgO," C. W. Bauschlicher, Jr., D. M. Silver, and D. R. Yarkony, J. Chem. Phys., 73, 2678 (1980).

"Spin Forbidden Radiative Transitions in Atomic Ca," R. N. Diffenderfer, P. J. Dagdigian, and D. R. Yarkony, J. Phys. B., 14, 21 (1981).

"On the Low-Lying Singlet States of BeO," C. W. Bauschlicher, Jr., B. H. Lengsfield and D. R. Yarkony, J. Chem. Phys., 73, 5702 (1980).

"On the Low-Lying States of MgO:II," C. W. Bauschlicher, Jr., B. H. Lengsfield, D. M. Silver, and D. R. Yarkony, J. Chem. Phys., 74, 3965 (1981).

"A Hybrid Method for Improving MCSCF Convergence," C. W. Bauschlicher, Jr., P. S. Bagus, D. R. Yarkony, and B. H. Lengsfield, J. Chem. Phys., 74, 3965 (1981).

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The broad goal of our research program was to study excited state chemistry, and electronic energy transfer and chemical energy redistribution processes, using the methods of ab initio electronic structure theory. In the course of this research we have contributed to the rapid growth in multi-configuration self-consistent field (MCSCF) methodology, initially, with the development of an MCSCF procedure based on the generalized Brillouins theorem and the approximate natural orbital method (GBT-NO MCSCF) and more recently with the extension of Lengsfield's density matrix driven quadratically convergent MCSCF procedure to treat state averaged wavefunctions (SA MCSCF). The later algorithm has significantly expanded the scope of problems in excited state chemistry amenable to treatment at the MCSCF/CI level.

As a prototypical system we chose reactions of the form

$$Me(Y) + N_2O(^1\Sigma^+) \rightarrow MeO(Z) + N_2\ (^1\Sigma_g^+)$$

where $Me(Y) = Mg(^1S, ^3P)$ and $Ca(^1S, ^3P)$. Although both the magnesium and calcium reactions are highly exoergic the reactivity and the distribution of product electronic states differs markedly for these two homologues.

Over the period of this grant we have studied the properties of several subspecies participating in this reaction including radiative decay of metastable atomic species, and the electronic structure, bonding and optical properties of the alkaline earth oxides. Ultimately we were able to characterize several regions of the lowest singlet and triplet potential energy surfaces of reaction 1 at the SCF/two configuration SCF(TCSCF)/CI level.

a. Radiative Properties of $Ca(^1D, ^3P)$ - Using GBT-NO MCSCF/CI methods the 1^1S, $1^{3,1}P$ and $1^{3,1}D$ states of calcium atom were characterized. Using an orthogonal orbital transition moment method and atomic spectral data, line strengths for $^1D \rightarrow {}^3P$, $^1D \rightarrow {}^1S$, $^3P \rightarrow {}^1S$ and other transitions were estimated. It was shown that the principal decay channel of $Ca(^1D_2)$ is the spin forbidden dipole allowed path through the ^3P state to the ^1S state.

b. Electronic Structure of Alkaline Earth Oxides - MCSCF/CI wavefunctions were determined for BeO, MgO and CaO with particular attention focused on the 1,2 $^{1}\Sigma^{+}$ states. It was shown that a viable starting point for the description of these states is necessarily multiconfugurational in character. In each case contributions from structures $Me^{+2}O^{-2}$ and $Me^{+}O^{-}$ must be considered simultaneously, and in the case of the $Me^{+}O^{-}$ structures alignment of the oxygen p-hole parallel and perpendicular to the axis must be included. Subsequently dipole allowed radiative transitions were studied for the 2 $^{1}\Sigma^{+}$ and 1 $^{2}\Pi$ states in MgO and CaO. Here the SA-MCSCF procedure proved to be essential.

c. The Reaction $Mg + N_2O = MgO + N_2$ - The lowest $^{3,1}A'$ surfaces of this reaction were characterized using SCF/TCSCF/CI methods. These calculations, which were made economically feasible with the purchase (with funds from AFOSR and NSF) of a dedicated minicomputer system, have enabled us to characterize the mechanism for the production of MgO(X $^{1}\Sigma^{+}$ and a $^{3}\Pi$) and also explain the disparities between the magnesium and calcium reactions. The importance of curve crossings with open shell structures corresponding to excited atomic states in the ground state reaction was demonstrated. A clear phenomenological description of this reaction has emerged. The $^{3,1}A'$ surfaces can be qualitatively partitioned into three contiguous, nondisjoint regions characterized by distinct values of an approximate reaction coordinate, ζ; a reactant region in which $\zeta = \zeta_1 \simeq R(Mg\text{-}O)$, a bending reaction in which $\zeta = \zeta_2 \simeq \angle NNO$ and a product region in which $\zeta = \zeta_3 \simeq R(N\text{-}O)$. Following charge transfer increases in ζ_2 are driven by a Rener-Teller instability in $N_2O^-(^{2}\Pi)$.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

RESEARCH EFFORTS COMPLETED IN FY 83

CHEMICAL REACTIVITY AND SYNTHESIS - DR. ANTHONY J. MATUSZKO

Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials AFOSR-79-0008	M. J. S. Dewar Department of Chemistry University of Texas Austin, TX 78712
Picosecond Laser Studies of Excited State Processes AFOSR-81 0009	Kenneth B. Eisenthal Department of Chemistry Columbia University New York, NY 10027
Studies of Polymer-Bound Macrocyclic Polytertiary Phosphines AFOSR-79-0090	Evan P. Kyba Department of Chemistry University of Texas Austin, TX 78712
Potential Energetic Materials Formed from Coupling of Substituted Halo-s-triazines AFOSR-82-0191	G. Fredric Reynolds Department of Chemistry and Chemical Engineering Michigan Technological University Houghton, MI 49931
Organosilicon Chemistry AFOSR-80 0006	William P. Weber Department of Chemistry University of Southern California Los Angeles, CA 90089-1062

COMPLETED PROJECT SUMMARY

1. TITLE: Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials

2. PRINCIPAL INVESTIGATOR: Professor M. J. S. Dewar
Department of Chemistry
University of Texas
Austin, TX 78712

3. INCLUSIVE DATES: 1 November 1978 - 31 October 1982

4. GRANT NUMBER: AFOSR-79-0008

5. COSTS AND FY SOURCE: $99,997, FY 79; $99,999, FY 80; $124,999, FY 81
$124,999, FY 82

6. SENIOR RESEARCH PERSONNEL:

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7. JUNIOR RESEARCH PERSONNEL:

F. Carrion
L. Chantranupong
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J. Friedheim
C. Reynolds
J. Ritchie
1.-P. Tien

8. PUBLICATIONS:

"MNDO Calculations of Molecular Electric Polarizabilities, Hyperpolarizabilities, and Nonlinear Optical Coefficients," M.J.S. Dewar, Y. Yamaguchi, and S. H. Suck, Chem. Phys. Lett., 59, 541 (1978).

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"Thermal and Electrical Properties of Organometallic Coordination Polymers Based on Centrosymmetric 1,5-Naphthyridine Derivatives," M.J.S. Dewar and S. B. Brown, J. Inorg. and Nuclear Chem., 42, 140 (1980).

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"Sigma Conjugation and Sigma Aromaticity," M.J.S. Dewar, Bull. Soc. Chim. Belg., 88, 957 (1980).

"Aspects of Cyclic Conjugation," M.J.S. Dewar and M. L. McKee, Pure and Applied Chem., 52, 1431 (1980).

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"Ionization Energies of p-Quinodimethane and 2,5-Dimethyl p-quinodimethane," M.J.S. Dewar, J.A.C.S., 104, 1447 (1982).

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"Proton Migration in Phenyl Cation?", Dewar and Reynolds, in preparation.

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"Ground States of Molecules. Part 67. Thermolysis of Molecules Containing NO_2 Groups," Dewar and Ritchie, in preparation.

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"MNDO Calculations for Molecules Containing Iodine," Dewar and Healy, in preparation.

"Thermal Decomposition of Compounds Containing the NO_2 Group," Dewar and Merz, in preparation.

"Mutual Conjugation in Radicals and Ions," Dewar, in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A new parametric SCF MO method (AM1) has been developed which seems to have overcome the remaining deficiencies of MINDO/3 and MNDO, in particular their failure to reproduce hydrogen bonds, overestimation of nonbonded repulsions, and poor results for compounds containing nitrogen and oxygen, specifically these containing the NO2 group. NMDO parameters have been devised for bromine and iodine, d-AOs have been introduced into MNDO and the resulting treatment (MNDOD) parameterized for P and S. This work was suspended to take advantage of AM1. The programs have been rewritten, improved, and combined into a single package (MOPAC) which will be sent to QCPE. The new programs run nearly three times faster.

Studies of the thermal decomposition of compounds containing the NO_2 group have led to new mechanisms, of significance in connection with the initiation of detonation in explosives. Methyl nitrate is found to decompose by an unprecedented bimolecular transfer of oxygen, nitromethane via rearrangement to methyl nitrite, and methyl nitrite by concerted elimination of HNO. Nitroethylenes and nitroacetylenes rearrange even more easily to nitrites, particularly if there is a NO_2 group β to the one rearranging. The rearrangements of tetranitroethylene and dinitroacetylene are extremely facile, suggesting that they may be obtainable only at low temperatures or as reaction intermediates. Introduction of NO_2 groups into cubane, on the other hand, is predicted to increase its thermal stability.

Studies of derivatives of norbornadiene suggest that fluoro derivatives should be especially effective for photochemical storage of energy, their photochemical conversion to quadricyclenes requiring less energetic photons than that of norbornadiene itself while the recoverable energy is greater.

Calculations for a wide variety of chelotropic reactions, and Diels-Alder reactions, indicate that these take place in steps or stages, via very unsymmetrical transition states. This work, in conjunction with our earlier studies, has led to a general rule restricting possible mechanisms of reactions which seems likely to have wide applications in chemistry.

Calculations for radicals derived from carboxylic acid derivatives are found to exist in distinct σ and π forms, the latter being the lower in energy for amides and imides and the former for carboxy radicals. The results agree nicely with experimental work by Skell and also account for some anomalous esr results for benzoyloxy radical. A similar calculation for the thermolysis and photolysis of β-perpropionolactone accounted nicely for recent experimental results. The photochemical rearrangement of cyclohexan-2,5-dienone to bicyclo[3,1,0]hex-2-ene-4-one is predicted to follow a mechanism analogous to, but different from, that suggested by Zimmerman, the first step being formation of a $\pi \rightarrow \pi^*$ excited triplet state, not a $n \rightarrow \pi^*$ one.

A detailed study of the three isomeric benzynes and their reactions has led to an alternative explanation of two recent investigations which had been interpreted in terms of 1,2 hydrogen shifts in phenyl cation, a reaction for which theoretical calculations have predicted very high activation energies.

The C_4H_4 potential surface has been surveyed in great detail. Nineteen chemically distinct species of relatively low energy were located together with the transition states for their interconversion.

Studies of the interactions between substituents in odd alternant radicals (e.g. allyl or benzyl) have confirmed the rules for mutual conjugation originally derived by Dewar in 1952 and "rediscovered" recently by other workers ("captodative effect"). A new PMO treatment and MNDO calculations led to the unexpected conclusion that the effect should be greater in cations than radicals, a result which explains some apparent anomalies in aromatic substitution.

A fact that the resonance integrals between different hybrid AOs of a given atom do not vanish even if the AOs are orthogonal has been known for many years but ignored. We have shown that a number of hitherto puzzling phenomena, can be explained in terms of such sigmaconjugative interactions.

Studies of biomimetic cyclizations indicate them to take place with intermediate π complexes and calculations for the reaction of singlet oxygen with limonene confirm the peroxirane mechanism. Benzene dication and its derivatives are predicted to exist in two isomeric forms of comparable stability, one a pentagonal pyramid and the other a chair. Their interconversion, and the energies of corresponding triplets, have been studied. Other topics include:

a. Refutation of the frontier orbital method.

b. A very detailed study of the carboranes, including all the species currently known.

c. An explanation of the aromaticity of large rings.

d. Calculations for the complexes from HBe and fluorine as models of the corresponding $(OC)_3Fe$ complexes.

e. A detailed comparison of the "half-electron" and generalized coupling operator RF SCF treatments of radicals and triplet states.

f. Calculations of the geometry, vibration frequencies, and electrical properties of polyethylene and polyperdeuterioethylene.

g. Calculations for a wide variety of haloolefins which explained results found puzzling at Allied Corp.

h. Calculations for allyl and crotyl anions accounted for some apparent anomalies that had been reported.

i. MNDO calculations for phenoxy radical and a wide range of its derivatives, for phenylchlorocarbene and the chlorocycloheptatrienylidenes, for phenylthiyl radical, for derivatives of t-butylaceylene and phenylphosphine, and for p-quinodimethane, have been used to assign their UPE spectra.

j. A MNDO study of reactions of carbon atoms with carbonyl compounds led to a new interpretation of Shevlin's experimental studies and proved on further investigation to be correct.

k. S_7 is predicted to occur as two freely pseudorotating isomers, one a chair and one a boat, separated by a significant energy barrier.

l. Calculations of reactions of chlorosilanes with nucleophiles indicates that the ease with which they take place is not due to participation by 3d AOs but merely to the fact that silicon, unlike carbon, is large enough to allow five or six groups to be attached to it without mutual steric repulsions.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Picosecond Laser Studies of Excited State Processes

2. PRINCIPAL INVESTIGATOR: Professor Kenneth B. Eisenthal
Department of Chemistry
Columbia University
New York, NY 10027

3. INCLUSIVE DATES: 1 October 1980 - 30 September 1983

4. GRANT NUMBER: AFOSR-81-0009

5. COSTS AND FY SOURCE: $106,033, FY 81; $84,939, FY 82; $98,952, FY 83

6. SENIOR RESEARCH PERSONNEL:

Dr. K. Gnadig	Dr. W. Hetherington
Dr. G. M. Korenowski	Dr. Y. Wang
Dr. F. Novak	Dr. E. V. Sitzmann
Dr. D. Millar	

7. JUNIOR RESEARCH PERSONNEL:

M. K. Crawford	M. J. McAuliffe
C. Dupuy	S. Y. Hou
L. Langan	

8. PUBLICATIONS:

"Picosecond Laser Studies of the Photodissociation of I_2 Aromatic Complexes and the Formation of I Atom-Aromatic Complexes in Solution," C. A. Langhoff, K. Gnadig, and K. B. Eisenthal, Chemical Physics, 46, 117 (1980).

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"Picosecond CARS as a Probe of the Multiphoton Photofragmentation of Benzene," W. M. Hetherington, G. M. Korenowski, and K. B. Eisenthal, Chemical Physics Letters, 77, 275 (1981).

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"Picosecond Laser Studies of Ultrafast Processes in Chemistry," Y. Wang, and K. B. Eisenthal, Journal of Chemical Education, 59, 482 (1982).

"Studies of the Generation and Energy Relaxation in Chemical Intermediates - Divalent Carbon Molecules and Singlet Oxygen," E. V. Sitzmann, C. Dupuy, Y. Wang, and K. B. Eisenthal, Picosecond Phenomena (Proceedings of the Third Topical Meeting on Picosecond Phenomena, Garmisch-Partenkirchen, West Germany) R. Hochstrasser, W. Kaiser, and C. V. Shank, Eds., (Springer Verlag, New York, NY, 1982).

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"Picosecond Laser Studies of Intramolecular Excited-State Charge-Transfer Dynamics and Small-Chain Relaxation," Y. Wang, M. C. Crawford, and K. B. Eisenthal, Journal of the American Chemical Society, 104, 5874 (1982).

"Picosecond Laser Studies on the Reaction of Excited Triplet Diphenylcarbene with Alcohols," E. V. Sitzmann, R. Wang, and K. B. Eisenthal, Journal of Physical Chemistry, 87, 2283 (1983).

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"Picosecond Laser Studies of the Charge-Transfer Reaction of Excited Triplet Diphenylcarbene with Electron Donors," E. V. Sitzmann, J. Langan, and K. B. Eisenthal, Chemical Physics Letters, 1983, accepted.

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"Singlet-Triplet Interconversion of Diphenylmethylene. Energetics, Dynamics and Reactivities of Different Spin States," K. B. Eisenthal, N. J. Turro, E. V. Sitzmann, I. Gould, G. Hefferon, J. Langan, and Y. Cha., Tetrahedron Symposium on Recent Aspects of Carbene Chemistry, submitted.

"Picosecond Dynamics of Barrier Crossing in Liquids: A Study of the Conformational Change of Excited State 1,1'-binaphthyl," D. Millar and K. B. Eisenthal, Journal of Chemical Physics, submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research has been to increase our understanding of important chemical and physical pathways by which molecules in excited electronic states dissipate their energy. We have studied two broad classes of chemical problems. One is the key role of excited state charge transfer (CT) interactions in energy decay phenomena via the formation of an excited state charge transfer complex, an ion pair, or by the intramolecular redistribution of charge generating a very large molecular dipole. We have used picosecond transient absorption and emission techniques to study these processes in two prototype systems: (a) excited anthracene + N,N^1- dimethylaniline, yielding exciplex and ion pair dynamics and (b) dimethylaminobenzonitrile $(CH_3)_2$-N-C_6H_5-C≡N (DMABN) representing the simplest case of a process now recognized to be common to a wide range of molecules, namely twisted internal charge transfer phenomena. From the studies on the anthracene system we obtained new information on molecular motions in liquids, on small chain dynamics using chromophores hooked together by a methylene chain, anthracene-$(CH_2)_3$- dimethylaniline, and new insights on the effects of geometry and solvent polarity on the dynamics of these processes. From this work we were able to develop ideas which explained a wide range of experimental findings appearing in the literature.

In our studies of twisted internal charge transfer in dimethylaminobenzonitrile, photo excitation of which leads to a twisting of the dimethylamino group perpendicular to the plane of the aromatic, we established that the stabilization of the twisted form is not only rapid in polar media but is in equilibrium with the initial, less polar excited form. We furthermore showed that for the case of alcohols as the solvent the stabilization is not only a long range dielectric polarization effect but also involves a short range complex between alcohol and the DMABN solute molecule.

The second class of problems is concerned with the kinetics and properties of short-lived chemical intermediates generated by laser excitation of precursor molecules. Two systems which we have studied are the divalent carbon fragments (carbenes) $R_1 - \ddot{C} - R_2$, implicated in an enormous variety of chemical reactions and singlet oxygen, $^1O_2$, a prime species in materials degradation.

The carbene that we have most extensively studied is diphenylcarbene, $C_6H_5 - \ddot{C} - C_6H_5$, which we generated by photodissociation of diphenyldiazomethane. We determined that the intersystem crossing time from the low lying singlet to the ground triplet state of diphenylcarbene took 90 ps in an alkane solvent. Combining this value with the measured triplet to singlet rate constant we obtained the equilibrium constant, free energy charge and an estimate of the singlet-triplet energy gap. We extended our studies into a heretofore untouched area, namely excited state carbene chemistry. We proposed that the key point, in the reactivity of the excited triplet state of diphenylcarbene ^{3*}DPC, is the presence of an empty low lying orbital. Comparing the orbital diagrams of ^{3}DPC, ^{1}DPC and ^{3*}DPC we noted that both ^{3*}DPC and ^{1}DPC have an empty low lying orbital and suggested that the origin of the reactivity of ^{1}DPC and ^{3*}DPC was the same. We then carried out experiments which showed that ^{3*}DPC indeed reacts with alcohols in the same way as ^{1}DPC. From our studies of the reaction of ^{3*}DPC with amines we established the first example of a charge transfer interaction of carbenes with electron donors. The reaction mechanism is not the same as with the alcohols where reactivity is determined by acidity, but rather by a charge transfer mechanism.

In the singlet oxygen research we showed that one of the pathways in the photofragmentation of the endoperoxides of substituted anthracene, yielded not only an excited oxygen, $^1O_2$, but also an electronically excited anthracene fragment. We established that though this route is conceptually important, i.e., generating two excited fragments, that the dominant decay pathway yielded the ground state (vibrationally hot) anthracene and $^1O_2$. From our kinetics we also found evidence, previously unexpected, that a chemical intermediate of about 45 ps lifetime, is involved in the dissociation process. We are presently seeking to identify the intermediate.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of Polymer-Bound Macrocyclic Polytertiary Phosphines

2. PRINCIPAL INVESTIGATOR: Professor Evan P. Kyba
Department of Chemistry
University of Texas
Austin, TX 78712

3. INCLUSIVE DATES: 1 February 1979 - 31 July 1983

4. GRANT NUMBER: AFOSR-79 0090

5. COSTS AND FY SOURCE: $104,643, FY 79; $54,998, FY 81; $50,000, FY 82

6. SENIOR RESEARCH PERSONNEL:

Dr. H. H. Heumuller
Dr. R. L. Harris
Dr. K. L. Hassett
Dr. P. N. Juri
Dr. B. Sheikh

7. JUNIOR RESEARCH PERSONNEL:

D. C. Alexander
C. N. Clubb
A. Hohn
S. P. Rines
D. R. Moore
J. E. Morningstar

8. PUBLICATIONS:

"Tertiary-arsinomacrocycles and their Molybdenum Carbonyl Complexes," E. P. Kyba and S.-S.P. Chou, J. Chem. Soc., Chem. Commun., 449 (1980).

"Group 6 Transition-Metal Complexes of Two Macrocycles Containing Tertiary-Phosphino and -Amino Ligating Sites," E. P. Kyba and S. B. Brown, Inor. Chem., 19, 2159 (1980).

"11-Membered Macrocycles Containing the Diars Moiety," E. P. Kyba and S.-S.P. Chou, J. Am. Chem. Soc., 102, 7012 (1980).

"High Dilution Syntheses of 14-Membered Tetradentate Microcycles Incorporating the Diars Moiety," E. P. Kyba and S.-S.P. Chou, J. Org. Chem., 46, 860 (1981).

"A Novel Synthesis of 1,2-Diphosphorylbenzenes," E. P. Kyba, S. P. Rines, P. W. Owens, and S.-S.P. Chou, Tetrahedron Lett., 22, 1875 (1981).

"Secondary Phosphino Macrocyclic Ligands," E. P. Kyba and H. H. Heumuller, ACS Symposium Series, 171, 473 (1981).

"Catalytic and Structural Studies of the Rhodium (I) Complexes of the Norphos and Renorphos Ligands," E. P. Kyba, R. E. Davis, P. N. Juri, and K. R. Shirley, *Inorg. Chem.*, *20*, 3616 (1981).

"Electrochemical Behavior of the Metal Tricarbonyl Complexes of Several Tridentate Macrocycles Containing Soft (P,S) Ligating Sites," M. A. Fox, K. Campbell, and E. P. Kyba, *Inorg. Chem.*, *20*, 4163 (1981).

"A Spectroscopic Method for the Determination of Optical Purities of Chiral, Chelating Diphosphines," E. P. Kyba and S. P. Rines, *J. Org. Chem.*, *47*, 4800 (1982).

"(Tertiary phosphinomacrocycle)cobalt(II) Halide Coordination Chemistry. Identification and Interconversion of Four Types of Complexes," E. P. Kyba, D. C. Alexander, and A. Hohn, *Organometallics*, *1*, 1619 (1982).

"Linked Bis (μ-phosphido) and Related Ligands for Metallic Clusters. 2. Reaction of 1,2,3-Triphenyl-1,2,3-triphosphaindane with Nonacarbonyldiiron," E. P. Kyba, R. E. Davis, K. L. Hassett, J. S. McKennis, and B. Sheikh, *Phosphorus and Sulfur*, *8* (1983), submitted.

"A Facile Synthesis of 1,2-Bis(phosphino)Benzene and Related Alkylated Species," E. P. Kyba, S.-T. Liu, and R. L. Harris, *Organometallics*, *2* (1983), submitted.

"Studies of Polymer-Bound Macrocyclic Polytertiary Phosphines," E. P. Kyba, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The goals of this research were to incorporate macrocyclic polyphosphines (MPP) into polymer supports and to study the properties of such polymer-bound species. Synthetic efforts were successful in the preparation of functionalized intermediates which could be elaborated into functionalized MPP, capable of incorporation into polymers. A Diels-Alder route to 1,2-bis(phosphoryl)-4-X-benzene, where X = CH_2OAc has been developed. The photochemical Arbuzov reaction of 1,2-dichlorobenzene and 3,4-dichlorotoluene has been studied, and gives access to 1,2-diphosphorylbenzenes and 3,4-diphosphoryltoluenes, respectively. The latter compound, as well as the Diels-Alder product can be used as precursors to functionalized MPP. Very recently an efficient method for the reduction of 1,2-diphosphorylbenzenes to 1,2-diphosphinobenzenes has been developed, which involves a reagent produced from the reaction of trimethylsilyl chloride and lithium aluminum hydride. Three MPP have been incorporated into polystyrene supports: *cis*-2,17-diphenyl-2,17-diphospha-6,13-dioxatricyclo$[16.4.0.0^{7,12}]$docosa-7(12),8,10,1(18),19,21-hexaene (14-P_2O_2); *cis*-2,10-diphenyl-6-phenyl-6-aza-2,10-diphosphabicyclo [9.4.0]pentadeca-11(1),12,14-triene (11-P_2NPh); and *cis*-2,10-diphenyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-11(1), 12,14-triene (11-P_2NH). The polymer attachment of the 14-P_2O_2 was on the dioxabenzo side, 11-P_2NPh via the N-Ph group, and the 11-P_2NH, via the nitrogen atom. The polymers used were 1% cross-linked macroreticular resins. The ability of polymer-bound (PB) MPP to coordinate transition metals was probed using Co(II). The PB-14-P_2O_2 and 11-P_2NPh gave complexes which had the stoichiometry (PB-MPP)$_2$CoX_2, by comparison of solid state UV spectra with those from non-PB-MPP CO(II) complexes. In one case the (MPP)$_2$CoX_2 structure was confirmed by a single crystal x-ray structure determination. Thus the polydentate MPP were acting as bidentate ligands and two such ligands were attached to each metal center, using 1% cross-linked polymer, i.e., site-site isolation is not achieved. Preliminary studies of the more highly cross-linked polymers indicated that site-site isolation is achievable. The PB-11-P_2NH behaves as a tridentate ligand towards Co(II) giving complexes of the type (PB-11-P_2N)CoL_2, by comparison of spectral properties with those of well-characterized non-PB-MPP complexes. Several approaches to precursors of optically active PB-MPP and related compounds have been investigated.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Potential Energetic Materials Formed from Coupling of Substituted Halo-s-triazines

2. PRINCIPAL INVESTIGATOR: Professor G. Fredric Reynolds
Department of Chemistry and
Chemical Engineering
Michigan Technological University
Houghton, MI 49931

3. INCLUSIVE DATES: 1 June 1982 - 31 May 1983

4. GRANT NUMBER: AFOSR-82-0191

5. COSTS AND FY SOURCE: $9,999, FY 82 (Mini Grant)

6. JUNIOR RESEARCH PERSONNEL:

R. Briggs	M. Huffman

7. PUBLICATIONS:

"Potential Energetic Materials Formed from Coupling of Substituted Halo-s-triazines," G. Fredric Reynolds, Final Technical Report.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Substituted halo-s-triazines possess both electrophilic and nucleophilic sites, provided that the non-halogen substituent on the triazine ring contains an acidic proton. The carbon atom to which the acidic proton is attached acts as a site for electrophilic substitution which can couple to the nucleophilic site on another molecule, namely, the carbon atom on the ring attached to halogen. The object of this research was to investigate conditions under which this coupling would occur, as well as to isolate pure compounds and study their structure by NMR, IR and mass spectroscopy.

During the course of this research, the following substituted s-triazines were prepared in good yield: 2,4-dichloro-6-dimethylmalonyl-s-triazine; 2,4-dichloro-6-ureido-s-triazine; 2,4-dichloro-6-(β-hydroxyethoxy)-s-triazine; and 2,4-dichloro-6-(4,6-dichlorpyrimidin-2-yldimethylmalonyl)-s-triazine. Also prepared in good yield were: 2-chloro-4,6-bis (4,6-dichloropyrimidin-2-yldimethylmalonyl)-s-triazine; 2,4,6-tris (4,6-dichloropyrimidin-2-yldimethylmalonyl)-s-triazine; 2,4,6-tris (β-hydroxyethoxy)-s-triazine; and 2,4,6-triureido-s-triazine. The structures of these compound were determined spectroscopically. Attempts were made to isolate compounds analogous to those listed above in which an additional s-triazine ring had been attached. To date, these attempts have not resulted in any significant yields of the desired products.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Organosilicon Chemistry

2. PRINCIPAL INVESTIGATOR: Professor William P. Weber
Department of Chemistry
University of Southern California
University Park
Los Angeles, CA 90089-1062

3. INCLUSIVE DATES: 1 October 1979 - 31 December 1982

4. GRANT NUMBER: AFOSR-80-0006

5. COSTS AND FY SOURCE: $62,881, FY 80; $70,421, FY 81; $77,771, FY 82

6. SENIOR RESEARCH PERSONNEL:

Prof. A. Marchand
Dr. D. Tzeng
Dr. H. Firgo

7. JUNIOR RESEARCH PERSONNEL:

J. Chihi
K. Steele
K. Kazoura
L.-J. Juang
S. Carr
T.-Y.Y. Gu
D. Tzeng
J. Mullis
Y.-M. Pai
M. Rubino
R. Swaim

8. PUBLICATIONS:

"Insertion of Dimethylsilylene into O-H and N-H Single Bonds," T.Y. Yang Gu and W. P. Weber, J. Organometal. Chem., 184, 7 (1980).

"Mechanism of the Reactions of Dimethylsilylene with Oxetanes," T.Y. Yang Gu and W. P. Weber, J. Am. Chem Soc., 102, 1641 (1980).

"Mass Spectrometry of Aryl-substituted Di- and Tri-Siloxanes," R. E. Swaim and W. P. Weber, J. Organic Mass Spectrometry, 15, 304 (1980).

"Mechanism of Reaction of Dimethylsilyl with $\alpha\beta$-Unsaturated Epoxides," D. Tzeng and W. P. Weber, J. Am. Chem. Soc., 100, 1451 (1980).

"Flash Vacuum Pyrolysis of 2-Methylbenzophenones and 2-Methyldiphenyl-Ketimines: Mechanism of the Vapor Phase Elbs Reaction," T.Y. Yang Gu and W. P. Weber, J. Organic Chemistry, 45, 2542 (1980).

"Insertion Reaction of Dimethylsilylene into Si-H and Si-OR Bonds," T.Y. Yang Gu and W. P. Weber, J. Organometal. Chem., 195, 29 (1980).

"Solvent Modified Reactivity of Dimethylsilylene," K. P. Steele and W. P. Weber, J. Am. Chem. Soc., 102, 6095 (1980).

"Kinetic Isotope Effects for Silylene Insertions into Oxygen-Hydrogen and Silicon-Hydrogen Bonds," K. P. Steele and W. P. Weber, Inorganic Chem., 20, 1302 (1981).

"Regiospecific Synthesis of Allylic Dimethylmethoxysilanes," D. Tzeng and W. P. Weber, J. Org. Chem., 46, 265 (1981).

"Reactions of Allylic and Benzylic Methyl Ethers with Sodium and Trimethylchlorosilanes. Evidence for the Intermediacy of Allylic and Benzylic Radicals and Anions," D. Tzeng and W. P. Weber, J. Org. Chem., 46, 693 (1981).

"Insertion Reactions of Dimethylsilylene into Silicon-Sulfur and Sulfur-Sulfur Single Bonds," A. Chihi and W. P. Weber, J. Organometal. Chem., 210, 163 (1981).

"Reaction of Dimethylsilylene with Allylic Methyl Sulfide," A. Chihi and W. P. Weber, Inorganic Chemistry, 20, 2822 (1981).

"Evidence for the Intermediacy of 1,1-Dimethyl-2-phenyl-1-sila-1,3-butadiene in the Photochemistry and Pyrolysis of 1,1-Dimethyl-2-phenyl-1-sila-2-cyclobutene," D. Tzeng, R. H. Fong, and W. P. Weber, J. Organometal. Chem., 219, 153 (1981).

"Mechanistic Studies of the Reaction of Oxetanes with Methylthio-trimethylsilane," H. Firgo and W. P. Weber, J. Organometal. Chem., 222, 201 (1981).

"Oxidation of Alkenyldisilane by m-Chloroperbenzoic Acid," T. A. Dixon, K. P. Steele, and W. P. Weber, J. Organometal. Chem., 231, 291 (1982).

"Insertion Reactions of Dimethylsilylene: Relative Reactivity Towards Oxygen-Hydrogen, Silicon-Hydrogen, and Silicon-Alkoxy Bonds," K. P. Steele, D. Tzeng, and W. P. Weber, J. Organometal. Chem., 231, 291 (1982).

"Mass Spectrometry of Allyloxy Di- and Trimethylsilanes", K. P. Steele and W. P. Weber, J. Organic Mass Spectrometry, 17, 222 (1982).

"Regiospecificity of Reactions of Epoxides and Oxetanes with Trimethyl silyl Cyanide," J. C. Mullis and W. P. Weber, J. Org. Chem., 47, 2873 (1982).

"Reaction of Secondary and Tertiary Alkyl Lithium Reagents with Vinyl Di- and Tisiloxane. Synthesis of α-Silyl Silanols," H. Firgo and W. P. Weber, Organometallics, 1, 649 (1982).

"Mechanism of Reactions of Oxetanes with Sodium and Dimethyldichloro-silanes, Synthesis of 1-oxa-2-silacyclopentanes," D. Tzeng and W. P. Weber, J. Org. Chem., 47, 1976 (1982).

"Selectivity in the Reactions of Alkyl Lithium Reagents with α,ω-Dichloropermethylsiloxanes," S. A. Kazoura and W. P. Weber, J. Organometal. Chem., 243, 149 (1983).

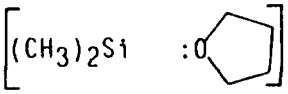
"Organosilicon Chemistry," W. P. Weber, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The chemistry and reactivity of silylenes have been explored. The object has been to discover novel reactions for the preparation of organosilicon compounds. The insertion reaction of dimethylsilylene into O-H bonds of primary, secondary, and tertiary alcohols has been shown to provide an efficient route to alkoxydimethylsilanes.

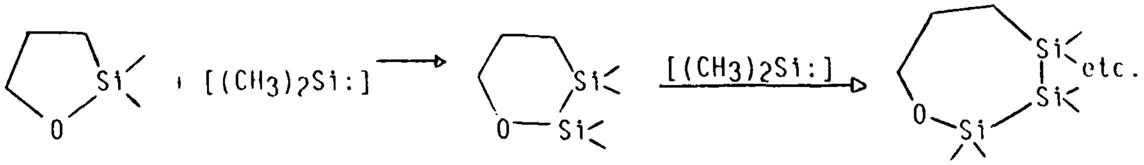
$$[(CH_3)_2Si:] + ROH \qquad RO\text{-}Si(CH_3)_2\text{-}H$$

Solvent significantly affects the reactivity of dimethylsilylene in such reactions. Specifically, dimethylsilylene shows no discrimination between primary and tertiary alcohols in hexane solvent but demonstrates considerable selectivity in favor of primary alcohols in ether solvents such as THF. This decreased reactivity and increased selectivity in ether solvents may result from formation of a complex between the electrophilic silylene and the oxygen of the ether. This selectivity provides a method to control the reaction products.



Dimethylsilylene reactivity also depends on the concentration of alcohol in hydrocarbon solvents. Apparently different alcohol aggregates, monomer versus dimers for example, show different reactivity toward dimethylsilylene.

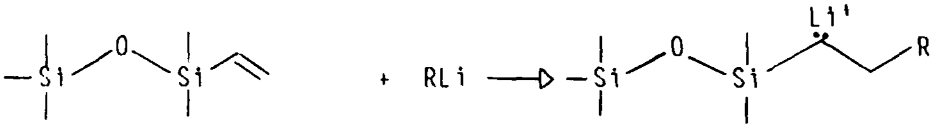
The insertion of dimethylsilylene in Si-O bonds of alkoxysilanes has permitted the synthesis of a novel series of cyclic polysilanes.



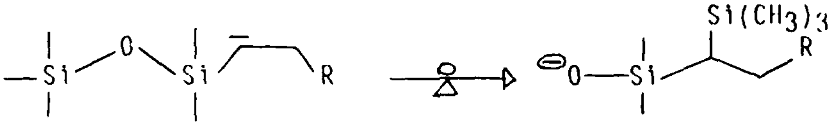
We have discovered that the reaction of dimethylsilylene with ring strained ethers, such as epoxides and oxetanes, occurs by initial complexation of the silylene with the ether oxygen to form a zwitterionic intermediate which rearranges to yield new silicon heterocyclic products.

The regiospecific reaction of dimethylsilylene with allylic methyl ethers to yield allylic dimethylmethoxysilanes may proceed though an analogous zwitterionic intermediate which undergoes 2,3-sigmatropic rearrangement to yield products.

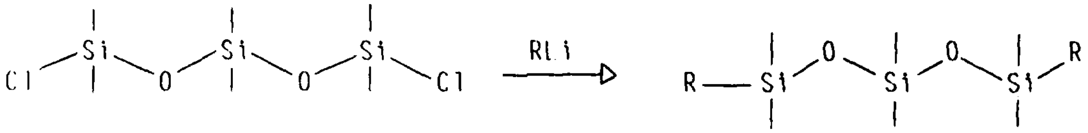
A second objective has been to develop reactions which can be carried out on siloxane polymers without breaking the siloxane polymer backbone. We have found that secondary and tertiary alkyl lithium reagents will add to the carbon carbon bond of vinyl di- or trisiloxanes at low temperatures to yield α-lithio di- or trisiloxanes with no attack by the alkyl lithium reagent on the siloxane bond.



However, on warming these undergo rearrangement to yield sterically hindered α-silyl silanols.



We have also found that alkyl lithium reagents react selectively with the Si-Cl bonds of α,ω-dichloro permethylsiloxanes with no cleavage of Si-O bonds to yield α,ω-dialkyl permethylsiloxanes.



AFOSR Program Manager: Dr. Anthony J. Matuszko

RESEARCH EFFORTS COMPLETED IN FY 83

ATMOSPHERIC SCIENCES - LT COL TED S. CRESS

Analysis and Prediction of Severe Storm Environment AFOSR-79-0125	Richard A. Anthes Department of Meteorology The Pennsylvania State University University Park, PA 16802
Large Electrical Discharges Over Charged Dielectric Surfaces AFOSR-MIPR-83-00007 to ONR	Ernesto Barreto Atmospheric Sciences Research Center State University of New York 1400 Washington Avenue Albany, NY 12222
Fabry-Perot Determinations of Equatorial F-Region Neutral Winds and Temperatures AFOSR-82-0055	Manfred A. Biondi Department of Physics and Astronomy University of Pittsburgh Pittsburgh, PA 15260
MITHRAS, A Program of Simultaneous Radar Observations of the High-Latitude Auroral Zone F49620-81-C-0042	Odile de la Beaujardiere John V. Evans Radio Physics Laboratory and Haystack Observatory SRI International Menlo Park, CA 94025 Massachusetts Inst. of Tech. Westford, MA 01886
Atmospheric Temperature Profiles from Earth Limb Infrared Measurements AFOSR-82-0153	R. D. Harris Center for Atmospheric and Space Sciences Utah State University Logan, UT 84322
A Laboratory Study of Aircraft Precipitation Static Charging AFOSR-81-0189 and AFOSR-82-0323	Anthony J. Illingworth Department of Pure & Applied Physics UMIST, Sackville Street Manchester MGO 1QD England
Studies on Light Scattering and Absorption Properties of Ice Clouds for Visible and Infrared Laser Wavelengths F49620-79-C-0198	Kuo-Nan Liou Department of Meteorology The University of Utah 819 Wm. C. Browning Bldg. Salt Lake City, UT 84112

Investigation into the Nature of Snowflake Aggregation in the Vicinity of the Melting Layer in Stratiform Clouds AFOSR-82-0173	Steven B. Newman Department of Physics/Earth Sciences Central Connecticut State University New Britain, CT 06050
Rainfall Studies Using the Differential Reflectivity Radar Techniques AFOSR-ISSA-82-00043 to NSF	Thomas A. Seliga Department of Electrical Engineering Ohio State University Columbus, OH 43212
Upper Atmosphere Structure and Dynamics AFOSR-ISSA-81-00039 AFOSR-ISSA-82-00042 to NSF	Gene E. Tallmadge Radio Physics Laboratory SRI International 333 Ravenswood Ave Menlo Park, CA 94025
Latitudinal Variations of Auroral-Zone Ionization Distribution F49620-80-C-0014	James F. Vickrey Radio Physics Laboratory SRI International Menlo Park, CA 94025
A Systematic Study of Light Scattering by Irregularly Shaped Particles AFOSR-MIPR-81-00022; AFOSR-MIPR-82-00052; AFOSR-MIPR-83-00063 to ARO	Ru T. Wang Donald W. Schuerman (Deceased) Space Astronomy Laboratory University of Florida Gainesville, FL 32601
Phase Fluctuations of Trans-ionospheric Signals Under Multiple Scattering Conditions AFOSR-80-0187 and F49620-82-C-0058	Bruce J. West Center for Studies of Nonlinear Nonlinear Dynamics La Jolla Institute 8950 Villa La Jolla Drive La Jolla, CA 92037

COMPLETED PROJECT SUMMARY

1. TITLE: Analysis and Prediction of Severe Storm Environment

2. PRINCIPAL INVESTIGATOR: Prof. Richard A. Anthes
Department of Meteorology
The Pennsylvania State University
University Park, PA 16802

3. INCLUSIVE DATES: 30 September 1979 - 29 December 1982

4. GRANT NUMBER: AFOSR-79-0125

5. COSTS AND FY SOURCE: $62,118, FY 79; $67,896, FY 80; $73,000, FY 81

6. SENIOR RESEARCH PERSONNEL:

Dr. T. N. Carlson
Dr. M. J. Fritsch
Dr. N. L. Seaman
Dr. T. T. Warner
Dr. R. J. Farrell

7. JUNIOR RESEARCH PERSONNEL:

M. N. Schwartz
T. Grazians
S. G. Benjamin
J. D. Goldman
J. M. Lanicci
Y. N. Kuo

8. PUBLICATIONS:

"The Evolution of the Mesoscale Environment of Severe Local Storms: Preliminary Modeling Results," R. A. Anthes, Y. N. Kuo, S. G. Benjamin, and Y. F. Li, Mon. Wea. Rev., 110, 1187 (1982).

"Some Effects of Surface Heating and Topography on the Regional Severe Storm Environment," S. G. Benjamin, Ph.D. Thesis, Department of Meteorology, The Pennsylvania State University (1983).

"Numerical Simulations of the Severe Storm Environment for 10-11 April 1979 (SESAME I) Case," S. G. Benjamin and T. N. Carlson, 12th Conference on Severe Local Storms, Amer. Meteor. Soc., Boston, MA, 201 (1982).

"A Simple Scheme for Objective Analysis in Curved Flow," S. G. Benjamin and N. L. Seaman, Mon. Wea. Rev., submitted.

"The Role of the Lid in Severe Storm Formation: Some Synoptic Examples from SESAME," T. N. Carlson, 12th Conference on Severe Local Storms, Amer. Meteor. Soc., Boston, MA, 221 (1982).

"Analyses and Prediction of Severe Storms Environment," T. N. Carlson, R. A. Anthes, M. Schwartz, S. G. Benjamin, and D. G. Baldwin, *Bull. Amer. Meteor. Soc.*, *61*, 1018 (1980).

"Elevated Mixed Layers and the Regional Severe Storm Environment: Conceptual Model and Case Studies," T. N. Carlson, S. G. Benjamin, G. S. Forbes, Y. F. Li, *Mon. Wea. Rev.*, *111*, 1453 (1983).

"The Lid Strength Index as an Aid in Predicting Severe Local Storms," T. N. Carlson and R. J. Farrell, *Nat. Wea. Digest*, *8*, 29 (1983).

"Analysis and Prediction of the Severe Storm Environment," T. N. Carlson, T. T. Warner, and M. J. Fritsch, Final Technical Report (1983).

"A Conceptual Model and Its Application in the Analysis of Severe Convective Storm Situations," J. D. Goldman, M.S. Thesis, Department of Meteorology, The Pennsylvania State University (1981).

"Diagnostic Study of Severe Storm Environment," Y. H. Kuo, Ph.D. Thesis, Department of Meteorology, The Pennsylvania State University (1983).

"Synoptic and Mesoscale Stability Analyses of the Red River Valley Severe Storm Outbreak of 10 April 1979," M. N. Schwartz, M.S. Thesis, Department of Meteorology, The Pennsylvania State University (1980).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A mesoscale numerical model was used to investigate the roles of planetary boundary layer processes, topography, and stability aloft in the development of severe convection. In particular, it was noted that advection of warm, dry air aloft from a hot and arid plateau tends to form a lid over relatively moist air near the surface. This process, which occurs over western Europe and Africa, as well as over the central plains of the U.S., enables the wet bulb potential temperature near the surface to become quite high while convection is limited by the thermal lid. Severe convection develops when the low level wet bulb potential temperature reaches a critical value or when the low level air emerges from under the lid, and the first thunderstorms occur over favorable topographical locations. Data sets from the 1979 SESAME project were used in the investigation. Analysis of thermal lids and underrunning of moist air showed the importance of differential surface heating and topography in establishing the severe storm environment. The correct formulation of soil moisture, cloud effects on the surface radiation budget, and topography are essential to accurate prediction of lid structure. The boundary layer parameterization in the model was significantly improved as a result of these studies. The underrunning process leads to front like circulations near the edge of the lid, an example of which is the so-called "dry line". The modeling tests also showed that differential heating associated with the Mexican plateau establishes a lee-side trough of low pressure near the surface, which in turn induces a strong southerly

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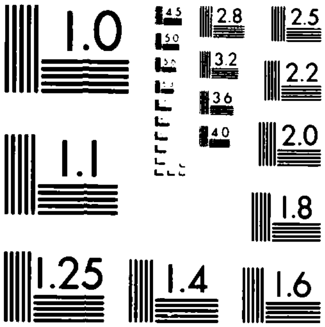
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low-level flow east of the plateau; this process is related to the formation of the low-level jet which is associated with outbreaks of severe convection. Other research included the response of precipitation to variations in surface parameterizations and the effect of the large-scale environment on the variations of convective heating profiles.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Large Electrical Discharges Over Charged Dielectric Surfaces

2. PRINCIPAL INVESTIGATOR: Dr. Ernesto Barreto
Atmospheric Sciences Research Center
State University of New York at Albany
1400 Washington Avenue
Albany, NY 12222

3. INCLUSIVE DATES: 15 October 1982 - 14 September 1983

4. INSTRUMENT NUMBER: AFOSR-MIPR-83-00007 to ONR

5. COSTS AND FY SOURCE: $11,500, FY 83 (One time help; This is a continuing program under ONR sponsorship)

6. PUBLICATIONS:

"The Gas Heating Phase In Electrical Breakdown," E. Barreto, Final Report, AFOSR-MIPR-83-00007, WPAFB-MIPR-FY145683N0018, Report No. AFWAL-TR-83-3124 (1983).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Under ongoing support from the Office of Naval Research (ONR), the Principal Investigator is conducting research on the initiation of electrical discharges over charged surfaces, including the physics of attachment of the discharge to the surface, the propagation of the discharge, and the physical characteristics of the discharge. In the experimental apparatus, discharges are prevented from changing into fully developed arcs by limiting the available energy and by studying discharges over charged dielectric surfaces. Observations suggest that in the initial stages of discharge development, the electrons behave as an ideal fluid, independent of the gas surrounding the electrodes. The gas heating that leads ultimately to full arc development is found to be due primarily to electron pressure rather than to the applied electric field directly. Predictions of larger scale phenomena based on observations and modeling at State University of New York, Albany, have been verified by observations at the Office National d'Etudes et de Recherches Aerospatiales (ONERA) in France. This AFOSR funding, together with support from AF Flight Dynamics Laboratory and ONR enabled the Principal Investigator to conduct additional research at ONERA. This effort was aimed at clarifying conditions pertinent to the initiation, propagation, and interaction of discharges in clouds and at the surfaces of charged aircraft. It has been found that in all cases gas heating is preceded by the formation of a weakly ionized plasma. The transformation to a strongly ionized gas requires additional ionization that can be associated with several different physical processes. In small gaps ($\leq$ 3.0 mm) with

metal electrodes, the influx of electrons from a cathode spot with at least a single cell is responsible for gas heating. In longer gaps (1 to 3 cm) highly luminous ionization waves are produced. These can be reflected at the electrodes and increase the degree of ionization. They are well known but not clearly explained in longer discharges. This stage is followed by the formation of hot filaments either at the electrodes or in mid gap. These seem to be associated with the onset of effective ion-electron interactions. In large surface discharges ($\sim$1.0 m) the glow and hot channel behind it constitute a stable propagating unit that seems to be controlled by three body electron-ion recombination. The properties of these gliding discharges are similar to those of lightning leaders. In all cases there is strong evidence to support the concept of fluid dynamic effects associated with the hot electron population in the weakly ionized gas. Thus the propagation of stable discontinuities, either strong (shocks) or weak, is shown to be possible.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Fabry-Perot Determinations of Equatorial F-Region Neutral Winds and Temperatures

2. PRINCIPAL INVESTIGATOR: Dr. Manfred A. Biondi
Department of Physics and Astronomy
University of Pittsburgh
Pittsburgh, PA 15260

3. INCLUSIVE DATES: 1 December 1981 - 31 May 1983

4. GRANT NUMBER: AFOSR 82-0055

5. COSTS AND FY SOURCE: $28,385, FY 82

6. SENIOR RESEARCH PERSONNEL: Dr. D. P. Sipler

7. PUBLICATIONS:

"OI 630.0 nm Optical Measurements of Neutral Winds, Temperatures and Airglow Enhancements during the BIME Program," M. A. Biondi, Final Technical Report.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A 100 mm aperture, field-widened Fabry-Perot interferometer was used in support of the Brazil Ionospheric Modification Experiment (BIME) F-region chemical release program to measure 630.0 nm nightglow line profiles and from this to determine the pattern of F-region thermospheric dynamics (neutral velocity vector $\vec{v}_n$ and neutral temperature T_n versus time) from 24 Aug 82 to 19 Sep 82 at Natal, Brazil. A 3-channel, sky-mapping filter photometer measured the temporal and spatial evolution of the 630.0 nm airglow enhancement produced by the first BIME release (8 Sep 82). Clouds over the observing site obscured the second BIME release (13 Sep 82). The neutral wind vectors exhibited some behavior patterns similar to those observed at equatorial (Kwajalein Atoll) and low (Arecibo, P.R.) latitudes. Typical values at the proposed rocket launch times ($\sim$2130 UT) were $\sim$100 m/sec at $\sim 110^\circ$ azimuth during the 24 Aug-19 Sep 82 period. The 630.0 nm airglow enhancement produced by the CO_2 from the rocket release ($O^+ + CO_2 \rightarrow O_2^+ + CO$, followed by $O_2^+ + e^- \rightarrow O^* + O^*$) was tracked for 6 minutes after release on 8 Sep, and enhanced brightness contours extending over a 250 x 250 km region were mapped.

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

COMPLETED PROJECT SUMMARY

1. TITLE: MITHRAS, A Program of Simultaneous Radar Observations of the High-Latitude Auroral Zone

2. PRINCIPAL INVESTIGATORS:

Dr. Odile de la Beaujardiere	Dr. John V. Evans
Radio Physics Laboratory	Haystack Observatory
SRI International	Massachusetts Institute of Technology
Menlo Park, CA 94025	Westford, MA 01886

3. INCLUSIVE DATES: 1 May 1981 - 31 March 1983

4. CONTRACT NUMBER: F49620-81-C-0042

5. COSTS AND FY SOURCE: $346,715, FY 81; $464,583, FY 82

6. RESEARCH PERSONNEL: SRI International

J. Petriceks
C. Senior
C. Dawson
C. Leger

Haystack Observatory

J. Holt
R. Wand
W. Oliver

7. PUBLICATIONS:

"Chatanika Radar Observations Associated with the MITHRAS Program," O. de la Beaujardiere, M. Baron, C. Senior, J. Petriceks, and C. Leger, Proc. Conf. Origins of Plasmas and Electric Fields in the Magnetosphere, Yosemite, CA (1982).

"Substorm Effects on Auroral Convection as Observed by the Millstone Hill Radar," J. M. Holt, J. V. Evans, and R. H. Wand, Proc. Conf. Origins of Plasmas and Electric Fields in the Magnetosphere, Yosemite, CA. (1982).

"High-Latitude Electric Fields Observed from Millstone Hill," J. V. Evans, R. H. Wand, J. M. Holt, and W. L. Oliver, Solar-Terrestrial Physics Symposium, Ottawa, Canada (1982).

"Millstone Hill Studies of the High-Latitude Ionosphere," R. H. Wand, J. M. Holt, J. V. Evans, and W. L. Oliver, Solar-Terrestrial Physics Symposium, Ottawa, Canada (1982).

"Simultaneous Measurements of the Electrodynamic Parameters of the Auroral Ionosphere by the EISCAT and Chatanika Radars,: G. Caudal, D. Alcayde', O. de la Beaujardiere, and G. Lejeune, EGS Symposium, Leeds, UK (1982).

"High-Latitude Neutral Atmosphere Temperature and Concentration Measurements from the First EISCAT Incoherent Scatter Observations," D. Alcayde, J. Fontanari, and P. Bauer, URSI Symposium, Fairbanks, Alaska (1982).

"Solar Cycle Variations of the High-Latitude Ionosphere as Observed with Incoherent Scatter Radar," M. J. Baron, C. J. Heinselman, and J. Petriceks, URSI Symposium, Fairbanks, Alaska (1982).

"High-Latitude Exospheric Temperature Observed over a Solar Cycle," J. D. Kelly, C. J. Heinselman, and J. Petriceks, URSI Symposium, Fairbanks, Alaska (1982).

"Millstone Hill Observations of the Trough: Boundary between the Plasma-pause and Magnetosphere or Not?" J. M. Holt, J. V. Evans, and R. H. Wand, URSI Symposium, Fairbanks, Alaska (1982).

"Early MITHRAS Results: The Electric-Field Response to Substorms," O. de la Beaujardiere, J. Holt, and E. Nielsen, URSI Symposium, Fairbanks, Alaska (1982).

"F-Region Ion Temperature Enhancements Resulting from Joule Heating," M. J. Baron, URSI Symposium, Fairbanks, Alaska (1982).

"F-Region Plasma Enhancements along the Equatorward Boundary of the Auroral Oval," R. T. Tsunoda, R. M. Robinson, and C. Senior, URSI Symposium, Fairbanks, Alaska (1982).

"Measures Simultanees des Champs Electriques de l'Ionosphere Aurorale par les Radars d'EISCAT et de Chatanika," G. Caudal, D. Alcayde, O. de la Beaujardiere, and G. Lejeune, Proc. GRECO Conf. Incoherent Scatter Obs., Grenoble, France (1982).

"Courants Alignes, Precipitations Diffuses et Electrojets dans le Secteur Nuit de Haute Latitude," C. Senior, Proc. GRECO Conf. Incoherent Scatter Obs., Grenoble, France (1982).

"F-Region Ion Temperature Enhancements Resulting from Joule Heating," M. J. Baron and R. H. Wand, J. Geophys. Res., 88, 4114 (1983).

"Some Properties of the Auroral Thermosphere Inferred from Initial EISCAT Observations," D. Alcayde, J. Fontanari, P. Bauer, and O. de la Beaujardiere, Radio Sci., 18, 881 (1983).

"Solar Cycle and Seasonal Variations of the Ionosphere Observed with the Chatanika Incoherent Scatter Radar," M. J. Baron, C. J. Heinselman, and J. Petriceks, Radio Sci., 18, 895 (1983).

"Early MITHRAS Results: The Electric-Field Response to Substorms," O. de la Beaujardiere, J. Holt, and E. Nielsen, Radio Sci., 18, 981 (1983).

"Millstone Hill Studies of the Trough: Boundary between the Plasmapause and Magnetosphere or Not?" J. M. Holt, J. V. Evans, and R. H. Wand, Radio Sci., 18, 947 (1983).

"High-Latitude Exospheric Temperature Observed over a Solar Cycle," J. D. Kelly, C. J. Heinselman, and J. Petriceks, Radio Sci., 18, 901 (1982).

"On the Control of Magnetospheric Convection by the Spatial Distribution of Ionospheric Conductivities," C. Senior and M. Blanc, J. Geophys. Res. (1982), submitted.

"Simultaneous Measurements of the Electrodynamic Parameters of the Auroral Ionosphere by the EISCAT and Chatanika Radars," G. Caudal, D. Alcayde, O. de la Beaujardiere, and G. Lejeune, Annales Geophysicae (1983), submitted.

"MITHRAS: A Program of Simultaneous Radar Observations of the High Latitude Auroral Zone," O. de la Beaujardiere, M. J. Baron, V. B. Wickwar, C. Senior, and J. V. Evans, Final Scientific Report (1982).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Between May 1981 and June 1982, an intensive campaign of thirty-three coordinated observations was carried out using three incoherent-scatter radars capable of probing the auroral zone. The objective of these experiments and subsequent analysis is to further our understanding of the interactions of the magnetosphere, the ionosphere, and the thermosphere by monitoring the auroral zone from stations widely separated in longitude. The three radars were Chatanika (Alaska), Millstone Hill (Massachusetts), and EISCAT (Scandinavia). Collaborative studies were undertaken using data from the Dynamics Explorer spacecraft and the STARE radar. There were three main types of MITHRAS experiments. MITHRAS #1 was aimed at large latitudinal coverage of F-region drifts, electron-densities, and temperatures. MITHRAS #2 was designed for very good height and time resolution. MITHRAS #3 was intermediate between the other two modes and provided both E- and F-region coverage over several degrees in latitude. Scientific collaborations between the various groups took place informally and during MITHRAS working meetings. Although the major analytical efforts will be completed under a follow-on contract, the following are the major scientific accomplishments to date.

a. Ionosphere - For a given electric field, the F-region ion temperature was higher in the postmidnight sector than in the premidnight sector. This asymmetry was explained by the fact that ion drag is less effective when the electron density is small, resulting in a decoupling between the neutral wind and the ion convection. In a separate study, ionospheric densities and temperatures were compared for the three radars for selected periods, and between the radars and a model ionosphere. Under similar geomagnetic conditions and solar illuminations, major differences were found. These differences were anticipated and are attributable to longitudinal effects that arise from the geomagnetic pole offset.

b Thermosphere - A method was developed to determine auroral zone altitude profiles of the neutral temperature and atomic oxygen concentration, even in the presence of Joule heating. As a result, it is now possible for the first time to examine the evolution of the high latitude neutral thermosphere from several auroral sites, with the ability to measure simultaneously the energy imput from Joule heating and particle precipitation.

c. Magnetosphere - Detailed case studies dealt with the effect of substorms on convection. A three-radar comparison of the substorm electric field signature revealed that the signature depends primarily on the local time where the observation is made. The cross-polar cap potential was also estimated from radar electric fields in the dawn or dusk sectors. In another study, it was shown that intense electric fields associated with substorms can be a dominant factor in the formation of ionospheric troughs. Subauroral electric fields were observed during a period of prolonged magnetic activity on 11 November 1981. During a long period of southward interplanetary magnetic field (IMF) on 18 November 1981 the electric field seen by Chatanika and EISCAT remained very intense in the dawn and dusk sectors, and the electric field reversal in the midnight sector occurred at a very early local time at both radars. These observations suggest that, for at least ten hours, the global plasma convection pattern remained fairly uniform, and was expanded and rotated toward early hours.

d. Models - Empirical models are being constructed to characterize the day and night conductivities, the electric fields, the E- and F-region densities, and the exospheric temperature. These models yield average values of the observed radar parameters as a function of quantities such as K_p, solar flux, IMF, solar zenith angle, and precipitation. A theoretical model of the temporal variation and global effects of ring-current shielding was developed. This model will be used to simulate the subauroral electric fields observations of 11 November 1981.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Atmospheric Temperature Profiles from Earth Limb Infrared Measurements

2. PRINCIPAL INVESTIGATOR: Professor R. D. Harris
Center for Atmospheric and
Space Sciences
Utah State University
Logan, UT 84322

3. INCLUSIVE DATES: 15 April 1982 - 30 September 1982

4. GRANT NUMBER: AFOSR-82-0153 (Mini Grant)

5. COSTS AND FY SOURCE: $9,777, FY 82

6. PUBLICATIONS:

"Atmospheric Temperature Profiles from Earth Limb Infrared Measurements," R. D. Harris, Final Technical Report.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A model of infrared radiation from CO_2 was developed that is applicable to earth limb radiation from the stratosphere. The kernel of this model is a numerical code to calculate the integrated transmittance of a single rotational line. By means of a non-linear iteration process it was shown that temperature or CO_2 density profiles in the stratosphere can be recovered from IR limb radiation measurements. A numerical code was developed to utilize two rotational lines of CO_2 to retrieve both temperature and CO_2 density simultaneously. This code is running but needs verification. If CO_2 is well mixed in the atmosphere a simultaneous retrieval of temperature and density will yield the atmospheric pressure profile and allow densities of other IR active species to be deduced. A computationally fast method for evaluation of transmittance was also studied. This interpolation scheme, first proposed by McMillin for vertically-pointing sensors, was reformulated for limb viewing. Preliminary results were very encouraging. It was recommended that the technique be evaluated with 12 to 20 model atmospheres to determine whether one set of expansion coefficients can be used for the entire atmosphere. The ultimate accuracy that can be obtained in a retrieval scheme in degrees of temperature or percent of density, using this method to calculate transmittance, will depend on the number of sets of expansion coefficients.

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

COMPLETED PROJECT SUMMARY

1. TITLE: A Laboratory Study of Aircraft Precipitation Static Charging

2. PRINCIPAL INVESTIGATOR: Dr. Anthony J. Illingworth
Department of Pure & Applied Physics
UMIST, Sackville Street
Manchester M60 1QD
England

3. INCLUSIVE DATES: 1 June 1981 - 31 July 1983

4. GRANT NUMBER: AFOSR-81-0189 and AFOSR-82-0323

5. COSTS AND FY SOURCE: $28,400, FY 81; $28,400, FY 82

6. SENIOR RESEARCH PERSONNEL: Dr. J. M. Caranti

7. JUNIOR RESEARCH PERSONNEL: S. J. Marsh

8. PUBLICATIONS:

"Static Charging by Collisions with Ice Particles," J. M. Caranti and A. J. Illingworth, Proc. Int. Conf. Aerospace Conf. Lightning and Static Electricity, Oxford, England (1982).

"The Contact Potential of Rimed Ice," J. M. Caranti and A. J. Illingworth, J. Phys. Chem., 87, 4125 (1983).

"The Frequency Dependence of the Surface Conductivity of Ice," J. M. Caranti and A. J. Illingworth, J. Phys. Chem., 87, 4078 (1983).

"Transient Workman-Reynolds Freezing Potentials," J. M. Caranti and A. J. Illingworth, J. Geophys. Res., 88, 8483 (1983).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An investigation into the charge transfer occurring when ice crystals collide with various materials was undertaken, with the aim of predicting the charging properties of the materials on the basis of laboratory observations. The research included individual ice crystal collisions with various targets, passage of various materials through ice crystal clouds, and a study of the electrical properties of ice. The results showed that neither the thermoelectric effect due to temperature difference between the ice and the target, nor the inductive effect due to external electric field, nor the Workman-Reynolds electric potential associated with the freezing of dilute aqueous solutions was of importance in the charging process under the conditions of interest. The most important result of the research was to show that the contact potential difference between ice and metals is the dominant charging mechanism.

Nickel, carbon, silver, and brass all received negative charge in ice crystal collisions; zinc charged predominantly negatively, but with some positive charge transfers; and magnesium always charged positively, due to its low work function (or contact potential). Measurements have yet to be conducted at higher collision speeds, more directly comparable to aircraft flight conditions, where ice crystal fracturing may also be a factor.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Studies on Light Scattering and Absorption Properties of Ice Clouds for Visible and Infrared Laser Wavelengths

2. PRINCIPAL INVESTIGATOR: Dr. Kuo-Nan Liou
Department of Meteorology
The University of Utah
819 Wm. C. Browning Bldg.
Salt Lake City, UT 84112

3. INCLUSIVE DATES: 1 June 1979 - 30 December 1982

4. CONTRACT NUMBER: F49620-79-C-0198

5. COSTS AND FY SOURCE: $11,987, FY 79; $13,204, FY 80; $32,000, FY 81;

6. SENIOR RESEARCH PERSONNEL: Dr. K. Sassen

7. PUBLICATIONS:

"Remote Sensing of Planar Ice Crystal Fall Attitudes," K. Sassen, J. Meteor. Soc. Japan, 58, 422 (1980).

"Infrared (10.6-μm) Scattering and Extinction in Laboratory Water and Ice Clouds," K. Sassen, Applied Optics, 20, 185 (1981).

"Light Scattering by Hexagonal Ice Crystals," R. F. Coleman and K. N. Liou, J. Atmos. Sci., 38, 1260 (1981).

"Infrared (10.6-μm) Radiation Induced Evaporation of Large Water Drops," K. Sassen, J. Optical Soc. America, 71, 887 (1981).

"Propagation of CO_2 Laser Radiation Through Ice Clouds: Microphysical Effects," K. Sassen and M. Griffin, J. Appl. Meteor., 20, 828 (1981).

"Theory of Time-Dependent Multiple Back-Scattering From Clouds," Q. Cai and K. N. Liou, J. Atmos. Sci., 38, 1452 (1981).

"Some Aspects of the Optical Properties of Ice Clouds," K. N. Liou, Clouds: Their Formation, Optical Properties, and Effects, (Academic Press), p.p. 315 (1981).

"Polarized Light Scattering by Hexagonal Ice Crystals: Theory," Q. Cai and K. N. Liou, Appl. Optics, 21, 3569 (1982).

"Scattering Phase Matrix Comparison for Randomly Hexagonal Cylinders and Spheroids," K. N. Liou, Q. Cai, P. W. Barber, and S. C. Hill, Appl. Optics, 22, 1684 (1983).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Measurements of the angular scattering and extinction of 10.6 μm wavelength laser radiation in laboratory water and ice clouds were made and compared with theoretical predictions for spheres. The measurements showed strong internal energy absorption. Dual-wavelength extinction measurements revealed information on the growth and dissipation of laboratory water clouds and the effects of cloud seeding. Experiments on the interactions of a 10.6 μm CO_2 laser beam with ice crystals revealed the disruptive effects on ice cloud content under some conditions due to high internal absorption in ice at this wavelength. Observed effects ranged from instantaneous fragmentation of large crystal branches to changes in the habit of growing ice crystals. Measurements of the evaporation rate of water drops of diameters about 1-2.5 mm suspended in a CO_2 laser beam showed an increase of about 1.6 μm/second relative to the evaporation rate produced by an irradiance of 1.65 W/m^2 at the same wavelength. Observations of planar ice crystals showed that these fall in a stable configuration for Reynolds Numbers between 1 and 100 and that crystal diameters greater than 0.1-0.2 mm are required to generate the optical displays.

A time-dependent transfer model for multiple backscattering of a pulsed laser beam in clouds was developed. This included a general four-by-four scattering phase matrix and required no specific physical approximations. Effects of the transmitter beam width and receiver field of view on the multiple backscattered return, depolarization, and polarization characteristics were investigated for wavelengths of 0.7 and 10.6 μm. A model was developed for light scattering by hexagonal ice crystals, involving complete polarization information for arbitrarily oriented hexagonal columns and plates on the basis of ray tracing which includes contributions from geometric reflection and refraction and Fraunhofer diffraction. Comparisons of the computed scattering phase function, degree of linear polarization, and depolarization ratio for randomly oriented columns and plates with experimental data obtained previously by these investigators showed close agreement, especially for the depolarization ratio. Comparisons with results calculated by the T-matrix method for randomly oriented hexagonal cylinders and equivalent spheroids showed general agreement for the phase functions, except for the 22° and 46° halo features and the backscattering maximum. The linear polarization component differed in the forward directions, where hexagonal cylinders have two positive polarization maxima. Large differences were found in the other matrix elements.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Investigation into the Nature of Snowflake Aggregation in the Vicinity of the Melting Layer in Stratiform Clouds

2. PRINCIPAL INVESTIGATOR: Dr. Steven B. Newman
Department of Physics/Earth Sciences
Central Connecticut State University
New Britain, CT 06050

3. INCLUSIVE DATES: 1 May 1982 - 31 December 1982

4. GRANT NUMBER: AFOSR-82-0173 (Mini Grant)

5. COSTS AND FY SOURCE: $9,915, FY 82

6. PUBLICATIONS:

"A Preliminary Investigation of Snowflake Aggregation Near the Melting Layer in Stratiform Clouds," S. B. Newman, Proc. Conf. Cloud Physics, Amer. Meteor. Soc., Boston, p.p. 381 (1982).

"An Investigation into the Nature of Snowflake Aggregation in the Vicinity of the Melting Layer in Stratiform Clouds," S. B. Newman, Final Technical Report, submitted to J. Atmos. Sci. (1983).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A model of snowflake aggregation developed previously (during a SCEEE/USAF Summer Faculty Research Fellowship) was refined to more accurately model the snowflake size distribution. Data from the AFGL cloud physics research aircraft were used to verify the accuracy of the model and to confirm the existence of an aggregation and breakup cycle in snowflake evolution near the melting layer. Changes in the observed relative numbers of large and small particles were related to occurrence of aggregation and breakup, and the temperatures at which these processes were occurring as deduced from the observations agreed well with temperatures predicted by the model.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Rainfall Studies Using the Differential Reflectivity Radar Techniques

2. PRINCIPAL INVESTIGATOR: Dr. Thomas A. Seliga
Department of Electrical Engineering
Ohio State University
Columbus, OH 43212

3. INCLUSIVE DATES: 15 May 1982 - 30 September 1982

4. INSTRUMENT NUMBER: AFOSR-ISSA-82-00043 to National Science Foundation

5. COSTS AND FY SOURCE: $10,000, FY 82

6. SENIOR RESEARCH PERSONNEL: Dr. K. Aydin

7. JUNIOR RESEARCH PERSONNEL: H. Direskeneli

8. PUBLICATIONS:

"Disdrometer Measurements During a Unique Rainfall Event in Central Illinois and Their Implication for Differential Reflectivity Radar Observations," T. A. Seliga, K. Aydin, and H. Direskeneli, 21st Conf. on Radar Meteorology, Amer. Meteor. Soc., Boston, 467 (1983).

"Differential Reflectivity (Z_{DR}) Measurements of Rainfall Compared With Ground-Based Disdrometer Measurements," H. Direskeneli, T. A. Seliga, and K. Aydin, 21st Conf. on Radar Meteorology, Amer. Meteor. Soc., Boston, 475 (1983).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This funding was in partial support of an expansion of a pre-existing National Science Foundation grant to Ohio State University. The original grant supported field operations in 1981, using a newly modified radar to obtain differential reflectivity measurements in convective storms on the high plains. The differential reflectivity, which is the ratio of reflectivity measured with horizontally polarized signals to that measured with vertically polarized signals, provides a direct measure of the average shape of scatterers. The research involved use of this parameter together with the absolute reflectivity to infer size distributions of raindrops, rainfall rates, and thermodynamic phase of scatterers. AFOSR funding enabled the conduct of a second field measurement program which included raindrop size measuring instruments (disdrometers) on loan from AF Geophysics Laboratory in addition to the radar and other surface instrumentation. Empirical relationships between the radar observable parameters and the rainfall parameters where developed from the drop size

distribution measurements. The results from applying these relationships to the radar data supported the original premise that representative and accurate interpretations of rainfall rates and drop sizes are possible with differential reflectivity radar measurements.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Upper Atmosphere Structure and Dynamics

2. PRINCIPAL INVESTIGATOR: Dr. Gene E. Tallmadge
Radio Physics Laboratory
SRI International
333 Ravenswood Ave
Menlo Park, CA 94025

3. INCLUSIVE DATES: 1 July 1981 - 30 September 1982

4. INSTRUMENT NUMBERS: AFOSR-ISSA-81-00039
AFOSR-ISSA-82-00042

5. COSTS AND FY SOURCE: $30,000, FY 81; $40,000, FY 82

6. SENIOR RESEARCH PERSONNEL:

Dr. R. I. Presnell	Dr. N. S. Stafford

7. PUBLICATIONS:

"Upper Atmosphere Structure and Dynamics," G. E. Tallmadge, Final Technical Report, National Science Foundation Grant ATM-8025353 (1982).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This funding was in partial support of a $700,000 grant to SRI from NSF for upgrading of the VHF radar of the Jicamarca Radio Observatory in Peru. The radar transmitter bandwidth and peak transmitted power were increased by modifying the last two amplifier stages of the transmitter and adding a penultimate driver stage. One of the final amplifer cavities was modified to accommodate a modern EIMAC 8973 tetrode tube in place of the obsolete original RCA 6949 triode power tube. The result of this work was the restoration of the original 6 MW peak transmitted power and improved reliability of the transmitter. The value of this facility in ongoing and future ionospheric research is thus enhanced.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Latitudinal Variations of Auroral-Zone Ionization Distribution

2. PRINCIPAL INVESTIGATOR: Dr. James F. Vickrey
   Radio Physics Laboratory
   SRI International
   Menlo Park, CA 94025

3. INCLUSIVE DATES: 1 December 1979 - 30 November 1982

4. CONTRACT NUMBER: F49620-80-C-0014

5. COSTS AND FY SOURCE: $59,500, FY 80; $66,747, FY 81; $125,090, FY 82; $10,224, FY 83

6. SENIOR RESEARCH PERSONNEL:

Dr. R. R. Vondrak	Dr. C. L. Rino
Dr. R. T. Tsunoda	

7. JUNIOR RESEARCH PERSONNEL:

S. J. Matthews	R. Robinson

8. PUBLICATIONS:

"A Review of High-Latitude Ionospheric Irregularities-Experimental Results," J. F. Vickrey, IAGA Fourth Scientific Assembly, Edinburgh, Scotland (1981).

"Recent Results in Auroral-Zone Scintillation Studies," C. L. Rino and J. F. Vickrey, URSI, XXth General Assembly, Washington, DC (1981).

"Irregularities and Instabilities in the Auroral F-Region," J. F. Vickrey and M. C. Kelley, Nobel Symposium on Problems in High-Latitude Magnetospheric/Ionospheric Plasma Physics and Strategies for the Solution, Kiruna, Sweden (1982).

"Structured Plasma in the Auroral Ionosphere," J. F. Vickrey and M. C. Kelley, Intl. Conf. on Plasma Physics, Goteborg, Sweden (1982).

"Joint Incoherent-Scatter and Scintillation Observations of High Latitude Ionospheric Irregularities - Implications for Global Morphology," J. F. Vickrey and C. L. Rino, URSI International Symposium on Radio Probing of the High-Latitude Ionosphere and Atmosphere: New Techniques and New Results, Fairbanks, Alaska (1982).

"Irregularities and Instabilities in the Auroral F-Region," J. F. Vickrey and M. C. Kelley, High Latitude Space Plasma Physics, (Plenum Publishing Corp., New York, NY), 95 (1983).

"The Diurnal and Latitudinal Variation of Auroral-Zone Ionospheric Conductivity," J. F. Vickrey, R. R. Vondrak, and S. J. Matthews, J. Geophys. Res., 86, 65 (1981).

"On the Origin and Spatial Extent of High Latitude Irregularities," M. C. Kelley, J. F. Vickrey, C. W. Carlson and R. Tobert, J. Geophys. Res., 87, 4469 (1982).

"The Effects of a Conducting E-Layer on F-Region Cross-Field Plasma Diffusion," J. F. Vickrey and M. C. Kelley, J. Geophys. Res., 87, 4461 (1982).

"Energy Deposition by Precipitating Particles and Joule Dissipation in the Auroral Ionosphere," J. F. Vickrey, R. R. Vondrak and S. J. Matthews, J. Geophys. Res., 87, 5184 (1982).

"High Latitude F Region Irregularities Observed Simultaneously with ISIS 1 and the Chatanika Radar," D. B. Muldrew and J. F. Vickrey, J. Geophys. Res., 87, 8263 (1982).

"Recent Results in Auroral Zone Scintillation Studies," C. L. Rino and J. F. Vickrey, J. Atmos. Terr. Phys., 44, 875 (1982).

"HF Ray Tracing in the Auroral Zone Using Measured Meridional Electron Density Distributions," J. P. Villain, R. A. Greenwald, and J. F. Vickrey, Radio Sci. (1982), submitted.

"Evidence of East-West Structure in Large-Scale Auroral F-Region Ionization Enhancements," R. T. Tsunoda and J. F. Vickrey, J. Geophys. Res. (1983), submitted.

"Relative Contribution of Ionospheric Conductivity and Electric Field to the Auroral Electrojets," Y. Kamide and J. F. Vickrey, J. Geophys. Res., 88, 7989 (1983).

"Variability of the Harang Discontinuity as Observed by the Chatanika Radar and the IMS Alaska Magnetometer Chain," Y. Kamide and J. F. Vickrey, Geophys. Res. Lett., 10, 159 (1983).

"On the Latitudinal Variations of the Ionospheric Electric Field During Magnetospheric Disturbances," C. A. Gonzales, M. C. Kelley, R. A. Bahnke, J. F. Vickrey, R. Wand, and J. Holt, J. Geophys. Res., 88, 9135 (1983).

"Low Altitude Image Striations Associated with Bottomside Equatorial Spread F - Observations and Theory," J. F. Vickrey, M. C. Kelley, and R. Pfaff, J. Geophys. Res. (1983), accepted.

"Electric Conductivities, Electric Fields, and Auroral Particle Energy Injection Rate in the Auroral Ionosphere and Their Empirical Relations to the Horizontal Magnetic Disturbances," B.-H. Ahn, R. M. Robinson, Y. Kamide, and S. -I. Akasofu, Planetary and Space Science, 31, 641 (1983).

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

I INTRODUCTION

The research has been concentrated in two broad areas: (i) the electrodynamics and structure of the auroral E layer, and (ii) the origin, evolution, and morphology of high-latitude F-region plasma density structure. The principal experimental resource used in this research has been data collected with the Chatanika incoherent-scatter radar; however, ancillary measurements from rockets and satellites have been used where appropriate. In addition to experimental investigations, we have contributed new theoretical concepts in the areas of cross-field plasma diffusion and global plasma-density irregularity morphology.

II AURORAL E-REGION STUDIES

The auroral E-region studies were principally based on eight days of synoptic Chatanika radar data in which the radar beam scanned the magnetic meridian. The days represent a variety of seasonal and magnetic conditions. With this technique, the radar is able to measure the altitude-latitude distribution of electron density and line-of-site plasma drift, from which the electric field, conductivity, and current are determined. From many such successive scans, the latitude-local time variations of the auroral ionosphere may be determined. Although the limits of the scans vary slightly from one experiment to another, gathering useful data to a minimum elevation angle of 15° is generally possible. Thus, at the 100-km altitude, geomagnetic latitudes from 62° to 68° are scanned.

A. Auroral Zone Ionospheric Conductivity

A key element in modeling the magnetosphere-ionosphere circuit is the auroral zone ionospheric conductivity because it represents the "load" on the magnetospheric generator and, in large part, determines the ionospheric closure path for field-aligned currents. A consistent description of the gross, large-scale features of auroral zone conductivity morphology is beginning to emerge. These observations, as well as those of others, indicate, however, that the temporal and spatial microstructure of high-latitude ionospheric phenomena seldom shows consistently repeatable patterns, particularly during substorms. Among the conductivity patterns that seem typical are:

(1) During the daytime ($\chi \lesssim 87^{o}$), the solar contribution to conductivity is well represented by $\Sigma p = 5 \cos^{1/2}(\chi)$ and $\Sigma_H = 10 \cos^{1/2}(\chi)$, where χ is the solar zenith angle. These conductivities can be considered as the minimum present, with substantial increases occuring during substorms.

(2) The nighttime height-integrated Hall and Pedersen conductivities within the diffuse aurora are generally 4 mho to 12 mho and 2 mho to 6 mho, respectively. South of the diffuse aurora, within the trough, they are at times < 0.5 mho. During substorms, the Hall and Pedersen conductivities increase to values exceeding 50 mho and 25 mho, respectively.

(3) The typical latitude/local-time precipitation pattern expands southward during substorm conditions and intensifies, thus enhancing the ionospheric conductivity. Later, as the recovery phase begins, the precipitation pattern contracts northward and diminishes. The precipitation onset and cessation can, at times, be as abrupt as a few minutes.

(4) The southern boundary of the diffuse aurora in the midnight sector moves equatorward with increasing magnetic activity.

B. Relationship Between Ionospheric Conductivity and Birkeland Currents

Triad satellite field-aligned current measurements were combined with Chatanika radar electron-density measurements to study the latitudinal distribution of conductivity in the various field-aligned current regions. In the Region 2 field-aligned current sheet of the evening sector, the Pedersen conductivity increases linearly with latitude across the current sheet. The value of the Pedersen conductivity at the equatorward edge of the sheet varied inversely with the width of the current sheet. Also, the total change in Pedersen conductivity was large if the conductivity at the equatorward edge was small. In Region 1, enhanced conductivities were found more often in the poleward portion of the current sheet. In the Region 2 current sheet of the morning sector, the Pedersen conductivity was between 8 and 16 mho and relatively uniform across the current sheet. The Hall conductivity was higher and showed much larger latitudinal variations. The ionization in the Region 2 current sheet of the morning sector was produced by precipitating electrons from a Maxwellian source of density between 0.3 and 0.5 cm^{-3}. This source was hotter and denser than the source of precipitation in the Region 2 current sheet of the evening sector. When incorporated into auroral electrodynamic models, these results may be important in realistically accounting for observed variations in electric field and current.

C. Relative Contributions of Conductivity and Electric Field to the Auroral Electrojets

A fundamental question of auroral physics is whether the magnetosphere is a constant-voltage source or a constant-current source. Examination of the relationships between the magnitude of the electrojet currents and the electric field and conductivity, combining Chatanika radar profiles of electric field and conductivity versus latitude with data from the Alaska magnetometer chain, determined that the character of the electrojets is a function of local time. In the region of moderate-to-large eastward electrojet ($j_x \gtrsim 0.2$ A/m) in the evening sector, the northward electric field is the main contributor to the magnitude of electrojet current, in the sense that the field magnitude is larger compared with the southward field magnitude in the westward electrojet. However, when the eastward electrojet is very weak, say $j_x > 0.2$ A/m, the electric field can maintain a reasonably large value of 10 to 20 mV/m. Thus, the intensification of an already moderate eastward electrojet seems principally to be caused by an enhancement of the northward electric field. If the eastward electrojet current density is very small, however, any increase or decrease may depend on small changes (maximum 10 mho) in the Hall conductivity.

That the westward electrojet seems to have two modes: one in which the contributions to the electroject magnitude are "conductivity dominant," and the other in which the contributions to the electrojet magnitude are "electric-field dominant." Statistically, the westward electrojet near midnight and in early morning hours is principally characterized by the relatively high Hall conductivity, whereas the westward electrojet in the late morning sector is dominated by the large southward electric field. The latter behavior is similar to that of the eastward electrojet in the evening sector, although the sense of the electric field is reversed. However, an important difference is that the Hall conductivity can become high in the late morning westward electrojet (as high as 50 mho) while the maximum conductivity for the evening eastward electrojet was less than 20 mho in our data set. In other words, both the southward field and the Hall conductivity appear to be important contributors to the intense westward electrojet in the late morning sector.

D. Variability of the Harang Discontinuity

Traditionally, the Harang discontinuity has been defined in terms of ground magnetic-field variations. Often, the electrojet currents are assumed Hall currents; hence, the current reversal coincides with the reversal of the convection electric field. For purposes of modeling, the reversal of the electric field is of greater significance because the physical processes occurring within the Harang discontinuity can be most effectively understood in terms of electric-field signatures. The Chatanika observations and Alaska magnetometer chain data made possible a comparison of the electric-field signatures and ground magnetic fluctuation signatures of the Harang discontinuity.

The Harang discontinuity, as defined by the reversal of the north-south electric field, is 1 to 2° poleward of the discontinuity identified by ground magnetic perturbations. During relatively quiet times and the early stage of a substorm, a conductivity enhancement occurs only on the poleward side of the Harang discontinuity defined by the electric-field reversal, whereas the enhancement surges equatorward extending beyond the discontinuity during the maximum to recovery phase of a substorm.

E. Energy Deposition by Precipitating Particles and Joule Dissipation in the Auroral Ionosphere

The contribution to high-latitude thermospheric heating by particle precipitation and Joule dissipation of electric fields often dominates the direct solar EUV input. This energy deposition by particles and electric fields, which can be highly structured, spatially and temporally, can perturb the atmospheric electron density, ion composition, electron and ion temperatures, and neutral air motion. (Joule heating preferentially heats ions while precipitating electrons preferentially heat thermal electrons through the production of low-energy secondaries; hence the thermospheric response to, and the altitude of, energy deposition may be different for the two sources.) Because the day-to-day variability of auroral phenomena is very large, any particular day's data may appear quite different from any composite characterization. Nevertheless, a characterization of the morphology of auroral energy deposition is as follows:

(1) The Joule heating rate and the precipitating particle energy deposition rate increase with increasing electrojet current, i.e., with increasing substorm intensity.

(2) The pattern of precipitating particle energy deposition in the auroral zone moves rapidly southward and intensifies during a substorm, recedes northward,and diminishes during the substorm recovery phase.

(3) The particle energy deposition rate associated with the morning-sector westward electrojet is higher than that for the evening-sector eastward electrojet.

(4) The rate of increase in particle energy deposition with increasing westward electrojet current equals to or exceeds that for an eastward electrojet current.

(5) The Joule heating rate for a given magnitude of electrojet current is higher in the evening-sector eastward electrojet than in the morning-sector westward electrojet.

(6) The rate of increase of Joule heating with electrojet current intensity is larger for an eastward electrojet than for a westward electrojet.

(7) Joule heating generally dominates particle energy deposition in the premidnight sector. However, the daily averages of both energy inputs are roughly equal.

(8) Energy is deposited by both Joule heating and precipitating particles at lower altitudes in the morning sector than in the premidnight sector.

Banks' description of the Joule heating pattern as "horseshoe shaped" and corresponding to the auroral oval with a minimum in the midnight sector is generally valid for both particle precipitation and Joule heating. However, the Harang discontinuity, where the minimum of Joule heating occurs, can be very narrow in local time. Moreover, if a substorm occurs near local midnight, there may be no minimum at all. Perhaps more importantly, the horseshoe must be viewed as asymmetrical with respect to local midnight. The opposing asymmetries of particle and Joule heating are self-consistent when viewed in terms of the change in ionospheric conductivity between the evening and morning sectors. Morning-sector precipitation tends to be harder than evening-sector precipitation, and thus enhances the Hall-to-Pedersen conductivity ratio (see Section II.A.). As a result, the westward electrojet current vector is more nearly perpendicular to the electric field, and therefore less dissipative than is the eastward electrojet current.

III AURORAL F-REGION IONIZATION STRUCTURE

The plasma in the auroral F layer is structured horizontally (perpendicularly to the earth's magnetic field) on scales ranging from tens of kilometers to meters. This structure can result from a variety of sources, including structured particle precipitation, structured electric-field patterns, and plasma instabilities. The great range of irregularity scale sizes present in the auroral F region makes it necessary to combine different experimental techniques. For example, the Chatanika incoherent-scatter radar can resolve irregularities of about 10-km scale size. Scintillation measurements are sensitive to irregularities in the medium scale regime ($\lesssim 1$ km), and in situ probes can resolve structure down to meters. These F-layer studies have benefitted greatly from drawing upon all of these techniques and we foresee that future studies, by necessity, will also require multi-instrument observations.

A. A Model of High-Latitude Irregularity Morphology

A simple model of irregularity morphology at high latitudes based on specifying (i) the "source function" in latitude and local time of irregularity production, (ii) the (scale-size dependent) lifetime of irregularities once produced, and (iii) the redistribution of irregularities by convection during their lifetime. Although this model framework is simple, it has proven very useful in the interpretation of a wide range of observations. For example the model reproduces the following key aspects of irregularity morphology:

(1) Observations of irregularities throughout the polar regions.

(2) A reduction of irregularity amplitude in the central polar cap.

(3) A steep gradient in irregularity intensity at the equatorward edge of the nighttime magnetospheric convection zone.

(4) An asymmetry between the dusk and dawn sectors of the equatorward boundary of the high-latitude irregularity zone during magnetically quiet times.

Because F-region irregularities are observed over a much larger area of the polar ionosphere than is structured precipitation, convection must play an important role in distributing these irregularities. However, because the diffusive lifetime of irregularities is proportional to the square of the scale size, 100-m scale structures cannot survive the transit of the polar cap without an additional production source. The $\bar{E} \times \bar{B}$/current convective instability, which can be driven by field-aligned currents, electric fields, or both, may be the key process that provides a source of wave energy at the intermediate scale and that drift waves play an important role at smaller scales. The lifetime of large-scale (10-km) irregularities may be reduced slightly below that expected from classical diffusion, but not enough to prevent their crossing the polar cap. On the other hand, these combined processes increase the time during which smaller-scale structure is observed in the plasma.

B. E-Region Effects on F-Region Cross-Field Diffusion

The dominant process involved in determining the lifetime of F-region irregularities is the diffusion of plasma across magnetic field lines. Because these field lines electrically couple the E and F regions, the plasma populations in the two zones interact. Thus, the presence of a dense E region, as is often the case in the auroral zone, can strongly affect the F-region diffusion rate, and, hence, the lifetime of F-layer irregularities. A simple model of classical cross-field diffusion that includes E-region coupling shows that:

(1) The classical cross-field plasma diffusion rate in the F-region ionosphere can be increased by an order of magnitude or more when the magnetic field lines connect to a highly conducting E layer below.

(2) The cross-field diffusion rate is strongly affected by the height of the F layer and the ratio of E- to F-region Pedersen conductivities.

(3) The presence of a conducting E region slows instability growth and limits the lifetime of small-scale F-region irregularities, once their production source is removed, but does not prevent the routine operation of instabilities in the high-latitude ionosphere.

(4) E-region image striations tend to slow F-region diffusion but are themselves damped by recombination if the background E-region electron density exceeds a value, n_c, given by $n_c \approx 2 \times 10^4/\lambda^2$ cm^{-3}, where λ is measured in kilometers.

A simple linear model of image formation, developed to further examine image striations, shows that this process is scale size selective. By comparing the model to equatorial rocket measurements it was shown that the spectrum of density structure observed off the magnetic equator is consistent with that expected from the image formation process (which depends on scale size and density) driven by the gravitational Rayleigh-Taylor instability operating on the bottomside F layer at the equator itself.

C. Coordinated Radar Measurements with ISIS 1

In addition to the studies involving only the radar data (and to some extent plasma theory), coordinated measurements were conducted with the Chatanika radar and the ISIS 1 satellite. These simultaneous measurements include the topside sounder and cylindrical electrostatic probe (CEP) when the satellite was at a height of about 700 m.

Two scatter signatures observed on the ISIS ionograms were associated with two particular large-scale irregularities that were identified in the radar data. The scattering detected by the sounder was caused by 30-to-60-m wavelength irregularities (small scale) that presumably were created by instabilities operating on the edges of the large-scale irregularities. The small scale irregularities, however, were observed outside the region in which the gradient-drift instability operates. These irregularities thus either convected to the point of observation or were field-aligned extensions of irregularities generated at lower heights. A statistical study using ISIS 1 data indicated that spread F caused by irregularities near the satellite height have, in general, a sharp equatorial boundary that tends to occur a few degrees equatorward of the region where keV electrons precipitate. This agrees with the modeling results described in Section III-A.

D. East-West Structure in the Auroral F-Region

As has been alluded to in the earlier discussion, large-scale plasma density enhancements appear to be an integral feature of the auroral F region. These enhancements, also known as "blobs," were initially discovered and studied using Chatanika radar data that were taken with the radar scanning the magnetic meridian. Although these early studies provided a great deal of information on the latitudinal structure of the enhancements, they were not optimized for detecting east-west structure.

A campaign to measure and study the east-west structure of the enhancements in November 1981 shown that the zonal density gradients are generally less steep than meridional ones, but, nevertheless, can be significant. In one particular enchancement, the observed longitudinal structure was consistent with production by precipitation at the largest scales ($\gtrsim$ 500 km) and by the gradient drift instability at scale sizes of $\sim$150 km. Although the smaller scale structure was consistent with the gradient drift process, it may have also been produced by structured precipitation. The resolution of which process is dominant will require experiments that combine in situ particle detector data with the radar measurements.

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

COMPLETED PROJECT SUMMARY

1. TITLE: A Systematic Study of Light Scattering by Irregularly Shaped Particles

2. PRINCIPAL INVESTIGATORS: Dr. Ru T. Wang
Dr. Donald W. Schuerman (Deceased)
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3. INCLUSIVE DATES: 1 March 1981 - 30 September 1983

4. INSTRUMENT NUMBERS: AFOSR-MIPR-81-00022; AFOSR-MIPR-82-00052; AFOSR-MIPR-83-00063 to Army Research Office

5. COST AND FY SOURCE: $49,422, FY 81; $30,000, FY 82; $30,000, FY 83

6. SENIOR RESEARCH PERSONNEL:

Dr. B. Gustafson	Dr. J. Weinberg

7. JUNIOR RESEARCH PERSONNEL:

R. Mitchell	S. S. Hong

8. PUBLICATIONS:

"Microwave Analog and Theoretical Light-Scattering Results for Ensembes of Identical Disks, Cylinders, and Spheroids," D. W. Schuerman, R. T. Wang, B.A.S. Gustafson, and R. W. Schaefer, Proc. of the 1981 CSL Sci. Conf. on Obscuration and Aerosol Research, R. Kohl, Ed., U.S. Army Chemical Systems Laboratory, Aberdeen, MD (1982).

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"Dependence of Side Scattering by an Ensemble of 43 Cylinders on Their Configuration," B.A.S. Gustafson, Aerosol Science and Technology, 2, 161, (1983).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Under joint support by AFOSR and Army Research Office, work being done by Dr. Donald Schuerman, Dr. R. T. Wang, and others at State University of New York at Albany was resumed following the move of the Principal Investigator and the microwave analog measurement facility to University of Florida. Dr. Wang assumed leadership of the research following the untimely death of Dr. Schuerman. The goal of this research was to define the information content of scattered visible and infrared radiation. Issues included (1) the physical nature of dust particles as deduced from scattered radiation, (2) applicability of spheroid scattering theory to the interpretation of measurements, and (3) the uniqueness of particular "signatures" in the scattered radiation. Scattering from micrometer-sized and smaller particles is scaled to a wavelength of 3.18 cm, so that objects with dimensions of a few centimeters can be constructed, mounted, and controlled for the scattering measurements.

Measurements conducted under this grant included scattering from various configurations of 2, 4, and 8 spheres as a function of their mutual separation and scattering from aggregates of particles. A series of measurements was made to evaluate the effects of surface roughness and to better define the joint roles of particle shape and roughness in the scattering process. Effects of refractive index were studied both by measurements and by calculations from scattering theory.

Several important results have emerged from this research.

a. Unless a non-sphere possesses unusually high refractive index or aspect ratio, its volume-equivalent extination efficiency can be predicted by Mie theory for the equal-volume sphere to within 16%, provided that the volume-equivalent phase shift parameter falls within a specified range.

b. Significant departures from the Mie theory prediction occur beyond the first major resonance (for relatively large particles) and near the Rayleigh scattering region (for relatively small particles). Non-spheres can thus have significantly higher extinction efficiencies than spheres of comparable volume.

c. Effects of sharp edges and interstices on scattering were found to be more pronounced than expected, especially in the orientation-dependence of polarization by extinction.

d. Close similarities exist between light-wave and scalar-wave extinction efficiencies for spheres with low refractive indices.

e. For randomly oriented spheroids of low refractive index, the Eikonal Approximation was found to be a powerful method in estimating the extinction signatures.

f. For some aggregated particles, signatures of angular scattering can be approximated very well by an interference theory using only four dominant parameters.

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

COMPLETED PROJECT SUMMARY

1. TITLE: Phase Fluctuations of Transionospheric Signals Under Multiple Scattering Conditions

2. PRINCIPAL INVESTIGATOR: Dr. Bruce J. West
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3. INCLUSIVE DATES: 1 May 1980 - 30 April 1983

4. GRANT/CONTRACT NUMBER: AFOSR-80-0187 and F49620-82-C-0058

5. COSTS AND FY SOURCE: $45,248, FY 80; $68, 903, FY 81; $31,400, FY 82; $41,017, FY 83

6. SENIOR RESEARCH PERSONNEL: Dr. V. Seshadri

7. PUBLICATIONS:

"Brownian Motion of Harmonic System with Fluctuating Parameters. III. Scaling and Moment Instabilities," K. Lindenberg, V. Seshadri, and B. J. West, Physica, 105A, 445 (1981).

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"Fractal Phase Screens," B. J. West, Final Technical Report, to be published.

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8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this study was to develop theoretical concepts that would be of assistance in understanding the statistical properties of the fluctuations in the ionospheric plasma density. A path integral approach was suggested to analyze the scintillation statistics of radio waves propagating through the ionosphere. In addition, the application of scaling concepts in the statistical distribution formation was also suggested as a way of characterizing the multi-scale nature of the ionosphere fluctuations. These analyses show that the weak scatter theory is not universally applicable. A comparison of Born and Rytov weak scatter calculations showed the latter to be superior. However, of more interest in these studies has been the statistical properties of systems having fluctuations spanning a number of decades in scale.

The instabilities in the ionospheric plasmas lead to a power law spectrum of fluctuations in the electron density. These fluctuations induce random scintillation of the phase and amplitude of electromagnetic signals propagating through the ionosphere. The power law scintillation spectrum for radio waves is observed to make a transition from a k^{-3} spectrum to a high frequency plateau in which the slope of the scintillation spectrum is significantly different. We have demonstrated how a multi-scale medium such as the ionosphere can give rise to a power law spectrum of the radio wave scintillations. In the model of plasma fluctuations discussed in this study, we show how a superposition of Gaussian spectra for the electron density fluctuations can yield a power law spectrum of the form $k^{-\mu-2}$. The quantity μ is the intermittency parameter. The high frequency plateau of the scintillation spectrum is explained herein as a transition from a $k^{-\mu-2}$ to a $k^{\mu-2}$ spectrum due to the effects of small-scale irregularities in the plasma. The small scale irregularities give rise to saturated scattering, as opposed to the unsaturated scattering generated by the large-scale irregularities.

The prototypical propagation problem in the phase screen approximation is that of a plane wave emergent from a scattering layer modeled as a boundary value problem. The wave is specified at $z = 0^+$ by a unit amplitude and a phase prescribed by a homogeneous isotropic random function with a power law spectrum and Gaussian statistics. This power law spectrum results directly from the electron density fluctuations in the ionosphere. The statistics of the wave propagating in free space away from the boundary cannot be Gaussian, except perhaps in the far field where the scattering is saturated. Further, the amplitude and intensity spectra of this wave each satisfy specific scaling relations. Such a wave is called a diffractal. A study of the scintillation index S_4 indicates that a diffractal is a reasonable model of a radio wave passing through the ionosphere as in satellite communication.

The above scintillation results are contingent on the power law form of the plasma fluctuations. A modest study was made, in which a recently developed theory of the properties of stochastic differential equations for complex systems was applied to the tearing-mode instability observed in Tokamak operation. The experimentally observed power law for the fluctuations was properly predicted by the theory, but the theory has not as yet been applied to the geophysical problem of interest.

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

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