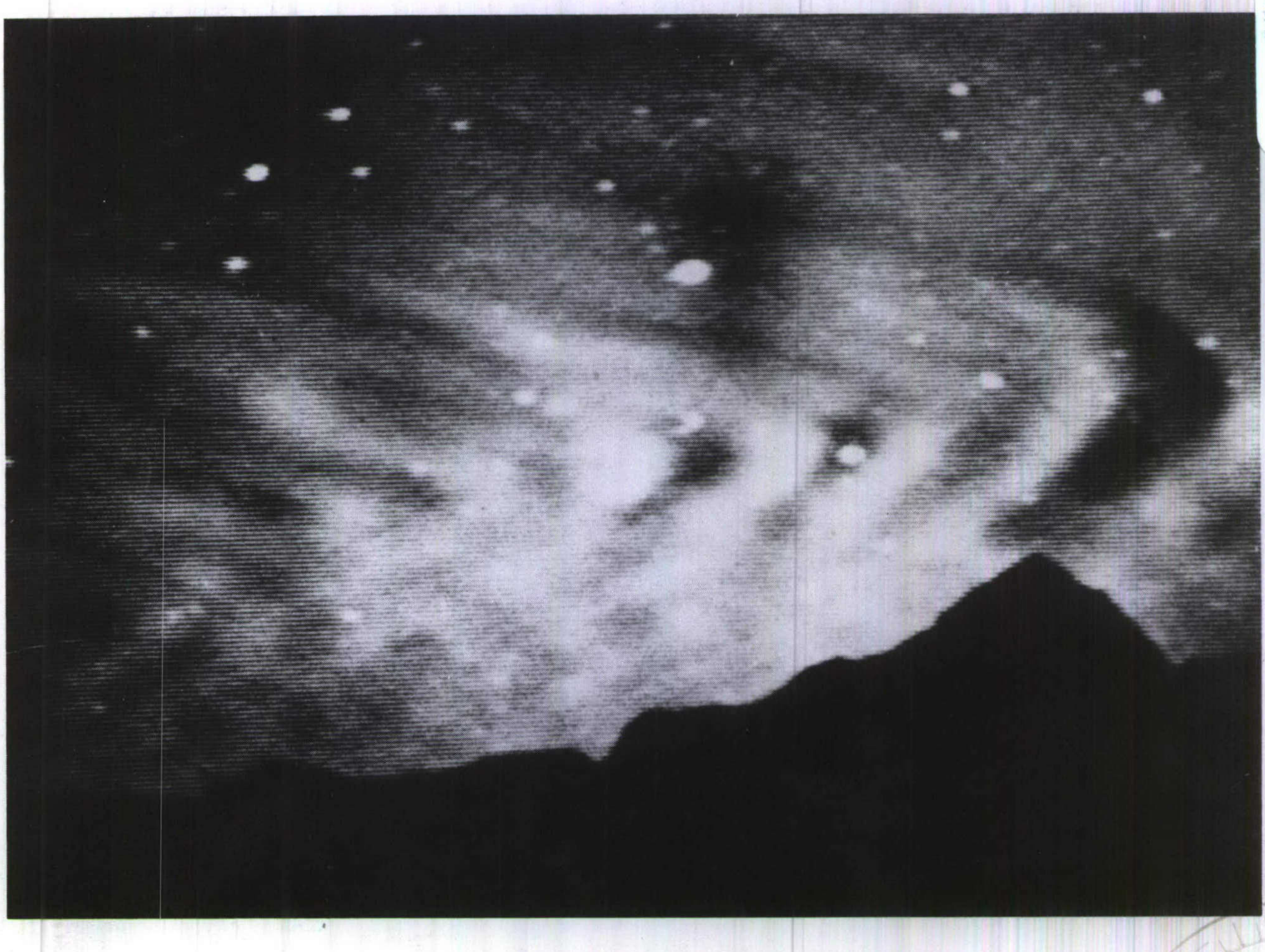
# CHEMICAL & ATMOSPHERIC SCIENCES
# FY-88 REVIEW



AFGL/AFOSR MIDDLE ATMOSPHERE PERIODIC STRUCTURE-ASSOCIATED RADIANCE (MAPSTAR) PROGRAM FOR UNDERSTANDING PERIODIC STRUCTURE IN THE INFRARED RADIANCE OF THE MIDDLE ATMOSPHERE. WAVE-LIKE OSCILLATIONS APPEAR IN IR IMAGE OF THE EARTH'S MIDDLE ATMOSPHERE (APPROX 90 KM ATTITUDE)

USAF 33rd edition

# COVER

Cover photo shows an IR image of the earth's middle atmosphere. The bright area of the sky is caused by OH and OI emissions near 85 to 95 km altitude (near the boundary between the mesosphere and thermosphere). These waves could have significant impact on IR surveillance systems and are the subject of the middle atmospheric periodic-structure-associated radiance (MAPSTAR) research task at AFGL, sponsored by AFOSR. Visible in this image are a series of waves that appear to be concentric on a point somewhere to the left of the photograph. The source of these types of waves is still somewhat a mystery. Recent studies, however, present strong evidence that disturbances in the lower atmosphere are often the ultimate cause. One such study of the event shown in the cover photo pinpoints a particularly vigorous thunderstorm as the source. In that case it appears that the storm punched into the stratosphere and set off a series of gravity waves. These waves then propogated upward into the mesosphere and caused the pattern seen in the photo.

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A review is presented of research efforts sponsored by the Directorate of Chemical and Atmospheric Sciences which have completed their period of support. Illustrated accounts resulting from the basic research programs in the Atmospheric and Chemical Sciences are highlighted. The Atmospheric Sciences is concerned with meteorology and upper atmospheric structure and dynamics. The Chemical Sciences deal with chemical techniques, chemical structures, surface chemistry, chemical dynamics, synthesis and properties of materials, and computational chemistry.

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# 33RD AFOSR
# CHEMICAL AND ATMOSPHERIC SCIENCES
# PROGRAM REVIEW
# FY88

FRANCIS J. WODARCZYK, EDITOR
CATHERINE B FAUSTMAN, MANAGING EDITOR
JULY 1990

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
DIRECTORATE OF CHEMICAL AND ATMOSPHERIC SCIENCES
BUILDING 410
BOLLING AIR FORCE BASE
WASHINGTON, DC 20332-6448

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# EDITORS' FOREWORD

The format of this 33rd edition of the Chemical and Atmospheric Sciences Review is similar to that of the 32nd edition. Included is a short assessment of each program area by program manager. We have organized the active research programs and completed project summaries by program area. This will help users of the review to locate material most relevant to their interests. We invite your comments and suggestions on methods to improve our Chemical and Atmospheric Sciences Review. The program review request for this purpose is below. Please return if you wish to continue to receive the program review in the future or additional copies.

The editors wish to thank all of the Directorate of Chemical and Atmospheric Sciences staff for their assistance in preparing this document. Major Richard M. Guidry and Lt Col James P. Koermer helped with much of the initial editing of this document. Special thanks go to our secretarial staff for the long hours and dedication to completion of this year's review.

Francis J. Wodarczyk

Francis J. Wodarczyk

Catherine B. Faustman

Catherine B Faustman

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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.

July 1990

Dear Reader

This issue of our Program Review once again summarizes our ongoing program of research together with indications of planned changes in emphasis. Since the mid 1950's we have produced this report to acquaint the scientific public with just what we have done and what we feel the future holds. It has taken a lot of effort over the years, but we think it's worth it. We hope that you will let us know what you think when you return the survey request provided in this volume on page 1.

Sincerely

Donald L Ball

DONALD L. BALL
Director of Chemical and
Atmospheric Sciences

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Operating Under Contract
F49620-87-C-0120 with National
Research Council
Principal Investigator:
Dr Robert Simon
Board on Chemical
Science and Technology
National Academy of Sciences
2101 Constitution Avenue
Washington, DC 20418

## CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY88 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.

### Mini-Conference on Key Problems in Silicon Chemistry

8-9 October 1987
US Air Force Academy, Colorado Springs, CO
Sponsored by - North Dakota State University
Fargo, ND 58105

### Joint International Symposium on Molten Salts

18-23 October 1987
Honolulu, HI
Sponsored by - The Electrochemical Society
Pennington, NJ 08534-2896

### Symposium on Spectroelectrochemistry and Electroanalytical Science

18-23 October 1987
Honolulu, HI
Sponsored by - The Electrochemical Society, Inc
Pennington, NJ 08534-2896

### Microstructure and Properties of Catalysts

30 November 2 December 1987
Boston, MA
Sponsored by - Materials Research Society
Pittsburgh, PA 15237

### Polymer Surfaces, Interfaces and Adhesion

30 November - 4 December 1987
Boston, Massachusetts
Sponsored by - Materials Research Society Fall 87 Meeting
Boston, Massachusetts

### Nonlinear Optical Properties of Polymers

30 November - 5 December 1987
Boston Massachusetts
Sponsored by - Materials Research Society
Boston, Massachusetts

### 1988 Gordon Conference on Polymers (West)

4-8 January 1988
Sheraton Hotel, Ventura, CA

### 1988 Sanibel Symposia

12-19 March 1988
Whitney Marine Laboratory, Marineland FL
Sponsored by - University of Florida
Gainesville, Florida 32611

### Symposium on Better Ceramics Through Chemistry III

5-8 April 1988
Reno Nevada
Sponsored by - Materials Research Society
Pittsburgh, PA

### Organic and Polymeric Nonlinear Optical Materials

16-19 May 1988, Cavalier Hotel
Virginia Beach, VA
Sponsored by - American Chemical Society, Polymer Division

### Joint Workshop on Interface Phenomena: Adhesion and Friction

23-27 August 1988
Dalhousie University, Halifax, Nova Scotia, Canada
Sponsored by - University of Maine, Dalhousie University

# ACTIVE RESEARCH EFFORTS

## CHEMISTRY

As of 30 September 1988

Alphabetically by Principal Investigator

### CHEMICAL TECHNIQUES - DR JOHN S. WILKES

| | |
|---|---|
| Fundamental Studies of Surface Processes and Trace Analysis Using Solid Electrodes<br>AFOSR-87-0037 | Stanley Bruckenstein<br>Department of Chemistry<br>State University<br>of New York<br>Buffalo, NY 14214 |
| Metal/Metallion System in Low Temperature Molten Salts<br>AFOSR-88-0079 | Francis M. Donahue<br>Department of Chemical<br>Engineering<br>University of Michigan<br>Ann Arbor, MI 48109-1092 |
| X-Ray Absorption Spectroscopy of Electrochemically Generated Species<br>AFOSR-88-0089 | William R. Heineman<br>Richard C. Elder<br>Department of Chemistry<br>University of Cincinnati<br>Cincinnati, OH 45221 |
| Electrochemistry of Metal Surfaces<br>AFOSR-86-0200 | Arthur T. Hubbard<br>Department of Chemistry<br>University of Cincinnati<br>Cincinnati OH 45221 |
| Electrochemical and Spectroscopic Studies of Molten Halides<br>AFOSR-88-0307 | Gleb Mamantov<br>Department of Chemistry<br>University of Tennessee<br>Knoxville, TN 37916 |
| Ionically and Electronically Conductive Composite Polymer Membranes<br>AFOSR-87-0173 | Charles R. Martin<br>Dept of Chemistry<br>Texas A and M University<br>College Station<br>Texas 77843-3255 |
| In-Situ Laser Activation of Electrochemical Charge Transfer Kinetics<br>AFOSR-88-0071 | Richard L. McCreery<br>Department of Chemistry<br>Ohio State University<br>120 West 18th Avenue<br>Columbus, OH 43210 |
| Chemical and Electrochemical Studies in Ionic Liquids<br>AFOSR-87-0088 | Robert A. Osteryoung<br>Department of Chemistry<br>State University<br>of New York<br>Buffalo, New York 14214 |

Atomic and Molecular Gas Phase
Spectrometry
AFOSR-86-0015

James D. Winefordner
Department of Chemistry
University of Florida
Gainesville, FL  32611

# SURFACE CHEMISTRY - LT COL LARRY W. BURGGRAF, USAF

| | |
|---|---|
| Surface Intermediates in Thin Film Deposition on Silicon<br>AFOSR-86-0050 | Jay B. Benziger<br>Department of Chemical Engineering<br>Princeton University<br>Princeton, NJ 08544 |
| Mechanisms of Reactive Etching<br>AFOSR-85-0209 | Steven E. Bernasek<br>Department of Chemistry<br>Princeton University<br>Princeton, NJ 08544 |
| Picosecond Laser Studies of Energy Transfer in Molecules on Surfaces<br>AFOSR-ISSA-88-0006 | Richard R. Cavanagh<br>John C. Stephenson<br>National Bureau of Standards<br>Molecular Spectroscopy Div<br>Washington, DC 20234 |
| Charge Exchange in Ion-Surface Scattering at Hyperthermal (1-100eV) and KeV Energies<br>AFOSR-88-0069 | Barbara Cooper<br>Department of Physics<br>Cornell University<br>531 Clark Hall<br>Ithaca, NY 14853 |
| A Combined XPS-AES-ISS-SIMS-Modulated Molecular Beam Investigation of The Reactions of Oxygen and Fluorine With Silicon Surfaces<br>AFOSR-87-0166 | Thomas Engel<br>Department of Chemistry<br>University of Washington<br>Seattle, WA 98195 |
| High Resolution Electron Energy Loss Spectroscopy Studies of Chemisorbed Species on Metal Surfaces<br>AFOSR-86-0109 | James L. Erskine<br>Department of Physics<br>University of Texas<br>Austin, TX 78712 |
| Kinetics of Surface Reactions Studies by Laser Desorption With FTMS Detection<br>AFOSR-89-0019 | John C. Hemminger<br>Department of Chemistry<br>University of California<br>Irvine, CA 92717 |
| High Translational Energy Induced Reactions in Semiconductor<br>AFOSR-88-0335 | Wilson Ho<br>Department of Physics<br>Cornell University<br>120 Day Hall<br>Ithaca, NY 14853-2801 |
| Center for Surface Radiation Damage Studies<br>AFOSR-86-0344 | Laurence D. Marks<br>Department of Materials Science and Engineering<br>Northwestern University<br>Evanston, IL 60201-9990 |

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| Dynamics of Gas-Surface Interactions<br>AFOSR-88-0194 | Steven J. Sibener<br>Department of Chemistry<br>University of Chicago<br>Chicago, IL 60637 |
| Experimental and Theoretical Investigation of Photodissociation on MgO(001)<br>AFOSR-88-0297 | Peter C. Stair<br>Department of Chemistry<br>Northwestern University<br>Evanston, IL 60201 |
| Investigation of Coupled Surface and Bulk Reaction Phenomena Using CEAPS<br>AFOSR-84-0301 | Bruce J. Tatarchuk<br>Department of Chemical Engineering<br>Auburn University<br>Auburn, AL 36849 |
| Surface Reactions in the Space Environments<br>F49620-86-C-0125 | Norman H. Tolk<br>Richard F. Haglund, Jr.<br>Dept of Physics and Astronomy<br>Vanderbilt University<br>Nashville, TN 37235 |
| The Structure and Reactivity of Boron Surfaces<br>AFOSR-88-0111 | Michael Trenary<br>Department of Chemistry<br>University of Illinois at Chicago<br>P O Box 4348<br>Chicago, Illinois 60680 |
| Studies of Ions and Neutrals Desorbed from Solid Surfaces by and Electron Bombardment<br>AFOSR-85-0028 | Nicholas Winograd<br>Department of Chemistry<br>Pennsylvania State University<br>152 Davey Laboratory<br>University Park, PA 16802 |
| The Orientation of Chemical Bonds at Surfaces-A Key to Understanding The Structure and Bonding of Surface Species<br>AFOSR-86-0107 | John T. Yates<br>Department of Chemistry<br>Surface Science Center<br>University of Pittsburgh<br>Pittsburgh, PA 15260 |

## CHEMICAL STRUCTURES - DR DONALD R. ULRICH

| | |
|---|---|
| Microdesigning of Lightweight/<br>High Strength Ceramic Materials<br>AFOSR-87-0114 | Ithan A. Aksay<br>Department of Mining<br>Metallurgical<br>University of Washington<br>Seattle, WA 98195 |
| Basic Research on Processing of<br>Ceramics for Space Structures<br>F49620-84-C-0097 | H. K. Bowen<br>Materials Processing<br>Massachusetts Institute of<br>Technology<br>Cambridge, MA 02139 |
| Multifunctional Macromolecules<br>F49620-87-C-0109 | Gordon W. Calundann<br>Celanese Research Company<br>Summit, NJ 07901 |
| Surface Protected Electronic Circuits<br>F49620-86-C-0110 | Grish Chandra<br>Down Corning Corporation<br>Midland, MI 48640-0994 |
| Development of Processible Electroactive<br>Oligomers and Polymers<br>F49620-88-C-0071 | Larry R. Dalton<br>Department of Chemistry<br>University of Southern<br>California<br>Los Angeles, CA 90089-0482 |
| Design of Polymers with Semiconductor<br>NLO and Structural Properties<br>F49620-87-C-0100 | Larry R. Dalton<br>Department of Chemistry<br>University of Southern<br>California<br>Los Angeles, CA 90089-0482 |
| Fundamental Studies of Near<br>Surface Modification of<br>Carbon Fibers<br>F49620-85-C-0147 | Mildred S. Dresselhaus<br>Department of Elec Engrg<br>and Comp Science<br>Massachusetts Institute of<br>Technology<br>Cambridge, MA 02139 |
| Ordered Polymer Nonlinear<br>Optical Materials<br>F49620-88-C-0065 | Mark A. Druy<br>Foster-Miller Inc<br>350 Second Avenue<br>Waltham MA 02254 |
| FTIR Sensing of Molecular Orientation<br>for Nonlinear Optic Films<br>F49620-87-C-0075 | Mark A. Druy<br>Foster-Miller Inc<br>350 Second Avenue<br>Waltham MA 02254 |

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| Ultrastructure Processing of<br>Ordered Polymers<br>AFOSR-87-0320 | Ronald K. Eby<br>Department of Materials<br>Science<br>and Engineering<br>Johns Hopkins University<br>Baltimore MD 21218 |
| Organic Heterostructure<br>Thin Films<br>F49620-88-C-0008 | W. C. Egbert<br>Research and Development<br>Minnesota Mining and<br>Manufacture Company<br>St Paul, MN 55144 |
| X-Ray Diffraction Studies of<br>the Structure or Ordered Polymers<br>Related Electro-Active Materials<br>AFOSR-88-0044 | Albert Fratini<br>Department of Chemistry<br>University of Dayton<br>Dayton, OH 45469 |
| Molecular Optics: Nonlinear Optical<br>Processes in Organic and Polymeric<br>Crystals and Films<br>F49620-88-C-0127<br>F49620-85-C-0105 | A. F. Garito<br>Department of Physics<br>University of Pennsylvania<br>Philadelphia, PA 19104 |
| Organic and Polymeric<br>Nonlinear Optical Materials<br>AFOSR-88-0221 | Diana J. Gerbi<br>Research Specialist<br>Minnesota Mining and<br>Manufacture Co.<br>Corporate Research Labs<br>3M Center Bldg 201-2E-08<br>St Paul, MN 55144 |
| Novel Liquid Crystalline Polymers<br>As Nonlinear Optical Materials<br>F49620-88-C-0068 | Anselm C. Griffin<br>Department of Chemistry and<br>Polymer Science<br>University of Southern<br>Mississippi<br>Hattiesburg, MS 39406 |
| Multi-Investigator Research Program<br>The Science of Ultrastructural<br>Sol-Gel Materials<br>F49620-88-C-0073 | Larry L. Hench<br>Gel-Tech, Inc<br>1 Progress Blvd<br>Alachua, FL 32615 |
| Research and Development on New<br>Thermosplastic/Rigid Rod Molecular<br>Composites<br>F49620-86-C-0057 | Wen-Fang Hwang<br>Dow Chemical Company<br>Midland, MI 48640 |
| Preparation of SIC/AIN Solid<br>Solutions Using Organometallic<br>Precursors<br>F49620-85-K-0019 | Leonard V. Interrante<br>Department of Chemistry<br>Rensselaer Polytech Inst<br>Troy, NY 12180-3590 |

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| Polymer Blends<br>F49620-88-C-0014 | M. Jaffe<br>H. C. C. Celanese<br>Research Company<br>86 Morris Avenue<br>Summit, NJ 07901 |
| Fluids Gels and Glasses Under Extreme Conditions of Pressure and Temperature<br>AFOSR-87-0045<br>AFOSR-85-0345 | Jiri Jonas<br>Department of Chemistry<br>University of Illinois<br>Urbana, IL 61801 |
| Ultrastructure Processing and Characterization of Polymers<br>AFOSR-88-0046 | Frank E. Karasz<br>Department of Polymer Science and Engineering<br>University of Massachusetts<br>Amherst, MA 01003 |
| Functional Polymers and Guest-Host Polymer Blends for Optical and Electronic Applications: A Molecular Engineering Approach<br>F49620-87-C-0111 | Frank E. Karasz<br>Department of Polymer Science and Engineering<br>University of Massachusetts<br>Amherst, MA 01003 |
| URI Proposal for a Center for Advanced Electrical and Structural Polymers<br>F49620-87-C-0027 | Frank E. Karasz<br>Department of Polymer Science and Engineering<br>University of Massachusetts<br>Amherst, MA 01003 |
| Fundamental Studies of Time-Dependent Response and Fracture of Cross-Linked Polymers<br>F49620-86-C-0032 | Frank N. Kelley<br>Maurice Morton<br>Institute of Polymer Science<br>University of Akron<br>Akron, OH 44325 |
| Intelligent Processing of Materials<br>F49620-86-C-0036 | Brian G. Kushner<br>BDM Corporation<br>McLean, VA 22102-3396 |
| Microcomposite Processing and Applications<br>F49620-87-C-0022 | Richard Lusignea<br>Foster-Miller<br>350 Second Avenue<br>Waltham, MA 02254 |
| Preparation and Properties of New Inorganic Glasses and Gel-Derived Solids<br>AFOSR-88-0066 | John D. Mackenzie<br>Department of Material Science and Engineering<br>School of Engineering and Applied Science<br>University of California<br>Los Angeles, CA 90024 |

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| Third International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites<br>AFOSR-87-0085 | John D. Mackenzie<br>Department of Material Science and Engineering<br>School of Engineering and Applied Science<br>University of California<br>Los Angeles, CA 90024 |
| International Collaboration Program on Innovative Chemical Processing of Superior Electronic and Optical Materials<br>F49620-87-K-0011 | John D. Mackenzie<br>Department of Material Science and Engineering<br>School of Engineering and Applied Science<br>University of California<br>Los Angeles, CA 90024 |
| Nonlinear Optical Materials<br>F49620-86-C-0104 | Paul J. Marinaccio<br>Foster Miller, Inc<br>350 Second Avenue<br>Waltham, MA 02254 |
| PBT, PBO-Based Hybrid Polymeric Materials with Nonlinear Optical Properties<br>F49620-88-C-0122 | Tobin J. Marks<br>Stephen H. Carr<br>Department of Chemistry<br>Northwestern University<br>Evanston, IL 60201 |
| Colloid and Interface Chemistry Aspects of Ceramics<br>F49620-85-C-0142 | Egon Matijevic<br>Department of Chemistry<br>Clarkson University<br>Potsdam, NY 13676 |
| Synthesis of Polysiloxanes for Sol-Gel Glasses<br>AFOSR-86-0133 | James E. McGrath<br>Department of Chemistry<br>Virginia Polytechnic Institute and State University<br>301 Burruss Hall<br>Blacksburg, VA 24061 |
| Ceramic Processing of Structure Ceramics and Composites<br>F49620-85-C-0118 | Madan G. Mendiratta<br>Metals and Ceramics Research<br>Universal Energy Systems Inc<br>Dayton, OH 45432 |
| Design of Non-Linear Optical Materials Based on Coordination Organometallic Compounds<br>AFOSR-88-0141 | Michael P. Mingos<br>Inorganic Chemistry Lab<br>University of Oxford<br>South Parks Road<br>Oxford, GB OX13QR |
| Surface Chemistry and Structural Effects in the Stress Corrosive of Glass and Ceramic Materials<br>F49620-86-K-0005<br>F49620-88-C-0074 | Carlo G. Pantano<br>Associate Professor<br>Materials Science & Engineering<br>Pennsylvania State University<br>University Park, PA 16802 |

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|---|---|
| Molecular Engineering, Dynamics of Electron Transport and NLO Interaction in Langmuir-Blodgett Films Organic<br>F49620-87-C-0097 | Paras N. Prasad<br>Department of Chemistry<br>State University of New York<br>Buffalo, NY 14260 |
| Design, Ultrastructure, and Dynamics of Nonlinear Optical Interact Ions in Polymeric Thin Films<br>F49620-87-C-0042 | Paras N. Prasad<br>Department of Chemistry<br>State University of New York<br>Buffalo, NY 14260 |
| Linear (Passive) and Non-Linear Guided Wave Studies in Glass<br>AFOSR-88-0199 | V. Ramaswamy<br>Department of Electrical Engineering<br>University of Florida<br>Ginesville, FL 32611 |
| Chemical Like Behavior of Electrodes and Holes in Polymeric Conductors<br>F49620-86-C-0060 | Howard Reiss<br>Department of Chemistry and Biochemistry<br>University of California<br>Los Angeles, CA 90024 |
| Studies in Support of Oxidation-Resistant Composite Materials<br>F49620-86-C-0011 | George Reynolds<br>G A Technologies, Inc<br>Ceramics and Chemistry Department<br>San Diego, CA 92138 |
| Crystallization of Nanocomposite Glasses Made by the SSG Process<br>F49620-88-C-0134 | Rustum Roy<br>Materials Research Laboratory<br>Pennsylvania State University<br>University Park, PA 16802 |
| Organosilicon Polymers Incorporating the Bicyclo-(2.2.2) Octane Moiety<br>AFOSR-87-0123 | Mukund Sibi<br>Department of Chemistry<br>Atlanta University<br>Atlanta GA 30314-4391 |
| Nonlinear Optical Properties of Organic Materials<br>F49620-87-C-0115 | James Stamatoff<br>Celanese Research Company<br>Summit NY 07901 |
| Organo-Optics: Development of Improved Nonlinear Optical Materials and Related Applications Based on Organic Small Molecules and Polymers<br>F49620-86-C-0129 | James Stamatoff<br>Celanese Research Company<br>Summit NY 07901 |
| Molecular Composites from High Temperature Polyquinolines<br>F49620-86-C-0102 | John K. Stille<br>Department of Chemistry<br>Colorado State University<br>Fort Collins, CO 80523 |

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| Phase Transofmations and Structure Development from Rigid-Rod Polymer Solutions<br>AFOSR-85-0275 | Edwin L. Thomas<br>University of Massachusetts<br>Polymer Science and Energy<br>Amherst, MA 01003 |
| Ceramics Derived From Organo-Metallic Precursors<br>F49620-88-C-0064 | Donald R. Uhlmann<br>Department of Material Science<br>University of Arizona<br>Tucson AZ 85721 |
| Synthesis and Crystallization Behavior of Fluoride Glasses<br>AFOSR-86-0350 | Donald R. Uhlmann<br>Department of Material Science and Engineering<br>University of Arizona<br>Tucson, AZ 85821 |
| New Non-Linear Optical Polymers<br>F49620-88-C-0078 | Gary E. Wnek<br>Department of Chemistry<br>Rensselaer Polytechnic Institute<br>Troy, NY 12180-3590 |
| Second-Generation Ordered Polymers<br>F49620-88-K-0001 | James F. Wolfe<br>Polymer Science Department<br>SRI International<br>333 Ravenswood Avenue<br>Menlo Park, CA 94025 |
| Ordered Polymers for Space Applications<br>F49620-85-K-0015 | James F. Wolfe<br>Polymer Sciences Department<br>SRI International<br>333 Ravenswood Avenue<br>Menlo Park, CA 94025 |
| Local Structure of Network Resins<br>AFOSR-87-0220 | A. H. Windle<br>Dept of Metallurgy and Material<br>University of Cambridge<br>Cambridge UK CB2 3QZ |
| Non-Linear Optical Polymers<br>F49620-85-C-0151 | Gary E. Wnek<br>Department of Materials Science and Engineering<br>Massachusetts Institute of Technology<br>Cambridge, MA 02139 |

## MOLECULAR DYNAMICS - DR FRANCIS J. WODARCZYK

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|---|---|
| Energy Disposal in Ion-Molecule Reactions<br>AFOSR-86-0059 | Michael T. Bowers<br>Department of Chemistry<br>University of California<br>Santa Barbara, CA 93106 |
| Dynamic Constraints on Stochastic Behavior in the Chemistry Highly Excited Molecules<br>AFOSR-87-0165 | Barry K. Carpenter<br>Department of Chemistry<br>Cornell University<br>Ithaca, NY 14853 |
| Energy Flow and Decomposition of Energetic Molecules from Metastable Vibrational States<br>FOSR-ISSA-88-0001<br>AFOSR-ISSA-87-0048 | Michael Casassa<br>John Stephenson<br>Molecular Spectroscopy Div<br>National Institute of Standards and Technology<br>Gaithersburg, Maryland 20899 |
| Physical Chemistry of Energetic Nitrogen Compounds<br>AFOSR-87-0210 | R. D. Coombe<br>Department of Chemistry<br>University of Denver<br>Denver, CO 80208 |
| Collisional Energy Transfer in High Vibrationally Excited Polyatomic Molecules<br>AFOSR-86-0033 | F. Fleming Crim<br>Department of Chemistry<br>University of Wisconsin<br>Madison, WI 53706 |
| Collaborative Experimental and Theoretical Study of the Photo-Dissociation and Reactions of the Azide Radical<br>F49620-88-C-0056 | Paul J. Dagdigian<br>Department of Chemistry<br>Johns Hopkins University<br>Charles and 34th Streets<br>Baltimore, MD 21218 |
| Rotational Energy Transfer in Metastable States of Heteronuclear Molecules<br>F49620-86-C-0061 | Steven J. Davis<br>Physical Sciences Inc.<br>Research Park<br>P. O. Box 3100<br>Andover, MA 01810 |
| Rotational and Vibrational Spectra of Molecular Clusters<br>F49620-87-C-0072 | Thomas R. Dyke<br>Department of Chemistry<br>University of Oregon<br>Eugene, OR 97403 |
| Vibrationally Energized Molecules: Unimolecular Energy Flow, and Level Specific Chemistry<br>AFOSR-88-0062 | Robert W. Field<br>James L. Kinsey<br>Department of Chemistry<br>Room 6-223<br>M I T<br>Cambridge, MA 02139 |

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| Thermal Decomposition of TNT and Related Materials in the Condensed Phase<br>F49620-87-C-0003 | Ira B. Goldberg<br>Rockwell International<br>Science Center<br>1049 Camino Dos Rios<br>Thousand Oaks, CA 91360 |
| Spectroscopic Studies of the Products of the Reactions of Electronically Excited Atoms and Small Molecules<br>AFOSR-86-0123 | Michael F. Golde<br>Department of Chemistry<br>University of Pittsburgh<br>Pittsburgh, PA 15260 |
| Production and Characterization of High-Energy Hypervalent Hydrides<br>F49620-87-C-0092 | Edward R. Grant<br>Department of Chemistry<br>Purdue University<br>West Lafayette, IN 47907 |
| Relaxation Dynamics of Highly Excited Halogens in their Electronic Ground States<br>AFOSR-88-0249 | Michael Heaven<br>Department of Chemistry<br>Illinois Institute of Technology<br>Chicago, IL 60616 |
| Electronically Metastable Molecules of High Symmetry<br>F49620-87-K-0002 | Hanspeter Helm<br>Molecular Physics Department<br>SRI International<br>333 Ravenswood Ave<br>Menlo Park, CA 94025 |
| Molecular Dynamics in the Vacuum Ultraviolet<br>AFOSR-86-0017 | Paul L. Houston<br>Department of Chemistry<br>Cornell University<br>Ithaca, NY 14853 |
| Energy and Chemical Change<br>AFOSR-86-0011 | James L. Kinsey<br>Raphael D. Levine<br>Department of Chemistry<br>Massachusetts Institute of Technology<br>Cambridge, MA 02139 |
| Boron Combustion Model Development with Kinetic Sensitivity Analysis and Measurement of Key Chemical Rate Parameters<br>F49620-88-C-0048 | C. E. Kolb<br>Aerodyne Research Inc<br>45 Manning Road<br>Billerica, MA 01821 |
| State-Resolved Dynamics of Ion-Molecular Reactions in a Flowing After Glow<br>AFOSR-86-0018 | Stephen R. Leone<br>Veronica M. Bierbaum<br>Department of Chemistry<br>University of Colorado<br>Boulder, CO 80309 |
| Measurement of Radiative Lifetimes of Virbrational States of Ions<br>AFOSR-87-0390 | Rose Marx<br>Laboratoire de Physico<br>University of Paris<br>Paris, France |

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| Infrared Transition Moments and<br>Collisional Dynamics of<br>Vibrationally Excited OH Radicals<br>F49620-86-C-0056 | David Nesbitt<br>Joint Institute for<br>Laboratory Astrophysics<br>University of Colorado<br>Boulder, Colorado 80309-0440 |
| Spectroscopy of the Transition<br>State Region in Chemical Reactions<br>AFOSR-87-0341 | Daniel M. Neumark<br>Department of Chemistry<br>University of California<br>Berkeley, CA 95720 |
| Transient Behaviors in<br>Chemical Reactions<br>AFOSR-86-0054 | G. Pimentel<br>Department of Chemistry<br>University of California<br>Berkelely, CA 94720 |
| Theory and Experimental and<br>Chemical Instabilities<br>AFOSR-87-0120 | John Ross<br>Department of Chemistry<br>Stanford University<br>Stanford, CA 94305 |
| State Resolved Chemistry of<br>NF, PF, and $N_3$<br>AFOSR-88-0279 | Donald W. Setser<br>Department of Chemistry<br>Kansas State University<br>Willard Hall<br>Manhattan, Kansas 66506 |
| $NO_2$ Photodissociation Dynamics<br>F49620-87-K-0004 | Tom G. Slanger<br>Molecular Physics Department<br>SRI International<br>333 Ravenswood Avenue<br>Menlo Park, CA 94025 |
| Reactions of Laser-Generated<br>Free Radicals at Semi-Conductor<br>Surfaces<br>F49620-86-C-0003 | Jeffrey I. Steinfeld<br>Department of Chemistry<br>Massachusetts Institute of<br>Technology<br>Cambridge, MA 02139 |
| State Identification of<br>Reaction Dynamics<br>F49620-86-C-0016 | Richard N. Zare<br>Department of Chemistry<br>Stanford University<br>Stanford, CA 94305 |
| Ultrafast Chemical Dynamics<br>of Reactions in Beams<br>AFOSR-87-0071 | A. H. Zewail<br>Department of Chemistry<br>California Institute of<br>Technology<br>Noyes Laboratory 127/72<br>Pasadena, CA 91125 |

## CHEMICAL REACTIVITY AND SYNTHESIS - DR ANTHONY J. MATUSZKO

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|---|---|
| New Inorganic-Organic High Polymer Systems<br>AFOSR-84-0147 | Harry R. Allcock<br>Department of Chemistry<br>Pennsylvania State University<br>152 Davey Laboratory<br>University Park, PA 16802 |
| High Energy Molecules of High Symmetry<br>F49620-85-C-0056 | William S. Anderson<br>John Guimont<br>United Technologies Corp<br>P O Box 50015<br>San Jose, CA 95150-0015 |
| New Nitration Concepts<br>F49620-86-K-0011 | Clifford D. Bedford<br>Chemistry Laboratory<br>SRI International<br>Menlo Park, CA 94025 |
| New Approaches to the Synthesis of Novel Organosilanes<br>AFOSR-88-0060 | Philip Boudjouk<br>Department of Chemistry<br>North Dakota State University<br>Fargo, ND 58105 |
| New Approaches to Fluorocarbon Synthesis<br>AFOSR-85-0009 | Donald J. Burton<br>Department of Chemistry<br>University of Iowa<br>Iowa City, IA 52242 |
| A New Approach to Highly Fluorinated Lubricants<br>AFOSR-87-0324 | R. D. Chambers<br>Department of Chemistry<br>University of Durham<br>Durham, England DH1 3LE |
| Development of Practical MO Techniques for the Prediction of Properties and Behavior of Materials<br>AFOSR-86-0022 | Michael J. S. Dewar<br>Department of Chemistry<br>University of Texas<br>Austin, TX 78712 |
| The Synthesis and Properties of Transition Metal Complexes with Bridging Nitride Ligands<br>AFOSR-87-0362 | Nancy M. Doherty<br>Department of Chemistry<br>University of Washington<br>Seattle WA 98195 |
| Synthesis and Reactions of Cyclic Organoboranes and Carboranes<br>AFOSR-85-0108 | John J. Eisch<br>Department of Chemistry<br>State University of New York<br>Binghamton, NY 13901 |
| Picosecond Laser Studies of Chamical Intermediates<br>AFOSR-88-0014 | Kenneth B. Eisenthal<br>Department of Chemistry<br>Columbia University<br>New York, NY 10027 |

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| Biological Synthesis of<br>Substituted O-Aminophenols<br>F49620-88-C-0016 | Herman L. Finkbeiner<br>Biological Sciences Branch<br>General Electric Co<br>P O Box 8<br>Schenectady, NY 12301 |
| A Biotechnological Approach<br>To Studies on the Biodegradation<br>Lorobenzenes and Trichloroethylene<br>AFOSR-88-0225 | David T. Gibson<br>Department of Microbiology<br>University of Iowa<br>Iowa City, IA 52242 |
| Polyparaphenylene from Bioproducts:<br>1,4-Polymerization of Dihydrocatechol<br>Derivatives<br>AFOSR-88-0094 | Robert H. Grubbs<br>Division of Chemistry and<br>Chemical Engineering<br>California Institute<br>of Technology<br>Pasadena, CA 91125 |
| Heat and Hydrolytically Stable Polymers<br>for Fabricable Films and Laminates<br>AFOSR-87-0104 | Henry Hall<br>Department of Chemistry<br>University of Arizona<br>Tucson, AZ 85721 |
| Perfluorinated Ligands in<br>Organometallic Chemistry<br>AFOSR-86-0075 | Russell P. Hughes<br>Department of Chemistry<br>Dartmouth College<br>Hanover, NH 0375 |
| Synthesis of Primary-Alcohol-Terminated<br>Polyepichlorohydrin with Molecular<br>Weight of 4000 to 12000<br>AFOSR-87-0223 | C. Sue Kim<br>Department of Chemistry<br>California State University<br>Sacramento CA 95819-2694 |
| New Experimental Challenges<br>in Elemental Fluorine Chemistry;<br>An Emerging Technology<br>AFOSR-88-0084 | Richard J. Lagow<br>Department of Chemistry<br>University of Texas<br>Austin, TX 78712 |
| Synthesis and Chemistry of<br>Strained and Conjugated<br>Fluorocarbons<br>AFOSR-86-0130 | David M. Lemal<br>Department of Chemistry<br>Dartmouth College<br>Hanover, NH 03755 |
| Synthesis of Novel, Substituted<br>Polycyclic Cage Systems<br>AFOSR-88-0132 | Alan P. Marchand<br>Department of Chemistry<br>North Texas State University<br>Box 5068<br>Denton, TX 76203-5068 |
| Structure and Properties of Novel<br>Compounds of Silicon Germanium,<br>and Tin<br>AFOSR-87-0001 | Josef Michl<br>Department of Chemistry<br>University of Texas<br>Austin, TX 78713-7726 |

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| Synthesis of Energetic Acid<br>Labile Lova Binders<br>F49620-86-K-0012 | Subhash Narang<br>Robert Schmitt<br>SRI International<br>333 Ravenswood Avenue<br>Menlo Park, CA 94025 |
| Heterocycles Based on Group III, IV, and V Elements Precursors for Novel Glasses and Ceramics<br>F49620-85-C-0042 | Kay L. Paciorek<br>Chemical and Materials Research<br>Ultrasystems, Inc<br>1685 Von Karman Avenue<br>Irvine, CA 92714 |
| Processing of Ceramics<br>with Biopolymers<br>AFOSR-88-0135 | Mehmet Sarikaya<br>Department of Materials Science & Engineering<br>University of Washington<br>Roberts Hall, FB-10<br>Seattle, WA 98195 |
| Highly Fluorinated Nitrogen-Containing Compounds.<br>New Stable Fluids<br>AFOSR-87-0067 | Jean'ne M. Shreeve<br>Department of Chemistry<br>University of Idaho<br>Moxcow, ID 83843 |
| Heteronuclear Metal Cluster Compounds: Synthesis and and Reactivity<br>AFOSR-86-0125 | F. G. A. Stone<br>Department of Inorganic Chemistry<br>University of Bristol<br>Bristol, BS8 1TS, UK |
| Meta-Hydroxyphenylacetylene Biotransformation<br>F49620-88-C-0032 | Kestutis Tautvydas<br>Research and Development<br>Minnesota Mining and Manufacture Company<br>St Paul, MN 55144 |
| Early Transition of Silicon Compounds and their Roles in the Synthesis of New Polymeric and Ceramic Materials<br>AFOSR-88-0273 | T. Don Tilley<br>Department of Chemistry<br>University of California<br>La Jolla, CA 92093 |
| Synthesis and Chemistry of Unsaturated Metal-Nitrogen Compounds<br>AFOSR-86-0027 | William C. Trogler<br>Department of Chemitry<br>University of California<br>LaJolla, CA 92093 |
| Dynamics and Stabilization of Materials Possessing High Energy Content<br>AFOSR-88-0043 | Nicholas J. Turro<br>Department of Chemistry<br>Columbia University<br>New York, NY 10027 |

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| Atrane and Quadruped Frameworks in Early Transition Metal and Silicon Group Stereochemistry: Monomers and Oligomers<br>AFOSR-88-0081 | John G. Verkade<br>Department of Chemistry<br>Iowa State University<br>Ames, Iowa 50011 |
| Synthesis of High-Nitrogen-Content Heterocyclic Nitramines and Energetic Internal Plasticizers<br>F49620-85-C-0036 | Rodney L. Willer<br>Morton Thiokol Inc<br>P O Box 241<br>Elkton, MD 21921 |
| Synthesis and Reactivity Studies of Early Metal Alkoxide/Siloxide Complexes and Sol-Gel Precursors<br>AFOSR-87-0103 | Peter T. Wolczanski<br>Department of Chemistry<br>Cornell University<br>Ithaca NY 14853 |

## COMPUTATIONAL CHEMISTRY - LT COL LARRY P. DAVIS, USAF

| | |
|---|---|
| Quantum-Theoretical Methods and Studies Relating to Properties of Materials<br>AFOSR-86-0146 | Carl S. Ewig<br>John R Van Wazer<br>Department of Chemistry<br>Vanderbilt University<br>Nashville, TN 37235 |
| Molecular Dynamics and Spectroscopy at Gas-Solid Interfaces<br>F49620-86-C-0009 | Thomas F. George<br>239 Fronczak Hall<br>Department of Chemistry<br>State University of New York<br>Buffalo, NY 14620 |
| Microscopic Theoretical Modelling of the Chemical and Tribological Properties of Ceramic Surfaces and Interfaces<br>AFOSR-88-0051 | William A. Goddard III<br>Dept of Chemistry and Physics<br>California Institute of Technology<br>Pasadena, CA 91125 |
| Theoretical Studies of Silicon Chemistry<br>AFOSR-87-0049 | Mark S. Gordon<br>Department of Chemistry<br>North Dakota State University<br>Fargo, ND 58105 |
| Theoretical Studies of Time-of-Flight Atom and Molecular Surface Scattering<br>AFOSR-87-0075 | Eric J. Heller<br>Department of Chemistry<br>University of Washington<br>Seattle, WA 98195 |
| Analytic Methods Using Computer Algebra with Slater-Type Orbitals for Problems in Ab Initio Quantum Chemistry<br>AFOSR-86-0149 | Herbert W. Jones<br>Charles A. Weatherford<br>Department of Physics<br>Florida A & M University<br>Tallahassee, FL 32307 |
| Chaotic Spectra of Small Molecules<br>AFOSR-88-0049 | Michael E. Kellman<br>Department of Chemistry<br>Northeastern University<br>360 Huntington Avenue<br>Boston, MA 02115 |
| Energy and Chemical Change<br>AFOSR-86-0011 | James L. Kinsey<br>Raphael D Levine<br>Department of Chemistry<br>Massachusetts Institute of Technology<br>Cambridge, MA 02139 |
| Theoretical Investigations of Metastability and Energy Storage Molecular Systems<br>AFOSR-88-0042 | Kate P. Kirby<br>Astrophysical Observatory<br>Smithsonian Institution<br>60 Garden Street<br>Cambridge, MA 02138 |

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| Studies of Resonantly Enhanced Multiphoton Ionization Processes in Molecules<br>AFOSR-87-0039 | Vincent McKoy<br>A.A. Noyes Laboratory of Chemical Physics<br>California Inst of Tech<br>Pasadena, CA 91125 |
| Theory of Electron Scattering from Adsorbates<br>AFOSR-MIPR-86-0004<br>AFOSR-MIPR-87-0010 | Horia I. Metiu<br>Department of Chemistry<br>University of California<br>Santa Barbara, CA 93106 |
| Potential Energy Surfaces and Stability of High Energy Content Excited Bound Clusters<br>AFOSR-87-0348 | C. A. Nicolaides<br>Theoretical & Physical Chemistry Institute<br>Natl Hellenic Research Inst<br>48 Vas. Constantinou Avenue<br>Athens 11635, GREECE |
| Computational Studies of Energetic Strained Molecules: Properties and Syntheses of Tetrahedrane and Triprismane Systems<br>AFOSR-88-0068 | Peter Politzer<br>Department of Chemistry<br>University of New Orleans<br>New Orleans, Louisiana 70148 |
| Gas-Solid Dynamics at Disordered and Adsorbate Covered Surfaces<br>F49620-87-C-0045 | Herschel Rabitz<br>Department of Chemistry<br>Princeton University<br>Princeton, NJ 08544 |
| Theoretical Studies of Heterogeneous Reactions in CVD and Catalysis<br>AFOSR-86-0043 | Lionel M. Raff<br>Donald L. Thompson<br>Department of Chemistry<br>Oklahoma State University<br>Stillwater, OK 74078 |
| Fundamental Studies of Carbon, NH, and Oxygen Rings and Other High Energy Density Molecular Systems<br>AFOSR-88-0167 | Henry F. Schaefer III<br>Department of Chemistry<br>University of California<br>Berkeley, CA 94720 |
| Evaluation of Chemical and Atmospheric Sciences Research<br>F49620-87-C-0120 | Robert Simon<br>Board on Chemical Science and Technology<br>National Academy of Sciences<br>2101 Constitution Avenue<br>Washington, DC 20418 |
| Theoretical Studies of Spin-Forbidden Processes Within the Breit-Pauli Approximation<br>AFOSR-86-0110 | David R. Yarkony<br>Department of Chemistry<br>Johns Hopkins University<br>Baltimore, MD 21218 |

# ATMOSPHERIC SCIENCES

## LT COL JAMES P. KOERMER, USAF
## MAJOR JAMES I. METCALF (USAF Reserve)

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|---|---|
| Mesospheric Wind Measurement<br>AFOSR-86-0241 | Gene W. Adams<br>Utah State University<br>Center for Atmospheric<br>and Space Sciences<br>Logan, UT 84322 |
| Mithras Studies of the Auroral<br>Oval and Polar Cap<br>F49620-87-K-0007 | Odile de la Beaujardiere<br>SRI International<br>333 Ravenswood Avenue<br>Menlo Park, CA 94025 |
| Numerical Modeling of Middle and<br>High Level Clouds with the<br>Colorado State University<br>Regional Atmospheric Modeling System<br>AFOSR-88-0143 | William R. Cotton<br>Department of Atmospheric<br>Sciences<br>Colorado State University<br>Fort Collins, Colorado 80523 |
| A Proposal for the Establishment<br>of a Center of Excellence in<br>Theoretical Geoplasma Research<br>Physics<br>F49620-86-C-0128 | Tom Chang<br>Center for Space Research<br>Center for Theoretical Geoplasma<br>M I T<br>Cambridge, MA 02139 |
| Nonlinear Internal Gravity-<br>Wave Propagation, Saturation,<br>and Adsorption in the Atmosphere<br>F49620-86-C-0065 | Timothy J. Dunkerton<br>Northwest Research Associates<br>(formerly Physical Dynamics)<br>P O Box 3027<br>Bellevue, WA 98005 |
| Propagation and Saturation<br>of Nonlinear Inertia-Gravity<br>Wave in the Atmosphere<br>F49620-86-C-0026 | Timothy J. Dunkerton<br>Northwest Research Associates<br>(formerly Physical Dynamics)<br>P O Box 3027<br>Bellevue, WA 98005 |
| Self-Consistent Modelling of the<br>Ionosphere-Thermosphere-<br>Magnetosphere System<br>F49620-88-C-0111 | Jeffrey M. Forbes<br>College of Engineering<br>Boston University<br>110 Cummington Street<br>Boston, MA 02215 |
| Electromechanical Feedback<br>Processes in the Ionosphere<br>AFOSR-85-0048 | Jeffrey M. Forbes<br>College of Engineering<br>Boston University<br>110 Cummington Street<br>Boston, MA 02215 |
| Multi-Instrument Studies of the<br>Auroral Ionosphere<br>AFOSR-86-0023 | John C. Foster<br>John M. Holt<br>Massachusetts Institute of<br>Technology<br>Haystack Observatory<br>Westford, MA 01886 |

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| Gravity Wave and Turbulence Studies Using a Portable, High-Resolution ST Radar<br>F49620-87-C-0024 | David C. Fritts<br>Geophysical Institute<br>University of Alaska<br>Fairbanks, AK 99775 |
| NAS Board on Atmospheric Science and Climate (BASC)<br>AFOSR-ISSA-87-0075 | Alan D. Hecht<br>NOAA/NCPO<br>Rockville, MD 20852 |
| Polarisation Radar Studies of Precipitation: Implementation Technique and Data Interpretation<br>AFOSR-88-0121 | Anthony J. Illingworth<br>Department of Physics<br>University of Manchester<br>Manchester, M60 1QD, UK |
| Comprehensive Mapping of Electron Precipitation and its Effect on the Atmosphere<br>F49620-88-C-0072 | William L. Imhof<br>Space Sciences Lab<br>Lockheed Missiles and Space Co Inc<br>3251 Hanover Street<br>Palo Alto, CA 94304 |
| A Numerical Study of the Role of Meso Beta and Meso Gamma Scale Vertical Exchange Processes in the Evolution of Upper Tropospheric Frontal Systems<br>F496209-86-C-0044 | Michael Kaplan<br>Mesoscale Environment Simulations & Operations Inc<br>6 Assembly Court<br>Newport News, VA 23606 |
| Cloud/Cryosphere Interaction<br>AFOSR-86-0053 | George Kukla<br>David A Robinson<br>Columbia University<br>Lamont-Doherty Geological Observatory<br>Palisades, NY 10964 |
| Wind Profiler Investigation of Low-Frequency Inertia-Gravity Around Jet Streams and Frontal Zones<br>F49620-88-C-0121 | Miguel F. Larsen<br>Department of Physics and Astronomy<br>Clemson University<br>Clemson, SC 29631 |
| Studies of Frontal Zone Dynamics with a High Resolution Wind Profiling System<br>AFOSR-85-0216 | Miguel F. Larsen<br>Department of Physics and Astronomy<br>Clemson University<br>Clemson, SC 29631 |
| Sources and Causes of Upper Atmospheric Disturbances<br>AFOSR-88-0217 | Min-Chang Lee<br>Research Laboratory of Electronics<br>Room 36-389<br>Massachusetts Institute of Technology<br>Cambridge, MA 02139 |

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| Development and Verification of a Physical Cloud-Moisture Model for Use in General Circulation Models<br>AFOSR-87-0294 | Kuo-Nan Liou<br>Department of Meteorology<br>University of Utah<br>Salt Lake City, UT 84112 |
| Aircraft Investigation of the Turbulent Transport of Electric Charge Through the Planetary Bouldary Layer<br>F49620-86-C-0013 | Ralph J Markson<br>Airborne Research Associates<br>46 Kendal Common Road<br>Weston, MA 02913 |
| An Investigation of Atmospheric Emission in Ultraviolet, Vacuum Ultraviolet and Extreme Ultraviolet Wavelengths<br>AFOSR-86-0057 | Ching -I Meng<br>Johns Hopkins University<br>Applied Physics Laboratory<br>Laurel, MD 20707 |
| The Interaction and Variation of Waves and Turbulence from MST Radar Data<br>F49620-86-C-0027 | Gregory D. Nastrom<br>Control Data Corporation<br>Minneapolis, MN 55420 |
| Investigation of Solar Wind Control of Magnetospheric Current Systems Using Wiener Filtering Techniques<br>AFOSR-ISSA-87-0053 | A.M. Peterson<br>C.R. Clauer<br>Stanford Electronics Labs<br>Stanford University<br>Stanford, California 94305 |
| 41st, 42nd, 43rd International Symposium on Molecular Spectroscopy<br>AFOSR-86-0065 | K. Narahari Rao<br>Department of Physics<br>Ohio State University<br>Research Foundation<br>Columbus, OH 43210 |
| Mesoscale Severe Weather Development Under Orographic Influences<br>F49620-86-C-0080 | Elmar Reiter<br>Colorado State University<br>Fort Collins, CO 80523 |
| USN Center of Excellence in Theory and Analysis of the Geo-Plasma Environment<br>F49620-86-C-0109 | Robert W. Schunk<br>Center for Atmospheric and Space Sciences<br>Utah State University<br>Logan, UT 84322 |
| Study of the Continuous/Diffuse (C/D) Aurora Using Particle Observations from the Dynamics Explorer Satellites<br>F49620-85-C-0029 | James R. Sharber<br>Southwest Research Institute<br>6220 Culebra Road<br>San Antonio, TX 78284 |
| Sensitivity Evaluation Plan for Lowtran<br>F49620-87-C-0057 | Ken Tomiyama<br>Dep of Electrical Engineering<br>Pennsylvania State University<br>University Park, PA 16802 |

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| Infrared and Ionization Structure of the Polar Mesosphere<br>AFOSR-85-0163 | James C. Ulwick<br>K. A. Baker<br>A. Steed<br>Utah State University<br>Space Dynamics Laboratory<br>Logan, Utah 84322 |
| Modeling and Observational Studies of Mesoscale Air-Mass Boundaries and Warm-Season Convective Precipitation<br>AFOSR-88-0050 | Thomas T. Warner<br>Department of Meteorology<br>Pennsylvania State University<br>University Park, PA 16802 |

# CHEMICAL TECHNIQUES

### Dr John S. Wilkes

The Chemical Techniques program encompasses research in the traditional chemical sub-disciplines of analytical chemistry and electrochemistry especially emphasizing electrochemistry.

The electrochemistry work funded in this program included electroanalytical methods and physical electrochemistry. The electroanalytical effort concerned new electrochemically based methods that could ultimately result in improved chemical sensors in liquids or gases. An electrochemical method for the detection of gases dissolved in a flow stream was developed, and work on quartz crystal microbalance was continued. The quartz crystal microbalance was also used in electrode studies.

Research projects in physical electrochemistry concentrated on the nature of electrode processes and on non-traditional electrolytes. Work in non-traditional electrolytes was in polymer electrolytes and molten salts. Work in molten salts concerned the behavior of electrochemical couples in low melting chloroaluminate melts, and the possible applications of the melts as battery electrolytes. Spectroscopic and electrochemical studies in higher melting chloroaluminates continued. A project combining electrochemistry and surface analytical techniques revealed important details about the orientation of electroactive materials on electrodes. New composite ionically and electronically conducting polymers were developed for use as electrochemical materials. Laser activation of carbon electrode surfaces improved the kinetics of electrode surfaces.

Research in analytical chemistry was limited to one project concerned with detection. The detection and diagnosis of plasma and conventional flames was studied and new analytical techniques were developed.

# SURFACE CHEMISTRY

Lt Col Larry W. Burggraf, USAF

The AFOSR surface chemistry program emphasizes novel interface chemistry critical to selection and creation of materials for future aerospace systems. Chemistry at interfaces may enhance or degrade performance of materials for structure, lubrication, power, electronics or optics. This research not only produces understanding of materials performance in demanding environments but it is producing new ways of modifying surfaces for optimum performance in challenging aerospace applications. The program is divided into four application areas; (1) surface, interface structures, (2) electronics, electro-optic materials processing chemistry, (3) aerospace hyperthermal surface reactions and (4) high-temperature lubrication. Researchers are developing and employing novel thin-film deposition and surface characterization tools to investigate fundamental reactions producing hydride, oxide, fluoride, nitride and carbide structures on surfaces which modify surface reactivity. Also, researchers are studying elementary surface reactions and structures for electronics and electro-optic materials, especially silicon germanide and gallium arsenide heterostructural materials in support of semiconductor research programs at the Wright Research and Development Center (WRDC) Materials Laboratory. Surface reactions initiated by energetic species in earth orbit which degrade system performance are being studied. Sponsored research is examining fundamental electronic processes at dielectric, semiconductor and metal interfaces induced by energetic species which produce structural damage and emission. These programs support research in the Space Physics Division of the Geophysics Laboratory and in the Electromagnetic Materials and Survivability Division of WRDC Materials Laboratory. The high-temperature lubrication effort is concerned with surface chemistry to produce low-wear, ultimately smooth, lubricated surfaces for high-temperature applications. Theoretical and experimental surface science techniques are being applied to ceramic and diamond substrate surfaces lubricated by novel dichalcogenide, fluorocarbon, and fluoride films. In each area our fundamental knowledge of how material interfaces react and interact with demanding environments is critical to design of future aerospace systems. Emphasis is given to experimental-theoretical collaborations to create fundamental molecular models of surface chemical processes at well-characterized surfaces.

In 1988 the surface chemistry program continued to expand experimental efforts to model tribochemical systems of potential interest including fluorocarbon lubricants on metals and ceramics as well as novel nickel-doped molybdenum disulfide films. WRDC Materials Laboratory researchers are preparing novel materials for tribological applications using electronics processing technology.

Future initiatives will emphasize novel surface chemistry techniques to characterize _in situ_ buried interfaces applied to problems of binder adhesion to solid oxidizers in rocket motors and buried interfaces in carbon composites.

# CHEMICAL STRUCTURES

Dr Donald R Ulrich

The Chemical Structures program addresses research on the materials chemistry and structure-property-processing relationships of polymers, ceramics, glass, electrooptic materials and advanced composites.

The scientific approaches being emphasized in ceramics and polymers are:

Polymers

- Ordered Polymers and Molecular Composites
- Nonlinear Optical Polymers
- Multifunctional Macromolecular Ultrastructure

Ceramics and Glass

- Solution Ceramics
- Ultrastructure Processing
- Halide and Chalcohalide Optical Glass

There have been several major advances in these areas.

## Chemical Processing of Ceramic Superconductors

Since 1979 ceramic research has focused on the control of microstructural features at the 10 to 1000 Angstrom level (ultrastructure) by chemical processing. There have been several major advances in this area for structural, optical and electronic ceramics. This experience was brought to bear on processing of newly discovered ceramic super conductors since these materials require precise control of grain boundary, interphase, and crystallite development. Only through chemical processing approaches can the mechanical properties, anion-defect chemistry, environmental stability and superconducting properties, including $T_c$ and current density be tailored to achieve reproducibility and reliability.

Professor Ilhan Aksay of the University of Washington has achieved the first production of single phase $YBa_2Cu_3O_{(7-x)}$ without secondary or tertiary compounds. Very thin grain boundaries were produced the phase of which was identified as $Cu_2O$, not CuO. These materials continuously demonstrated $T_c$'s at 90°K. Professors Kent Bowen, Wendal Rhine and Michael Cima of MIT developed the concept of microreactors for complex ceramic compositions to control the chemistry, morphology and size of superconducting ceramic particles. Reactions are conducted in emulsion droplets to form particles by combined sol-gel and emulsion techniques. Phase separation or spinodal decomposition in the microemulsion just above room temperature produces narrow-size distributions of $Ba_2YCu_3O_{6.9}$ particles. Patterned super conductors have been sintered with excellent uniformity and very little change in particle size and excellent grain boundary control. Again a $T_c$ in the vicinity of 90°K was observed.

Successful sol-gel approaches have been demonstrated by Professor John D Mackenzie of UCLA and Dr Danial Yu of Universal Energy Systems. Professor Egon Matijevic of Clarkson University has demonstrated multicomponent particle formation with excellent control of phase composition and particle shape through unique solution and aerosol chemistry approaches.

## Nonlinear Optical Polymers

Drs Jim Stamatoff and John Riggs of Hoechst Celanese and Professor Anthony Garito of the University of Pennsylvania have successfully developed a pendant side chain polymer family which has a second harmonic generation coefficient, which is 10 times larger than that of inorganic single crystal lithium niobate. In addition the electrooptic coefficient is higher than that of lithium niobate. This is a major advance since in the past the electrooptic coefficient was only 3% that of the lithium niobate, which arises from lattice phonon contributions.

The performance projection is that for polymer electrooptic modulators, such as travelling-wave electrode Mach-Zendher Modulators, the maximum frequency is limited to 50 GHz only by conventional electrodes. Lithium niobate is limited to 24 GHz even in aperiodic structures due to velocity mismatch. The power and switching voltages for the polymers are, respectively, 0.03 watts and 3.5 volts.

This research is jointly supported by AFOSR and DARPA with Dr John Neff as the DARPA program manager.

The Rome Air Development Center has already initiated a development program to utilize these polymers in Bragg Cells for frequency doubling.

## Densification of Carbon-Carbon Composites by Supercritical Fluid Processing

Current oxidation protection systems for carbon-carbon composite turbine engine candidates rely on conversion or CVD derived outer coatings and glassy sealers. Thermal expansion mismatch between the SiC coating and carbon-carbon substrate results in coating cracks and oxidation at temperatures below 1500°F.

Dr R Wagner of Babcock and Wilcox dissolved polycarbosilane in supercritical propane. This was precipitated in the internal porosity of 2D and 3D carbon/carbon composites. Thermally stable deposits were produced by insitu pyrolysis.

Supercritical fluid enhanced densification was demonstrated. Increased oxidation resistance, bend strength, and polymer char yield resulted. Fiber coating was also demonstrated. This advancement is contributing to several carbon-carbon composite turbine engine development programs being supported by the Air Force Wright Aeronautical Laboratory Materials Laboratory. It was jointly supported by DARPA and AFOSR with Dr Philip Parrish and Major Steve Wax as the DARPA program managers.

# MOLECULAR DYNAMICS

Dr Francis J. Wodarczyk

The Molecular Dynamics Program focuses on elementary physical and chemical processes in the gas phase. The study of these elementary processes allows us to understand and to predict such diverse phenomena as neutral and ion-molecule processes giving rise to natural airglow, interactions present in a low earth orbit environment, chemical laser kinetics, and energy release mechanisms in advanced propellants. These topics reflect the basic research interests of the Air Force laboratories with which this program most frequently interacts, namely, the Air Force's Geophysics Laboratory at Hanscom AFB near Boston, Mass.; the Weapons Laboratory at Kirtland AFB near Albuquerque, N.M.; and the Astronautics Laboratory at Edwards AFB outside Lancaster, Calif.

In FY1988 the Molecular Dynamics Program consisted of four subareas, each accounting for roughly one quarter of the total Task: Atmospheric Chemistry, Interactive Dynamics, Chemical Lasers and Energetic Materials. Descriptions of typical research supported in the subareas follows.

Molecular and chemical processes pertinent to development of new electronic transition chemical lasers are studied. Chemical reactions which produce electronically excited species permit the determination of reaction rate constants, photon yields, branching ratios, and quenching mechanisms. Atomic and molecular electronic states with promising spectroscopic features are examined experimentally to evaluate laser potential. Important items for evaluation include radiative lifetime, susceptibility to collisional quenching, and potential energy curves. Experimental techniques that are used include laser-induced fluorescence, molecular beam and flow tube chemiluminescence techniques, and pure spectroscopy. Chemical excitation schemes involve direct chemical and photochemical pumping as well as energy transfer from metastable molecules. Interesting chemical systems include halogen azides, dioxetanes, interhalogens, and alkali, alkaline earth, and Group III metals.

Detailed kinetics of the reactions of important atmospheric species are investigated by a combination of laser-induced multiphoton dissociation and flow tube analysis. Flowing afterglow and molecular beam studies determine molecular processes occurring in the natural and perturbed atmosphere. Energy distributions in bimolecular ion-molecule reactions are studied using ion cyclotron resonance spectroscopy for reactions at or near thermal energies. Emphasis is placed on reactions of atmospheric ions and clusters.

The dynamics of multiphoton dissociation processes producing free radicals are investigated using double resonance absorption, laser-induced fluorescence, and Raman scattering techniques. Free radical-surface interactions are investigated under conditions close to those in actual plasma systems. Products are identified and the resulting gaseous products and surfaces are analyzed by spectroscopic techniques. State-resolved collision-induced kinetics of vibrationally excited molecules interacting with gases or surfaces are studied using molecular beam techniques in an ultra-high vacuum environment. Ultra-short laser pulses are used to probe reaction dynamics on a femtosecond time scale. Spectroscopic studies of a bimolecular transition state are performed by detaching a negative ion having a structure similar to the transition state for the neutral bimolecular reaction. The role of reactions between suprathermal atoms and ions with surfaces is evaluated with particular emphasis on those interactions which can lead to the emission of optical radiation.

Funding in the Energetic Materials area is projected to increase slightly due to efforts to look for novel sources of high-energy density propellants. Since total AF funding for basic research is projected to continue to decrease for the next few years, the Chemical Laser, Atmospheric Chemistry, and Interactive Dynamics areas are programmed for slightly decreased funding in the near term.

# CHEMICAL REACTIVITY AND SYNTHESIS

Dr Anthony J. Matuszko

Chemical reactivity and synthesis covers a broad area of novel synthesis techniques and new descriptive chemistry relevant to Air Force requirements for the future. All reports that our budgets for basic research have been increasing over the past few years may be somewhat misleading. In reality, the core budget has been decreasing while increasing amounts have been designated for special programs or new initiatives. Our research continues to place emphasis on the synthesis, properties and reactivity of inorganic and organometallic compounds, particularly the chemistry of main group and early transition metals. We will be taking a close look at new inorganic and organic polymer forming reactions. Our small program in organic and inorganic fluorine chemistry has been scientifically quite productive in the past; this program will be continued at the present level. We plan to continue some research in the energetic materials area. And finally, we are in the process of starting a brand new initiative in the area of Biotechnology Approaches to the Synthesis of Aerospace Materials.

In the areas of inorganic and organometallic chemistry we will be continuing to do research on the synthesis and properties of organopolysilanes, silazanes, siloxanes and other organometallics and intermetallics. This chemistry has provided an important foundation for transitioning into potential applications in ceramic matrix materials and precursors for low temperature processing of high strength fibers, ceramics, and glasses. We are exploring the chemistry of intermetallic organometallics containing elements such a B, P, Si, Ge, Hf, Zr, Ti and Ta and taking a look at the corresponding organometal oxide polymers.

The program in fluorine chemistry involves the exploration of new techniques for the fluorination of organic compounds together with approaches to the functionalization of these compounds. Air Force interests include their use as non-flammable, wide temperature range fluids, lubricants and elastomers capable of withstanding future state-of-the-art use temperatures without significant degradation. This work will be in support of the Air Force Materials Laboratory's program in the area of fluorocarbon ether lubricants.

The research in energetic materials involves new chemical syntheses of high energy compounds and improved routes to propellant ingredents and explosives with emphasis on new energetic oxidizers and energetic polymeric binders. Our effort in this area is being cut back due to funding limitations.

Programs have commenced under the new Biotechnology Initiative. The types of research efforts include potentially lower-cost biosynthetic pathways to key chemical intermediates for aerospace materials, studies of the structure of strong, tough natural systems to model for improved synthetic structures, understanding the molecular mechanism which tailors the formation of natural structures, and biodegradation of hazardous waste chemicals such as chlorocarbons. Air Force laboratories actively participating in this research effort are the Air Force Materials Laboratory at Wright Patterson AFB, Ohio, the Environics Group at Tyndall AFB, Florida, and the Air Force Academy at Colorado Springs, Colorado.

# COMPUTATIONAL CHEMISTRY

Lt Col Larry P. Davis, USAF

The Computational Chemistry Program grew modestly in FY 88 compared with FY 87, thanks chiefly to a new initiative in the area of tribology. This new initiative was designed to develop a molecular-level understanding of the mechanisms of friction and wear, and has both an experimental component (managed under Task A2, Surface Chemistry) and a theoretical component. The theoretical component of the program has grown slightly during FY 89 and then is expected to level off.

For the first time, the Computational Chemistry Program was divided officially into three areas: a core program, the tribology area, and the high energy density materials area. The largest component of the core program involved the modelling of surfaces and processes which take place among surface-adsorbed species and gas-phase species, including interactions of surface species with electromagnetic radiation and electrons. Another large component of the core program encompassed studies of energy flow in isolated molecules, including high levels of vibrational excitation and multiphoton absorption leading to ionization. Finally, studies of basic silicon chemistry using molecular orbital techniques were performed in support of Task A3, Structural Chemistry Task. We expect molecular orbital theory to play an increasingly important role in all areas of the program into the foreseeable future. The core program is expected to decrease at a moderate rate over the next few years due to cuts in the overall budget. Of increasing importance for successful proposals in this area is the strength of the collaboration with experimentalists within the AFOSR and Air Force laboratory basic chemistry research programs.

The High Energy Density Materials Program (HEDM) remained an integral part of the Computational Chemistry Task. The experimental part of the program was managed under Task B1, Molecular Dynamics. The overall goal for this area is to determine "the limits of metastability," or how much energy can be stored for how long a time in a molecular system. We expect that this area of research will continue at approximately the same level for at least the next few years.

Several of the Air Force laboratories continued and expanded viable programs in computational chemistry. Frank J Seiler Research Laboratory maintained its leadership role within the Air Force and within the computational community as a whole in the further development of semi-empirical molecular orbital theory, in addition to performing extensive calculations on energetic molecules, biochemical molecules, and molten salt species. The Geophysics Laboratory continued to do ab initio quantum chemical calculations on atmospheric species. The Astronautics Laboratory maintained and expanded its considerable effort in the theoretical treatment of high energy density species. The Materials Laboratory expanded its effort in computations of the physical properties of polymers and began calculations on their nonlinear optical properties as well. The Armament Test Laboratory continued its contractural programs to provide theoretical support for its explosives decomposition programs. There has also been an important increase in interaction among laboratory scientists and AFOSR principal investigators.

# ATMOSPHERIC SCIENCES

Lt Col James P. Koermer, USAF
Maj James I. Metcalf, USAFR

AFOSR, as the single manager of basic research in the Air Force, manages both an extramural program of grants and contracts for atmospheric research and an in-house basic research program at the Geophysics Laboratory (GL). The AFOSR extramural program is administered in two tasks, of which one focuses on the meteorology of the troposphere and stratosphere and the other emphasizes the dynamics and physics of the ionosphere and the neutral upper atmosphere. While 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, AFOSR concentrates its funding in a few topical areas in order to coordinate research efforts in these areas and maximize the likelihood of significant progress. The meteorlogy program emphasizes mesoscale dynamics, cloud processes, and gravity wave phenomena. The upper atmosphere program emphasizes the observation, understanding, and modeling of the auroral zone and the dynamics of the neutral upper atmosphere.

Mesoscale meteorology aims at improved understanding of atmospheric processes at horizontal scales of 10 to 1000 km, using numerical models and a variety of remote and *in situ* sensing techniques. Research completed at the National Aeronautics and Space Administration (NASA) Goddard Laboratory for Atmospheric Sciences showed the role of upper-level frontogenesis in the dynamics of mid-latitude baroclinic waves. Scientists at Technion - Israel Institute of Technology developed a numerical simulation of local instabilities in strongly sheared, slightly viscous, rotating stratified flows. Ongoing research efforts are aimed at improved forecasts of precipitation, severe convective storms, and cirrus clouds.

Research in the physics of cloud processes includes studies of water nucleation, precipitation development, optical and infrared scattering and transmission in clouds, and atmospheric electrical processes. Under the Small Business Innovation Research Program, Micro Science, Inc, of Leesburg, Va., designed, developed, and demonstrated a cloud imaging system based on a pair of solid state electronic cameras, each of which incorporates a charge injection device (CID). Scientists at the Naval Research Laboratory investigated natural and triggered lightning to identify sources of high-frequency (HF) radiation and to relate this radiation to electric currents in lightning return strokes. A new research effort at the University of Manchester, England, will use observations by polarimetric radar to develop techniques for precipitation measurement and for detection of hail in convective storms. Scientists at the Pennsylvania State University are conducting an evaluation of the sensitivity of the LOWTRAN transmission code to variations in atmospheric conditions, particularly the presence of clouds. Scientists at the University of Utah are developing a new model of moisture and clouds for incorporation into models of the general circulation of the atmosphere.

Research on gravity waves encompasses the planetary boundary layer, the transport of momentum and energy, and the dynamical coupling of the troposphere and stratosphere. Research completed at the National Oceanic and Atmospheric Administration (NOAA) Aeronomy Laboratory showed the azimuthal anisotropy of gravity waves and the relationship of their dissipation to the vertical profile of the buoyancy (Brunt-Väisälä) frequency in the troposphere and lower stratosphere. The University of Alaska, in a new research effort, will use a recently developed portable very high frequency (219 MHz) radar and other sensors to study the momentum flux and its divergence in the upper troposphere and lower stratosphere.

A variety of measurement and modeling techniques are used to study the structure and dynamics of the ionosphere. The University of Alaska developed a new three-dimensional time-dependent model of the polar F region of the ionosphere to study the response of the ionosphere to disturbances of the interplanetary magnetic field. In a research program funded jointly with the National Science Foundation (NSF) scientists at The Johns Hopkins University used a HF (8-20 MHz) radar to study the structure and motion of electron density irregularities in the E and F regions of the ionosphere. Research completed at Utah State University involved the use of a three-dimensional ionospheric model to simulate the temporal and spatial variation of parameters observed by radars during the Magnetosphere Ionosphere Thermosphere Radar Studies (MITHRAS) of 1981 and 1982. SRI International is undertaking scientific studies of ionospheric structure based on these data and on more recent radar observations. New research on the coupling of the solar wind, the magnetosphere, and the ionosphere was begun at Stanford University.

Research on the dynamics and composition of the upper atmosphere includes both theoretical and experimental efforts. Two research efforts were completed at University College London. One was a multi-faceted program of modeling the structure and dynamics of the upper mesosphere and lower thermosphere. The other, in collaboration with AFGL, was the development of a Doppler lidar for the measurement of winds at 80-110 km altitude. The University of Michigan began an investigation of the dynamics of the mesosphere and thermosphere based on interferometric measurements of optical and infrared emissions from selected atomic and molecular species.

AFOSR collaborates closely not only with AFGL but also with other government laboratories and research funding organizations, including the Army Research Office, the Office of Naval Research, NSF, NASA, and NOAA. Programs are frequently funded jointly with these other agencies. In addition to its support of individual scientists and research organizations, AFOSR contributes to the support of research planning and coordinating agencies and committees, including the National Academy of Sciences (NAS) Board of Atmospheric Sciences and Climate and the NAS Committee on Solar-Terrestrial Research. In these ways AFOSR attempts to maximize the benefits to the Air Force that result from the nation's basic research programs.

# RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - CHEMICAL TECHNIQUES

DR JOHN S. WILKES

| | |
|---|---|
| Fundamental Studies of Surface Processes and Trace Analysis Using Solid Electrodes<br>AFOSR-87-0037 | Stanley Bruckenstein<br>Department of Chemistry<br>State University of New York<br>Buffalo, New York 14214 |
| Chemical and Electrochemical Properties of Potential Battery Systems in Room Temperature Molten Salts<br>AFOSR-85-0027 | Francis M. Donahue<br>Department of Chemical Engineering<br>University of Michigan<br>Ann Arbor, MI 48109-2136 |
| Electrochemical and Spectroscopic Investigations of Molten Chloroaluminates and Related Solvents<br>AFOSR-85-0321 | Gleb Mamantov<br>Department of Chemistry<br>University of Tennessee<br>Knoxville, TN 37996-1600 |

# COMPLETED PROJECT SUMMARY

TITLE: Fundamental Studies of Surface Processes and Trace Analysis Using Solid Electrodes

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

INCLUSIVE DATES: 1 November 1986 - 31 July 1988

CONTRACT/GRANT NUMBER: AFOSR-87-0037

COST AND FY SOURCE:
$130,000, FY 89;
$43,607, FY 88

SENIOR RESEARCH PERSONNEL:
C. Paul Wilde
A. R. Hillman
Maria Hepel

JUNIOR RESEARCH PERSONNEL:
Nancy Adinolfe
Kenneth Kanige
Eugene Mensah
Michael Shay
Robert Holt

PUBLICATIONS:

"Ohmic Potential Drop at Electrodes Exhibiting Steady-State Diffusional Currents" Stanley Bruckenstein, Anal. Chem., 1987, 59, 2098.

"Interpretation of Polyazulene Electrochemistry Considering the Faradaic Current Efficiency and Capacitive Current Effects During the Growth and Redox Switching Steps". Stanley Bruckenstein, and John W. Sharkey, J. Electroanal. Chem. and Interfacial Chem. 1988, 241, 211-230.

"Voltammetry at a Rotating and a Stationary Very Thin Ring Electrode". Stanley Bruckenstein, and James S. Symanski, J. Electrochem. Soc., 135, 1985, (1988).

"Determination of Hg(I) Adsorption Accompanying the Coulostatic Underpotential Deposition of Mercury on Gold Using the Quartz Crystal Microbalance". M. Shay, and S. Bruckenstein, Langmuir, 1989, 5, 280-282.

"Observation of Kinetic Effects During Interfacial Transfer at Redox Polymer Films Using the Quartz Crystal Microbalance". Stanley Bruckenstein, C. Paul Wilde, Michael Shay, A Robert Hillman, and David C. Loveday, J. Electroanal. Chem., 258, (1989), 457-462.

"Tracking Anion Expulsion During Underpotential Deposition of Lead at Silver Using the Quartz Crystal Microbalance". Maria Hepel, and S. Bruckenstein, Electrochimica Acta. In Press.

"Mechanistic Studies of the Deposition and Cathodic Stripping of Thioacetamide at a Silver Electrode in Alkaline Media". Maria Hepel, and S. Bruckenstein. Electroanalysis, 1 117-123 (1989).

"Induction in Stripping Voltammetry at Solid Electrodes". Maria Hepel, and S. Bruckenstein. Electroanalysis, 1, 311-315 (1989).

"The Formation and Electroreduction of Silver Sulfide Films on Silver Metal". Maria Hepel, S. Bruckenstein, and G. C. Tang. J. Electroanal. Chem., 261, 389-400 (1989)

"*In Situ* Underpotential Deposition Study of Lead on Silver Using the Electrochemical Quartz Crystal Microbalance. Direct Evidence for Pb(II) Adsorption Before Spontaneous Charge Transfer". Maria Hepel, Kenneth Kanige, and Stanley Bruckenstein. J. Electroanal. Chem., 266, 409-421 (1989).

"Experimental Observations on Transport Phenomena Accompanying Redox Switching in Polythionine Films Immersed in Strong Acid Solutions". S. Bruckenstein, A. R. Hillman, and C. P. Wilde, J. Phys. Chem., (In Press).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Physical electrochemical and electroanalytical studies were undertaken at silver, gold, and platinum electrodes. The goal was to study 1) phenomena controlling the formation of submonolayer and thicker films at solid electrodes, 2) the behavior of such films, and apply the fundamental information obtained in these studies to electroanalysis.

Underpotential deposition (UPD) studies were undertaken at polycrystalline silver electrodes. Using the electrochemical quartz crystal microbalance, it was shown that Pb(II) species are adsorbed at silver when the Pb(II) exists as an anion in solution. The anionic Pb(II) adsorbate is ultimately reduced to a underpotential Pb(0) with concomitant anion (ligand) expulsion from the electrode surface. Adsorption of sulfide ion (UPD without faradaic charge transfer) also occurs at silver from alkaline sulfide solutions. Three distinct UPD states were identified. The coulostatic formation of UPD Hg(0) at a gold electrode was studied in sulfuric acid using the EQCM. It was found that a monolayer of Hg(0) is formed along with an overlayer of mercury (I) bisulfate. The formation of silver sulfide during the electrooxidation of thioacetamide was established. A theoretical analysis of cathodic stripping peaks based on a hemispherical model with progressive nucleation was performed. The results were used in interpreting inductions times associated with the formation of cathodic stripping peaks at silver electrodes. The uncompensated ohmic potential drop at microelectrodes under steady state diffusion conditions was shown to be susceptible to a theoretical analysis. All microelectrodes under such conditions have the same ohmic potential drop, which was calculated. A very thin rotating electrode was investigated and its behavior characterized and interpreted in terms of existing theory. Studies of modified electrodes were undertaken. A method for determining the current efficiency for the electropolymerization process was developed and confirmed using azulene. The details of ion and neutral species transport on redox switching of polythionine was studies using the EQCM and the mobile species determined in strong acid solutions. Kinetic effects in this system were also studied and it was shown that mass and charge transport are decoupled when the electrode potential changes rapidly.

AFOSR Program Manager: Dr John S. Wilkes

# COMPLETED PROJECT SUMMARY

TITLE: Chemical and Electrochemical Properties of Potential Battery Systems in Room Temperature Molten Salts

PRINCIPAL INVESTIGATOR:
Francis M. Donahue
Department of Chemical Engineering
The University of Michigan
Ann Arbor, MI 48109-2136

INCLUSIVE DATES: 1 December 1984 - 30 November 1987

CONTRACT/GRANT NUMBER: AFOSR-85-0027

COST AND FY SOURCE: \$118,444, FY 85; \$141,603, FY 86; \$118,571, FY 87

SENIOR RESEARCH PERSONNEL:
Peter A. S. Smith
David S. Newman

JUNIOR RESEARCH PERSONNEL:
Russell Moy
Sarah Borns
John Ross
Leif Simonsen
Steven Blaine

PUBLICATIONS:

"Analgamated Aluminum Electrodes in Acidic Chloroaluminate Molten Salts." R. Moy and F. M. Donahue, *Electrochem. Acta*, *33*, 721 (1988).

"Viscosity Measurement of Low Temperature Molten Salts." F. M. Donahue and J. F. Ross, Accepted for publication in *J. Appl. Electrochem.*

"Chemistry and Electrochemistry of Aluminum and Its Ions in a Low Temperature Molten Salt With Reactive Solvents." F. M. Donahue, L. R. Simonsen, and R. Moy, *J. Electrochem. Soc.* (Submitted)

"Batteries Based on Modified Low Temperature Molten Salt Electrolytes." L. R. Simonsen and F. M. Donahue, to *33d International Power Sources Symposium*. (Submitted)

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The following areas had been proposed:

1. Electrochemistry/Chemistry of Aluminum

Aluminum electrodes were studied in basic and acidic melts. Dissolution was possible in both environments, but deposition was possible only in acidic melts. Extensive studies in acidic melts indicated that the exchange current density was relatively low (even at = 100°C, it was = 1 mA/cm$^2$) and that some passivation occurred at high current densities / overpotentials. However, the dissolution behavior at moderate rates ( 10 mA/cm$^2$) indicated relatively low polarization (sufficient for battery applications).

The $Al_2Cl_7^-$ anion was found to react with some basic, organic solvents (nitriles and amines) forming tetrahedral and octahedral aluminum coplexes (ions and neutral molecules) with the organic base. The structure was determined from $^{27}Al$ nmr. The electrochemistry of the complexes formed with nitriles indicated that the dissolution process was significantly altered (e.g., passivation was not observed) while deposition was not possible (due to the quantitative removal of $Al_2Cl_7^-$).

Aluminum electrodes were found to behave well in battery configurations with $FeCl_3$ and $CuCl_2$ 'positives'. Acidic, binary melts were completely reversible and were found to operate at current densities in excess of 15 $mA/cm^2$.

## 2.Magnesium Electrodes

Corrosion of magnesion was essentially nil in basic and neutral melts (these melts were essentially free of impurities) indicating that the cation (1-methyl-3-ethylimidazolium and tetrachloroaluminate anion were not electrochemically attacked by the metal. On the other hand, magnesium reacted with $Al_2Cl_7^-$ in acidic melts to form aluminum and a magnesium ionic species. Since $^{25}Mg$ nmr spectra could not be obtained at the concentration levels found in the melts, the structure of this magnesium species could not be determined. Magnesium was found to be stable in ternaries of acetonitrile and (initially acidic) binary melts.

## 3. Zinc Electrodes

Electrodissolution of zinc is more robust than aluminum (e.g., the exchange current densities in basic solutions are on the order of 0.1 $mA/cm^2$ at room temperature). Dissolution forms the anionic complex, $ZnCl_4^{2-}$, which was verified by the stoichiometry for the diffusivity measurement of $Cl^-$. Since $^{67}Zn$ nmr spectra could not be obtained at the concentration levels found in the melts, the structure could not be corroborated in this manner.

Zinc electrodes were found to behave well in primary battery configurations with $FeCl_3$ and $CuCl_2$ 'positives'.

## 4. Chlorine Studies

The problems encountered in previous studies with chlorine (see FJSRL-TM-84-0002) continue, i.e., significant solubility of chlorine in the melts (including melts containing the chlorinated cation) which leads to self-discharge of anode, eliminates the chlorine electrode as a reasonable candidate for battery systems.

## 5. Silver/Silver Chloride Studies

Since this electrode system was partially predicated on potential battery systems with magnesium (which has not been studied extensively), this system was not considered.

AFOSR Program Manager: Dr John S. Wilkes

# COMPLETED PROJECT SUMMARY

TITLE: Electrochemical and Spectroscopic Investigations of Molten Chloroaluminates and Related Solvents

PRINCIPAL INVESTIGATOR:
Glem Mamantov
Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

INCLUSIVE DATES: 15 September 1985 - 14 September 1988

CONTRACT/GRANT NUMBER: AFOSR-85-0321

COST AND FY SOURCE: $140,025, FY 86; $128,413, FY 87; $138,826, FY 88

SENIOR RESEARCH PERSONNEL:
J. P. Schoebrechts
G. Hance
S. Williams
T. Blackburn
S. W. Orchard
Y. Sato
B. Gilbert
G. Shankle
K. Ogle

JUNIOR RESEARCH PERSONNEL:
Paul Flowers
Karl Sienerth
Horst Clauberg
Ed Settle
David Trimble
Zhong Da Wu
Jim Selkirk

PUBLICATIONS:

"Infrared Spectroscopic Determination of Oxide in Molten Chloroaluminates," P.A. Flowers and G. Mamantov, Anal. Chem., 59, 1062 (1987).

"A New Room Temperature Molten Salt Solvent System: Organic Cation Tetrachloroborates", S.D. Williams, J.P. Schoebrrchts, J. C. Selkirk, and G. Mamantov, J. Amer. Chem. Soc., 109, 2218 (1987).

"A Brief Introduction to Electrochemistry in Molten Salts and Chloroaluminate Melts," G. Mamantov, in Molten Salt Chemistry; An Introduction and Selected Applications, G. Mamantov and R. Marassi, eds., Reidel Publishing Company, pp 259-270 (1987).

"An Electrochemical Approach for the Determination of Oxide Impurities in Acidic Alkali Chloroaluminates," J.-P. Schoebrechts, P.A. Flowers, and G. Mamantov, in Proceedings of the Joint International Symposium on Molten Salts, G. Mamantov, M. Blander, C. L. Hussey, C. B. Mamantov, M. L. Saboungi, and J. S. Wilkes, eds., The Electrochemical Society, Pennington, NJ, pp 437-444 (1987).

"Raman Spectroscopy of Fluoride-Containing Chloroaluminate Melts," B. Gilbert, S.D. Williams and G. Mamantov, Inorg. Chem., 27, 2359 (1988).

"Electrochemical and Spectroscopic Studies of Tungsten Hexachloride in an Acidic Sodium Chloroaluminate Melt. Determination of Dissolved Oxide," J. -P. Schoebrechts, P.A. Flowers, G.W. Hance, and G. Mamantov, J. Electrochem. Soc., 135, 3057 (1988).

"Thin-Layer Transmittance Cell for Infrared Spectroelectrochemistry," P. A. Flowers and G. Mamantov, Anal. Chem., 61, 190 (1989).

"Voltammetry of Ag(I) in Solid $NaAlCl_4$," T. R. Blackburn and G. Mamantov, J. Electrochem Soc., 136, 580 (1989).

"An Introduction to Electrochemistry in Molten Salts," G. Mamantov, C. L. Hussey, and R. Marassi, in Techniques for Characterization of Electrodes and Electrochemical Processes, R. Varma and J. R. Selman, etd., John Wiley (in press).

"Infrared Spectroscopic and Spectroelectrochemical Investigation of Chloranil in Molten Sodium Chloroaluminates," J. Electrochem. Soc. (in press).

"Infrared Spectroscopic and Spectroelectrochemical Studies in Molten Sodium Chloroaluminates," P.A. Flowers, PhD Dissertation, University of Tennessee, Knoxville, May 1988.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project involved several aspects of electrochemistry and spectroscopy in molten chloroaluminates and related solvents. The following topics were investigated:

(1) Development of spectroelectrochemical and other methodology for alkali chloroaluminates. This research included UV-visible absorption spectroelectrochemistry, infrared and Raman spectroscopy and spectroelectrochemistry, and studies with ultramicroelectrodes.

(2) Electrochemical and chemical studies of selected redox systems in sodium chloroaluminates, including tungsten and tantalum species, $CO_2$, HCl, and iridium carbonyls.

(3) Studies related to molten salt batteries. Such studies included examination of $Na^+$ conducting glasses in $AlCl_3$-NaCl melts, studies of cobalt electrodes in these melts, and studies with $FeCl_3$-NaCl melts.

(4) Investigations of new molten salt solvents, including fluoride-containing chloroaluminate melts, room temperature organic tetrachloroborates, and calcium halide melts.

AFOSR Program Manager: Dr John S. Wilkes

# RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - SURFACE CHEMISTRY

LT COL LARRY W. BURGGRAF, USAF

| | |
|---|---|
| In-Situ Surface Analysis During Laser-Controlled Chemical Processing of Surfaces<br>AFOSR-86-0094 | Alan Campion<br>Department of Chemistry<br>University of Texas at Austin<br>Austin, Texas 78712 |
| Surface Analysis System and Surface Raman Spectroscopy<br>AFOSR-87-0070 | Alan Campion<br>Department of Chemistry<br>University of Texas at Austin<br>Austin, Texas 78712 |
| Resonant Charge Exchange Studies with Hyperthermal Energy Ion Beams: Development of Multi-Detection Capabilities and a Data Acquisition System<br>AFOSR-87-0048 | Barbara H. Cooper<br>Laboratory of Atomic and Solid State Physics<br>Cornell University<br>Ithaca, NY 14853-2501 |
| LASST-ACSIS Workshop on "Diffusion at Interfaces: Microscopic Concepts"<br>AFOSR-87-0325 | M. Grunze<br>Laboratory for Surface Science<br>University of Maine<br>Barrows Hall<br>Orono, ME 04469 |
| Dynamics of Gas-Surface Interactions<br>AFOSR-84-0073 | Steven J. Sibener<br>The James Franck Institute and Department of Chemistry<br>University of Chicago<br>5640 S. Ellis Avenue<br>Chicago, Illinois 60637 |
| The Influence of Surface Structural Defects on Surface Chemistry<br>AFOSR-83-0302 | Peter C. Stair<br>Department of Chemistry<br>Northwestern University<br>Evanston, Illinois 60208 |
| Investigation of Coupled Surface and Bulk Reaction Phenomena Using CEAPS<br>AFOSR-84-0301 | Bruce J. Tatarchuk<br>Chemical Engineering Department<br>Auburn University<br>Auburn, AL 36849 |
| Electronic Interactions of Electrons Photons and Atoms with Material Surfaces<br>AFOSR-86-0150 | Norman H. Tolk<br>Richard F. Haglund, Jr<br>Department of Physics and Astronomy, and Center for Atomic and Molecular Physics at Surfaces<br>Vanderbilt University<br>Nashville, TN 37235 |

Scanning Tunneling Microscopy as
as a Surface Chemical Probe
AFOSR-86-0235
AFOSR-85-0042

**Ellen D. Williams**
**Department of Physics and**
**Astronomy**
**University of Maryland**
**College Park, MD 20742**

# COMPLETED PROJECT SUMMARY

TITLE: In-Situ Surface Analysis During Laser-Controlled Chemical Processing of Surfaces

| | |
|---|---|
| PRINCIPAL INVESTIGATOR: | Alan Campion<br>Department of Chemistry<br>University of Texas at Austin<br>Austin, Texas 78712 |
| INCLUSIVE DATES: | 1 May 1986 - 29 February 1988 |
| GRANT NUMBER: | AFOSR-86-0094 |
| COSTS AND FY SOURCE: | $75,000 FY 86 |
| SENIOR RESEARCH PERSONNEL: | Kathryn Lloyd, PhD |
| JUNIOR RESEARCH PERSONNEL: | Scott Perry |

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Experiments designed to assess the utility of several methods of surface analysis under reaction conditions are described. The goal of the research was to develop new methods with which to understand the mechanisms associated with the preparation of materials of electronic interest by chemical vapor deposition, with an emphasis on laser control of the reactions. The focus of the work was to improve the sensitivity of unenhanced surface Raman spectroscopy through the combined use of ultraviolet lasers, Cassegrain optical systems and charge-coupled device detectors. Model systems to test these technical improvements were designed and an understanding of the factors that govern sensitivity has been achieved. Construction of a system for laser direct writing as well as the installation of a multipurpose surface analysis system are also described.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

## COMPLETED PROJECT SUMMARY

TITLE: Surface Analysis System and Surface Raman Spectroscopy

PRINCIPAL INVESTIGATOR:
Alan Campion
Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

INCLUSIVE DATES: 01 November 1986 - 31 December 1987

GRANT NUMBER: AFOSR-87-0070

COSTS AND FY SOURCE: $80,000 FY86-87

SENIOR RESEARCH PERSONNEL: Kathryn Lloyd, PhD

JUNIOR RESEARCH PERSONNEL:
Kristi Allan
Xudong Jiang
Yuanfang Dai

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A multipurpose surface analysis chamber equipped with X-ray photoelectron spectroscopy, ion scattering spectroscopy, secondary ion mass spectrometry and Auger electron spectroscopy has been constructed and installed. The Leybold LHS-12 system which was partially funded from this grant, comprises both high pressure and ultrahigh vacuum sample preparation and reaction chambers, thermal evaporation and radiofrequency sputtering sources and a rapid entry load lock. This system is fully operational, meeting all specifications, and is being used in a wide variety of surfaces science and other applications. These include the XPS study of the decomposition of alkyl halides in support of our surface Raman spectroscopy efforts, an XPS study of the X-ray induced degradation of thin polymer films and a study of the role of peroxide ions in the mechanism of high temperature superconductivity.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Resonant Charge Exchange Studies with Hyperthermal Energy Ion Beams: Development of Multi-Detection Capabilities and a Data Acquisition System.

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|---|---|
| PRINCIPAL INVESTIGATOR: | Barbara H. Cooper<br>Laboratory of Atomic and Solid State Physics<br>Cornell University<br>Ithaca, NY 14853-2501 |
| INCLUSIVE DATES: | 15 November 1986 - 14 May 1988 |
| GRANT NUMBER: | AFOSR-87-0048 |
| COSTS AND FY SOURCE: | $79,000 FY87, 88 |
| JUNIOR RESEARCH PERSONNEL: | David M. Goodstein<br>Greg A. Kimmel<br>David R. Peale |

PUBLICATIONS:

"An Efficient Algorithm for the Simulation of Hyperthermal Energy Ion Scattering", D.M. Goodstein, S.A. Langer, and B.H. Cooper, J. Vac. Sci. Tech., A 6(3) 703 (1988).

"The Design and Performance of a UHV Beamline to Produce Low and Hyperthermal Energy Ion Beams", D.L. Adler and B.H. Cooper, Rev. Sci. Instrum., 59, 137 (1988).

"Design and Performance of Ion Optics for Hyperthermal (10-100 eV) and keV Ion Scattering", D.L. Adler, B.H. Cooper, and D.R. Peale, J. Vac. Sci Tech., A6(3), 804 (1988).

"A Versatile Apparatus for Low Energy and Hyperthermal Energy Ion Scattering Spectroscopy", R.L. McEachern, D.L. Adler, D.M. Goodstein, G.A. Kimmel, B.R. Litt, D.R. Peale, and B.H. Cooper, Rev. Sci. Instrum., in press.

"Source for Producing Alkali Ion Beams for Low Energy Surface Scattering Spectroscopies", D.R. Peale, D.L. Adler, B.R. Litt, and B.H. Cooper, Rev. Sci. Instrum. (1988) (submitted).

"Trajectory Analysis of Low Energy and Hyperthermal Ions Scattered from Cu(110)", R.L. McEachern, D.M. Goodstein, and B.H. Cooper, Phys. Rev. B (1988) (submitted).

"Low Energy Alkali Ion Scattering as a Probe of Resonant Charge Exchange on Cesiated Cu(110)", G.A. Kimmel, D.M. Goodstein, and B.H. Cooper, J. Vac. Sci. Tech., AVS conference proceedings (1988) (submitted).

"Hartree-Fock Potentials for Alkali Ion-Metal Scattering Below 500 eV", D.M. Goodstein, R.L. McEachern, and B.H. Cooper, (1988) (in preparation).

"Rainbow Scattering for 100 to 400 eV $Na^+$ from Cu(110)", D.L. Adler, R.L. McEachern, D.M. Goodstein, nd B.H. Cooper, (1988) (in preparation).

"Resonant Charge Exchange Studies with Hyperthermal Energy Ion Beams: Development of multi-detection capabilities and a data acquisition system", B.H. Cooper, Final Technical Report to AFOSR (1988).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of the instrumentation development were to complete the overall apparatus, to design and construct multi-detectors for the scattered ions, and to configure a computer system that could handle real-time data acquisition from the multi-detectors.

Progress in instrumentation includes: the successful production of low phase-space alkali and noble gas beams ranging in energy from 10eV to several keV, completion of two hemispherical analyzers for detecting scattered ions (one with high-resolution capabilities, the other for large angle scattering studies), position-sensitive pulse-counting detectors for multi-energy detection, and a Macintosh II-based data acquisition system which receives and stores data from the storage buffers of the multi-detectors.

The scientific objectives are to investigate the interactions of hyperthermal (10-100 eV) and keV ions with metal surfaces. Particular emphasis is placed on the study of ion-surface charge transfer processes.

Scientific progress includes; Measurements of 50eV to 4keV alkali scattering from clean and cesium-covered Cu(110), simulations using Hartree-Fock pair potentials that give good agreement with the 100 to 400 eV $Na^+$ scattering from Cu(110), trajectory analysis to identify peaks in the $Na^+$ energy spectra, measurements of charge transfer probabilities for alkalis scattering from Cu(110) with low coverages (1/10 monolayer) of Cs adsorbates, and ongoing development of a model that includes both local and collective effects of the Cs adsorbates in determining charge transfer probabilities.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

## COMPLETED PROJECT SUMMARY

TITLE: LASST-ACSIS Workshop on "Duffusion at Interfaces: Microscopic Concepts"

PRINCIPAL INVESTIGATOR: M. Grunze
Laboratory for Surface Science and Technology
University of Maine
Barrows Hall
Orono, ME 94469

INCLUSIVE DATES: 1 August 1987 - 31 July 1988

GRANT NUMBER: AFOSR-87-0325

COSTS AND FY SOURCE AFOSR ($4,100); ONR ($5,000)

SENIOR RESEARCH PERSONNEL: M. Grunze
H. J. Kreuzer

JUNIOR RESEARCH PERSONNEL: J. J. Weimer

PUBLICATIONS:

The proceedings of the Conference have been published as "Diffusion at Interfaces: Microscopic Concepts", edited by M. Grunze, H.J. Kreuzer and J.J. Weimer, Springer Series in Surface Sciences, Volume 12, (1988), Springer Verlag, Berlin, (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of the workshop was to review the experimental and theoretical results on surface bulk diffusion and to discuss them in view of microscopic concepts. The papers presented and discussions, summarized by the chairpersons, are published as a Volume in "Springer Series in Surface Sciences." A particular accomplishment of the conference was that theoretical and experimental criteria to distinguish between single particle and collective diffusion behavior were developed.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Dynamics of Gas Surface Interactions

PRINCIPAL INVESTIGATOR:
Professor Steven J. Sibener
The James Franck Institute and
Department of Chemistry
The University of Chicago
5640 S. Ellis Avenue
Chicago, IL 60637

INCLUSIVE DATES: 1 April 1984 - 31 May 1988

CONTRACT/GRANT NUMBER: AFOSR 84-0073

SENIOR RESEARCH PERSONNEL: Steven J. Sibener

JUNIOR RESEARCH PERSONNEL:
Barbara Gans
Dan Koleske
Yaw-Wen Yang
Scott Silence*
Suzanne King
Glenn Tisdale
Mark Kramer*
Joe Zwanziger*
(*Undergraduate Research Students)

PUBLICATIONS:

"Surface Phonon Spectroscopy of a Partially Disordered and Multiply Reconstructed Surface: Si(100) · (2x1)," Y. W. Yang, D. D. Koleske, and S. J. Sibener, Phys. Rev. B, (submitted).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research initiative deals with the interaction of atomic, molecular, electron, and optical beams with well-characterized single crystal surfaces. These studies are motivated by the desire to understand and control catalytic surface chemistry, the technological need to characterize the physical properties of thin films and surfaces, and the desire to understand how energy and momentum are exchanged at the surface of a material when it is subjected to gas-surface collisions, electron-surface collisions, optical illumination, or chemical reaction. During the past grant period two major new ultra-high vacuum scattering instruments were designed and successfully completed. One is a high performance neutral particle scattering apparatus, which routinely achieves an energy resolution of about 300 micro-electron volts. The other instrument is a new electron energy loss spectrometer which has achieved, with high signal throughout about 5 millelectron volt energy resolution, and operation with beam energies of up to 240 eV. Both of these instruments have independently rotating detectors, allowing scattering information to be collected over a range of final angles without varying the incident kinematics-this is the optimal situation for facilitating comparisons with theoretical scattering calculations. These new ultra-high vacuum instruments have performed at or exceeded their respective design goals, allowing experiments aimed at elucidating the structural and dynamical properties of surfaces to be pursued. Emphasis is initially being placed on inelastic single phonon measurements in order to determine the surface phonon dispersion relations for a wide variety of clean and adsorbate covered surfaces. Such measurements yield unambiguous information on the forces present at material interfaces, and in particular indicate to what extent surface forces differ form bulk behavior. The neutral particle instrument has performed elastic diffraction and inelastic measurements on alkali halide, semiconductor, and metallic surfaces. Si(001)-(2x1) phonon dispersion measurements differ from prior theoretical calculations, and suggest that the dynamical properties of partially disordered surfaces merit increasing attention in this program. Initial experiments in the electron scattering laboratory are examining the surface force field of Ni(111). Lattice dynamics and quantum scattering computer codes that support the above experimental effort are now operational. A molecular dynamics program is currently under development.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

## COMPLETED PROJECT SUMMARY

TITLE: The Influence of Surface Structural Defects on Surface Chemistry

PRINCIPAL INVESTIGATOR: Peter C. Stair
Department of Chemisstry
Northwestern University
Evanston, Illinois 60208

INCLUSIVE DATES: 1 September 1983 - 31 July 1988

CONTRACT/GRANT NUMBER: AFOSR-83-0302

COST AND FY SOURCE: $119,849 FY 83; $96,472 FY 84;
$99,459 FY 85; $78,193 FY 87

JUNIOR RESEARCH PERSONNEL: Anne L. Testoni, Jeffery Bruns, John L. Grant

PUBLICATIONS:

"The Role of Surface Defects in Aluminum Surface Oxidation," A. L. Testoni, and P. C. Stair, J. Vac. Sci. Technol. A4, 1430, (1986).

"The Effects of Surface Facets on the Oxidation of Aluminum (111) Surfaces," A. L. Testoni, and P. C. Stair, Surface Sci., 171, L491 (1986).

"Pulsed Laser-Induced Desorption from Metal Surfaces," peter C. Stair, and Eric Waltz, J. Opt. Soc. Am., B4, 255 (1987).

"The Role of Steps in the Oxidation of Al(111) Surfaces," A. L. Testoni, and P. C. Stair, Surface Science (submitted).

"The Instrument Response Function for a Digital Pulse Counting LEED Instrument," A. L. Testoni, and P. C. Stair, Rev. Sci. Instrum (submitted).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research objectives associated with this project were divided into three categories:

1. Develop digital low-energy electron diffraction (LEED) as a tool for quantitative analysis of extended and point surface structural defects.

2. Characterize the nature and concentration of defects produced by sputtering and annealing treatments of single crystal surfaces. A systematic examination of the defects produced by surface fabrication and cleaning procedures was needed to evaluate the effect of these treatment on surface properties.

3. Determine the influence of surface defects on surface chemistry. A central hypothesis of this research project was that surface defects strongly influences the rates of surface chemical reactions associated with oxidation and corrosion and the morphologies of resulting oxide layers. A comparison of the chemical behavior of relatively perfect, well annealed single crystal surfaces with interfaces having known defect structures was performed to prove this hypothesis.

Accomplishments of the research were:

1. Construction of the first computer-interfaced digital LEED instrument with high resolution diffraction images (512x512 pixels) and high sensitivity for quantitative measurements of beam shapes and background intensity distributions.

2. The nature and concentration of extended surface structural defects (steps, strain, mosaic boundaries) produced on Al(111) single crystals by various preparation procedures were determined. The most commonly observed defects were randomly oriented steps.

3. Studies of the influence of steps on the oxidation of Al(111) revealed a) that steps do not effect the sticking coefficient of molecular oxygen on the surface and, b) steps lower the critical atomic oxygen coverage required to nucleate the oxide phase. This letter result suggests that oxide nucleation occurs preferentially at step sites.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Investigation of Coupled Surface and Bulk Reaction Phenomena Using CEAPS

PRINCIPAL INVESTIGATOR:
Bruce J. Tatarchuk
Chemical Engineering Department
Auburn University
Auburn, AL 36849

INCLUSIVE DATES: 1 September 1984 - 30 April 1988

GRANT NUMBER: AFOSR-84-0301

COST AND FY SOURCE: Cumulative Project Funding: \$96,350 (9/1/84 - 10/31/85), \$94,571 (11/1/85 - 10/31/86), \$93,265 (11/1/86 - 10/31/87), \$48,800 (11/1/87 - 4/30/88)

JUNIOR RESEARCH PERSONNEL:
J. S. Zabinski
T. S. Lee
J. H. Sanders

PUBLICATIONS:

"Backscatter Mossbauer Spectroscopy: Applications to Surface and Catalytic Phenomena," with J. A. Dumesic, in Chemistry and Physics of Solid Surfaces, Volume 5, Chapter 4, 65-109 (1984), Published by Springer Veriag.

"Electron Intensities Obtained During Backscatter-Mossbauer Spectroscopy: I. Comparison Between Theory and Experiment," T. S. Lee, T. D. Placek and J. A. Dumesic, Nuclear Instruments and Methods in Physics Research, B18, 182, (1987).

"Generation of Low Energy Resonant Electrons During Relaxation of $^{57}$Fe,"J. S. Zabinski, Hyperfine Interactions 41, 737, 1988.

"A Theoretical Model for the Analysis of Backscattered-Conversion Electron Mossbauer Spectroscopy: Angular and Energy Distributions," with T. S. Lee. Hyperfine Interactions 42, 1149, 1988.

"Electron Intensities Obtained During Backscattered-Mossbauer Spectroscopy: II. Emergent Energy and Angular Distributions," T. S. Lee and J. S. Zabinski. Nuclear Instruments and Methods in Physics Research, B30, 196, 1988.

"Resonant Low Energy Electrons and Their Impact on Sampling Depth During Backscatter-Electron Mossbauer Spectroscopy," J. Zabinski. Nuclear Instruments and Methods in Physics Research, B31, 576, 1988.

"Generation of Low Energy Resonant Electrons During Relaxation of $^{57}$Fe," International Conference on the Applications of the Mossbauer Effect, August, 1987, Melbourne, Australia, Volume III, Proceedings of the International Conference on the Applications of the Mossbauer Effect, J. C. Baltzer AG, Scientific Publishing Co., Basel-Switzerland, 1988, with J. Zabinski.

"A Theoretical Model for the Analysis of Backscattered-Conversion Electron Mossbauer Spectroscopy: Angular and Energy Didstributions," T. S. Lee. International Conference on the Applications of the Mossbauer Effect, August, 1987, Melbourne, Australia, Volume III, Proceedings of the Interantional Conference on the Applications of the Mossbauer Effect, J. C. Baltzer AF, Scientific Publishing Co., Basel-Switzerland, (1988).

"Surface Chemical Characterization of Internal Interfaces Generated Within Thin-Film Hydrides," J. H. Sanders. Fall National Meeting of the Materials Research Society, December, 1987, Boston, MRS Symposium Proceedings, Microstructure and Properties of Catalysts, Volume III, 369-374, (1988).

"Chemical Characterization of the Deactivation and Protection of FeTi Thin-Films Using Complementary Nondestructive Techniques," J. H. Sanders. Journal of Thin Solid Films. (in press).

"Resonant Low Energy Electrons and Their Impact on Nondestructive Depth-Profiling of Thin-Film Samples," J. S. Zabinski. Surface and Coatings Technology (accepted for publication).

"Deactivation Mechanisms for Thin-Film Iron-Titanium Hydrides," J. Sanders Journal of the Less-Common Metals. (submitted).

"Passivation Mechanisms for Thin-Film Iron-Titanium Hydrides," J. Sanders The Journal of Physics F: Metals. (submitted).

"Characterization of Reactions Occurring at Buried Interfaces Between Iron and Titanium Thin-Films," J. Sanders, The Journal of Materials Research. (in preparation).

"Generation mechanisms for Low Energy Electrons Produced During Relaxation of $^{57}$Fe and Their Utilization for Depth-Deconvolution," J. S. Zabinski Hyperfine Interactions. (in preparation).

"Electron Intensities Obtained During Backscattered-Mossbauer Spectroscopy: III. Emergent Energy and Angular Distributions Resulting from Shakeoff and Secondary Events," T. S. Lee and J. S. Zabinski, Nuclear Instruments and Methods in Physics Research. (in final preparation).

"Nucleation and Intercalation of Iron Overlayers on $MoS_2$ Single Crystal Substrates," J. S. Zabinski, Surface Science. (in preparation for submission).

"Empirical Procedures for the Depth-Deconvolution of Low Energy Electron Mossbauer Spectra," J. S. Zabinski, Nuclear Instruments and Methods in Physics Research. (in preparation for submission).

PRESENTATIONS:

"Applications of Surface Specific Mossbauer Spectroscopy," invited paper at the Symposium on Techniques for the Characterization of Electrode Surfaces, 188th National Meeting of the American Chemical Society, Division of Colloids and Surface Chemistry, Philadelphis, 1984, with J. S. Zabinski and T. R. Nolen.

"Applicatons of Combined-Backscatter-Conversion Electron and Backscatter-Photon Mossbauer Spectroscopy to Thin-Film Studies," Annual Meeting of the Florida Chapter of the American Vacuum Society, Clearwater, FL, February 1987, with J. S. Zabinski, J. H. Sanders and T. S. Lee,.

"A Theoretical Model for Interpretation of Backscatter-Conversion Electron Mossbauer Spectra Obtained from Thin-Film Substrates," Annual Meeting of the Florida Chapter of the American Vacuum Society, Clearwater, FL, February 1987, with T. S. Lee, J. S. Zabinski and J. H. Sanders.

"Characterization of Surface Chemical Effects Occurring at Internal Interfaces Using Novel Spectroscopic Probes," Rice University, Department of Chemical Engineering, December, 1987.

"Resonant Low Energy Electrons and Their Impact on Nondestructive Depth-Profiling of Thin-Film Samples," invited paper to the 15th International Conference on Metallurgical Coatings, San Diego, California, April, 1988 with J. S. Zabinski.

"Investigation of Internal Interfacial Reactions of the FeTi-Hydride Systems," 15th International Conference on Metallurgical Coatings, San Diego, Califonia, April, 1988 with J. H. Sanders.

"Interfacial Chemical Reactions Between $MoS_2$ Lubricants and Bearing Materials," Symposium S -- New Materials Approaches to Tribology: Theory and Practice, Fall National Meeting of the Materials Research Society, December, 1988, Boston, with J. S. Zabinski.

"Application and Performance of Silicon-Based Atomic Oxygen Protective Coatings," invited presentation to the 34th International SAMPE Symposium: Tomorrows Materials Today, Session on Space Environmental Effects, May, 1989, Reno, Nevada, with J. H. Sanders, R. T. Booher and P. B. Lloyd.

THESES IN PROGRESS:

"Theoretical and Experimenal Studies of Backscattered-Mossbauer Spectroscopy," T. S. Lee, Ph.D. Dissertation.

"Studies of Ion Beam Induced Mixing and Internal Hydride Formation by Means of Backscattered-Mossbauer Spectroscopy," J. Sanders, Ph.D. Dissertation.

"Significance of Low Energy Resonant Electrons and Photons During Backscattered-Mossbauer Spectroscopy," J. Zabinski, Ph.D. Dissertation.

GRADUATE STUDENT AWARDS:

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|---|---|
| Jeffrey Sanders: | NASA-Graduate Student Researchers Program Fellowship, 6/16/85 to 6/15/88. |
| | Graduate Student Research Award presented by the Materials Research Society, National Meeting, Boston, Massachusetts, December, 1987. |
| | Graduate Student Research Award presented by the International Congress on Metallurgical Coatings, San Diego, California, April, 1988. |

| | |
|---|---|
| Jeffrey Zabinski: | Southeastern Regional Ph.D. Fellowship in Chemical Engineering, September 1985 to September 1989.<br>American Vacuum Society - Tennessee Valley Chapter Graduate Student Research Award, 1988-1989.<br>Travel Grant awarded by the international Congress on the Applications of the Mossbauer Effect (ICAME), Melbourne, Australia, August 1987. |
| Teh-Shing Lee: | Travel Grant awarded by the International Congress on the Applications of the Mossbauer Effect (ICAME), Melbourne, Australia, August 1987. |

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS;

The influence and manipulation of chemical phenomena occurring at internal interfaces has major technological importance to the Air Force, yet is an area of basic science which has received relatively little attention in the past due to the characterization problems posed by such systems. Better characterization techniques, providing both nondestructive and depth-profiled chemical and structural insights, are needed so that important issues in: surface chemistry, interfacial adhesion, microelectronics, corrosion, metallurgy, protective coatings, thin-film science, etc., can be accurately diagnosed and subsequently manipulated for technological advantage.

As a result of the above noted realization, we have constructed a device to nondestructively depth-profile thin-film samples from the topmost monolayers to ca. 20 $\mu m$. The device combines backscatter-conversion electron and backscatter-photon Mossbauer spectroscopy (CEAPS) to provide depth-resolved chemical, electronic, magnetic, and morphological information over this range. An Air Force sponsored study involving the theorectical and experimental development of CEAPS as well as the testing and demonstration of this technique on a number of model systems has been completed. During our efforts:

- CEAPS has been used to study interfacial reactions that occur between solid-lubricants and bearing materials after vacuum annealing and reactive gas ($H_2$,$O_2$) treatments. The reaction products (FeS, Fe-oxides, $FeMo_2S_4$, etc.) affect both the tribological and adhesive properties of the lubricant/bearing system.
- CEAPS has provided better than monolayer sensitivity for appropriate nuclei and permitted nondestructive analysis from the topmost monolayer to as deep as 20 um into the specimen; and has provided surface information from one monolayer in as short a time as one hour permitting Mossbauer spectra to be collected from clean surfaces in laboratory vacuum for the first time.
- Monte Carlo simulations of electronic relaxation following nuclear decay have been conducted to identify generation mechanisms for low energy electrons containing surface information.

- New theoretical treatments for backscattered-Mossbauer spectroscopy have been developed and experimentally verified which accurately predict angular electron distributions, energy distributions and measured signal-to-background ratios thereby allowing more detailed nondestructive depth-profiling of layered substrates. Inclusion of low energy electrons in theoretical models permits the analysis of very thin surface layers, and provides enhanced surface sensitivities.

- CEAPS studies have revealed the chemical and morphological sources of deactivation in FeTi-hydride systems.

- The above noted deactivation pathways have been eliminated by means of a protective palladium coating, the chemical and structural integrity of the buried-interface (i.e., coating/FeTi) has been examined using CEAPS to verify performance criteria.

- We have discovered low energy resonant electron signals below 15 eV (i.e., signatures), which are produced in the topmost monolayers of the sample, and which permit easy deconvolution of the layer from the remainder of an infinitely thick substrate. This procedure permits CEAPS to be used in a more complementary fashion with other surface science techniques.

- CEAPS was used to monitor monolayer equivalent oxidation of substrates with 30 nm silica coatings to verify coating effectiveness for corrosion resistance when exposed to simulated LEO environments.

- Ion beams mixing of a buried Fe/Sn interface was studied from both Fe Mossbauer and Sn Mossbauer perspectives revealing the intermetallic compounds responsible for the adhesive and corrosion resistant properties of this system.

AFOSR Program Manager: Lt. Col. Larry W. Burggraf, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Electronic Interactions of Electrons, Photons and Atoms with Material Surfaces

PRINCIPAL INVESTIGATORS:
Norman H. Tolk
Richard F. Haglund, Jr
Department of Physics and Astronomy, and
Center for Atomic and Molecular Physics at Surfaces
Vanderbilt University
Nashville, TN 37235

INCLUSIVE DATES: 15 April 1986 - 14 April 1988

CONTRACT/GRANT NUMBE: AFOSR-86-0150

COSTS AND FY SOURCE: $90,000 FY87; $114,921 FY88

SENIOR RESEARCH PERSONNEL:
Marcus H. Mendenhall
Joel Tellinghuisen
Alan V. Barnes
Peter Nordlander
Royal G. Albridge
Dwight P. Russell

JUNIOR RESEARCH PERSONNEL:
Doug Harper
Doug Cherry
Shirley Oyog
Mike Albert
Mike Shea

PUBLICATIONS:

"Energy Shifts and Broadening of Excited Hydrogen-Atom Levels in the Vicinity of a Metal Surface," P. Nordlander and J.C. Tulley, Phys Rev. Letters 61, 990 (1988).

"Electronic Transitions in Surface and Near-Surface Radiation Effects", R.F. Haglund, Jr. M. H. Mendenhall, N.H. Tolk, G. Bertz, and W. Husinsky, Nucl Instr. and Meth. B32, 321 (1988).

"Extended Huckel Theory for Ionic Molecules and Solids: An Application to Alkali Halides", Y. Wang, P. Nordlander, and N.H. Tolk, to be published in the October 1988 issue of J. Chem. Phys.

"Ultraviolet Spectroscopy of $CN^-$ in Alkali Halides: Dynamics of the Metastable Triplet State", M. Mendenhall, A. Barnes, P. Bunton, R. Haglund, L. Hudson, R. Rosenberg, D. Russell, J. Sarnthein, P. Savundararaj. N. Tolk, and J. Tellinghuisen, Chem. Phys. Letters 147, 59 (1988).

"PSD of Excited Hydrogen from KCl", L.T. Hudson, A.V. Barnes, N.J. Halas, R.F. Haglund, M.H. Mendenhall, P. Nordlander, N.H. Tolk. Y. Wang, and R.A. Rosenberg, in Desorption Induced by Electronic Transitions, DIET III ed by R.H. Stulen and M.L. Knotek (Springer-Verlag, Berlin, 1988) p 274.

"Optical Radiation from Electron, Photon and Heavy Particle Bombardment of Lithium Fluoride and Lithium-Dosed Surfaces,"N. H. Tolk, R.G. Albridge, A.V. Barnes, R.F. Haglund, Jr., L. T. Hudson, M.H. Mendenhall, D.P. Russell, J. Sarnthein, P.M. Savundararaj. and P.W. Wang, in Desorption Induced by Electronic Transitions, DIET III, ed. by R.H. Stulen and M.L. Knotek (Springer-Verlag, Berlin, 1988) p. 284.

"Long Lifetime of Bulk Luminescence Observed in Spectrosil Glasses Under Electron Bombardment", P.W. Wang, R.F. Haglund, Jr., L.T. Hudson, D.L, Kinser, M.H. Mendenhall, N.H. Tolk and R.A. Weeks, in Desorption Induced by Electronic Transitions, DIET III, ed. by R.H. Stulen and M.L. Knotek (Springer-Verlag, Berlin, 1988) p 289.

"Intracavity Optical Damage Due to Electrons, Ions and Ultraviolet Photons," R.F. Haglund, Jr. SPIE 895, 182 (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The intent of this research program is to elucidate the microscopic mechanisms by which the energy of incoming beams of atoms, ions, electrons and photons is absorbed, localized the redirected to produce neutral-particle desorption from surfaces and subsequent surface modification or restructuring. In particular, we emphasized (1) heavy-particle-, electron-, and photon-induced desorption measurements for the case of the model system LiF, (2) kinematically-complete experiments in which all the neutral species desorbed from a surface are detected, in order to form a complete picture of the energy balance in electronically induced desorption processes for the LiF model system, (3) Parametric and time resolved studies of electronically-stimulated desorption as a function of incident-beam energy, beam intensity, and substrate conditions, and (4) comparison of the results of the above experiments with measurements of electronically desorbed Li-atoms coadsorbed with O-atoms on well defined crystals.

These comparative studies of electron, photon and ion bombardment of the same sample surface probed the various channels through which incident particle energy is dissipated. Electron or photon irradiation of alkali halides results in the swift ejection of halide atoms, leaving behind an enriched alkali metal surface from which the alkali atoms thermally desorb. Ion bombardment involves momentum transfer as well as electronic mechanisms, which results in a different surface stoichiometry at the time of desorption. This study explored how the degree of surface metallization influences the choice of the final excitation state of the desorbing particle. Measurements were made to compare the desorption of excited state neutral lithium from lithium fluoride by electron, photon and ion bombardment and from lithium-dosed tungsten and lithium-dosed glass by electron and photon bombardment.

In the electron and photon desorption experiments, we observed only the first lithium resonance line. These results contrast with the ion sputtering results, where emissions from higher excited states are observed. This suggests that the presence of a metal rich surface provides a channel for de-excitation of excited lithium states which are above the lithium metal Fermi energy. This quenching of the higher excited lithium lines is less likely when the sample is excited by ions. These studies have shown substantial success and have pointed the way for significant future progress.

Further studies presently supported by AFOSR on another contract involve careful surface analysis of the stiochiometry of lithium fluoride during ion, electron and photon irradiation. The ultimate aim of this research program is to characterize the final states of all the desorption products and the extent to which they are influenced by the surface, exciting beam and secondary processes.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Scanning Tunneling Microscopy as a Surface Chemical Probe

PRINCIPAL INVESTIGATOR: Ellen D. Williams
University of Maryland
Department of Physics and Astronomy
College Park, MD 20742

INCLUSIVE DATES: 8/1/86-01/31/88

CONTRACT/GRANT NUMBER: AFOSR-86-0235

SENIOR RESEARCH PERSONNEL: Ellen D. Williams

JUNIOR RESEARCH PERSONNEL: Xue-sen Wang, Jill Goldberg, Romel Gomez

PUBLICATIONS:

"Apperance Potenial Study of Ba-Activated Oxidation of Nickel," R. D. Gomez and E. D. Williams, Surface Science, (in press) (1988).

"Comparison of LEED and STM Measurements of Vicinal Si(III)," X-S. Wang, P. J. Phaneuf and E. D. Williams, J. Microscopy, (in press) (1988).

"Measurement-Dependent Corrugations of Graphite," R. D. Gomez and E. D. Williams, (in preparation) (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research effort was to improve the instrumentation in support of grant number AFOSR-85-0042. The following equipment was put into effect:

1. A micro-computer dedicated to real-time control and data-acquisiton of the STM. Software has been developed to drive the STM scans under computer control while simultaneously reading the output of the feedback circuit. The data are then displayed on the monitor (in low resolution) and stored in an array in memory.

2. A sophisticated commerical graphics software package to allow data manipulation and three-dimenstional displays after data acquisition in complete.

3 A quadrupole mass spectrometer which is mounted on the UHV system housing the STM. It is used for partial pressure analysis of the background and for measurement of thermal desorption spectra following STM scans of adsorbed overlayers.

4. An X-Y recorder used for routine acquisition of Auger and Appearance Potential spectra of samples.

5. A rear-view LEED optics which are mounted on the vacuum system housing the STM. They are used for qualitative display of the diffraction structure of the samples. An existing video detector is used to acquire quantitative beam profile measurements for comparison with the STM images.

6. A liquid-nitrogen cooled sample manipulator. The cooling feature will be used to monitor the kinetic processes of surface facetting over temperature ranges down to 100 K.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Scanning Tunneling Microscopy as a Surface Chemical Probe

PRINCIPAL INVESTIGATOR: Ellen D. Williams
University of Maryland
Department of Physics and Astronomy
College Park, MD 20742

INCLUSIVE DATES: 11/1/84-6/30/88

CONTRACT/GRANT NUMBER: AFOSR-85-0042

SENIOR RESEARCH PERSONNEL: Ellen D. Williams

JUNIOR RESEARCH PERSONNEL: Xue-sen Wang, Romel Gomez, Jill Goldberg

PUBLICATIONS:

"Apperance Potenial Study of Ba-Activated Oxidation of Nickel," R. D. Gomez and E. D. Williams, Surface Science, (in press) (1988).

"Comparison of LEED and STM Measurements of Vicinal Si(111)," X-S. Wang, P. J. Phaneuf and E. D. Williams, J. Microscopy, (in press) (1988).

"Measurement-Dependent Corrugations of Graphite," R. D. Gomez and E. D. Williams, (in preparation) (1988).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objectives of this research effort were:

1) To develop a capability to perform scanning tunneling microscopy
2) To develop an ultra-high vacuum surface analytical system incorporating scanning tunneling microscopy.
3) To characterize the properties of clean solid surfaces using scanning tunneling microscopy in combination with more standard techniques such as Auger Electron Spectroscopy (AES) and Low-Energy Electron Diffraction (LEED).

Fulfillment of objective 1 required design and construction of the scanning tunneling microscope and associated electronics, development of computer I/O for experiment control and data acquisition, and development of graphical data display. The capabilities of the system were demonstrated by a detailed study of the effect of varying experimental parameters on the imaging of the graphite surface.

An ultra-high vacuum system equipped with a hemipherical retarding field optics for electron spectroscopics and LEED, with a quadrupole mass spectrometer, gas handling and sample manipulation was set up to fulfill objective 2. The capabilities of this system were demonstrated by an investigation of the Ba-catalyzed oxidation of nickel.

The scanning tunneling microscope was installed in the ultra-high vacuum system and used in combination with LEED to investigate the properties of a vicinal Si(III) surface. STM was shown to be a far more sensitive probe than LEED for surface disorder. STM characterization was used to develop methods for preparing a smooth, uniform surface.

AFOSR Program Manager: Lt Col Larry W. Burggraf, USAF

# RESEARCH EFFORTS COMPLETED IN FY88
## COMPLETED PROJECT SUMMARIES - CHEMICAL STRUCTURES
### DR DONALD R. ULRICH

| | |
|---|---|
| Physical-Chemical Studies<br>of Solutions Processings<br>of Nematic Polymers<br>F49620-85-C-0140 | Guy C. Berry<br>Department of Chemistry<br>Carnegie-Mellon University<br>Pittsburgh, PA 15213 |
| Symposium on "Better Ceramics<br>Through Chemistry III"<br>AFOSR-88-0145 | David E. Clark<br>Dept of Materials Science<br>and Engineering<br>University of Florida<br>Gainesville, FL 32611 |
| | C. Jeffrey Brinker<br>Division 1846<br>Sandia National Laboratory<br>Albuquerque, New Mexico 87185 |
| | John B. Ballance<br>Materials Research Society<br>9800 McKnight Road, Suite 327<br>Pittsburgh, PA 15237 |
| Development of Conducting Polymers<br>of High Structural Strength<br>F49620-85-C-0096 | Larry R. Dalton<br>Department of Chemistry<br>University of Southern California<br>Los Angeles, CA 90089-0482 |
| Structure and Refinement of<br>Ordered Aromatic Heterocyclic<br>Polymers by Diffraction Methods:<br>Application of Results to<br>Electro-optic Phenomena<br>AFOSR-84-0364 | Albert V. Fratini<br>Department of Chemistry<br>University of Dayton<br>Dayton, Ohio 45469 |
| Novel Liquid Crystals-Polymers<br>and Monomers - As Nonlinear<br>Optical Materials<br>AFOSR-84-0249 | Anselm C. Griffin<br>Chemistry and Polymer Science<br>University of Southern Mississippi<br>Hattiesburg, MS 39406 |
| Ultrastructure Processing and<br>Environmental Stability of<br>Advanced Structural and<br>Electronic Materials<br>F49620-85-C-0079 | Larry L. Hench<br>Advanced Materials Research Center<br>College of Engineering<br>University of Florida<br>One Progress Blvd, #14<br>Alachua, Florida 32615 |
| Studies in Support of<br>Oxidation - Resistant<br>Composite Materials<br>F49620-86-C-0011 | James L. Kaae<br>Senior Technical Advisor<br>General Atomics Company<br>P. O. Box 85608<br>San Diego, CA 92138-5608 |

# RESEARCH EFFORTS COMPLETED IN FY88
# COMPLETED PROJECT SUMMARIES - CHEMICAL STRUCTURES
## DR DONALD R. ULRICH

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|---|---|
| Third International Conference<br>on Ultrastructure Processing of<br>Ceramics, Glasses and Composites<br>AFOSR-87-0085 | John D. Mackenzie<br>Department of Materials Science and<br>Engineering<br>University of California<br>Los Angeles, CA 90024-1595 |
| High-Performance Polymeric<br>Materials<br>AFOSR-83-0027 | J. E. Mark<br>Department of Chemistry<br>University of Cincinnati<br>Cincinnati, OH 45221 |
| PBT, PBO-Based Hybrid Polymers<br>with Nonlinear Optical Properties<br>or High Electric Conductivity<br>AFOSR-86-0105 | Tobin J. Marks<br>Stephen H. Carr<br>Department of Chemistry<br>Northwestern University<br>Evanston, IL 60208-3113 |
| Surface Chemistry and<br>Structural Effects in the<br>Stress Corrosion of Glass<br>and Ceramic Materials<br>F49620-86-K-0005 | Carlo G. Pantano<br>Department of Materials Science<br>and Engineering<br>Pennsylvania State University<br>University Park, PA 16802 |
| Organo-Metallic Elements<br>for Associative Information<br>Processing<br>AFOSR-85-0169 | Theodore O. Poehler<br>Richard S. Potember<br>Johns Hopkins University<br>Applied Physics Laboratory<br>Laurel, Maryland 20707 |
| Ion-Exchanged Waveguides<br>for Signal Processing<br>Applications - A Novel<br>Electrolytic Release<br>AFOSR-84-0369 | Ramu V. Ramaswamy<br>Department of Electrical<br>Engineering<br>University of Florida<br>Gainesville, FL 32611 |
| Exploitation of the Sol-Gel Route<br>in Processing of Ceramics and<br>Composites<br>F49620-85-C-0069 | Rustum Roy<br>Materials Research Laboratory<br>Pennsylvania State University<br>University Park, PA 16802 |
| Synthesis and Crystallization<br>Behavior of Fluoride Glasses<br>AFOSR-86-0350 | Donald R. Uhlmann<br>Department of Materials Science<br>and Engineering<br>University of Arizona<br>Tucson, Arizona 85721 |

# RESEARCH EFFORTS COMPLETED IN FY88
## COMPLETED PROJECT SUMMARIES - CHEMICAL STRUCTURES
### DR DONALD R. ULRICH

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|---|---|
| A New Process for Final Densification of Ceramics<br>F49620-85-C-0053 | Richard A. Wagner<br>Lynchburg Research Center<br>Babcock and Wilcox<br>Lynchburg, VA 24505 |
| Development of a High Efficiency Q-Switched Glass Laser Via Sol-Gel Processing<br>F49620-87-C-0087 | Shi Ho Wang<br>William Moreshead<br>GelTech, Inc<br>One Progress Blvd #18<br>Alachua, Florida 32615 |
| New Non-Linear Optical Polymers<br>F49620-85-C-0151 | Gary E. Wnek<br>Department of Chemistry<br>Rensselaer Polytechnic Institute<br>Troy, NY  12180-3590 |

## COMPLETED PROJECT SUMMARY

TITLE: Physical-Chemical Studies of Solutions Processing of Nematic Polymers

PRINCIPAL INVESTIGATOR: Guy C. Berry
Department of Chemistry
Carnegie-mellon University
Pittsburgh, PA 15213

INCLUSIVE DATES: 1 September 1985 - 31 August 1988

CONTRACT/GRANT NUMBER: F49620-85-C-0140

COST AND FY SOURCE: $163,327, FY 86; $140,255, FY 87;
$159,978, FY 88.

SENIOR RESEARCH PERSONNEL:
K. Se
K. Suresh
G. B. Sohoni
L. Du

JUNIOR RESEARCH PERSONNEL:
C. Wei-Berk
C. S. Kim
C. P. Spencer
M. Srinivasarao

PUBLICATIONS:

"Studies on Dilute Solutions of Rodlike Macroions. III. Integrated Intensity and Photon Correlation Light Scattering Investigation of Association", Y. Elinaga and G. C. Berry, in Micordomains in Polymer Solutions, Ed. by P. Dubin, Plenum Publishing Co. New York 1985, Chapter 11.

"Rheological Properties of Rodlike Polymers in Solution. 2. Linear and Nonlinear Transient Behavior", S. Venkatraman, G. C. Perry and Y. Einaga, J. Polym. Sci., Polym. Phys. Ed., 23, 1275-1295, (1985).

"Rheological Properties of Rodlike Polymers in Solution. 3. Transient and Steady-State Studies on Nematic Solutions", Y. Einaga, G. C. Berry, and S.-G. Chu, Polym. J., 17, 239, (1985).

"Rheological and Rheo-optical Studies of a Constitutive Equation for Nematogenic Solutions of Rodlike Polymers", G. C. Berry, Disc. Faraday Soc. No. 79, 141-148, (1985).

"Studies on Dilute Solutions of Rodlike Macroions. 4. Aggregation with Enhanced Orientational Correlation", R. Furukawa and G. C. Berry, Pure Appl. Chem., 57, 912-920, (1985).

"Rheological and Rheo-Optical Properties of Solutions of Rodlike Polymers", G. C. Berry, Polym. Mater. Sci. Eng., 52, 82, (1985).

"Light Scattering Studies of Orientational Order in Supramolecular Aggregates of Rodlike and Multipli-Broken Rodlike Molecules", G. C. Berry, C. C. Wei and R. Furukawa, Polym. Preprints, Am. Chem. Soc., 27(1), 228, (1985).

"Rheological and Rheo-Optical Studies with Nematogenic Solutions of a Rodlike Polymer: A Review of Data on Poly(phenylene benzoliethiazole)", G. C. Berry, in Institute for Mathematics and its Applications, Vol. 5, Theory & Applications of Liquid Crystals, Ed. By J. L. Erickson, and D. Kinderleher, Springwer-Yerlag, New York, (1987), p. 1.

"Nematic Solutions of Rodlike Polymers. 1. Light Scattering from Nematic Solutions with Complex Teature; and Phase Separation in Poor Solvents", Kazunori Se, and G. C. Berry, in Reversible Polymer Gels and Related systems, Ed. by P. S. Russo, Am. Chem. Soc. Symposium Series, (1987), p. 129.

"Frank Elastic Constants and Leslie-Ericksen Viscosity Coefficients of Nematic Solution of a Rodlike Polymer", Kazunori Si, and G. C. Berry, Mol. Cryst. Liq. Crystal., 153, 133, (1987).

"Rheological Rheo-optical and Light Scattering Studies on Nematic Solutions of Poly(1,4-phenylene-2,6-benzobisthiazole)", G. C. Berry, Kazunori Se, and Mohan Srinivasaro, in High modulus Polymers, Ed. by A. E. Zachariades and R. S. Porter, Marcel Dekker, New York, p. 195. (1988).

"Rheological Studies on Blends of Rodlike and Flexible Chain Polymers", C. S. Kim, V. S. Sullivan, and G. C. Berry, Confr. Proceed, 46th. Tech. Confr., Soc. Plastics Engineers, 34, 890, (1988).

"Rheological Properties of Nematic Solutions of Rodlike Polymers", G. C. Berry, Mol. Cryst. Liq. Cryst., 165, 272, (1988).

"Studies on Aligned Nematic Solutions of a Rodlike Polymer", G. C. Berry, and M. Srinivasarao, Abetracts, Int'l. Symp. on Dynamics of Macromolecules by Electic and Optical Methods, Tokyo, (8-10 August, 1988).

"Properties of Solutions of Rodlike Chains from Dilute Solutions to the Nematic State", G. C. Berry, Proceedings, Materials Research Society, Boston, November, 1988.

"Molecular Composites Formed by Solutions of a Rodlike Polymer (PBT) in Polyphosphonic Acid", A. F. Charlet, and G. C. Berry, Polymer, (in press).

"Studies on Dilute Solutions of Rodlike Macroions. 5. Electrostatic Effect on intermolecular Association", C. Wei-Berk, and G. C. Berry, (to be submitted).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Investigations have involved solutions of the rodlike chain poly(1,4-phenylene-2,6-benzobisthiazole), PBT, and related copolymers containing a small fraction of the phenylene replaced by bipyridyl ether. Studies include: 1) The kinetics of polymerization of PBT in the nematic phase; 2) The supramolecular structure of PBT in solution; 3) The phase equilibria of blends of PBT and nylon in solution; 4) The rheological properties of blends of PBT and nylon in solution; and 5) The properties of fully aligned monodomains if nematic solutions of PBT.

The polymerization kinetics of PBT did not show any change in rate at the isotropic to an anisotropic phase transition for the solutions studied. At higher conversions (above 80%), the polymerization rate constant decreases markedly. This is attributed to effects on the diffusion of the chains along their axes, and comparisons are made to available theroretical models.

Static and dynamic light scattering and viscometric studies on solutions of a PBT copolymer show that its conformation is controlled by intromolecular electrostatic interactions. These cause the chain to expand with decreasing ionic strength of the solvent, but do not lead to a rodlike conformation for the PBT copolymer, even at the lowest ionic strength encountered ($10^{-3}$ mol/l) in this work. In some solvents PBT or its copolymer tend to aggregate. This can lead to a thermochromic effect accompanied by enhanced intermolecular order if the solvent becomes thermodynamically poorer with change in temperature. Such behavior, which can be understood on the basis of theroretical work by Flory and coworkers, could have undesirable effects in solution processing.

The rheological properties of isotropic blends of rodlike PBT and flexible chain nylon show some dramatic effects, including a higher viscosity for the blend than is observed for either component. This behavior is understood in terms of constraints on the diffusion of the rodlike chains caused by the flexible chains. The effect occurs only if the reptational diffusion of the latter is slow enough to make its time constant at least as long as that for diffusion of the rod along the contour. Otherwise, the presence of the flexible chains merely alters the local mobility, such that the viscosity for the blend may be representd by the expression for the viscosity of an isotropic rodlike solution, with the solvent viscosity in the latter replaced by the viscosity of the flexible chain solution.

Fully aligned (monodomains) samples of nematic PBT solutions have been prepared and used in static and dynamics light scattering experiments to study the Frank elastic constants and the Leslie-Erickson viscosities of nematic PBT solutions. The effects of magnetic folds and shear deformations on the director alignment has also been studied with the monodomain sample. It has been found that shear flow is stable only if initiated from an aligned state with the director in the flow directions. Flow instabilities develop otherwise, explaining some of the features previously observed in the shear flow of nematic solutions of PBT.

AFOSR Program Manager: Dr Donald R. Ulrich

# COMPLETED PROJECT SUMMARY

TITLE: Symposium on "Better Ceramics Through Chemistry III"

PRINCIPAL INVESTIGATORS:

David E. Clark
Department of Materials Science and Engineering
University of Florida
Gainesville, FL 32611

C. Jeffrey Brinker
Division 1846
Sandia National Laboratory
Albuquerque, New Mexico 87185

John B. Ballance
Materials Research Society
9800 McKnight Road, Suite 327
Pittsburgh, PA 15237

INCLUSIVE DATES: 4/1/88 - 3/31/89

GRANT NUMBER: AFOSR 88-0145

COST AND FY SOURCE: 20,395 FY 88

PUBLICATIONS: Symposium Proceedings entitled "Better Ceramics Through Chemistry III" edited by C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, Vol. 121, Materials Research Society, Pittsburgh, Pennsylvania, 1988.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This third MRS symposium on Better Ceramics Through Chemistry was held April 5-9, 1988 in Reno, Nevada. It was intended to unite chemists and physicists with ceramists and material scientists in order to synthesize new and better ceramic materials by solution routes involving molecular precursors. This year's symposium was distinguished from the previous two by several factors: (1) the participation of a greater number of chemists and chemical engineers; (2) more extensive use of *in situ* methods of characterization; (3) emphasis on sol-gel derived films, and (4) the inclusion of a session on "Better Superconductors Through Chemistry."

Highlights included the session on sol-gel chemistry of silicates where lively discussions focused on evidence for thermodynamic versus kinetic control in silicate polymerization pathways. Silicate speciation and hydrolysis and condensation kinetics were elucidated in several studies using $^{29}$Si NMR, the most sophisticated approach employing 2D INADEQUATE $^{29}$Si NMR. In addition to NMR, other in situ methods discussed in the characterization and poster sessions included small angle scattering, photophysical probes, surface acoustic wave (SAW) techniques, cryogenic transmission electron microscopy (TEM) $^1$H spin relaxation, and positronium decay.

In the session on films, ellipsometric imaging was employed to study film formation in situ. An approach to thick films based on organic modification was presented, and an approach to novel zeolite/gel composites for sensor surfaces was described.

AFOSR Program Manager: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

TITLE: Development of Conducting Polymers of High Structural Strength

| | | |
|---|---|---|
| PRINCIPAL INVESTIGATOR: | Larry R. Dalton<br>Department of Chemistry<br>University of Southern California<br>Los Angeles, CA 90089-0482 | |
| INCLUSIVE DATES: | 01 June 1985 - 31 May 1988 | |
| GRANT/CONTRACT NUMBER: | F49620-85-C-0096 | |
| COSTS AND FY SOURCE: | $36,000 FY84; $109,869 FY85; $110,687 FY86;<br>$67,677 FY87 | |
| SENIOR RESEARCH PERSONNEL: | David W. Polis<br>Julie Thomson<br>Daniel Davidov | Malcolm R. McLean<br>H.S. Nalwa<br>A. I. Vistnes |
| JUNIOR RESEARCH PERSONNEL: | Robert Montogomery<br>Christy Young<br>H. Kim<br>C. Johnston | Lu-ping Yu<br>Paul Bryson<br>A. Morrobel-Sosa |

PUBLICATIONS:

"Evidence for Soliton-Phonon Interaction in trans-Polyacetylene: Temperature and Frequency Dependence of Electron Spin-Lattice Rexation Data", B.H. Robinson, J.M. Schurr, A.L. Kwiram, H. Thomann, H. Kim, A. Morrobel-Sosa, P. Bryson, and L.R. Dalton, J. Phys. Chem., 89, 4994 (1985).

"Direct Observation of Coulomb Correlation Effects in Polyacetylene", H. Thoman, L. R. Dalton, M. Grabowski, and T.C. Clarke, Phys. Rev. B., 31, 3141 (1985).

"Electrical and Optical Properties of Chemically Synthesized Polypyrrole", H.S. Nalwa, L.R. Dalton, W.F. Schmidt, and J.G. Rabe, Polym. Commun., 26, 240 (1985).

"Dielectric Properties of Copper Phthalocyanine Polymers", H.S. Nalwa, L.R. Dalton, and P.L. Vasudevan, Eur Polym. J., 21, 943 (1985).

"Electrical Conductivity of the Charge Transfer Complexes of Polypyrrole", H. S. Nalwa, J.G. Rabe, W.F. Schmidt, and L.R. Dalton, Makromol Chem. Rapid Commun., 7, 533 (1986).

"ESR and ENDOR of Conducting Polymers", C.L. Young, D. Whitney, A.I. Vistnes, and L. R. Dalton, Annual Reviews of Physical Chemistry, 37, 459 (1986).

"The Role of Extensively Delocalized pi-Electrons in Electrical Conductivity, Non-Linear Optical Properties and Physical Properties of Polymers", L.R. Dalton, J. Thomson, and H.S. Nalwa, Polymer 28, 543 (1987).

"Role of Delocalized pi-Electrons in Nonlinear Optical and Electrical Conductivity Properties of Polymers", L.R. Dalton, Proc. SPIR, 682, 77 (1986).

"Electroactive Polymers: Consequences of Electron Delocalization", L.R. Dalton, Nonlinear Optical and Electroactive Polymers (P.N. Prasad and D.R. Ulrich, eds), Plenum, New York, 243 (1987).

"Polymer Precursors and Model Systems for Graphite Materials". L.R. Dalton, Ultrastructure Processing of Ceramics, Glasses, and Composites (J.D. MacKenzie and D.R. Ulrich, eds). John Wiley and Sons, New York (1987).

"Synthesis and Characterization of New Electroactive Polymers", L.R. Dalton Nonlinear Optical Properties of Polymers (A.J. Heeger, J. Orenstein and D.R. Ulrich, eds) Materials Research Society, Pittsburgh, 301 (1988).

"Design of Polymers with Desiirable Semiconductor, NLO, and Structural Properties," L.R. Dalton, Proc SPIR, 878, 201 (1988).

"Synthesis and Characterization of New Electroactive Polymers", L.P. Yu and L.R. Dalton, Synthetic Metals, (in press).

"Optical Magnetic Resonance, and Conductivity Studies of the Ladder Polymer BBL", F. Coter, Y. Belaish, D. Davidov, L.R. Dalton, E. Ehrenfreund, M.R. McLean, and H.S. Nalwa, Synthetic Metals, (in press).

"Synthesis of New Soluble and Processible Electroactive Polymers", L.P. Yu and L.R. Dalton, Progress in Rubber and Plastics Technology: Proceedings of the 1st International Conference on Electrical, Optical, and Acoustic Properties of Polymers, The Plastics and Rubber Institute (1988).

"Synthesis of New Nonlinear Optical Ladder Polymers", L.R. Dalton, Nonlinear Optical Effects in Organic Polymers (J. Messier, F. Kajzar, P.N. Prasad, and D.R. Ulrich, eds) NATO ASI Series No 971 (1988).

"Observation and Analysis of Soliton Localization in Durham Polyacetylene", L.R. Dalton, A.I. Vistnes, J. Thomson, C. Johnston, H. Thomann, and B.M. Hoffman, J. Phys Chem. (submitted).

"ESE Studies of Oxygen Effects in Polyacetylene", A. Morrobel-Sosa and L.R. Dalton, J. Phys Chem. (submitted).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The first objective of this research was to realized an improved understanding of electrical, magnetic, and optical properties in high symmetry polymers capable of supporting significant pi-electron delocalization. The second objective was to develop new synthetic approaches for the preparation of soluble electroactive polymers and to process these materials into forms appropriate for exploitation for their unique properties.

The project consisted of three parts. The first part focused on defining fundamental bond alternation defects (solitons and polarons) in prototype conducting polymers such as polyacetylene, polythiophene, etc. Accomplishments include the first ENDOR measurements of these materials which in turn provided the first quantitative definition of the extent and shape of the wavefunction of such defects. ENDOR and TRIPLE measurements also provided the first measurement of electron coulomb interactions, a quantity which together with electron phonon interactions determines electron localization/delocalization in pi-electron polymers. Subsequently, these measures of electron localization/delocalization were correlated with quantities, such as third order nonlinear optical susceptibility, which are theoretically predicted to depend upon electron delocalization.

The second area focused upon defining the optical, magnetic, and electrical properties of the well-known ladder polymers BBL and BBB. For example for BBL, our optical studies indicate a interband Pi-Pi* gap of approximately 1.8eV in the neutral undoped state and the presence of charged defects which increase a number upon doping. Electron paramagnetic resonance and ENDOR studies suggest that these defects are polarons. A highly anisotropic conductivity is observed over the temperature range 300-700 C which could be fit to Mott's model of variable range hopping. The conductivity anisotropy is attributed to anisotropic localization lengths of the localized states. Electron delocalization defined from the analysis of electrical conductivity data is considerably greater than that defined by ENDOR measurements. This disagreement can likely be attributed to the different timescales involved in the two experiments. ENDOR data are more appropriate for correlation with short timescale phenomena such as nonlinear optical activity. A third order susceptibility of approximately $2 \times 10^{-9}$ esu was measured by degenerate four wave mixing at 532 nm for a BBL sample characterized by a linear adsorption of 18 micron $^{-1}$ and an index of refraction of 2.3. The reversibility of BBL to thermal cycling over the temperature range 300-700 C was investigated; heating of the as-synthesized polymer results in decarbonylation and a subsequently thermally stable lattice.

A major research activity has been the synthesis of soluble electroactive polymers by derivatization and soluble precursor polymer methods. Of particular focus has been the synthesis of polyquinoxaline ladder polymers by such techniques. Ladder polymers were chosen for extensive investigation because their exhibit a molecular conformation optimizing pi orbital overlap, hence, electron delocalization. Polycondensation synthesis was pursued to permit synthesis of oligomeric model compounds and to facilitate soluble precursor polymer synthesis by careful control of the asymmetric condensation process. Asymmetric derivation has permitted the preparation of natural amphillic oligomers and polymers which have been utilized with Langmuir-Blodgett processing methods to prepare ordered films. Derivatization also influences liquid crystalline properties and ordered films have been processed from liquid crystalline solutions. An example of the preparation of derivatized ladder polymers is shown in the accompanying figure.

The optical nonlinearity of the vinylamine-derivatized polymers shown in this figure have been investigated by degenerate four wave mixing with third order susceptibilities in the range $10^{-9}$ to $10^{-11}$ esu typically observed for pristine polymers. Nonlinear optical data was correlated with extensive analytical data including elemental analysis, NMR, FTIR, mass spectroscopy UV-Vis, TGA, DSC, and chromatography data. Electron delocalization and optical nonlinearity appear to be limited by polymer imperfections associated either with incomplete condensation or air oxidation of imine nitrogens. Comparison of optical nonlinearity data for open-chain precursor polymers with data for fully-fused ring ladder polymes permits insight into the dependence of electron delocalization and optical nonlinearity on molecular conformation. The enhanced susceptibilities observed for ladder polymers are in agreement with preliminary theoretical calculations. Both electronic and thermal components of the third order susceptibility are observed to depend upon the nature of the vinylamine substituent. Finally, we note that, in addition to hompolymers, we have prepared a variety of copolymers and composite materials.

AFOSR Program Manager: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

TITLE: Structure and Refinement of Ordered Aromatic Heterocyclic Polymers by Diffraction Methods: Application of Results to Electro-optic Phenomena

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

GRANT NUMBER: AFOSR-84-0364

INCLUSIVE DATES: 30 September 1984 - 31 October 1987

COSTS AND FY SOURCE: \$32,602 FY85; \$33,320 FY86; \$33,178 and \$19,994 FY87

SENIOR RESEARCH PERSONNEL:
K. Baker
H. Knachel

JUNIOR RESEARCH PERSONNEL:
M Anater
E. Cross
J. Plashke
G Borchers
C. George
M. Sturtevant

PUBLICATIONS:

"$^{13}$C NMR and X-Ray Crystallographic Determination of the Structures of Some Isomeric Phenylquinoxalines", F. Hedberg, D. Bush, M. Ryan, R. Harvey, A. Fratini, D. Dudis, M. Barfield, S. Walter, D. Draney, and C. Marvel, Air Force Tech Report AFWAL-TR-85-4037, (1985).

"The Structure of Poly-2,5-benzoxazole (ABPBO) and Poly-2,6-Benzothiazole (ABPBT) Fibers by X-Ray Diffraction," A.V. Fratini, E.M. Cross, J.F. O'Brien and W.W. Adams, air Force Tech Report AFWAL-TR-85-4097, (1985).

"The Structure of Poly-2,5-benzoxazole (ABPBO) and Poly-2,6-benzothiazole (ABPBT) Fibers by X-Ray Diffraction", A.V. Fratini, E.M. Cross, J.F. O'Brien and W.W. Adams, J. Macromol. Sci. - Phys. B24 (1-4), 159-179 (1985-1986).

"Refinement of the Structure of PEEK Fibre in an Orthorhombic Unit Cell", A.V. Fratini, E.M. Cross, R.B. Whitaker and W.W. Adams, Polymer, 27, 861-865 (1986).

"Fluoro-Ketones IX. Hydration of Perfluoroalkylpolyketones and their Reactions Forming Novel Cyclic Compounds":; L.S. Chen, A.V. Fratini and C. Tamborski, J. Fluorine Chem., 31, 381-393 (1986).

"Structure of a Dioxabicyclic Fluoro Octane Derivative", P.G. Lenhert and A.V. Fratini, Acta Cryst., C43, 1929-1932 (1987).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research program was to obtain detailed x-ray structural data on the rodlike and stiff-chain, aromatic heterocyclic class of polymers. These polymers possess mechanical and thermal oxidative properties which are comparable or superior to those obtained with fiber reinforced composites. Of prime interest is an understanding, at the molecular level, of the characteristic mechanical, tensile, optical, electro-optical and processing properties of these materials. The work performed included the determination and refinement of the structure of oriented fibers of the following systems:

(1) The stiff-chain poly-2,5-benzoxazole (ABPBO) and poly-2,6-benzothiazole (ABPBT) polymers.
(2) The rigid rod poly(p-phenylenebenzobiosoxazole) (PBO) and poly(p-phenylenebenzobisthiazole (ABPBT) polymers,
(3) The benzimidazoisoquinoline ladder polymer (BBL) a potential organic conducting polymer.
(4) PBT modified by attaching pendant benzothiazole groups to the polymer backbone. This system allows an investigation of changes in the molecular and unit cell structure resulting from chemical modifications to the PBT backbone.
(5) Single crystal x-ray structures of several model compounds which contain pendant benzothiazole, benzoxazole and benzimidazole groups.

AFOSR Program Manager: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

TITLE: Novel Liquid Crystals-Polymers and Monomers - As Nonlinear Optical Materials

PRINCIPAL INVESTIGATOR: Anselm C. Griffin
Chemistry and Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406

INCLUSIVE DATES: 01 September 1984 - 31 December 1987

GRANT NUMBER: AFOSR-84-0249

COST AND FY SOURCE: $84,602 FY84; $84,700 FY86; $90,063 FY87

SENIOR RESEARCH PERSONNEL: A.M. Bhatti M.L. Steele

JUNIOR RESEARCH PERSONNEL: R.S.L. Hung C.R. Walton
G.A. Howell

PUBLICATIONS:

"Synthesis of Side Chain Liquid Crystal Polymers for Nonlinear Optics", A.C. Griffin, A.M. Ghatti and R.S.L. Huang, Proc. SPIR, 682, 65 (1987).

"Side Chain Liquid Crystalline Copolymers for NLO response", A.C. Griffin, A.M. Bhatti and R.S.L. Hung, Nonlinear Optical and Electroactive Polymers (P.N. Prasad and D.R. Ulrich, eds), Plenum Publishing Corp., NY, NY, 375 (1988).

"Side Chain Polymalonate Liquid Crystals for Nonlinear Optics", A.C. Griffin, A.M. Bhatti and R.S.L. Hung, Mol, Cryst. Liq. Cryst., 155, 129 (1988).

"Pyridine N-oxides as Polymeric Nonlinear Optical Materials", A.C. Griffin, A.M. Bhatti and G.A.Howell, Nonlinear Optical Properties of Polymers (A.J. Heeger, J. Orenstein and D.R. Ulrich, eds.), 109, Materals Research Society, Pittsburgh, PA 115 (1988).

"The Characterization of Langmuir-Blodgett Films of a Non-Linear Optical, Side Chain Liquid Crystalline Polymer", M.M. Carpenter, Paras N. Prasad and A.C. Griffin, Thin Solid Films, (in press).

"Side Chain Liquid Crystalline Polymers for Nonlinear Optics", A.C. Griffin and A.M. Bhatti, Organic Materials for Nonlinear Optics, Royal Society of Chemistry, London, England, (in preparation).

"The Dielectric and Electro-optical Properties of a Chiral Liquid Crystalline Polymer", G.S. Attard, K. Araki, J.J. Moura-Ramos, G. Williams, A.C. Griffin, A.M. Bhatti and R.S.L Hung, (in preparation).

"Novel Liquid Crystals - Polymers and Monomers - As Nonlinear Optical Materials", DARPA/DSO-AFOSR/NC Optical Processing Annual Review, McLean, VA (November 1984).

"Preparation of Linear Aliphatic Polyesters with Novel Side Chains", SE-SW Regional American Chemical Society Meeting, Memphis, TN (October 1985).

"Nitroaromatic Liquid Crystalline Polymers: Unique Structures for Nonlinear Optical Materials", International Conference on Ultrastructure in Organic and Inorganic Polymes, Amherst, MA (October 1985).

"Novel Liquid Crystals - Polymers and Monomers as Nonlinear Optical Materials", DARPA/DSO-AFOSR/NC Optical Processing Annual Review, McLean, VA (November 1985).

"Novel Liquid Crystals - Polymers and Monomers - as Nonlinear Optical Materials", Air Force Materials Laboratory, Dayton, OH (March 1986).

"Novel Polyesters as Nonlinear Optical Materials", 11th International Liquid Crystal Conference, Berkeley, CA (July 1986).

"Model Compounds for Liquid Crystalline Polymers", Gordon Research Conference on Polymer Liquid Crystals, New London, NH (July 1986).

"Synthesis of Side Chain Liquid Crystal Polymers for Nonlinar Optics", 30th SPIE Annual Technical Symposium, San Diego, CA (August 1986).

"Liquid Crystalline Polymers for Nonlinear Optics, Chemistry Department, Auburn University, Auburn, AL (January 1987).

"Liquid Crystalline Polymers for Nonlinear Optics", Chemistry Department, State University of New York at Buffalo, Buffalo, NY (January 1987).

"Side Chain Liquid Crystalline Copolymers for NLO response", American Chemical Society National Meeting, Denver, CO (April 1987).

"Liquid Crystalline Polymers as Nonlinear Optical Materials", Liquid Crystal Institute, Kent State University, Kent OH (April 1987).

"Liquid Crystalline Polymers for Nonlinear Optics", 3M Company, St Paul, MN (April 1987).

"Side Chain Polymalonate Liquid Crystals for Nonlinar Optics", International Confsrence on Liquid Crystal Polymers", Bordeaux, France (July 1987).

"Liquid Crystal Polymers", Chemistry Department, Queen Mary College, University of London, London, England (July 1987).

"Liquid Crystalline Side Chain Polymers as Nonlinear Optical Materials", American Chemical Society National Meeting, New Orleans LA (September 1987).

"Polyester Side Chain Liquid Crystalline Materials for Nonlinear optics", Materials Research Society National Meeting, Boston, MA (December 1987).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project involved the design, synthesis and characterization of liquid crystalline materials having a potentially nonlinear optically active (nlo) species as a fundamental consistent of the liquid crystalline structure. Compounds of interest were usually polymeric and, in particular, side chain liquid crystalline polymers were primary target materials. The design concept was to use a pi donor-pi acceptor linearly conjugated system as simultaneously both the nlo species and the liquid crystalline (mesogenic) moiety. Second order nlo properties were design goals. Specific results included (a) use of polycondensation reactions to synthesize polyester side chain liquid crystals containing nitroaromatic nlo active species, (b) use of chiral diols in the above reactions to generate chiral nlo polymers (c) preparation of pyridine N-oxide based side chain polymers having a push-pull pi electronic structure, (d) generation of a series of copolymers involving both an nlo component and a chiral non-nlo component to obtain a pi-transfer of chirality to the nlo species and to obtain a smectic A materials, and (e) the fine tuning of specific reaction conditions to produce nitroaromatic based nlo side chain liquid crystalline polymers of the methacrylate type without crosslinking or significant adverse side reactions.

Materials described above were prepared and characterized chemically and both as polymers and as liquid crystals and were also made available to other laboratories for evaluation of optical and related properties. Particularly fruitful collaborations have resulted in the finding of unusual and interesting electric field alignment behavior of a nitroaromatic polyester liquid crystal by Professor Graham Williams (University College of Wales, Aberystwyth) and in the examination of film properties and nlo behavior of a Langmuir Blodgett monolayer film from a nitroaromatic containing copolymer side chain liquid crystal by Professor Paras Prasad (SUNY-Buffalo)

AFOSR Program Manager: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

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

PRINCIPAL INVESTIGATOR:
Larry L. Hench
Advanced Materials Research Center
College of Engineering
University of Florida
One Progress Blvd., #14
Alachua, Florida 32615

INCLUSIVE DATES: 1 April 1985 - 31 March 1988

CONTRACT/GRANT NUMBER: F49620-85-C-0079

COSTS AND FY SOURCE: Cumulative Project Funding $1,618,574.00, FY 85, FY 86, FY 87

SENIOR RESEARCH PERSONNEL:
David E. Clark (MSE)
Robert W. Gould (MSE)
Brij M. Moudgil (MSE)
Carolyn M. Van Vliet (EE)
Gijs Bosman (EE)
Jon K. West (MSE)
Jean Phalippou (University of Montpellier)

JUNIOR RESEARCH PERSONNEL:
G. Orcel
S. Wallace
S. Park
S. H. Wang
W. J. McCracken
C. Campbell
R. Nikles
M. Y. Luo
K. Wistom
W. J. Dalzell
G. P. LaTorre
R. A. Stokell
R. H. Krabill
S. M. Kim
R. Li
Yeu-Chyi Cheng
B. I. Lee
S. Tehrani
J. S. Kim
J. L. Nogues
P. Y. Chu
T. Chia

PUBLICATIONS:

50 papers published and 30 patent disclosures submitted

### ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objective of our Multi-Investigator Research Program is to achieve an understanding of the science of chemically derived, ultrastructure processing of ceramics, glasses and composites. Five research areas were pursued.

(A) Sol-Gel Processing: Procedures for reliable and reproductible drying of sol-gel silica monoliths were developed using drying control chemical additives (DCCA's). Processes for chemical stabilization of ultraporous, optically transparent silica monoliths were also developed along with the means for chemically doping of optically active polymers. A method for dehydration and densification of the ultrapure silica monoliths was also achieved resulting in optical components with uniquely low optical transmission from 160 nm to 3500 nm. The gel-derived optical silica also has a uniquely low coefficient of thermal expansion over a broad temperature range. The processing and properties of GELSIL$^{TM}$ made by this new ultrastructure processing method are reviewed in:

"Gel-Silica Optics", L. L. Hench, S. H. Wang, and J. L. Nogues in Multifunctional Materials, Vol. 878, Robert L. Gunshor, ed., SPIE, Bellingham, WA, 1988, pp. 76-85.

(B) Sol-Gel Derived Processing of Ceramic Coatings and Composites: Electrophoretic and thermophoretic methods for depositing composite coatings onto a carbon/carbon substrate have been developed. A gradient coating has been achieved where a concentration of SiC whiskers is varied throughout the thickness.

"Chemically Derived Refractory Coatings", S. M. Sim, P. Y. Chu, R. H. Krabill, D. E. Clark, in 3rd Ultrastructure Conf., J. Wiley and Sons, D. G. Mackenzie and D. R. Ulrich, eds. (1988).

(C) Organometallic Precursor Processing of SiC Composites: A method for efficient chemical crosslinking of polysilanes has been developed and utilized in producing a range of composites containing SiC. After pyrolysis superior toughness to weight ratios are obtained for these ultrastructural composites to the nm scale of SiC reinforcement.

"Molecular Composites of $SiC/SiO_2$, $SiC/Al_2O_3$, and SiC/TiC", B. I. Lee and L. L. Hench, Am. Ceram. Soc. Bull. 66[10] (1987) 1432-1485.

(D) Electronic Characterization of High Band Gap Silicon Carbide: Significant advances have been made in measuring and interpreting the noise spectrum and transport properties of SiC single crystals. This work has led for the first time to verification of the general theory of space charged limited flow (SCL) of semiconductors developed by Prof. Van Vliet several years ago.

"New Perspectives of Silicon Carbide: An Overview with Special Emphasis on Noise and Space-Charge-Limited Flow", C. M. Van Vliet, G. Bosman, L. L. Hench, Ann. Rev. Mater. Sci. 8 (1988) 381-421.

(E) General Research on Inorganic Materials: A quantitative theory of technology tranfer has been developed using examples from the MIRP. Other investigation on glass surface chemistry and environmental resistance have also been pursued.

"Ceramics and the Challenge of Change", L. L. Hench, Advanced Ceramic Materials 3[3] (1988) 203-206.

## LIST OF PUBLICATIONS

"Use of Drying Control Chemical Additives (DCCAs) in Producing Gel Monoliths," L. L. Hench in Glass Current Issues, A. F. Wright and J. Dupuy, eds., Martinus Nijboff Publishers, Dordrecht, The Netherlands, pp. 259-262 (1985).

"NMR Raman Study of the Effect of Additives on the Sol-Gel Process," I. Artaki, M. Bradley, T. W. Zerda, J. Jonas, G. Orcel and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, pp. 73-80 (1986).

"Comparative Pore Distribution Analysis of Sol-Gel Derived Silica," S. Wallace and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, pp. 148-156 (1986).

"Physical Properties of Partially Densified $SiO_2$ Gels," S. Park and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, pp. 168-172 (1986).

"Sol-Gel Derived Silica Optical Filters," S. H. Wang and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, pp. 201-207 (1986).

"Processing and Structural Properties of $Li_2O$-$Al_2O_3$-$TiP_2$-$SiO_2$ Gels," G. Orcel and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, pp. 224-230 (1986).

"Physical-Chemical and Biochemical Factors in Silica Sol-Gels," L. L. Hench and G. Orcel, J. Non-Crystalline Solids 82 1-10 (1986) .

"Processing and Structural Evolution of ($xLi_2O$ $(1-x)Na_2O$) $Al_2O_3$ $2SiO_2$ Gels," G. Orcel, J. Phalippou, and L. L. Hench, J. Non-Crystalline Solids 82 301-306 (1986).

"Structural Changes of Silica Xerogels During Low Temperature Dehydration," G. Orcel, J. Phalippou and L. L. Hench, J. Non-Crystalline Solids 88 114-130 (1986).

"Effect of Formamide Additive on the Chemistry of Silica Sol-Gels, Part I: NMR of Silica Hydrolysis," G. Orcel and L. L. Hench, J. Non-Crystalline Solids 79 177-194 (1986).

"Sol-Gel Glass," L. L. Hench, McGraw Hill Yearbook of Science and Technology, pp. 221-223 (1987).

"Polarized Infrared Reflection Spectroscopy of Single Crystal Lithia-Silicates and Quartz," W. J. McCracken, W. B. Person, and L. L. Hench, J. of Materials Science 20 3853-3864 (1985).

"Sol-Gel Derived Ceramic Matrix Composites," D. E. Clark, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons. 237-246 (1986).

"Processing of Sol-Gel Derived Doped Powders and Substrates," K. W. Wistrom and D. E. Clark, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley & Sons, 272-277 (1986).

"Thermophoretic and Electrophoretic Deposition of Sol-Gel Composite Coatings," W. J. Dalzell and D. E. Clark, Ceramic Engineering and Science Proceedings, 7[7-8], 1014-1026 (1986).

"Use of FT-IRRS for Characterizing Thermal Stability of SiC Whiskers and Composites," G. P. LaTorre, R. A. Stokell, R. H. Krabill and D. E. Clark, Ceramic Engineering and Science Proceedings, 7[7-8], 933-944 (1986).

"Effect of Surface Hydration on Polymer Adsorption," Brij M. Moudgil and Yeu-Chyi Cheng, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley & Sons. 550-554 (1986).

"Electrophoretic Behavior and Surface Reactions of Sol-Gel Derived Alumina," B. I. Lee and L. L. Hench, Colloids and Surfaces 23 211-229 (1987).

"Crosslinking and Pyrolysis of Silane Precursors for Silicon Carbide," B. I. Lee and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, pp. 345-353 (1986).

"Silicon Carbide/Silica Gel Matrix Composites," B. I. Lee and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, pp. 231-236 (1986).

"Silicon Carbide/Silica Molecular Composites," B. I. Lee and L. L. Hench in Ceramic Engineering and Sciences Proceedings, Am. Ceram. Soc., Columbus, Ohio, pp. 994-997 (July-August 1986).

"Observation of Single Carrier Space-Charge Limited Flow in Nitrogen-Doped a-Silicon Carbide. I. I-V Characteristics and Impedance," S. Tehrani, J. S. Kim, L. L. Hench, C. M. Van Vliet and G. Bosman, J. Appl. Phys., 58[4] 1562-1570 (1985).

"Observation of Single Carrier Space-Charge Limited Flow in Nitrogen-Doped a-Silicon CArbide. II. I-V Electrical Noise," S. Tehrani, L. L. Hench, C. M. Van Vliet and G. Bosman, J. Appl. Phys., 58[4] 1572-1577 (1985).

"The Hole of Chemical Additives in Sol-Gel Processing," L. L. Hench, G. Orcel and J. L. Nogues in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds. Vol. 73, Materials Research Society, Pittsburgh, PA, pp. 35-47 (1986).

"SAXS Study of Silica Sols and Gels," G. Orcel, R. W. Gould and L. L. Hench in Better Ceramics Through Chemistry II, C. Jeffery Brinker, David E. Clark and Donald R. Ulrich, eds., Vol 73, Materials Research Society, Pittsburgh, PA, pp. 289-294 (1986).

"Processing and Properties of $xSiO_2$-$(1-x)Al_2O_3$ Gels," G. Orcel, J. Phalippou, and L. L. Hench, Rev. Int. Hautes Temper. Refract. Fe., 22 185-190 (1985).

"Optical Properties of Gel-Silica Glasses," Shi-Ho Wang, Candace Campbell and L. L. Hench to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Dielectric Relaxation Analysis of Gel Drying," S. Wallace and L. L. Hench to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Sol-Gel Coatings on Carbon/Carbon Composites," S. M. Sim, R. H. Krabill, W. J. Dalzell, Jr., P-Y. Chu, and D. E. Clarkin Better Ceramics Through Chemistry II, C. Jeffery Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, pp. 647-652 (1986).

"Drying Behavior of Sol-Gel Derived $Al_2O_3$-SiC Composites," R. H. Krabill and D. E. Clark in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, pp. 641-646 (1986).

"Chemically Derived Refractory Coatings," S. M. Sim, P-Y. Chu, R. H. Krabill and D. E. Clark, to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Surface Charge of Sol-Gel Derived Aluminas as a Function of Calcination Temperature," Burtrand I. Lee and Larry L. Hench, Particulate Science and Technology 4 213-223 (1986).

"Silicon Carbide from Organosilanes and Application in Silica Gel Glass Composites," B. I. Lee and L. L. Hench in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol 73, Materials Research Society Pittsburgh, PA, pp. 815-822 (1986).

"Observation of Single Carrier Space-Charge-Limited Flow in Nitrogen Doped a-Silicon Carbide. III. Computer Calculations," S. Tehrani, G. Bosman, L. L. Hench and C. M. Van Vliet, J. Appl. Physics., 60[7] 2386-2395 (1986).

"New Perspectives of Silicon Carbide: An Overview, With Special Emphasis on Noise and Space-Charge-Limited Flow," Carolyn M. Van Vliet, Gijs Bosman, and Larry L. Hench, Ann. Rev. Mater. Sci., 18 381-421 (1988).

"Gel-Silica Optics," L. L. Hench, S. H. Wang, and J. L. Nogues, in Multifunctional Materials, Vol. 878, Robert L. Gunshor, ed., SPIE, Bellingham, WA, pp. 76-85 (1988).

"Correlations Between processing Parameters, Ultrastructure, and Strength of Gel-Silica," J. K. West, R. Nikles, and G. LaTorre, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Physical Properties of Dried $Na_2O-SiO_2$ Monoliths," R. Li and L. L. Hench, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Physical and Structural Evolution of Sol-Gel Derived $TiO_2-SiO_2$ Glasses," Y. C. Cheng and L. L. Hench, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Dielectric Relaxation Analysis of Water Adsorption in Sol-Gel Derived Silica Gel Monoliths, S. Wallace and L. L. Hench to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Preparation and Characterization of Monolithic Si-Ce-O Gels," A. Sivade, G. Orcel, L. L. Hench, J. Bouaziz, R. Sempere, D. Bourret, presented at the 40th Pacific Coast Regional Meeting of the American Ceramic Society, San Diego, CA, Nov. 3, 1986.

"Gel-Silica Waveguides," R. V. Ramaswamy, T. Chia, R. Srivastava, A. Miliou and J. West, in Multifunctional Materials, Vol. 878, Robert L. Gunshor, ed., SPIE, Bellingham, WA, pp. 86-92 (1988).

"Coating Porous Substrates by the Sol-Gel Method," P-Y. Chu and D. E. Clark, presented at the 89th Annual Meeting and Exposition of the American Ceramic Soicety, Pittsburgh, PA, April 27, 1987.

"Molecular Composites of $SiC/SiO_2$, $SiC/Al_2O_2$, and SiC/TiC," Burtrand I. Lee and Larry L. Hench, Am. Ceram. Soc. Bull., 66[10] 1432-1485 (1987).

"Comparison of Polysilastyrene with Polycarbosilane as a Precursor to Silicon Carbide," B. I. Lee, presented at the Fiber Tex-87, Nov. 3-5, 1987, (in press).

"Mechanical Properties of Partially Densified $SiC/SiO_2$ Gel Matrix Composites," B. I. Lee and L. L. Hench, in Ceramic Engineering and Science Proceedings, Am. Ceram. Soc., Westerville, Ohio, 8[7-8], 685 (1987).

"Theory and Experiments of 1/f Noise in Sohottky-Barrier Diodes Operating in the Thermionic-Emission Mode," Min-Yih Luo, Gijs Bosman, Aldert van der Ziel, and Larry L. Hench, IEEE Transactions of Electron Devices 35[8] 1351-1356 (1988).

"Ceramics and the Challenge of Change," L. L. Hench, Advanced Ceramic Materials 3[3] 203-206 (1988).

"Corrosion of Silicate Glasses: An Overview," L. L. Hench, Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988 (to be published).

AFOSR Program Manager: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

TITLE: Studies in Support of Oxidation - Resistant Composite Materials

PRINCIPAL INVESTIGATOR:
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INCLUSIVE DATES: 16 October 1985 - 14 October 1987

CONTRACT/GRANT NUMBER: F49620-86-C-0011

SENIOR RESEARCH PERSONNEL:

Mildred Dresselhaus,
Massachusetts Institute of Technology

John MacKenzie
University of California, Los Angeles

Barry McQuillan
General Atomics Company

Robert Price
General Atomics Company

George Reynolds
Materials Science Northwest

Holger Streckert
General Atomics Company

Donald Tilley
University of California at San Diego

PUBLICATIONS:

"Deintercalation Reactions to Form Ceramic Coatings on Graphite Fibers", B.W. McQuillan and G.H. Reynolds, Graphite Intercalation Compunds, ed M.S. Dresselhaus, G. Dresselhaus, and S.A. Solin, Materials Research Society (1986).

"Growth of Alumina Fibers From Intercalated Graphite Precursor Fibers", B.W. McQuillan and G.H. Reynolds, Proceedings of the 3rd International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, ed. J.D. Mackenzie an D.R. Ulrich, Academic Press (in press).

"Surface Modification of Matrix Materials for Oxidation - Resistant Carbon-Carbon Composites", H.H. Streckert and F.C. Montgomery, Proceeding of the 3rd International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, ed, J.D. Mackenzie and D.R. Ulrich, Academic Press (in press).

"Preparation of Ceramic Oxide Fibers from Intercalated Graphite Fibers", B.W. McQuillan and G. Reynolds, Proceedings of the 18th Biennial Conference on Carbon, Worchester MA, July 1987 (in press).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Studies on elements required for oxidation resistant composite materials have been carried out in four areas.

1. investigations of moisture resistant sealant glasses for carbon-carbon composite materials and their interactions with oxidation barrier coatings.

2. investigations of the effects of electrochemical modification of carbon surfaces on the wetability of these surfaces by sealant glasses.

3. investigations of alkoxides sol-gel precursors of ceramic materials.

4. investigations of the formation of ceramic fibers through the oxidation of intercalated carbon fibers.

AFOSR Program Manager: Dr Donald Ulrich

# COMPLETED PROJECT SUMMARY

TITLE: Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites

PRINCIPAL INVESTIGATOR: John D. Mackenzie
Department of Materials Science and Engineering
University of California
Los Angeles, CA 90024-1595

INCLUSIVE DATES: 01 January 1987 to 31 December 1987

CONTRACT/GRANT NUMBER: AFOSR-87-0085

PUBLICATIONS:

"Ultrastructure Processing of Advanced Ceramics", edited by J.D. Mackenzie and D.R. Ulrich, John Wiley and Sons, New ork, New York (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives for this Third Conference were similar to those of the two previous ones (Florida, 1983 and 1985), namely to establish and to strengthen the scientific foundation of a new era in the processing of ceramics, glasses and composites for electronic, optical, structural and novel applications. In the past few years, attempts to understand and to control the processing of these materials on a submicron and even molecular scale through direct interactions between chemists, materials scientists, engineers and physicists, made possible by the support of AFOSR and others, have already led to new materials, novel processes and improved properties. Further progress would be enhanced through the sharing of research results and ideas via this forthcoming Third Conference.

The Conference was successfully organized and took place at the San Diego Princess Resort in San Diego, California from February 23 to 27, 1987. Two-hundred and fifth people attended. There were 60 oral presentations and 42 poster presentations. The conference proceedings will be published in the form of a book entitled "Ultrastructure Processing of Advanced Ceramics", edited by J.D. Mackenzie and D.R. Ulrich, in June 1988.

AFOSR Program Manager: Dr Donald R. Ulrich

# COMPLETED PROJECT SUMMARY

TITLE: High-Performance Polymeric Materials

PRINCIPAL INVESTIGATOR: J.E. Mark
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INCLUSIVE DATES:1 November 1982 - 31 October 1987

GRANT NUMBER: AFOSR-83-0027

COSTS AND FY SOURCE: $73,000, FY82; $87,513, FY83; $109,258, FY84; $118,807, FY85; $173,247, FY86

SENIOR RESEARCH PERSONNEL: H. H. Jaffe

JUNIOR RESEARCH PERSONNEL:
W. J. Welsh
D Bhaumik
Y.-P. Ning
W.D. Johnson
K.C. Metzger
G.S. Sur
L. DeBolt
S.J. Clarson
M.-Y. Tang
K. Nayay
C.-Y. Jiang
A. Letton
C.-C. Sun
Z. Rigbi
S. Liu

PUBLICATIONS:

"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., 21, 1111 (1983).

"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, in "Chemistry and Biology of Pteridines: Pteridines and Folic Acid Derivatives", ec by J.A. Blair, W. de Gruyter Pub Co, Berlin, 1983.

"A Theoretical Investigation of Chain Packing and Electronic Band Structure of the Rigid-Rod Polymer Trans-(p-Phenylene Benzobisthiazole) in the Crystalline State", D. Bhaumik and J.E. Mark, J Polym Sci, Poly Phys Ed., 21, 2543 (1983).

"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, Cancer Biochem, Biophys., 7 27 (1983).

"Band Structures, Geometry, and Partial Oxidation of Iridium Carbonyl Chloride Chains", D. Bhaumik and J.E. Mark, Synthetic Metals., 6, 299 (1983).

"Conformational Analysis and Solid-State $^{29}Si$ NMR Spectroscopy of Some Polysilanes", W.J. Welsh, J. Ackerman, and J.E. Mark, Polym Preprints, Div of Polym Chem, Inc, ACS, 24(1), 131 (1983).

"Theoretical Investigations on Some Rigid-Rod Polymers Used as High Performance Materials", W. J. Welsh, D. Bhaumik, H. H. Jaffe, and J.E. Mark, Polym Eng Sci., 24, 218 (1984)

"Particle Sizes of Reinforcing Silica Precipitated Into Elastomeric Networks", Y.-P. Ning, M.-Y. Tang, C.-Y. Jiang, J.E. Mark, and W.C. Roth, J Appl Polym Sci., 29, 3209 (1984)

"Dipole Moments of Some Poly(Dimethylsiloxane) Linear Chains and Cryclics", E. Riande and J.E. Mark, Eur Polym J., 20, 517 (1984)

"Treatment of Filler-Reinforced Silicone Elastomers to Maximize Increases in Ultimate Strength", Y.-P. Ning and J.E. Mark, Polym Bulletin, 12, 407 (1984)

"Effects of Ethylamine Catalyst Concentration in the Precipitation of Reinforcing Silica Filler in an Elastomeric Network", J.E. Mark, and Y.-P. Ning, Polym Bulletin, 12, 413 (1984)

"The Effect of Relative Humidity on the Hydrolytic Precipitation of Silica Into an Elastomeric Network", C.-Y. Jiang and J.E. Mark, Colloid Polym Sci., 262, 758 (1984).

"The Effects of Various Catalysts in the In-Situ Precipitation of Reinforcing Silica in Polydimethylsiloxane Networks", C.-Y. Jiang and J.E. Mark, Makromol Chemie., 185, 2609 (1984).

"Theoretical Studies of the Electronic Properties of Substituted Polyacetylenes, K.C. Metzger and W. J. Welsh, Polym Preprints, Div of Polym Chem, Inc, ACS, 25(1), 195 (1984).

"A Theoretical Investigation of the Electronic Band Structure in Doped Trans-Polyacetylene", D. Bhaumik and J.E. Mark, Polym Preprints, Div of Polym Chem, Inc, ACS, 25(2), 266 (1984).

"Geometry Optimization Using Symmetry Coordinates, H. Kondo, W. J. Welsh, H. H. Jaffe, and H. Y. Lee, J Comp Chem, 5, 84 (1984).

"Theoretical Studies in Electrical Conductivity in Polyynes", K. C. Metzger and W. J. Welsh, Polym Preprints, Div of Polym Chem Inc, ACS, 25(2), 270 (1984).

"Elastomeric Properties of Bimodal Networks Prepared by a Simultaneous Curing-Filling Technique", M.-Y Tang and J.E. Mark, Polym Eng Sci., 25, 29 (1985).

"Simultaneous Curing and Filling of Elastomers", J.E. Mark, C.-Y. Jiang, and M.-Y. Tang, Macromolecules, 17, 2613 (1984).

"Impact Resistance of Unfilled and Filled Bimodal Thermosets of Poly(dimethylsiloxane)", M.-Y. Tang, A. Letton, and J.E. Mark, Colloid Polym Sci., 262, 990 (1984).

"Molecular Orbital Conformational Energy Calculations of the Aromatic Heterocyclic Poly(5,5'-Bibenzoxazole-2,2'-Diyl-1,4-Phenylene) and Poly(2,5-Benzoxazole)", W. J. Welsh, and J.E. Mark, Poly Eng Sci., 25, 965 (1985).

"Bimodal Networks and Networks Reinforced by the In-Situ Precipitation of Silica", J.E. Mark, Brit Polym J., 17, 144 (1985).

"Effects of a Magnetic Field Applied During the Curing of a Polymer Loaded with Magnetic Filler", Z. Rigbi and J.E. Mark, J Polym Sci, Polym Phys Ed., 23, 1267 (1985).

"Hydrolysis of Several Ethylethoxysilanes to Yield Deformable Filler Particles", Y.-P. Ning, Z Rigbi and J.E. Mark, Polym Bulletin, 13, 155 (1985).

"Precipitation of Reinforcing Filler Into Poly(Dimethylsiloxane) Prior to Its End Linking Into Elastomeric Networks", Y.-P. Ning and J.E. Mark, J Appl Polym Sci., 30, 3519 (1985).

"Molecular Aspects of Rubberlike Elasticity", J.E. Mark, Acc Chem Res., 18, 202 (1985).

"A Theoretical Study of Conformations and Elastronic Band Structures for Two Benzoxazole Polymers", K. Nayak and J.E. Mark, Makromol Chemie, 186, 2153 (1985).

"Reinforcing Effects from Silica-Type Fillers Containing Hydrocarbon Groups", J.E. Mark and G.S. Sur, Polym Bulletin, 14, 325 (1985).

"Elastomeric Networks Cross Linked by Silica or Titania Fillers", G.S. Sur and J.E. Mark, Eur Polym J., 21, 1051 (1985).

"Electron Microscopy of Elastomers Containing In-Situ Precipitated Silica", J.E. Mark, Y.-P. Ning, C.-Y. Jiang, M.-Y. Tang, and W.C. Roth, Polymer, 26, 2069 (1985).

"Conformational Analysis of Some Polysilanes and the Precipitation of Reinforcing Silica Into Elastomeric Networks", J.E. Mark in Science of Ceramic Chemical Processing, ed by L.L. Hench and D. R. Ulrich, Wiley, New York (1986).

"Chain Packing in Two Aromatic Heterocyclic Polymes, One of Which Has a Ladder Structure", K. Nayak and J.E. Mark, Makromol Chemie., 187, 1547 (1986).

"Band Structure Analysis of a Bis(oxalato)platinate Complex", K. Nayak, D. Bhaumik and J.E. Mark, Synthetic Metals, 14, 309 (1986).

"Odd-Even Variations in the Melting Points of Some Ethylene Polyesters", D. Bhaumik and J.E. Mark, Makromol Chemie, 187, 1329 (1986).

"Theoretical Studies of Liquid-Crystalline Rodlike Polymers Used as High-Performance Materials", W. J. Welsh and J.E. Mark, Chemical Design Automation News, 1(6), 2 (1986).

"Conformational and Electronic Bank Structure Analysis of a New Type of High Performance Polybenzothiazole Polymers", K. Nayak, J Mat Sci., 21, 2232 (1986).

"Comparisons Among Some Tetra-Alkoxysilanes in the Hydrolytic Precipitation of Silica into Elastomeric Networks", G.S. Sur and J.E. Mark, Makromol Chemie 187, 2861 (1986).

"Conformational Energies and Unperturbed Chain Dimensions of Polysilane and Polydimethylsilylene", W. J. Welsh, L. DeBolt and J.E. Mark, Molecmolecules, 19, 2978 (1986).

"Ethylamine and Ammonia as Catalysts in the In-Situ Precipitation of Silica in Silicone Networks", Y.-P. Ning and J.E. Mark, Polym Comm., 26, 167 (1986).

"Precipitation of Iron Oxide Filler Particles Into an Elastomer", S. Liu and J.E. Mark, Polym Bulletin, 18, 33 (1987).

"Theoretical Studies of Electrical Conductivity in Polymers", W. J. Welsh, Chemical Design Automation News, 2(2), 4 (1987).

"Reinforcement of a Non-Crystallizable Elastomer by the In-Situ Precipitation of Silica", S. J. Clarson and J.E. Mark, Polym Comm., 28, 249 (1987).

"Conformational Characteristics of Some Liquid-Crystalline Aromatic Heterocyclic Polymers Useable as High-Performance Materials", W. J. Welsh, in Current Topics in Polymer Science Vol 1, ed by R. M. Ottenbrite, L.A. Utracki and S. Inoue, Hanser Publishers, New York, 1987.

"Polymer-Modified Silica Glasses. I. Control of Harness", J.E. Mark and C.-C. Sun, Polym Bulletin, 18, 259 (1987).

"Band-Structure Calculations on Polymeric Chains", W. J. Welsh, in Polymers for High Technology, ed by M.J. Bowden and S.R. Turner, Am Chem Soc, Washington, DC 1987.

"In-Situ Generation of Ceramic Particles in Elastomeric Matrices", J.E. Mark in Ultrastructure Processing of Ceramics, Glasses, and Composites, ed by J.D. Mackenzie and D.R. Ulrich, Wiley, New York, 1988.

"AM1 and MNDO/2 Molecular Orbital Conformational Energy Calculations on Model Compounds of Simple Polysilanes and Polygermanes", W.D. Johnson and W. J. Welsh, Proceedings of Silicon-Based Polymer Science Workshop, Polymer Division, ACS, Makaha, Hawaii, November 1987.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The first primary objective was to obtain an understanding of the properties of relatively stiff polymer chains, and to provide guidance on how these properties can be exploited to obtain high-performance polymeric materials. More specifically, one goal was to use semi-empirical and quantum-mechanical methods to obtain information on the physical properties of rigid-rod benzobisoxazole (PBO), benzobisthiazole (PBT), and structurally related polymers. These materials 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 structure 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.

One scientific study involved conformational energy calculations on two polymers (AAPBO and ABPBO) related to PBO. Another addressed chain packing in a ladder polymer (BBL), and a less stiff but structurally related polymer (BBB). Good agreement with experimental structural studies was obtained. All of the results obtained on these aspects of the program are summarized in several more general review articles.

Some theoretical and experimental investigations were also carried out on more tractable random-coil polymers in order to evaluate the theoretical methods and to obtain more insight into the properties of the structurally related rigid-rod polymers. These studies specifically involved some polysilanes, polygermanes, polysiloxanes, ethylens-based polyesters, and an enzyme inhibitor (DAMP).

Electronic band structure calculations were explored with regard to the types of conductivity which may be of interest for electronic applications of the rigid-rod polymers and related materials. Similar calculations were also carried out on relatively small molecules having structural features in common with the PBO and PBT polymers. Specific systems studied were PBO, two PBO-related polymers (AAPBO and ABPBO), PBT, two PBT-related polymers (AAPBT and ABPBT), substituted polyacetylenes, doped trans-polyacetylene, two polyynes, iridium carbonyl chloride chains, and a bis(oxalato)platinate complex. Several polymers were found to have relatively small band gaps, and could therefore be of considerable practical importance. Much of this work is summarized in two review articles.

In collaboration with Professor William J. Welsh (U Missouri-St Louis) and Mr Henry Kurtz (Memphis State U), theoretical studies of nonlinear optical effects in small molecules and polymers have been initiated. The goals of this project are: (1) to apply existing methodologies to calculate hyperpolarizabilities of small molecules and polymer subunits and (2) to develop new, more accurate methods for the calculation of such hyperpolarizabilities.

Another series of investigations explored the idea of precipitating fillers into elastomers. The goal was to provide reinforcement of these materials. Also, since the hydrolysis reactions used are very similar to those used in the new sol-gel-ceramics technology, advantageous connections between these two disciplines could be obtained.

In one series of studies, silica-type fillers were precipitated into uniomodal and bimodal siloxane polymers after the curing process. It was found that the precipitation could also be carried out during the curing process, or before it. Good reinforcement was observed for these elastomers, and for some thermosets as well. Titania particles and iron oxide prticles also gave good reinforcement. In some cases extraction procedures gave even larger increases in mechanical properties, and thus even better reinforcement.

It may also be possible to introduce some deformability into the filler particles by carrying along some hydrocarbon groups from the material being hydrolyzed. Magnetic filler particles have the advantage that they can be manipulated with an external magnetic field.

Particle sizes and particle size distributions have been studied by electron microscopy and small-angle x-ray scattering. Correlation of this information with hydrolysis conditions and mechanical properties is providing valuable guidance for the exploitation of these materials.

The major results obtained in these reinforcement studies are summarized in a series of review articles.

It is also possible to use compositions and hydrolysis conditions that make the silica the continuous phase, and the polymer the dispersed phase. Such polymer-modified ceramics could have extremely attractive properties, for example reduced brittleness.

AFOSR Program Manager: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

TITLE: PBT, PBO-Based Hybrid Polymers with Nonlinear Optical Properties or High Electric Conductivity

PRINCIPAL INVESTIGATOR:

Tobin J. Marks
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Stephen H. Carr
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INCLUSIVE DATES: 15 March 1986 - 30 November 1989

CONTRACT/GRANT NUMBER: AFOSR-86-0105

SENIOR RESEARCH PERSONNEL:

C. Ye
J. Park
N. Minami
D. Kanis

JUNIOR RESEARCH PERSONNEL:

P. De Pra
Y. Jin
J. Giesler
D. Dai

PUBLICATIONS:

"Phthalocyanine-Based Electrically Conductive, Processable Molecular/Macromolecular Hybrid Materials", T. Inabe, W.-B. Liang, J. F. Lomax, S. Nakamura, J. W. Lyding, W. J. McCarthy, S. H. Carr, C. R. Kannewurf, and T. J. Marks, *Synthetic Metals*., *13*, 219 (1986).

"Pi-Electron Calculations for Nonlinear Optical Properties of Molecules", D. Li, T. J. Marks, and Mark A. Ratner, *Chem. Phys. Lett*., *131*, 370 (1986).

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"Molecular and Macromolecular Nonlinear Optical Materials. Probing Architecture/Electronic Structure/Frequency Doubling Relationships Via An SCF-LCAO MECI pi Electron Formalism", DeQuan Li, Mark A. Ratner, and Tobin J. Marks, *J. Am. Chem. Soc.*, *110*, 1707 (1988).

"Synthesis of Molecular Arrays with Nonlinear Optical Properties. Second Harmonic Generation by Covalently Functionalized Glassy Polymers", C. Ye, T. J. Marks, J. Yang, and G. K. Wong, *Macromolecules*, *20* 2322 (1987).

"Rational Construction of Polymeric Nonlinear Optical Materials. Properties of Chromophore-Functionalized Polystyrenes", C. Ye, N. Minami, T. J. Marks, J. Yang, and G. K. Wong, *Mats. Res. Soc. Proc*., *109*, 263 (1988).

"Nonlinear Optical Materials Based on Benzobisthiazole. Electronic Structure/Molecular Architecture/Polarizability/Hyperpolarizability Relationships Derived from pi-Electron Theory", DeQuan Li, T. J. Marks, and M. A. Ratner, *Mats. Res. Soc. Proc.*, *109*, 149 (1988).

"Conductive Polymers Based upon Rigid-Rod Ultra-High-Modulus Macromolecules. Electrochemical Doping of Poly(*p*-phenylenebenzobisthiazole) (PBT)", P. A. De Pra, J. G. Gaudiello, and T. J. Marks, *Macromolecules*, *21*, 2215 (1988).

"Persistent, Efficient Frequency Doubling by Poled Annealed Films of a Chromophore-Functionalized Poly(*p*-hydroxystyrene), C. Ye, N. Minami", T. J. Marks, J. Yang, G. K. Wong, *Macromolecules*, *21*, 2899 (1988).

"Synthetic Approaches to Stable and Efficient Polymeric Frequency Doubling Materials. Second-Order Nonlinear Optical Properties of Poled, Chromophore-Functionalized Glassy Polymers", C. Ye, N. Minami, and T. J. Marks, J. Yang, and G. K. Wong, in "Nonlinear Optical Effects in Organic Polymers," J. Messier, F. Kajzar, P. N. Prasad, and D. R. Ulrich, eds., Kluwer Publishers, Dordrecht, pp 173-183 (1989).

"Approaches to Polymeric Nonlinear Optical Materials. Theoretical and Synthetic Design Strategies", D. Li, N. Minami, M. A. Ratner, C. Ye, T. J. Marks, J. Yang, and G. K. Wong, *Synthetic Metals*., *28*, D585 (1989).

"Poled Polymeric Second Harmonic Generation Materials. Chemical Manipulation of the Temporal Characteristics of Electric Field-Induced Noncentrosymmetry", M. A. Hubbard, N. Minami, c. Ye, T. J. Marks, J. Yang, and G. K. Wong, *SPIE Proc*. *971*, 136 (1988).

"Poled Polymeric Nonlinear Optical Materials. Enhanced Second Harmonic Generation Stability of Crosslinkable Matrix/Chromophore Ensembles", M. A. Hubbard, T. J. Marks, J. Yang, and G. K. Wong, *Chemistry of Materials*, *1*, 167 (1989).

"Third-Order Optical Susceptibilities of Molecular and Polymeric Materials. Symmetry, Frequency, and Chromophore Structure Dependence as Probed by pi-Electron Theory", D. Li, T. J. Marks, and M. A. Ratner, *Mats. Res. Soc. Proc*., (in press).

"Electrically Conductive Molecular Composites Based Upon PPBT and Metallophthalocyanines: Processing, Microstructure, and Electrochemistry", P. A. De Pra, J. M. Giesler, T. J. Marks, and S. H. Carr, *Mats. Res. Soc. Proc*., (in press).

"Polyphenylene Ether-Based Thin Film Nonlinear Optical Materials Having High Chromophore Densities and Alignment Stability", D. Dai, T. J. Marks, J. Yang, and G. K. Wong, (submitted for publication).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This program has involved a combined synthetic, processing, and physicochemical study of multifunctional, high-performance polymer systems rationally designed for certain unusual physical properties. In one thrust, the unique properties of the high modules/high strength macromolecules poly(p-phenylenebenzabisthiazole) (PBT) and poly(p-phenylenebisoxazole) (PBO) have been utilized to develop new kinds of electrically conductive polymeric and molecular/macromolecular hybrid materials. In the second thrust, several complementary approaches to the construction, evaluation, and fundamental understanding of new types of high-performance nonlinear optical materials have been pursued. Areas of emphasis have included chromophore-functionalized glassy polymers, chromophore-embedded crosslinkable matrices, inorganic/organic hybrid materials, crosslinked NLO films, the design of novel chromophores, and internally ordered polymeric NLO materials. Each research component has built upon past successes as well as upon strong on-going collaborations in laser optics and quantum theory.

AFOSR Program Manager: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

| | | |
|---|---|---|
| TITLE: | Surface Chemistry and Structural Effects in the Stress Corrosion of Glass and Ceramic Materials | |
| PRINCIPAL INVESTIGATOR: | Carlo G. Pantano<br>Department of Materials Science and Engineering<br>Pennsylvania State University<br>University Park, PA 16802 | |
| INCLUSIVE DATES: | 1 January 1982 - 31 May 1988 | |
| GRANT NUMBER: | F49620-86-K-0005 | |
| SENIOR RESEARCH PERSONNEL: | Rui M. Almeida<br>Jack J. Mecholsky | Cheryl A. Houser |
| JUNIOR RESEARCH PERSONNEL: | Jeffrey Chesson<br>Armando Gonzalez<br>Andrew Phelps<br>Alan Then | Dennis Coon<br>Martin Murtagh<br>Aleta Tesar |

PUBLICATIONS:

"Mechanical Properties of Silicon-Oxynitride Glasses," D. Coon, J. Rapp, R.C. Brandt and C. G. Pantano, J. Non-Crystl. Solids, 56, 161 (1983).

"Chemical Analysis of Fracture Surfaces," C.G. Pantano and J. F. Kelso, in Fractography of Ceramic and Metal Failures, ASTM STP 827, J. J. Mecholsky, Ed., ASTM, Philadelphia, pp 134-156 (1984).

"Transformation Range Viscosity of Fluorozirconate Glasses," J. E. Shelby, C. G. Pantano and A. Tesar, J. Am. Cer. Soc., 67(8), C164 (1984).

"Chemical Analyses of Sol/Gel Surfaces and Thin Films," C. G. Pantano, C.Z. Houser and R. K. Brown, in Better Ceramics through Chemistry, MRS Symposia Proc., Vol 32, North Holland, pp 255-267 (1984).

"Surface Chemical Studies of Oxides and Nitrides," C. G. Pantano, in Electronic Packaging Materials Science, MRS Symposia Proc., Vol 40, MRS, pp 303-316 (1985).

"Surface Chemistry in Relation to the Strength and Fracture of Silicate Glasses," C. G. Pantano, in Strength of Inorganic Glass, C. R. Kurkjian, Ed., Plenum, New York, pp 37-66 (1985).

"Surface Chemistry and Fracture of Fluoride Glasses," C. G. Pantano, Mater. Sci. Forum, 6, 285 (1985).

"Chemical Properties of Real and Ideal Glass Surfaces," C. G. Pantano, in Materials Characterization for Systems Performance and Reliability, McCauley and Volker, Eds., Plenum, New York, pp 127-148 (1986).

"Elastic Moduli of Silica Gels Prepared with Tetraethoxysilane," M. Murtagh, E. K. Graham and C. G. Pantano, J. Am. Ceram. Soc., 69 (11), 775 (1986).

"Secondary Ion Mass Spectroscopy," C. G. Pantano, in Vol 10 of the Metals Handbook: Materials Characterization, ASM, Ohio (1986).

"Surface Chemistry and Slow Crack Growth Behavior of Fluorozirconate Glasses," C. G. Pantano, in Halide Glasses for Infrared Fiberoptics, R. M. Almeida, Ed., Nijhoff, Netherlands, pp 199-218 (1987).

"Thermochemical Analysis of Interface Reactions in Carbon Fiber Reinforced Glass Matrix Composites," P. M. Benson, K. E. Spear and C. G. Pantano, in Ceramic Microstructures '86 Role of Interfaces, J. A. Pask and A. G. Evans, Ed., Plenum Press, New York, pp 415-426 (1987).

"Mechanical Properties of IR Glasses and Fibers," J. J. Mecholsky, J. A. Sycocki and C. G. Pantano, SPIE, 843, 21 (1987).

"Structural Changes in Stresses $As_2S_3$ Glass Fibers Determined by Raman Spectroscopy," D. S. Knight, J. J. Mecholsky and W. B. White, J. Am. Ceram. Soc., 70(8), 561 (1987).

"Hydrolysis Reactions at the Surface of Fluorozirconate Glass," R. K. Brow and C. G. Pantano, J. Am. Ceram. Soc., 17(7), 577 (1988).

"Fractoemission from Fused Silica and Sodium Silicate Glasses," J. T. Dickinson, S. C. Langford, L. C. Jense, G. L. McVay, J. F. Kelso and C. G. Pantano, J. Vac. Sci. Technol., A7(3), 1084 (1988).

"Glass Surfaces," C. G. Pantano, Review of Solid State Science, 3, 379 (1989).

"Characterization of Silica Gels by Infrared Reflection Spectroscopy," R. M. Almeida, T. A. Guiton and C. G. Pantano, J. Non-Crystl. Solids, (accepted for publication) (1990).

"Detection of the LO Mode in V-$SiO_2$ by Infrared Diffuse Reflectance Spectroscopy," R. M. Almeida, T. A. Guiton and C. G. Pantano, J. Non-Crystl. Solids, (submitted) (1990).

"Vibrational Spectra and Structure of Silica Gel Films Spun on c-Si Substrate," R. M. Almeida and C. G. Pantano, J. Mat. Sci., (submitted).

STUDENT THESES:

"Effects of Structure on the Fracture of $Na_2O.xAl_2O_3(3-x)SiO_2$ Glasses," Jeffrey Chesson, (1983).

"The Effects of Modifying Cation Substitutions on the Physical and Mechanical Properties of a Fluorozirconate Glass," Aleta A. Tesar (1984).

"The Elastic Moduli of Silicon Alkoxide Gels by Pulse Superposition Interferometry," Martin J. Murtagh (1985).

"Slow Crack Growth in Sodium Aluminosilicate Glasses," Dennis N. Coon (1986).

"Slow Crack Growth in Fluorozirconate Glass," Armando Gonzalez (1987).

"Fatigue Behavior in Fluorozorconate Glass," Alan Then (1987).

"Surface Layer Formation During the Aqueous Corrosion of Fluorozirconate Glass," Andrew Phelps (1988).

"Vacuum Crack Growth in Glass," Armando Gonzalez (1990) (expected).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this program has been to define the material dependences of glass fracture, and further, to verify the role of surface chemistry and corrosion in crack growth. The approach has been to independently study the surface chemistry using chemical and spectroscopic techniques, and the crack growth kinetics using fracture mechanics techniques. The studies have been carried out in a variety of environments on glass of different structure types (silicate vs fluoride vs chalcogenide), and glass systems whose composition could be varied to control ion-exchange kinetics and hydration rates. Silica gels have provided excellent models of surfaces for chemical and structural characterization. Most recently, the fracture of glass in vacuum has also been studied to examine intrinsic effects of composition and structure - especially the role of water in the glass structure, radiation-induced defects, and fractoemissions.

There is no question that crack growth in glass occurs in response to a chemical reaction, and a key feature of the reaction is that it depends upon the availability of highly strained bonds in the crack tip. But these studies reveal little or no correlation between the composition dependence of crack growth and the composition dependence of surface chemical reactions. We have found, however, that the elastic constants of the glasses can be related to the crack growth behavior. Although it can be argued that the elastic modulus controls the amount of strain in the crack tip bonds (and thereby, the reaction rate), it was concluded here that the effect of elastic modulus upon crack opening displacement is more important. There is, the elastic modulus controls the size of the crack-tip opening, and thereby, determines the stress intensity at which the size of the crack-tip opening is sufficient to admit certain molecules. And at stress intensities above this critical value (the so-called stress corrosion limit), the crack opening displacement controls the activity of these molecules in the crack-tip (and thereby, the reaction rate).

Perhaps the most interesting results of this program concerned the crack growth and fractoemission studies in vacuum. It was found that stable crack growth is exhibited by all glasses - i.e., silica, silicate, fluoride, fluorophosphate and chalcogenide - in vacuum. In contrast, the only crystalline material that could be found to exhibit stable crack growth in vacuum was sapphire. It was verified that this crack growth was not due to residual gas phase species in the vacuum, and further, it did not depend upon the water content of the glass, the reaction-induced defect concentration of the glass, or the glass composition.

In an effort to further investigate the mechanism of crack growth in vacuum, the electron, photon and ion emissions - so called fractoemissions - that accompany fracture were evaluated, and simultaneously, the fracture surfaces created in the process. A unique facility was developed to permit the detection of fractoemissions as a function of crack velocity; this is in contrast to the usual fractoemission studies of impact fracture. The key features of the instrument are:

(i) a neutral-beam gun for ion-desportion and static-SIMS of fracture surfaces,

(ii) a quadrupole mass spectrometer for detection of ionic species desorbed, sputtered or ejected during or after fracture,

(iii) an electron multiplier for detection of the electrons detected during crack-propagation, and

(iv) an in-situ fracture device where fracture surfaces can be created at any desired velocity.

The crack growth experiments were carried out in vacuum over the entire range of crack velocities, but there was no detectable electron ion, or photon emission up to $10^{-3}$ m/sec. Once the crack velocities exceeded $10^{-2}$ m/sec, the fractoemissions could be detected; these probably correspond to the fractoemissions measured during fast fracture. A rigorous interpretation of this effect has not yet been established. An important point is the fact that the detected emissions during fast fracture persist long after the fracture event. Thus, they could be associated with the rapid separation of charged surfaces, or reconstruction of the fracture surfaces; in either case, the effect would not be prevalent during slow fracture. Alternatively, there may exist a velocity threshold for fractoemission. These hypotheses can only be evaluated using theoretical approaches. Thus, molecular dynamics methods are being pursued to model the behavior of highly strained anion-cation pairs in the crack-tip regions. The objective is to define the range of stability (i.e., the crack opening displacement) as a function of applied stress intensity. The results will depend very much upon the potential function chosen, but many successful ones already exist for silica. If the crack growth behavior in vacuum can be modeled, then the possibility exists to introduce reactive molecular species into the simulation.

AFOSR Program Manage: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

TITLE: Organo-Metallic Elements for Associative Information Processing

PRINCIPAL INVESTIGATOR: Theodore O. Poehler and
Richard S. Potember
Johns Hopkins University
Applied Physics Laboratory
Laurel, Maryland 20707

INCLUSIVE DATES: 15 April 1985 - 15 April 1988

GRANT NUMBER: AFOSR-85-0169

SENIOR RESEARCH PERSONNEL: A. A. Burk, D. S.-W Hu

JUNIOR RESEARCH PERSONNEL:
K.R. Speck C.A. Viands
R.A. Murphy J Curry
R.C. Hoffman J.E. Cocchiaro

PUBLICATIONS:

"Reversible Electric Field Induced Bistability in Carbon Based Radical-Ion Semiconducting Complexes: A Model System for Molecular Information Processing and Storage," 2nd International Workshop on Molecular Electronic Devices, R.S. Potember, T.O.Poehler, R.C. Hoffman, K.R. Speck, and R.C. Benson, edited by F.L. Carter, (Marcel Dekker, Inc. NY) (1985).

"Molecular Electronics," R.S. Potember, R.C. Hoffman, and T.O. Poehler, Johns Hopkins Technical Digest, Vol 7, No. 2. (April-June 1986).

"Characterization of an Erasable Organometallic Optical Storage Medium," R.C. Hoffman, T.O. Poehler, and R.S. Potember, Digest of Technical Papers, CLEO, (9-13 June 1986).

"Electronic Devices from Conducting Organic Polymers," R.S. Potember, R.C. Hoffman, H.S-W. Hu, J.E. Cocchiaro, C.A. Viands, R. A. Murphy, and T. O. Poehler, Polymer, Vol 28, p 574 (1987).

"Bistable Optical Threshold Switching in Organic Photochromic Materials," R.S. Potember, T.O. Poehler, K.R. Speck, R.Cl Hoffman, and C.A. Viands, Bull Am. Phys. Soc., Vol. 31, p 657 (1986).

"$VO_2$ Films Formed by the Sol Gel Process from Vanadium (IV) Tetraalkoxyl Compounds," R.S. Potember, K.R. Speck and H.S-W. Hu, Patent Disclosure, The Johns Hopkins University, (March 1987).

"Molecular Devices for Optical Computing," R.S. Potember, R.C. Hoffman, H.S-W. Hu, and K.R. Speck, to appear in the 3rd International Workshop on Molecular Electronic Devices, ed. Forrest L. Carter (Elsevier, North-Holland) pp 663-677 (1988).

"Electronic Devices from Conducting Organic and Polymers," R.S. Potember, R.C. Hoffman, H.S-W. Hu, J.E. Cocchiaro, C.A. Viands, and T.O. Poehler, Polymer Journal, Vol. 19, No. 1, pp 147-156 (1987).

"Bistable Optical Switching in Organometallic Doped Gel Derived Silica Glasses," K.R. Speck, T.O. Poehler, and R.S. Potember, The Firth International Congress on Applications of Lasers and Electro-optics (1986).

"Optical Threshold Elements Based on the Excited State Photophysical Properties of Molecular Materials," R.S. Potember, R.C. Hoffman, K.A. Stetyick, and R.A. Murphy, Nonlinear Optical Properties of Polymers, Editors A. J. Huger, J. Orenstein, D.R. Ulrich, Materials Research Society Symposium Proceedings, 109, 29-34, (1987).

"Vanadium Dioxide Films Grown from Vanadium Tetrakis(t-Butoxide) by the Sol-Gel Process," K.R. Speck, H. S-W. Hu, R.A. Murphy, and R.S. Potember, Better Ceramics Through Chemistry III, Editors C. J. Brinker, D.E. Clark, and D. R. Ulrich, 121, 667-672 (1988).

"Vanadium Dioxide Films Grown from Vanadium Tetraisopropoxide by the Sol-Gel Process," K.R. Speck, H.S-W. Hu, M.E. Sherwin, R.S. Potember, Thin Solid Films, 165, 317-322 (1988).

"Organometallic Materials for Erasable Optical Storage," R.C. Hoffman, and R.S. Potember, Applied Optics (accepted for publication).

"Molecular Materials for Nonlinear Optics," R.S. Potember, R.C. Hoffman, K.A. Stetyick, R.A. Murphy, and K.R. Speck, Johns Hopkins APL Technical Digest, Vol 9, No 3, p 189 (1988).

CONFERENCES

"Bistable Threshold Switching in Organic Photochromic Materials," presented at the American Physical Society Meeting, Las Vegas, Nevada, 30 March - 4 April, 1986.

"Bistable Threshold Switching in Organic Materials," R.S. Potember, T.O. Poehler, K.R. Speck, R.C. Hoffmkan, and C.A. Viands, presented at the Nueral Networks for Computing Conference, Snowbird, Utah 13-16 April 1986.

"Electronic Devices from Conducting Polymers," presented at 2nd International Polymer Conference, Tokyo, Japan, 21 August 1986.

"Bistable Optical Switching in Organometallic Doped Gel-Derived Silica Glasses," K.R. Speck, T.O. Poehler, and R.S. Potember, The Fifth International Congress on Applications of Lasers and Electro-optics, Arlington, VA 13-13 November 1986.

"Electronic Devices from Conductive Organics," R.S. Potember, presented at Speciality Polymers 86, 6-8 August 1986, The Johns Hopkins University, Baltimore, MD.

"Optical Threshoild Materials for Symbolic Computing," R.S. Potember, AFOSR/DARPA Program Review, February 1987, Leesburg, VA.

"Molecular Optical Devices," R.S. Potember, Japan National Science Foundation Forum, Frontiers in Material Science, January 1987, Hakone, Japan.

"Molecular Devices for Optical Computing," R.S. Potember, Symposium on Molecular Electronic Devices, October 1986, Arlington, VA.

Symposium of Molecular Electronics and Biocomputers, "Molecular Optical Devices," Invited speaker, Budapest, Hungary, 24-27 August 1987.

National Academy of Science, National Research Council, "Opportunities in Molecular Materials," Invited speaker, Washington, D.C., October 1987.

Riken Institute, Japan, "Nonlinear Materials for Optical Computers," and "Sol-Gel Processing of $VO_2$ Thin Films," Invited speaker, October 1988.

Polymer Society Japan, "Optical Threshold Devices," Invited speaker, Fukurka, Japan, October 1988.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of the program were (1) to investigate the optical switching characteristics of organic thin films that exhibit reversible phase transitions, (2) to use these materials as a basis for a new class of devices for use in optical information processing, and (3) to use these materials as a basis for a new class of devices for use in high density content-addressable memories and associative processors.

AFOSR Program Manager: Dr Donald R. Ulrich

## COMPLETED PROJECT SUMMARY

TITLE: Ion-Exchanged Waveguides for Signal Processing Applications - A Novel Electrolytic Release

PRINCIPAL INVESTIGATOR:
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Department of Electrical Engineering
University of Florida
Gainesville, FL 32611

INCLUSIVE DATES: 1 September 1984 - 31 October 1987

CONTRACT/GRANT NUMBER: AFOSR-84-0369

SENIOR RESEARCH PERSONNEL:
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Huo Zhenguang
S. Iraj Najafi

JUNIOR RESEARCH PERSONNEL:
Rajendra K. Lagu
Paul G. Suchoski, Jr
Paul Chludzinski
Hsing C. Cheng
C.K. Kao
Amalia Miliou
David K. Lewis
Christopher P. Hussell

PUBLICATIONS:

"Fabrication of Single Mode Glass Waveguide by Electrolytic Release of Silver Ions," R. K. Lagu and V. Ramaswamy, *Appl Phys Lett.*, *45*, pp 117-118 (1984).

"Fabrication of Ion-Exchanged Glass Waveguides by Electrolytic Release of Silver Ions," R. K. Lagu and V. Ramaswamy, Seventh Topical Meeting on Integrated and Guided-Wave Optics, Post Deadline Paper PD-8, April 24-26 (1984).

"*In Situ* Measurement of Ionic Concentration During Fabrication of Ion-Exchanged Waeguides," R. K. Lagu, S.I. Najafi and V. Ramaswamy, *Appl Opt*., *23*, 3925 (1984).

"Fabrication of Ion-Exchanged Glass Waveguides Through Electrolytic Release of Silver Ions," R.V. Ramaswamy, R. K. Lagu and S.I. Najafi, SPIE PROCEEDINGS, 1st International Conference on Integrated Optical Circuit Engineering, Cambridge, MA (21-26 October 1984).

"Fabrication and Characterization of Buried Glass Waveguides with Symmetric Index Profiles," R. K. Lagu, R.V. Ramaswamy and S.I. Najafi, Digest of 3rd European Conference on Integrated Optics (ECIO), Paper II-R, pp 75-80, Berlin, (May 1985).

"An Improved Method for Fabricating Ion-Exchanged Waveguides Through Electrolytic Release of Silver Ions," S.I. Najafi, R. V. Ramaswamy and R. K. Lagu, IEEE J. Lightwave Tech., *LT-3*, pp 763-66 (1985).

"$Ag^+$-Diffused Graded-Index Glass Waveguides: Diffusion and Modal Characterization," S.I. Najafi and R.V. Ramaswamy, Conference Digest-Gradient-Index Optical Imaging Systems Conference, Palermo, CA pp 142-145 (26-27 September 1985).

"Process and Waveguide Parameter Relationships for the Design of Planar Silver Ion-Exchanged Glass Waveguides," R. K. lagu and R.V. Ramaswamy, IEEE J. Lightwave Tech., LT-4, pp 176-181 (1986).

"Silver Ion-Exchanged, Buried Glass Optical Waveguides with Symmetric Index Profile," R. K. Lagu and R.V. Ramaswamy, Appl. Phys Lett., 48, pp 19-20 (1986).

"Planar, Buried, Ion-Exchanged Glass Waveguides: Diffusion Characteristics," R.V. Ramaswamy and S.I. Najafi, IEEE J. Quantum Electron., QE-22, pp 883-891, (1986).

"A Variational Finite-Difference Method for Analyzing Channel Waveguides with Arbitrary Index Profiles," R.K. Lagu and R.V. Ramaswamy, IEEE J. Quantum Electron., QE-22, pp 968-976 (1986).

"Diffusion and Model Characterization of $AG^+$-$Na^+$ Exchanged Channel Waveguides," S.I. Najafi and R.V. Ramaswamy, Technical Digest-Conference on Integrated and Guided Wave Optics, Atlanta, Pp 60-61 (26-28 February 1986).

"Wavelength Dependent Propagation Characteristics of $Ag^+$-$Na^+$ Exchanged Planar Glass Waveguides," S.I. Najafi, R.Srivastava and R.V. Ramaswamy, Appl Opt., 25, pp 1840-1843 (1986).

"Guided Waves in Graded-Index Planar Waveguides with Nonlinear Cover Medium," R.K. Varshney, M.A. Nahme, R. Srivastava and R.V. Ramaswamy, NSF Workshop on Optical Nonlinearities, Fast Phenomena and Singal Processing, Tucson AZ, pp 185-199, (May 1986).

"Silver Film-Diffused Glass Waveguides: Diffusion Process and Optical Properties," S.I. Najafi, P.G. Suchoski, Jr and R.V. Ramaswamy, IEEE J. Quantum Electron., QE-22, pp 2213-2218 (1986).

"Guided Waves in Graded-Index Planar Waveguides with Nonlinear Cover Medium," R.K. Varshney, M.A. Nahme, R. Shrivastava and R.V. Ramaswamy, Appl Opt., 25, pp 3899-3902 (1986).

"Buried $Na^+$-$Ag^+$ Ion-Exchanged Glass Waveguides: Theory and Experiment," N.C. Cheng, R.V. Ramaswamy and R. Shrivastava, Seventh Topical Meeting on Gradient-Index Optical Imaging Systems (GRIN'87), Reno, NV, Paper TuC2-1, (January 1987).

"Influence of $Ag^+$-$Na^+$ Ion-Exchanged Equilibrium on the Index Profile of Single-Mode Glass Waveguides," R.V. Ramaswamy, R.Shrivastava and P. Chludzinski, Seventh Topical Meeting on Gradient-Index Optical Imaging Systems (GRIN '87), Reno, NV, Paper ThB2-1, (January 1987).

"Microstructural Definition of Ion-Exchanged Glass Optical Waveguides," P. Chludzinski, R.V. Ramaswamy and T.J. Anderson, Proceedings of the Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, Vacation Village, San Diego, CA, paper 51 (Wiley & Sons), (23-27 February 1987).

"Fabrication and Characterization of Single-Mode Glass Waveguides," R. Shrivastava, R.V. Ramaswamy, H.C. cheng and H. Zhenguang, Proc, SPIE, 835, pp 288-295 (1987).

"Ion-Exchange Between Soda-Lime Silicate Glass and Sodium Nitrate-Silver Nitrate Molten Salts," P. Chludzinski, R. V. Ramaswamy and T.J. Anderson, Phys Chem Glasses, 5, pp 169-173 (October 1987).

"WKB Analysis of Planar Surface Waveguides with Truncated Index Profiles," R.Srivastava, C.K. Kao and R. V. Ramaswamy, J. Lightwave Tech., LT-5, pp 1605-1609, (November 1987).

"Gel Silica Waveguides," R.V. Ramaswamy, T. Chia, R. Shrivastava, A. Miliou and J. West, SPIE's Symposium on Optical Signal Processing, Los Angeles, CA, pp 86-93 (January 1988).

"Nonlinear Prism Coupling and Power Limiting in Ion-Exchanged Waveguides," H. Zhenguang, R. Shrivastava and R.V. Ramaswamy, Topical Meeting in Integrated & Guided Wave Optics, (IGWO '88), Santa Fe, NM, Paper MF16, (March 1988).

"Buried Low-Loss Fiber Compatible Single-Mode Ion-Exchanged Channel Waveguides," H.C. Cheng, H. Zhenguang, A. Miliou, R. Srivastava and R.V. Ramaswamy, Topical Meeting in Integrated & Guided Wave Optics, (IGWO '88), Santa Fe, NM Paper MC1, (March 1988).

"Influence of $Ag^+$-$Na^+$ Ion-Exchange Equilibrium on Waveguide Index Profile," R.V. Ramaswamy, R. Shrivastava, P. Chludzinski and T. J. Anderson, IEEE Journal of Quantum Electron, QE-24, pp 780-786, (May 1988).

"Process Optimization of Buried $Ag^+$-$Na^+$ Ion-Exchanged Waveguides: Theory and Experiment," R.V. Ramaswamy, H.C. Cheng and R. Shrivastava, Appl Opt., 27, pp 1814-1819, (May 1988).

"Ion-Exchanged Waveguides: A Review," R. V. Ramaswamy and R. Shrivastava, INVITED PAPER, Special Joint Issue on Integrated Optics by IEEE Journal of Quantum Electronics and Journal of Lighwave Tech., 6, pp 984-1002 (June 1988).

"Ion-Exchanged Waveguides for Optical Signal Processing," R. V. Ramaswamy, R. Srivastava, H.C. Cheng, A. Miliou nd H. Zhenguang, INVITED PAPER, Sixth European Conf on Fiber Optic Communications and Local Area Network, FOC-LAN'88, Amsterdam, The Netherlands, paper 4.3., (June 1988).

"Sol-Gel Waveguides: Problems and Prospects," R.V. Ramaswamy and R. Srivastava, INVITED PAPER, US/UK Joint Conference on Optical Glass and Macromolecular Materials, Pitlochry, Scotland, paper Th. 5., (June 1988).

"Recent Advances in Ion-Exchanged Optical Waveguides and Components," R.V. Ramaswamy and R. Shrivastava, Journal of Modern Optics, 35, pp 1049-1067 (June 1988).

"Single-Mode Buried Channel Waveguide by Single-Step Electromigration Technique Using Silver Film," H. Zhenguang, R. Shrivastava and R.V. Ramaswamy, Appl Lett., 53, pp 1681-1683, (October 1988).

"Laser-Assisted Fabrication of Optical Waveguides in Gel-Silica Glasses," A. Miliou, R. Shrivastava, R.V. Ramaswamy and R.W. Slocumb, Topical Meeting on Integrated and Guided Wave Optics, (IGWO '89), Houston, TX (February 1989).

"Low Loss Near-Adiabatic Single-Mode Passive Waveguide Tapers," H. Zhenguang, R. Shrivastava and R.V. Ramaswamy, Paper TuBB3, Topical Meeting on Integrated and Guided Wave Optics, (IGWO '89), Houston, TX, (February 7, 1989).

"Single Mode Cross-Coupler 3dB Power Dividers by Ion-Exchange," C.P. Hussell, H.C. Cheng, R. Srivastava, R.V. Ramaswamy and J. L. Jackel, MOD, GRIN '89, Tokyo, Japan (July 1989).

"Fiber-Compatible $K^+$-$Na^+$ Ion-Exchanged Channel Waveguides: Fabrication and Characterization," A. Miliou, H. Zhenguang, H.C. Cheng, R. Srivastava and R.V. Ramaswamy, Journal of Quantum Electron., 25, pp 1889-1897 (August 1989).

"Low-Loss, Small-Mode Passive Waveguides and Near-Adiabatic Tapers in BK7 Glass," H. Zhenguang, R. Srivastava and R.V. Ramaswamy, IEEE J. Lightwave Tech., Special Issue, 7, pp 1590-1596 (October 1989).

ABSTRACT OF OJBECTIVES AND ACCOMPLISHMENTS:

The primary objective of the project was to investigate theoretically as well as experimentally the ion-exchange process for fabrication of passive waveguide components in commercial glasses. Two cation pairs, $Ag^+$-$Na^+$ and $K^+$-$Na^+$, were investigated. Since passive components require extremely high reproducibility this factor was given utmost attention in the case of $Ag^+$-$Na^+$ pair and a novel electrolytic release technique for silver ions was developed which provided on-line control of the silver concentration in the melt. The ion-exchange equilibrium at the melt-glass interface was studied to understand the dependence of the silver incorporation into the glass on the melt concentration. A large value of the equilibrium constant was obtained which also meant that for single-mode waveguide devices, very low melt concentrations were needed. While low concentrations required precise control of silver ions, the waveguides exhibited low loss due to reduced scattering. A commercial glass (BK7) was extensively investigated and low-loss (∼0.2 dB/cm at 1.3 µm wavelength) waveguides were routinely fabricated. The entire process has been modeled and the software developed allows prediction of device performance from the knowledge of fabrication conditions. Both surface guides as well as guides buried by two-step ion exchange process with or without the aid of an external electric field were studied. We have discovered that single-mode surface channel waveguides can be fabricated with excellent fiber-compatibility using $Ag^+$-$Na^+$ exchange in BK7 glass. This simplifies the process and ensures large reproducibility. Using this technique, several devices have been fabricated and analyzed. A near-adiabatic taper and a 2 X 2 cross-coupler for 3dB power splitting were demonstrated.

Ion-exchange technique was extended to fabrication of nonlinear waveguides by $K^+$-$Na^+$ exchange in semiconductor-doper glasses. These materials exhibit intensity dependent refractive index and have been suggested to be potentially useful for all-optical signal processing applications. We have studies nonlinear prism coupling and observed power limiting tat 20 MW threshold power from an Argon ion laser. The effect has been identified to be thermal in origin. The fast electronic nonlinearity was not investigated due to the lack of short pulse capability.

AFOSR Program Manager: Dr Donald R. Ulrich

# COMPLETED PROJECT SUMMARY

TITLE: Exploitations of the Sol-Gel Route in Processing of Ceramics and Composites

PRINCIPAL INVESTIGATOR:
Rustum Roy
Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802

INCLUSIVE DATES: 15 July 1987 - 14 June 1988

CONTRACT/GRANT NUMBER: F49620-85-C-0069

SENIOR RESEARCH PERSONNEL:
Sridhar Komarneni
C.G. Pantano

JUNIOR RESEARCH PERSONNEL:
Qaide Deng
Dongxin Qi
Lalba Rani

"Enhancing Densification of 93% $Al_2O_3$-7% MgO Triphasic Zerogels with Crystalline a-$Al_2O_3$ and $MgAl_2O_4$ Seeds", S. Komarneni, Y. Suwa and R. Roy, J. Mat. Sci. Lett., 6, 525-527 (1987).

"Microstructural Evolution in Sintering of AlOOH Gels", W.A. Yarborough and R. Roy, J. Mat. Res., 2, 494-515 (1987).

"Ceramics Via the Solution-Sol-Gel Route", R. Roy, Science, 238, 1664-1669 (1988).

"Some New Advances with SSG Derived Nanocomposites", R. Roy, S. Komarneni and W.A. Yarborough, Ultrastructure Processing Ceramics, Glasses and Composites (Eds J.D. Mackenzie and D.R. Ulrich), Pub. by Wiley and Sons, New York (in press) (1988).

"Effect of Epitaxial Seeding on Crystallization Process and on Densification in Diphasic $Al_2O_3$-MgO Xerogel", Y. Suwa, R. Roy and S. Komarneni, Proceedings of 87 International Symposium and Exhibition on Science and Technology of Sintering, Tokyo, Japan (in press) (1988).

"Hydrothermal Preparation of Low-Expansion 'NZP' Family of Materials", S. Komarneni, Int. J. High Tech. Ceramics (in press) (1988).

"The $Al_2O_3$-$SiO_2$ Phase Diagram: Metastability and Order Disorder", R. Roy, Proceedings of 1st International Workshop on Mullite - Advances in Ceramics (Eds. R.F. Davis, J.A. Pask and S. Somiya), Publ. by the American Ceramic Society, Columbua, OH (in press) (1988).

"Mullite Derived from Diphasic Gels", S. Komarneni and R. Roy, Proceedings of 1st International Workshop on Mullite - Advances in Ceramics (Eds. R.F. Davis, J.A. Pask and S. Somiya), Pub by The American Ceramic Society, Columbia OH (in press) (1988).

"Multi-phasic Nanocomposite Sol-Gel Processing of Cordierite", A.K. Kijowski, S. Komarneni and R. Roy, Better Ceramics Through Chemistry, Vol 3(Eds. C.J. Brinker, D.E. Clark and D.R. Ulrich), Publ. by Materials Research Society, Pittsburgh, PA (in press) (1988).

"Microwave Preparation of Mullite Powders", S. Komarneni, E. Breval and R. Roy, Proceedings of Microwave Processing of Materials (Eds. M.H. Broos, I.J. Chabinsky and W.H. Sutton), Publ. by Materials Research Society, Pittsburgh, PA (in press) (1988).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objective of this program was to explore and develop novel processing techniques for ceramics based on the solution-sol-gel (SSG) route.

Perhaps the most important accomplishment that AFOSR support has made possible is the development of the very concept of nanocomposites and di-phasic gels. The nanocomposite sol-gel processing has been shown to have profound effects on lowering crystallization temperatures, enhancing densification and improving microstructure of ceramics. Using compositionally di- or multi-phasic xerogels, enhanced densification has been achieved in the sintering of cordierite, $Mg_2Al_4Si_5o^{18}$ and mullite $Al_6Si_2O_{13}$. Such sintering of compositionally di- and multi-phasic gels at much lower temperatures may be attributed, at least in part, to the heat of reaction of the discrete phases at the sintering temperature. Using a structurally di- or multi-phase xerogels, "seeding" has been shown to have profound effects on microstructural evolution lowering crystallization temperature, enhancing densification and sintering of $Al_2O_3$ and $Al_2O_3$-MgO xerogels. The crystalline seeds are of the phase(s) expected in the final equilibrium assemblage and those lower the energy barrier for crystallization through epitaxy resulting in lower crystallization temperatures. Thus the above nanocomposite approach was shown to be superior to the monophasic or single phase SSG route.

The novel microwave processing was utilized in conjunction with sol-gel processing to make fine powders of mullite using single phase gels.

AFOSR Program Manager: Dr Donald R. Ulrich

# COMPLETED PROJECT SUMMARY

TITLE: Synthesis and Crystallization Behavior of Fluoride Glasses

PRINCIPAL INVESTIGATOR:
Donald R. Uhlmann
Department of Materials Science and Engineering
University of Arizona
Tucson, Arizona 85721

INCLUSIVE DATES: 1 September 1985 - 30 September 1988

CONTRACT/GRANT NUMBER: AFOSR-86-0350

COST AND FY SOURCE:

| | |
|---|---|
| First Year | \$60,000 |
| Second Year | \$79,752 |
| Third Year | \$80,248 |

SENIOR RESEARCH PERSONNEL: Donald R. Uhlmann

JUNIOR RESEARCH PERSONNEL:
M. Aronson
G. Dale
G. Berry
T. Gudgel
Kim Hamm
G. Tecwee
M. Denesuk
M. Choudry
M. Smith

PUBLICATIONS:

"Superconducting and Structural Properties of Spattered Thin Films of YBa$_2$Ca$_3$O$_{t-x}$," J. L. Makous, L. Maritato, C. M. Falco, J. P. Cronin, G. P. Rajendran, E. V. Uhlmann, and D. R. Uhlmann, *App. Phys. Lett., 51* 2164-2166 (1987).

"Wet Chemical Processing of High T$_c$ Superconducting Films, " B. Dutta, B. Samuels, J. P. Cronin, G. Dale, G. Tecwee, G. Rajendran, E. D. Zanotto, E. V. Uhlmann, B. D. Fabes, and D. R. Uhlmann, pp. 501-510 in M. F. Yan, Ed., *Ceramic Superconductors II*, (ACS, Westerville, 1988).

"Melt Processing of Bi-Ca-Sr-Cu-O Superconductors," E. D. Zanotto, J. P. Cronin, B. Dutta, B. Samuels, S. Subramoney, G. L. Smith, G. Dale, T. J. Gudgel, G. Rajendran, E. V. Uhlmann, M. Denesuk, B. D. Fabes, and D. R. Uhlmann, pp. 406-418 in M. F. Yan, Ed., *Ceramic Superconductors II* (ACS, Westerville, 1988).

"Bi-Ca-Sr-Cu-O Superconductors of (2122) Composition by Melt Processing," T. J. Gudgel, E. D. Zanotto, G. L. Smith, G. Dale, S. Subramoney, E. V. Uhlmann, M. Denesuk, J. P. Cronin, B. Dutta, G. Rajendran, B. Fabes, and D. R. Uhlmann, pp. 419-427 in M. F. Yan, Ed., *Ceramic Superconductors II* (ACS, Westerville, 1988).

"Wet Chemistry-Derived Barrier Layers for Ceramic Superconductor Films," J. P. Cronin, T. J. Gudgel, L. Zanotto, B. Dutta, G. P. Rajendran, G. Dale, E. D. Zanotto, E. V. Uhlmann, G. L. Smith, M. Denesuk, B. D. Fabes, and D. R. Uhlmann, pp. 511-523 in M. F. Yan, Ed., Ceramic Superconductors II, (ACS, Westerville, 1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objectives of the program were as follows:

1. Exploration of wet chemical synthesis routes to the preparation of metal-organic precursors for heavy metal fluoride glasses.

2. Exploration of synthesis conditions for converting precursors to multicomponent oxide gels for conversion to heavy metal fluoride glasses.

3. Exploration of chemistries and conditions for converting multicomponent oxide gels to heavy metal fluoride glasses.

4. Exploration of chemical approaches to passivating the surfaces of heavy metal fluoride glasses.

5. Exploration of the possibility of developing a computer model to describe crystallization during a cycle of cooling-reheating-recooling a liquid to form a glass (the cycle used in forming fluoride glass fibers).

6. Exploration of wet chemical synthesis routes to the formation of high temperature oxide superconductors.

7. Exploration of the feasibility of forming glasses of high temperature superconductor compositions, and of the crystallization behavior of such glasses if obtainable.

8. Exploration of wet chemical synthesis routes to the formation of barrier layers for use with high temperature oxide superconductor films on ceramic substrates.

The accomplishments of the program were as follows:

1. Several wet chemical synthesis routes to the preparation of metal-organic precursors for heavy metal fluoride glasses were developed. Particular attention was directed to the synthesis of double alkoxides and multialkoxides containing various combinations of the desired heavy metal cations.

2. Using selected precursors, it was demonstrated that multicomponent oxide gels could be prepared which contained the heavy metal cations in concentration ratios corresponding to those in the fluoride glass analogues.

3. Conversion of multicomponent oxide gels based on heavy metal cations to the corresponding fluorides was demonstrated.

4. Improved passivation of the surfaces of heavy metal fluoride glasses was accomplished through reaction with sulfuric acid. This reaction converted the heavy metal fluorides in a surface layer to the corresponding heavy metal sulfates, which are characterized by much lower rates of chemical attack in aqueous environments. The kinetics of such attack were measured.

5. A computer model was developed which describes in detail the number and size distributions in an initially liquid body which is cooled to temperatures below the glass transition at an arbitrary rate $R_1$, reheated at an arbitrary rate $R_2$ to an arbitrary temperature above the glass transition (as the draw temperature), and recooled at an arbitrary rate $R_3$ to form the final body. The model provides the capability of predicting material and process parameters which are critical in obtaining good glasses.

6. It was demonstrated that high temperature superconductors in both the Y-Ba-Cu-O and Bi-Ca-Sr-Cu-O systems could be formed by wet chemical routes. The preferred synthesis route involved the use of nitrate solutions. Critical temperatures for superconducting behavior similar to those of the best vapor-deposited films were demonstrated. The approach has significant commercial potential, and a patent disclosure was filed.

7. For a range of compositions in the Bi-Ca-Sr-Cu-O systems, it was demonstrated that glasses could be formed. The ability to form glasses was related to chemistry and knowledge of the kinetic processes involved in glass formation. The crystallization behavior of the glasses was determined, and superconductivity of the resulting crystallized bodies was demonstrated.

8. Using wet chemical synthesis routes based on sol-gel methods, barrier layers having a broad range of chemistries were prepared; and their effectiveness as barriers to interaction between superconducting films and substrates was evaluated. Improvement in critical temperature for superconductivity through the use of such barrier layers was demonstrated.

AFOSR Program Manager: Dr Donald R. Ulrich

# COMPLETED PROJECT SUMMARY

TITLE: A New Process for Final Densification of Ceramics

PRINCIPAL INVESTIGATOR:
Richard A. Wagner
Lynchburg Research Center
Babcock and Wilcox
Lynchburg, VA 24505

INCLUSIVE DATES: 15 February 1985 - 14 May 1988

CONTRACT/GRANT NUMBER: F49620-85-C-0053

SENIOR RESEARCH PERSONNEL:
R. A. Wagner, Babcock and Wilcox
Val J. Krukonis, Phasex Corporation

JUNIOR RESEARCH PERSONNEL:
D. R. Petrak
L. R. Okes
M. P. Coffey
J. M. Smith
N. W. White

PUBLICATIONS:

"Characterization of Matrix Inhibited 2D Carbon/Carbon Composites," Richard A. Wagner and Daniel R. Petrak, Proceedings of the XVIII Biennial Conference on Carbon 496 (1987).

"A Novel Impregnation Process: Application to Carbon/Carbon Composites," Richard A. Wagner, Val J. Krukonis, and M. P. Coffey, Proceedings of the 12th Annual Conference on Composites and Advanced Ceramics (1988).

"Supercritical Fluid Applications in Advanced Materials Processing," Richard A. Wagner, Val J. Krukonis, and M. P. Coffey, 1988 Materials Research Society Better Ceramics Through Chemistry III Symposium Proceedings.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Current oxidation protection systems for carbon/carbon composites rely on conversion or CVD silicon carbide coatings and glassy sealers. Coating cracks caused by thermal expansion mismatch between the silicon carbide coating and carbon/carbon substrate result in decreased oxidation resistant below 800°C (1500°F).

The objective of this program was to demonstrate the feasibility of using supercritical fluids to dissolve, transport, and precipitate ceramic precursors within the internal porosity of carbon/carbon composites to improve their low temperature thermochemical properties.

The solubility behavior of candidate silicon carbide precursors was determined in supercritical propane and carbon dioxide. Selected precursors were also fractionated using supercritical fluids and the char yield was found to increase with molecular weight of the fraction. These solubility and fractionation results were then used to guide the impregnation program.

Silicon carbide precursors (eg. polycarbosilane parent polymer and high molecular weight fractions) were dissolved in supercritical propane and precipitated in the internal porosity of 2D and 3D carbon/carbon composites. Multiple impregnation/pyrolysis cycles were employed to achieve weight increases of up to eight percent with corresponding changes in the bulk density and apparent porosity of the substrate material. Supercritical fluids were also used to coat ceramic fibers with a silicon carbide precursor in a demonstration of their potential to control the fiber/matrix interface of composites.

Microstructural characterization revealed significant silicon carbide accumulations in the porosity and along fiber/matrix interfaces in both 2D and 3D composites. Increased bending strength and oxidation resistance were both attributed to these deposits of polymer derived silicon carbide. The results of this program needs to be integrated with state-of-the-art coatings and sealers to optimize the overall oxidation protection system.

AFOSR Program Manager: Dr Donald R. Ulrich

# COMPLETED PROJECT SUMMARY

TITLE: Development of a High Efficiency Q-Switched Glass Laser Via Sol-Gel Processing

PRINCIPAL INVESTIGATOR: Shi Ho Wang/William Moreshead
GELTECH, Inc
One Progress Blvd #18
Alachua, Florida 32615

INCLUSIVE DATES: 15 August 1987 - 14 February 1988

CONTRACT/GRANT NUMBER: F49620-87-C-0087

SENIOR RESEARCH PERSONNEL: Jean-Luc Nogues, PhD

JUNIOR RESEARCH PERSONNEL: Robert Krabil

PUBLICATIONS:

A publication is planned for the next few months on the properties of neodymium and neodymium/erbium glasses prepared by the sol-gel method.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research effort attempted to determine the feasibility in preparing potential laser glasses using the sol-gel process. The sol-gel process is a logical choice for silica-based laser glasses, since it requires lower processing temperatures than traditional melt glass techniques, and allows good control of purity.

As a result of this six-month research program the following objectives were achieved:

1. Preparation of Nd doped sol-gel monoliths.
2. Preparation of gels of three different neodymium concentrations.
3. Preparation of gels codoped with neodymium and erbium.
4. Definition of a process to prepare Nd doped glass with a density close to the theoretical density of Nd silica glass, and higher than the density of pure silica.
5. Collection of a set of characteristics of Nd doped glass, such as texture and optical properties.
6. Fluorescence testing of the gels to determine the feasibility of using the sol-gel process to prepare Nd and Nd/Er doped materials for laser applications.

AFOSR Program Manager: Dr Donald R. Ulrich

# COMPLETED PROJECT SUMMARY

TITLE: New Non-Linear Optical Polymers

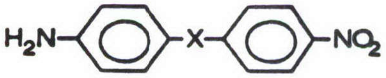
| | |
|---|---|
| PRINCIPAL INVESTIGATOR: | Gary E. Wnek<br>Department of Chemistry<br>Rensselaer Polytechnic Institute<br>Troy, NY 12180-3590 |
| INCLUSIVE DATES: | 1 October 1985 - 31 December 1987 |
| CONTRACT/GRANT NUMBER: | F49620-85-C-0151 |
| COSTS AND FY SOURCE: | $119,282 FY85; $119,053 FY86 |
| SENIOR RESEARCH PERSONNEL: | Donald R. Uhlmann<br>Yen Wei |
| JUNIOR RESEARCH PERSONNEL: | Ilya Gorodisher<br>Prakob Kitipichai |

PUBLICATIONS:

"Transmission of Electron Density Through Moieties Between Donors and Acceptors: Possible Implications for Nonlinear Optics," G.E. Wnek, P. Kitipichai, G. Frysinger, G.M. Korenowski, I. Gorodisher, D.R. Uhlamnn, and Y. Wei, MRS Symp. on Nonlinear Optical Properties of Polymers, A.J. Heeger, J. Orenstein and D.R. Ulrich, eds., Materials Research Society, p 139-141, Pittsburgh (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

(1) Determination of the ability of atoms or groups such as S, O, and $CH_2$ to transmit electron density when situated between donors and acceptors. This study was motivated by considering options for the synthesis of polymers with flexible pivots in the backbone between donors and acceptors but which still would allow for communication between these units. A number of molecules were synthesized wherein the donor and acceptor were p-aminophenyl and p-nitrophenyl, respectively.



When X is S, the compound is NLO-active, with an SHG powder efficiency 9-11x that of urea. Interestingly, the methylene bridge derivative was found in some cases to be NLO-active (SHG ca. 2x urea), even though the bridge is anticipated to be an 'insulator'. Apparently the SHG activity is the result of through-space charge transfer, which may be intra- or intermolecular. The crystal structure of the NLO-active form of this compound has been determined.

(2) Study of the photophysical properties of molecules in (1) in collaboration with the Jet Propulsion Laboratory. This program was initiated toward the end of the contract period in an effort to better understand the role of the bridging atom or group in transmitting electron density. Preliminary results suggest that the excited state of the sulfide (X=S) is dominated by charge transfer from aminophenyl to nitrophenyl. The implications of this result on the NLO-activity of this compound are being studied in detail.

(3) Synthesis of polymers containing NLO-active moieties. A new diol monomer, N-bis-2-hydroxyethyl-p-nitroaniline was synthesized. Several polyesters have been prepared from this monomer and diacyl chlorides. Also, using this diol, polyurethanes have been prepared from several diisocyanates. The rapid kinetics of the isocyanate/alcohol reaction is attractive in that it may be possible to pole the polyurethanes in an electric field during synthesis. Poling and SHG studies of these new polyesters and polyurethanes are in progress. Finally, the diamine N-bis-2-aminoethyl-p-nitroaniline has been prepared, extending the scope of potentially NLO-active polymers to polyamines and ureas.

AFOSR Program Manager: Dr Donald R. Ulrich

# RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - MOLECULAR DYNAMICS

DR FRANCIS J. WODARCZYK

| | |
|---|---|
| State-Specific Energy Transfer in Diatomic Radicals<br>F49620-85-K-0010 | David R. Crosley<br>Molecular Physics Lab<br>SRI International<br>333 Ravenswood Avenue<br>Menlo Park, CA 94025 |
| Laser Spectroscopy of Excited States in Atmospheric Molecules<br>AFOSR-85-0054 | Edward E. Eyler<br>Department of Physics<br>Yale University<br>New Haven, CT 06511 |
| Spectrometric Studies of Gas Phase Collision Processes<br>AFOSR-87-0323 | John B. Fenn<br>Department of Chemical Engineering<br>Yale University<br>P O Box 2159 Yale Station<br>New Haven, CT 06520-2159 |
| Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties<br>AFOSR-85-0381 | Robert W. Field<br>James L. Kinsey<br>Department of Chemistry<br>M I T<br>Cambridge, MA 02139 |
| Thermal Decomposition of TNT and Related Materials in the Condensed Phase<br>F49620-87-C-0003 | Ira B. Goldberg<br>Manager, Physical Chemistry<br>Rockwell International<br>Science Center<br>Thousand Oaks, CA 91360 |
| The Spectroscopy and Energy Transfer Kinetics of the Interhalogens<br>AFOSR-87-0197<br>AFOSR-85-0210 | Michael C. Heaven<br>Department of Chemistry<br>Illinois Institute of Tech<br>Chicago, Illinois 60616 |
| Electronic Energy Transfer Processes in the Alkali/Alkaline Earth Metal Vapors<br>AFOSR-84-0272 | Stephen R. Leone<br>Alan C. Gallagher<br>Joint Institute for Laboratory Astrophysics<br>University of Colorado and National Institute of Standards and Technology<br>Boulder, Colorado 80309 |
| The Use of Laser-Powered Homogeneous Pyrolysis to Determine the Initial Steps in the Homogeneous Gas-Phase Decomposition of Cyclic Nitramines<br>F49620-85-K-0006 | Donald F. McMillen<br>Chemical Kinetics Department<br>Chemistry Laboratory<br>SRI International<br>Menlo Park, CA 94025 |

# RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - MOLECULAR DYNAMICS
DR FRANCIS J. WODARCZYK

| | |
|---|---|
| Transient Behaviors in Chemical Reactions: Nanosecond Infrared Spectroscopy, Chemically Pumped Visible and Near-IR Lasers<br>AFOSR-87-0044 | George C. Pimentel<br>Department of Chemistry<br>University of California<br>Berkeley, CA 94720 |
| Free Radical Surface Interactions Using Multiphoton Ionization of Free Radicals<br>F49620-86-K-0001 | Michael J. Rossi<br>SRI International<br>Menlo Park, California 94025 |
| The Kinetics and Dynamics of Iodine Monofluoride Formation in Gas-Phase Collisions<br>AFOSR-85-0039 | J. C. Whitehead<br>Chemistry Department<br>Manchester University<br>Manchester, M13 9PL, U.K. |
| State to State Collision Induced Dissociation and Gas/Surface Interactions<br>F49620-86-C-0004 | Curt Wittig<br>Hanna Reisler<br>Department of Chemistry<br>University of Southern CA<br>Los Angeles, CA 90089-0482 |

## COMPLETED PROJECT SUMMARY

TITLE: State-Specific Energy Transfer in Diatomic Radicals

PRINCIPAL INVESTIGATOR:
David R. Crosley
Molecular Physics Laboratory
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

INCLUSIVE DATES: 1 May 1985 - 1 October 1988

CONTRACT/GRANT NUMBER: F49620-85-K-0010

SENIOR RESEARCH PERSONNEL:
Jay B. Jeffries
Richard A. Copeland
Karen J. Rensberger
Ingrid J. Wysong

JUNIOR RESEARCH PERSONNEL: Michael L. Wise

PUBLICATIONS:

"State-Specific Collision Dynamics of OH Radicals and N Atoms," R. A. Copeland, D.R. Crosley, and J.B. Jeffries, in *Advances in Laser Science-I*, W. C. Stwalley and M. Lapp, Eds., Am. Inst. Phys. Conf. Proc. 146, 545 (1986).

"Collisional Quenching and Energy Transfer in OH," D.R. Crosley and R.A. Copeland, in *Laser Applications to Chemical Dynamics*, M.A. El-Sayed, Ed., Proceedings of the Society of Photoinstrumentation Engineers 742, 6 (1987).

"Vibrational Energy Transfer and Quenching of OH($A^2\Sigma^+$, v=1)," R.A. Copeland, M.L. Wise, and D.R. Crosley, *J. Phys. Chem.*, 92, 5710 (1988).

"Vibrational Relaxation of OH($X^2\Pi_i$, v=2)," K.J. Rensberger, J.B. Jeffries, and D.R. Crosley, *J. Chem. Phys.*, 90, 2174 (1989).

"Vibrational and Rotational Energy Transfer in $X^2\Pi$ OH," D.R. Crosley, K.J. Rensberger, and J.B. Jeffries, *Am. Inst. Phys. Conf. Proc.*, in press, (1989).

"Collisional Quenching and Energy Transfer of NS $B^2\Pi$," I.J. Wysong, J.B. Jeffries, and D.R. Crosley, *Am. Inst. Phys. Conf. Proc.*, in press, (1989).

"Rotational and Translational effects in collisions of Electronically Excited Diatomic Hydrides," D.R. Crosley, *J. Phys Chem.*, (in press) (1989).

"Intramultiplet Energy Transfer in the Collisions of 3p $^4D^o$ Nitrogen Atoms with Nitrogen Molecules," J.B. Jeffries, R.A. Copeland, and D.R. Crosley, *J. Chem. Phys.*, (submitted) (1989).

"Quenching and Vibrational Energy Transfer in the $B^2\Pi$ State of NS," I.J. Wysong, J.B. Jeffries, and D.R. Crosley, *J. Chem. Phys.*, (submitted) (1989).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The effect of rotational level J′ on vibrational energy transfer (VET) and on electronic quenching was investigated for the $A^2\Sigma^+$ state of the OH radical. A strong dependence is found which appears to sample the entrance region of the collision surface. The final-J distribution following VET samples the exit channel. Rotational energy transfer (RET) in the same state shows unexpected propensities, in particular a large amount of $\Delta J > 1$ transfer in collisions with He. The J′ dependence, which is characteristic of both VET and total removal of the excited electronic state (quenching), can be interpreted in terms of an anisotropic potential. This concept, which we advocated qualitatively, has now been confirmed by independent ab initio results. The surprising magnitude of the $\Delta J > 1$ RET is predicted by a similar theoretical calculation.

A subject of considerable interest and importance is the fate of the electronic energy when an excited state in quenched. This question was studies in OH colliding with $H_2O$, using a two-laser pump-and-probe method. The results show that high vibrational (v) levels of OH are populated, contrary to the low-v levels that would correspond to previously assumed Franck-Condon-governed quenching collisions. In a different pump-probe experiment, VET and RET in ground electronic state ($X^2\Pi i$) OH are being investigated. In the RET we are looking at correlation in the transfer among states with different rotation, spin-orbin, $\lambda$-doublet, and orientational quantum numbers. For nonpolar colliders, VET occurs two to three orders of magnitude more slowly than in the $A^2\Sigma^+$ state. VET from v=2 of $X^2\Pi_i$ takes place 2.5 to 5 times faster than from v=1, depending on collider. Each of these facts contradicts expectations of simple theories of VET.

Measurements of the total collisional removal and VET rate constants for a series of vibrational levels of the $B^2\Pi$ state of the NS molecule show a surprising specificity on both collider and v′. For some colliders, the removal rate constants double from v′=0 to 1, are a minimum at 4, increase at 5, decrease at 6 and increase at 7; but for $O_2$ and $H_2$, they increase nearly monotonically with v′. For polyatomic colliders, a considerable amount of $\Delta v=2$ VET is observed.

Fine-structure transfer in the 3p $^4D^o$ state of nitrogen atoms was studied in collisions with He and $N_2$. This system is also amenable to ab initio calculation for detailed comparison with these state-specific results. Individual J levels are populated following two-photon absorption of laser light, and the final states are monitored by wavelength-resolved fluorescence. The results show that $\Delta J = 1$ transfer is faster than $\Delta J = 2$ or 3 and that the $m_J$ quantum number is not conserved in a J-changing collision.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: Laser Spectroscopy of Excited States in Atmospheric Molecules

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|---|---|
| PRINCIPAL INVESTIGATOR: | Edward E. Eyler<br>Department of Physics<br>Yale University<br>New Haven, CT 06511 |
| CO-PRINCIPAL INVESTIGATORS: | William A. Chupka and<br>Steven D. Colson<br>Department of Chemistry<br>Yale University<br>New Haven, CT 06511 |
| INCLUSIVE DATES: | 1 December 1984- 30 April 1988 |
| CONTRACT/GRANT NUMBER: | AFOSR-85-0054 |
| COST AND FY SOURCE: | \$100,000, FY 85; \$122,024, FY 86;<br>\$109,659, FY 87 |
| SENIOR RESEARCH PERSONNEL: | Edward E. Eyler<br>William A. Chupka<br>Steven D. Colson<br>Christian Cornaggia |
| JUNIOR RESEARCH PERSONNEL: | Andre Nussenzwig<br>Dorothea T. Biernacki<br>Peter Barnes<br>Tom Reagan |

PUBLICATIONS:

"Autoionization of the 4f Rydberg State of the NO molecule, E. E. Eyler, W. A. Chupka, Steven D. Colson, and D. T. Biernacki, Chem. Phys. Lett., 119, 177, (1985).

"Autoionization of Nonpenetrating Rydberg States of NO and $H_2$", E. E. Eyler, in Proceedings of the Workshop on Some Aspects of Autoionization in Atoms and Small Molecules, Argonne National Laboratory, ANL-PHY-85-3, pp. 245-252. Workshop was held May 2-3, 1985.

"Rydberg-Valence Interactions in the $\Pi_g$ States of $O_2$", Abha Sur, C. V. Ramana, W. A. Chupka, and Steven D. Colson, J. Chem. Phys., 84, 69 (1986).

"Autoionization of Nonpenetrating Rydberg States in Diatomic Molecules", E. E. Eyler, Phys. Rev., A34, 3881, (1986).

"Rotationally resolved double resonance spectra of NO Rydberg states near the first ionization limit", D. Therese Biernacki, Steven D. Colson, and E. E. Eyler, J. Chem. Phys., 88, 2099, (1988).

"Analysis of the 4f, v=3 state of NO", E. E. Eyler, and D. Therese Birnacki, J. Chem., Phys., 88, 2850, (1988).

"High resolution laser spectroscopy of NO: The A, well state and a series of nf, v=1 Rydberg states", D. Therese Biernacki, Steven D. Colson, and E. E. Eyler, J. Chem. Phys., 89, 2599, (1988).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The principal objectives of this project were to systematically investigate the structure and dynamics of molecular Rydberg states using high resolution laser spectroscopy. We have established a new laser facility for this purpose, and have used it to acccomplish several initial projects:

Autoionization rates have been measured for 28 levels of the 4f, v=3 state of nitric oxide. These are the first accurate determinations of decay rates in nonpenetrating molecular Rydberg states. The energy levels of these same states were measured and analyzed using a long-range interaction model to describe the perturbation of the distant Rydberg electron with the $NO^+$ core. The deviations from simple hydrogen atom binding energies were explained to an accuracy of 0.1% using this model.

To understand the decay rates, we have developed a theoretical model for autoionization of high $\ell$ Rydberg states that should be applicable to any small molecule. Decay rates for any state can be determined for knowledge of the polarizability, dipole and quadrupole moments of the molecular ion core as a function of internuclear separation. It was found that in nearly all cases where autoionization is energetically possible, it should occur more rapidly than radiative decay. Specific calculations were carried out for molecular hydrogen and compared with recent experiments.

Using optical double resonance, we have obtained completely resolved spectra of the n=7,8 and 9 Rydberg states of NO and conducted an extensive analysis. A previously unobserved quantum interference effect was observed an analyzed where the narrow 5f, v=2 levels are coincident with the broadly predissociative 8p, v=1 levels. We also obtained multiphoton ionization spectra of the 3s Rydberg state of $O_2$, and were able to characterize this state using photoelectron spectroscopy, showing evidence for Rydberg-valence interactions.

A new optical double resonance arrangement using a pulse-amplified cw dye laser and a collimated molecular beam was set up to allow studies of very highly excited states with 60 MHz resolution. This apparatus was used for a systematic study of the 3s, 7f, 12f and 15f states of NO. The natural linewidths were fully resolved, so that both energy levels and autoionization rates could be determined by measuring the line positions and their widths. A detailed analysis of this data yielded both an improved understanding of the Rydberg state structure and a much improved value for the ionization potential of NO. Preliminary experiments were also conducted on excited states of CO, about which comparatively little is known. These preliminary runs were very successful, and clearly demonstrate the feasiblity of a comprehensive study of this system using laser double resonance.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: Spectrometric Studies of Gas Phase Collision Processes

PRINCIPAL INVESTIGATOR: John B. Fenn
Department of Chemical Engineering
Yale University
P O Box 2159 Yale Station
New Haven, CT 06520-2159

INCLUSIVE DATES: 1 August 1987 - 31 July 1988

CONTRACT/GRANT NUMBER: AFOSR-87-0323

SENIOR RESEARCH PERSONNEL: Shida Shen

JUNIOR RESEARCH PERSONNEL: Takeshi Kodama

PUBLICATIONS:

"Microjet Burners for Molecular-beam Sources and Combustion Studies," W. Groeger and J. B. Fenn, Rev. Sci. Instrum., 59, 1971 (1988).

"Internal Energy Distribution of OCS Desorbing from a Hot Platinum Surface," W. Groeger and J. B. Fenn, J. Phys Chem., 93, 344 (1989).

"Rotational Relaxation of CO and $CO_2$ in Free Jets of Gas Mixtures," T. Kodama, S. Shen and J. B. Fenn, AIAA Series in Aeronautics and Astronautics, (Proc. 16th Int'l Symp. on Rarefied Gas Dynamics, M. Summerfield ed.).

"Superradiance in Free Jets of Discharge-Excited $CO_2$," S. Shen and J. B. Fenn. Chem. Phys. Lett., (in preparation).

"Gas Dynamic Modulation of Free Jet Beams," S. Shen and J. B. Fenn. Rev. Sci. Instrum., (in preparation).

"Terminal Distributions of Internal Energy in Free Jets of Discharge Excited CO and $CO_2$," J. Phys. Chem., (in preparation).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Measurements of total radiation intensity from free jets of CO and $CO_2$ excited in the source by a corona discharge showed sharp increases when source conditions led to condensation in jet. A new "microjet burner" was developed and showed promise for combustion studies and as a beam source for hot molecules. Measurements of internal energy distribution in OCS scattered by a hot surface showed different degrees of accommodation for the several internal energy modes. In admixture, CO and $CO_2$ showed no evidence of rotational coupling during free jet expansion.

AFOSR Program Manager: Dr Francis J. Wodarczyk

## COMPLETED PROJECT SUMMARY

TITLE: Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties

PRINCIPAL INVESTIGATOR:
Robert W. Field
James L. Kinsey
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

INCLUSIVE DATES: 01 October 1985 - 31 October 1987

CONTRACT/GRANT NUMBER: AFOSR-85-0381

COSTS AND FY SOURCE: $187,920 FY86; $200,000 FY87

SENIOR RESEARCH PERSONNEL:
S. Coy
J. P. Pique
F. Temps
C. Hamilton
R. Redington

JUNIOR RESEARCH PERSONNEL:
S. Halle
D. Jonas
S. Taddy
M. Hunter
J. Lundberg
P.H. Vaccaro

PUBLICATIONS:

"Stimulated Emission Pumping: New Methods in Spectroscopy and Molecular Dynamics," C.E. Hamilton, J.L. Kinsey, and R.W. Field, Ann. Rev. Phys. Chem., 37, 493-524 (1986).

"Collisional Energy Transfer in Highly Vibrationally Excited $H_2CO$ ($\tilde{X}^1A_1$)" F. Temps, S. Halle, P.H. Vaccaro, R.W. Field, and J.L. Kinsey, J. Chem. Phys., 87, 1895-1897 (1987).

"Polarization-Detected Transient Gain Studies of Relaxation Processes in $v_4 = 1\tilde{A}\ ^1A_2$ Formaldehyde-$h_2$", P.H. Vaccaro, F. Temps, S. Halle, J.L. Kinsey, and R.W. Field, J. Chem. Phys., 88, 4819 (1988).

"Laser Fluorescence, Excitation Spectrum of Jet-Cooled Tropolone: the $A^1B_2 - \tilde{X}^1A_1$ System", R.L. Redington, Y. Chen, G.J. Scherer, and R.W. Field, J. Chem. Phys., 88, 627 (1988).

"Vibrationally Excited Formaldelhyde: The Relationship between Vibrational Structure and Collisional Properties", F. Temps. S. Halle, P.H. Vaccaro, R.W. Field, and J.L. Kinsey, Faraday, Discussion of Molecular Vibrations, 1987, J. Chem. Soc., Faraday Trans., 2, 84, 1457 (1988).

"High Resolution Spectroscopic Studies of Small Molecules", R.W. Field J. de Physique, Conference Laser M2P, 12 Suppl C7-17 (1987).

"A Nomenclature for $\Lambda$ Doublet Levels in Rotating Linear Molecules", M.H. Alexander, P. Anderson, R. Bacis, R. Bersohn, F.J. Comes, P.J. Dagdigian, R.N. Dixon, R.W. Field, G.W. Flynn, K.-H. Gericke, B.J. Howard, J.P. Huber, D.S. King, J.L. Kinsey, K. Kleinermanns, A.C. Luntz, A.J. MacCaffery, B. Pouilly, H. Reisler, S. Rosenwaks, E. Rothe, M. Shapiro, J.P. Simons, R. Vasudev, J.R. Weisenfeld, C. Wittig, and R.N. Zare, J. Chem. Phys., 89, 1749 (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

### A. Spectroscopic Studies of Formaldehyde

We have performed Stimulated Emission Pumping (SEP) studies of $H_2CO$ and $D_2CO$ $\tilde{X}^1A_1$ at energies up to 12,000 $cm^{-1}$ Stark Quantum Beat (SQB) and Stark Anticrossing (SAC) studies of the $\tilde{A}^1A_2$ state, and SEP-Stark studies of the $\tilde{X}^1A_1$ state. The $\tilde{X}$-state experiments were designed to explore the effects of $E_{vib}^{TOT}$, excitation in specific vibrational modes, J, and $K_a$ on the assignability (i.e. localization) of the energy levels in terms of the traditional 3N-6 vibrational and 3 rotational quantum numbers. We found that regular behavior extends to surprisingly high energy at low-J values (also $J=K_a$ or $K_a=0$ where only one Coriolis mechanism is operational) and in overtones of mode-2 (the CO stretch) and that this regularity is manifest in regular vibrational energy level paterns, rotational constants, $\tilde{A}$-$\tilde{X}$ Franck-Condon transition intensities, and electric dipole moments.

The next logical step was to discover whether spectroscopic information about level "assignability" or localization has any relevance to collisional or chemical processes. Does the molecule remember that it is in a special, localized eigenstate or is the collision so violent that the molecule forgets the nature of its initial state? This is a very important question in light of the fact that spectroscopy identifies localized levels embedded in a dense manifold of non-localized or ergodic states. Ideally, we would want to look for level specific chemistry, but such a study would be vastly more difficult than the measurements of rotationally inelastic rates which we have recently been able to perform.

### B. Collisional Studies of $H_2CO$ $A^1A_2$

In order to develop and test methods capable of following single collision rotational state-to-state processes in the $\tilde{X}^1A_1$ state, we performed extensive rotational energy transfer (RET) studies in the $\tilde{A}^1A_2$ state. Two new techniques which are variants of SEP, were exploited: Transient Gain (TG) and Transient Polarization (TP). Populations (TG) or polarizations (TP) in the target level were monitored using a cw, single mode dye laser. These experiments provided a useful reference for comparing $\tilde{A}$-state RET adsolute rates and propensity rule patterns with our measurements in the $\tilde{X}$-state. They also showed that RET is dominated by electric dipole propensity rules, that polarization is surprisingly well preserved in $\Delta J \leq 2$ rotationally inelastic collisions, and provided a definitive explanation for highly nonlinear Stern-Volmer fluorescence quenching in the $H_2CO$ $\tilde{A}$ $4^1$ state. Rapid RET combined with strongly J-dependent unimolecular predissociation rates leads to nonlinear fluorescence quenching vs. pressure for rotationally unresolved detection whereas the single rotational level collisional depopulation rate monitored by TG or TP spectroscopy remains strictly linear vs pressure. Systematic studies of $\tilde{A}$-state RET with He, Ar, $N_2$, and $H_2CO$ collision partners have been performed.

### C. Collisional Studies of $H_2CO\ A^1A_1$

Two techniques (SEP-TA and SEP-TP) utilizing pulsed SEP to populate a single X-state rovibrationic level at $E = 11,400\ cm^{-1}$ and transient adsorption (TA) or transient polarization (TP) with a cw dye laser to monitor the evolution of population in the target level, have been developed. We have shown that, despite the $10^3$ higher vibrational density of states, than at E=0 in $\tilde{X}$ or at $\tilde{A}\ 4^1$, RET follows the same rotational propensity rules and proceeds at a slightly shower rate. This is remarkable because vibrational level spacing are smaller than $^JK_a \rightarrow {}^JK_a \rightarrow \pm 1$ level spacing. Somehow, even when the spectroscopy shows that the molecule is beginning to forget about 3N-6 vibrational quantum numbers, the rotational energy level pattern and RET propensity rules show that the molecule remembers the factorization of the wavefunction into a rotational and a vibrational part, even after offering a rotationally inelastic collision. This remarkable result implies that localized levels are likely to exhibit level specific chemistry which is sufficiently robust to be able to survive many nonreactive collisions. This experiment has motivated us to plan an experiment to look for level specificity in $NH_2 + O_2$ reactions during our next AFOSR grant.

### D. Quantum Chaos

A variety of statistical measures have been shown to provide information about the evolution of the dynamics from classically separable to classically chaotic. We have applied these measures to the pure sequence (single J, single rovibronic symmetry) spectra obtainable uniquely by SEP. Most of our recent work in this area has been focussed on averaged Fourier Transforms of SEP spectra of acetylene. That work is supported by the Department of Energy. During the next AFOSR grant period, we plan extensive experimental and theoretical statistical studies of SEP spectra of HCN/HNC.

### H-Atom Tunnelling

In collaboration with Professor R. Redington of Texas Tech, we have recorded fluorescence excitation spectra of tropolone $\tilde{A}^1B_2 - \tilde{X}^1A_1$ system. Tropolone is an example of an internally hydrogen-bonded molecule. Our studies have shown extreme vibrational mode-specificity on the $\tilde{A}$-state H-atom tunneling rates. This suggests that small displacements of heavy atoms remote from the light atom tunneling site can have enormous effects on the barrier to tunneling. We expect to continue these studies of H-atom tunneling during the next AFOSR grant period.

AFOSR Program Manager: Lt Col Larry P. Davis, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Thermal Decomposition of TNT and Related Materials in the Condensed Phase

PRINCIPAL INVESTIGATOR: Ira B. Goldberg
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Rockwell International Science Center
Thousand Oaks, CA 91360

INCLUSIVE DATES: 1 November 1986 - 30 September 1988

CONTRACT/GRANT NUMBER: F49620-87-C-0003

SENIOR RESEARCH PERSONNEL: Ted McKinney
Leslie F. Warren
Kwang Chung

JUNIOR RESEARCH PERSONNEL: Michael Cunningham

PUBLICATIONS:

"ESR Evidence for the Identity of Free Radicals Observed During Thermal Decomposition of Nitroaromatic Compounds," T. M. McKinney, I. B. Goldberg, and L. F. Warren, 1989 Pacific Conf. on Chemistry and Spectroscopy, October 1989, Abstract 135.

"Explosive Coke Formation at Early Stages of Trinitrotoluene Decomposition," T. M. McKinney, and I. B. Goldberg, (in preparation).

"Complicating Factors in the Reaction Mechanism Between Hexamethylbenzene and Trinitrotoluene," T. M. McKinney, and I. B. Goldberg, (in preparation).

"Effects of Acids, Bases, and Water on the Thermal Decomposition of Trinitrotoluene," T. M. McKinney, and I. B. Goldberg, (in preparation).

"Catalytic Effect of Known Decomposition Products of TNT on the Thermal Decomposition of pure TNT," T. M. McKinney, and I. B. Goldberg, (in preparation).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

2,4,6-Trinitrotoluene (TNT) undergoes thermal decomposition by a process that permits EPR observation on two distinctly different free radical species. The initial free radical has been ascribed to intermolecular coupling of two TNT moieties to produce a dibenzylnitroxide with distinctive hyperfine structure. The other species has a single featureless EPR absorption line. It appears to arise from a polymeric material that is called "Tar" or "Explosive Coke." The formation kinetics have been monitored by EPR. Analysis revealed that Tar is produced at an accelerated rate early in the reaction as compared to the autocatalytic (pseudo 1st order with respect to Tar) rate observed later. The following series of reactions was proposed and was found to be consistent with numerical simulation:

2 TNT --> Nitroxide $(k_1)$
TNT + Nitroxide --> Tar $(k_2)$
TNT + Tar --> Tar′ $(k_3)$
Nitroxide + Tar --> Tar" $(k_4)$

The nitroxide concentration remains small and behaves as a reactive intermediate. Known disproportionation reactions provide a reasonable model for the observed behavior. The nitrone that results from the disproportionation is a likely candidate for reactions leading to the Tar.

Hexamethylbenzene (HMB) and TNT react to form mixtures of spectrally similar nitroxide radicals. The kinetics may be simulated on the bases of a set of intermolecular condensation reactioss analogous to TNT. HMB and 2,4,6-trinitrobenzene (TNB) do not provide a clean model system for the TNT reaction because many different reaction products are observed. The relative amounts of different species depend on the ratios of reactants and the temperature. Charge transfer is suspected of being an important route to the formation of secondary nitroxides in systems with HMB.

Trace quantities of almost any material or small changes in the reaction conditions affect the course of thermal decomposition of TNT. This exacerbates the problem of mechanistic studies because seemingly inconsequential changes in experimental conditions may have a significant effect on reproducibility. Small quantities of different materials were intentionally added to learn more about the process.

The presence of moisture in TNT promotes high nitroxide concentrations at mild temperature relative to decomposition of pure TNT. It is not evident whether the water promotes nitroxide formation or inhibits nitroxide decomposition. Nucleophiles have a profound effect on TNT decomposition. Tar formation is enhanced by the nature of the Tar as reflected by the g-factor depends on the nucleophile. Acids appear to retard both radical and Tar formation. The effect is most pronounced with phosphoric acid. This may warrant further study as a means of desensitizing TNT or extending its storage life.

Known decomposition products of TNT, including, 2,4,6-trinitro-benzyl alcohol, benzaldehyde, and -benzoic acid, produce distinctive EPR spectra depending on whether they are thermolyzed in the pure state, in benzene solutions, or in the presence of TNT or HMB. Several spectra have been assigned on the basis of numbers and kinds of magnetic nuclei, but molecular structures have not been verified.

AFOSR Program Manager: Lt Col Larry P. Davis, USAF

# COMPLETED PROJECT SUMMARY

TITLE: The Spectroscopy and Energy Transfer Kinetics of the Interhalogens

PRINCIPAL INVESTIGATOR: Michael C. Heaven
Department of Chemistry
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Atlanta, Georgia 30322

INCLUSIVE DATES: 1 June 1987 - 31 May 1988

CONTRACT/GRANT NUMBER: AFOSR-87-0197

COSTS AND FY SOURCE: $64,678, FY 87

SENIOR RESEARCH PERSONNEL: Wafaa M. Fawzy

JUNIOR RESEARCH PERSONNEL: M. Michel Macler

PUBLICATIONS:

"Electronic Spectroscopy and Energy Transfer Pathways of Matrix Isolated $I_2$", M. Macler, J. P. Nicolai, and M. C. Heaven, J. Chem. Phys., 91, 174 (1989).

"Laser Excitation and Resolved Fluorescence Spectra for Matrix Isolated IBr", M. Macler and M. C. Heaven, (in preparation).

"Ultraviolet Emission Spectra from Matrix Isolated $I_2$", M. Macler and M. C. Heaven, (in preparation).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this program has been the determination of spectroscopic and radiative lifetime data for the low energy, metastable states of the halogens and interhalogens. This information was obtained by recording wavelength and time resolved laser excitation spectra for molecules isolated in rare gas matrices.

The spectroscopy, fluorescence decay lifetimes, and energy transfer dynamics of electronically excited $I_2$ and IBr have been investigated in solid rare gas matrices (Rg = Ar, Kr, and Xe). Visible laser excitation (460-800 nm) of dilute Rg/$I_2$ (1000:1) matrices resulted in emission from the $I_2$ $A^3\Pi(1_u)$ state. Re-analysis of the A --> X spectra provided revised molecular constants for matrix isolated $I_2$. A state lifetimes of 70 ± 20, 80 ± 20, and 110 ± 30 μs were observed in Ar, Kr, and Xe hosts respectively. The A state excitation spectrum closely followed the $I_2$ continuum absorption spectrum, indicating that transfer from the $B^3\Pi(0_u^+)$ and $^1\Pi(1_u)$ states was effective in populating $I_2$(A). At dilution ratios of 600:1 or lower the I $^2P_{1/2}$ - $^2P_{3/2}$ transition was observed in conjunction with the A-X bands. Excitation studies showed that isolated I atoms, trapped during the deposition process, were excited by electronic energy transfer from nearby $I_2^*$ molecules. A vibronic progression, similar to that of the A-X bands, but shifted to longer wavelengths, was noted in concentrated Rg/$I_2$ matrices (300:I). This system, which was emitted with a lifetime of about 10 ms, most probably originated from iodine dimers or $I_3$.

Excimer laser excitation (193 nm) of dilute Ar/$I_2$ matrices produced a single intense vibronic feature at 380 nm, the $I_2$ A-X bands, and the I $^2P_{1/2}$ - $^2P_{3/2}$ line. The uv emission exhibited a lifetime of about 5 ns, and was tentatively identified at the $D'^3\Pi/2g)$ - $A'^3\Pi/2u)$ transition. This assignment implies a gas phase to matrix red-shift of about 3100 $cm^{-1}$. With 193 nm excitation the atomic line was most probably produced by direct photodissociation. (Intermolecular energy transfer processes were not observed in dilute matrices.)

Laser excitation of Ar/IBr matrices at wavelengths within the 420-610 nm range resulted in emission from the IBr B-X and A-X systems. The former was completely diffuse, while the A-X bands formed a single vibronic progression from 980-1500 nm. Analysis of this progression revealed a matrix red-shift of $T_e(A)$ by 310 $cm^{-1}$, and minimal perturbation of the ground state vibrational constants ($\omega_e = 268$, $\omega_e x_e = 1.04$ $cm^{-1}$). Energy from IBr(A) to I $^2P_{1/2}$ was observed in concentrated matrices.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: The Spectroscopy and Energy Transfer Kinetics of the Interhalogens

| | |
|---|---|
| PRINCIPAL INVESTIGATOR: | Michael C. Heaven<br>Department of Chemistry<br>Illinois Institute of Technology<br>Chicago, Illinois 60616 |
| INCLUSIVE DATES: | 15 June 1985 - 14 November 1987 |
| CONTRACT/GRANT NUMBER: | AFOSR-85-0210 |
| COSTS AND FY SOURCE: | $80,182, FY85; $61,234, FY86 |
| SENIOR RESEARCH PERSONNEL: | Lambertus J. van de Burgt<br>Wafaa M. Fawzy |
| JUNIOR RESEARCH PERSONNEL: | Jean-Philippe Nicolai<br>Michael Macler |

PUBLICATIONS:

"Rate Constants for Collisional Deactivation of $Br_2(B)$ and $Br_2(X)$ by He", L.J. van de Burgt and M.C. Heaven, Chem. Phys., 103, 407 (1986).

"Electronic Quenching of $I_2(B)$ by He at Low Collision Energies", J.P. Nicolai and M.C. Heaven, J. Chem. Phys., 84, 6694 (1986).

"Fluorescence Decay Dynamics of the Halogens and Interhalogens", M.C. Heaven, Chem. Soc. Rev., 15, 405 (1986).

"Emission Spectra for Matraix Isolated IF: Observation of New Low-Lying Electronic States", J.P. Nicolai and M.C. Heaven, J. Chem. Phys., 87, 3304 (1987).

"Radiative Lifetime Measurements for the B State of Chlorine Monofluoride", L.J. van de Burgt and M.C. Heaven, (in preparation).

"The Spectroscopy and Energy Transfer Dynamics of Matrix Osolated Iodine", W. Fawzy, M. Macler, J.P. Nicolai, and M.C. Heaven, (in preparation).

ABSTGRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The kinetics of chemically and optically pumped halogen lasers are governed by the relative energies and stabilities of the low-lying metastable electronic states. The objective of this program has been the characterization of these states for selected halogens and interhalogens. Laser induced fluorescence techniques, applied to gas-phase and matrix isolated samples, have been used for this purpose.

The electronic spectra and energy transfer pathways of matrix isolated IF and $I_2$ have been investigated. Laser excitation of matrix isolated IF revealed the presence of three electronic states which had not been observed previously. The lowest energy state was identified as $A'^3\Pi(2)$. Determination of the position and lifetime of this state has provided a means for assessing its role in the chemical excitation of the B state. The two higher energy states have been tentatively assigned to a doubly excited electronic configuration.

The $I_2$ A→X system was studied in Ar, Kr, and Xe matrices. Analyses of the emission spectra showed that previous vibrational assignments were in error. The A state lifetime was found to be 50 ± 15 μs in all three matrix hosts. Polarization measurements and excitation spectra showed that the A state was populated via the A <- X and $^1\Pi$(1u) <- X transitions.

Emission from $I^*$ atoms was observed when low iodine to rare gas dilution ratios were used. Excitation spectra, recorded by monitoring the atomic emission intensity as a function of laser wavelength, were identical to those observed for the $I_2$ A-X system. Thus, the iodine atoms were excited by energy transfer from $I_2$(A). Electronic energy transfer was also noted in matrices which contained iodine co-deposited with oxygen. Excitation of $I_2$(A) resulted in emission from the $O_2$ a-X system. Both of these energy transfer processes are of relevance to the chemically pumped oxygen-iodine laser.

The radiative lifetime of ClF(B) was measured in the gas-phase. After correction for the effects of a strongly fluorescent contaminant, the lifetime was found to be 300 ± 50 us. This corresponds to an electronic transition dipole of 1 Rel = 0.1 ± 0.014 D. The rate for self-quenching was found to be $2.3 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. Preliminary calculations indicate that lasing of the ClF B-X transition can be achieved by optical pumping.

Continuous wave excitation and wavelength-resolved fluorescence techniques were used to study the self-quenching and energy transfer kinetics of $Br_2$(B). A self-quenching rate constant of $4 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ was observed for the levels with $v' > 10$, $J' > 15$, in excellent agreement with the results from pulsed measurements. The rate constant for rotational energy transfer (summed over all final states) was found to be $6 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. An upper bound of $5 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ was established for the vibrational transfer rate constant. These results are at variance with the energy transfer rate constants obtained from models of the time-resolved fluorescence decay kinetics.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: Electronic Energy Transfer Processes in the Alkali/Alkaline Earth Metal Vapors

PRINCIPAL INVESTIGATORS:
Stephen R. Leone
Alan C. Gallagher
Joint Institute for Laboratory Astrophysics
University of Colorado and
National Institute of Standards and Tech
Boulder, Colorado 80309

INCLUSIVE DATES: 5 August 1987 - 15 January 1988

CONTRACT/GRANT NUMBER: AFOSR-84-0272

SENIOR RESEARCH PERSONNEL:
D. Neuschafer
M. Harris
I. V. Hertel
W. Bussert
J. J. Kelly

JUNIOR RESEARCH PERSONNEL: M. O. Hale

PUBLICATIONS:

"Energy Transfer Processes of Aligned Excited States of Ca Atoms," D. Neuschafer, M. O. Hale, I.V. Hertel, and S. R. Leone, "Electronic and Atomic Collisions," D. C. Lorents, W.E. Meyerhof, and J. R. Peterson (eds.) Elsevier, 585-591 (1986).

"Orbital Alignment Effects in the $Ca(4s5_{p}{}^{1}P_{1})$ to $Ca(4s5_{p}{}^{3}P_{J})$ Electronic Energy Transfer with Molecular Collision Partners," W. Bussert and S. R. Leone, Chem. Phys. Lett., 138, 169-275 (1987).

"State-Specific Orbital Alignment Effects in Electronic Energy Transfer: $Sr(5s6_{p}{}^{1}P_{1}) + M \rightarrow Sr(5s6_{p}{}^{3}P_{J}, 4d5p{}^{3}F_{4}, {}^{3}F_{3}) + M$," W. Bussert and S. R. Leone, Chem. Phys. Lett., 138, 176-182 (1987).

"Observation of Three-body Collisional Transfer Between Atomic Levels," M. Harris, J.F. Kelly, and A. Gallagher, Phys. Rev., A36, 1512-1514 (1987).

"The Effect of Orbital Alignment on the Forward and Reverse Electronic Energy Transfer $Ca(4s5_{p}{}^{1}P_{1}) + M \rightarrow Ca(4s5_{p}{}^{3}P_{J}) + M$. With Rare Gases," W. Bussert, D. Neuschafer, and S.R. Leone, J. Chem. Phys., 87, 3833-3842 (1987).

"Collisional Transfer With the $Sr(5^{3}P_{J}{}^{o})$ Multiplet Due to Nearly Adiabatic Collisions with Noble Gases," J. F. Kelly, M. Harris, and A. Gallagher, Phys. Rev., A37, 2354-2360 (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Electronic energy transfer cross sections and effects of orbital alignment on energy transfer pathways are determined for a variety of alkaline earth atom collision systems. The rates of these processes are of interest in fundamental considerations of energy storage and pooling.

Cross sections have been measured for energy transfer among high-lying electronically excited states of calcium and strontium, induced by buffer-gas collisions. We combine both time-resolved kinetic techniques with emission amplitude measurements to define the absolute rates and branching pathways. The results have been analyzed in terms of current theoretical methodology to develop propensity rules which describe electronic energy transfer. We measured J mixing rates within the metastable $^3P$ states and collisional and stimulated radiation coupling between the lowest $^1P$, $^3P$, $^1D$, and $^3D$ states of Sr. Energy-pooling collisions have been investigated between several combinations of these low-lying, metastable states of Sr. These have led to major revisions and additions to understanding of high-density energy storage in these metastable states.

We also obtained a large array of new orbital alignment effects in electronic energy transfer, in order to determine the influence of orbital directionality on the cross sections of electronic energy transfer. The alignment effects are large, and have been observed both with rare gas and molecular collisions. In several cases, the determinations of these preferential orbital alignment effects are carried out both in the forward and reverse directions, providing a definitive measurement of the symmetry of the potentials involved in the curve crossing. Several highly state-selective effects are also observed, indicating that these orbital alignment determinations provide a remarkable new level of detail on the nature of electronic energy transfer pathways. These results have stimulated important new quantum mechanical calculations of electronic energy transfer.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: The Use of Laser-Powered Homogeneous Pyrolysis to Determine the Initial Steps in the Homogeneous Gas-Phase Decomposition of Cyclic Nitramines.

PRINCIPAL INVESTIGATOR:
Donald F. McMillen
Chemical Kinetics Department
Chemistry Laboratory
SRI International,
Menlo Park, CA 94025

INCLUSIVE DATES: 1 January 1985 - 31 December 1987

CONTRACT/GRANT NUMBER: F49620-85-K-0006

| SENIOR RESEARCH PERSONNEL: | | |
|---|---|---|
| | Donald P. McMillen | Jay B. Jeffries |
| | David M. Golden | Jean-Michel Zellwager |
| | Paul H. Stewart | Roberta P. Saxon |
| | S. Esther Nigenda | |

PUBLICATONS:

"Pulsed-Laser Pyrolysis of Dimethylnitramine and Dimethylnitrosamine", Donald F. McMillen, S. Esther Nigenda, Alicia C. Gonzales, and David M. Golden, Spectrochimica Acta Parta A, Molecular Spectroscopy, 43 (2), 237. (1987).

"Synthesis of N,N,-Dimethylnitramine by Nitrodephosphorlyation of Hexamethylphosphoramide", Jeffrey C. Bottar, Clifford D. Bedford, Robert J. Schmitt, and Donald F. McMillen, J. Org. Chem., 33, 4140 (1988).

"Thermal Decomposition of Dimethylnitramine and Dimethylnitrosamine by Pulsed Laser Pyrolysis", S. Esther Nigenda, Donald F. McMillen, and David M. Golden, J. Phys. Chem., 92 (1988).

"Theoretical Study of Nitro-Nitrite Rearrangement of $NH_2NO_2$", Roberta P. Saxon and Megumu Yoshimine, J. Phys. Chem., April, 1988 (submitted).

"Molecular-Beam-Sampled Laser Pyrolysis of Dimethylnitramine", Paul H. Stewart, Jay B. Jeffries, Jean-Michel Zellweger, Donald F. McMillen, and David M. Golden, J. Phys. Chem., April 1988 (submitted).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The principal objective of this project has been to identify and determine the thermal rate parameters for, the initial and/or rate-limiting steps in the gas-phase decomposition of nitramines. Our approach to this goal, which has also received support from the Army Research Office (ARO), has involved two experimental laser pyrolysis approaches and theoretical calculations, applied to dimethylnitramine and unsubstituted nitramine itself. The laser pyrolysis approaches, developed and refined during the course of this work, involved the use of pulsed infrared laser heating via an unreactive absorber bath gas. The theoretical approach involved application of large basis set MCSCF ab initio quantum mechanical calculations to a tractable analog of the cyclic nitramines. Although the acyclic nitramines cannot undergo all of the reactions of the cyclic nitramines, they do have many reactions in common, particularly those rapid secondary reactions that can lead either to oxidized amino radicals or to ultrosamines, and that help control the branching that determines when selfsustaining decomposition is achieved.

Our studies, unlike those reported in the literature, indicate that a nitro-nitrate rearrangement pathway is competitive with the expected (and previously invoked) N-$NO_2$ bond scission. This rearrangement pathway has been obscured because it can lead to some of the same products as are yielded by the bond scission route. The principal evidence for the nitro-nitrite rearrangement is (1) Arrhenius parameters for decomposition ($\log k/s^{-1} = 13.5 \pm 0.6 - [37.4 \pm 2.5]/2.3RT$) that are two orders of magnitude too low to be consistent with simple N-$NO_2$ bond scission as the sole rate-determining step; (2) molecular-beam, mass-spectrometrically-sampled laser pyrolysis studies that show direct detection of NO and the nitroxyl radical $(CH_3)_2NMO\cdot$ on a time scale too short to allow for the production of these substances in secondary bimolecular reactions; and (3) ab initio calculations that find a rearrangement pathway at slightly lower energy than that of simple bond scission. These results suggest that such rearrangement pathways may be a common feature of nitramine decomposition, as other studies have recently shown them to be for C-$NO_2$ compounds. In the course of repeated synthesis of dimethylnitramine, we also developed a new method of synthesis via the nitrodephosphorylation of phosphoramides, which has marked convenience, yield, and safety advantages for certain ultramines.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: Transient Behaviors in Chemical Reactions: Nanosecond Infrared Spectroscopy, Chemically Pumped Visible and Near-IR Lasers

PRINCIPAL INVESTIGATOR: George C. Pimentel
Department of Chemistry
University of California
Berkeley, CA 94720

INCLUSIVE DATES: 1 November 1986 - 31 October 1987

GRANT/CONTRACT NUMBER: AFOSR-87-0044

JUNIOR RESEARCH PERSONNEL: Mark Young

PUBLICATIONS:

"Nanosecond Infrared Detection of Gaseous Free Radicals: $CF_3$ and $C_2F_5$," Mark Young and G.C. Pimentel (in preparation).

"The Rate of Reaction Between $CF_3$ and $Br_2$," Mark Young and G.C. Pimentel (in preparation).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this grant was to provide funds for acquisition of an excimer dye laser to complete construction of our nanosecond infrared spectrometer. The grant funds have been expended as per the grant request and the instrument is now operating with 10 nsec temporal resolution and 0.5 $cm^{-1}$ spectral resolution over the spectral region 1400 - 900 $cm^{-1}$. The free radical $CF_3$ has served as a prototype example, displaying nascent vibrational excitation and permitting kinetic studies.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: Free Radical Surface Interactions Using Multiphoton Ionization of Free Radicals

PRINCIPAL INVESTIGATOR: Michel J. Rossi
Chemical Kinetics Department
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

INCLUSIVE DATES: 1 October 1985 - 30 September 1988

CONTRACT/GRANT NUMBER: F49620-86-K-0001

SENIOR RESEARCH PERSONNEL: David M. Golden
Robert M. Robertson
Nur Selamoglu

PUBLICATIONS:

"Kinetics of Surface Reactions of $CF_3$ Radicals," R. M. Robertson, M. J. Rossi, and D. M. Golden, J. Vac. Sci. Technol., A5, (6) 3351 (1987).

"Summary Abstract: Spontaneous Thermal Etching of Silicon by $CF_3$ RAdicals," R. M. Robertson, D. M. Golden, and M. J. Rossi, J. Vac. Sci. Technol., A6(3), 1407 (1988).

"In Situ Radical Detection Under Very Low Pressure Photolysis Conditions Using Resonance-Enhanced Multiphoton Ionization. Kinetics of $CF_3$ Radicals Produced from IR Multiphoton Dissociation of Hexafluoroacetone," R. M. Robertson, D. M. Golden, and M. J. Rossi, J. Phys. Chem., 92, 5338 (1988).

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"Atom- and Radical-Surface Sticking Coefficients Measured Using Resonance Enhanced Multiphoton Ionization (REMPI)," R. M. Robertson, and M. J. Rossi, Proceedings of the Materials Research Society, Vol. 131, Chemical Perspectives of Microelectronic Properties, M. E. Gross, J. T. Yates, Jr., and J. Jasinski (Eds.), p. 251, (1989).

"Sticking Coefficients of the $SiH_2$ Free Radical on a Hydrogenated Silicon-Carbon Surface," R. M. Robertson, and M. J. Rossi, Appl. Phys. Lett., 54, 185 (1989).

"Atom- and Radical-Surface Sticking Coefficients Measured Using Resonance Enhanced Multiphoton Ionization (REMPI)," R. M. Robertson, and M. J. Rossi, J. Chem. Phys., (accepted).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this work was the study of the interaction of neutral transients such as atoms and polyatomic free radicals with surfaces of technical interest, such as single crystal silicon, GaAs and $SiO_2$. The specific goal of this study is to provide kinetic input data such as free radical sticking coefficients and surface reactivity parameters of free radicals in support of chemical kinetic modeling of the neutral component of semiconductor processing plasmas. Therefore, the pressure regime chosen was in the millitorr range and the experiments were conducted in a Knudsen reactor.

The strategy chosen was to generate the free radicals from IR-multiphoton or UV single photon photolysis of appropriate precursors *in situ* within the Knudsen cell that contains the sample surface. The free radical density as a function of time was followed by Resonance-Enhanced Multiphoton Ionization (REMPI) of the free radical, and the stable reaction products resulting from the radical-surface reaction were monitored using molecular beam modulated mass spectrometry. We spent considerable time developing and testing the methodology, and in the end we obtained quantitative information on unimolecular and biomolecular free radical reaction pathways in the presence of active surfaces. This requires the knowledge of absolute densities of free radicals as a function of time, a goal that was achieved by calibrating the REMPI signal using the mass spectrometer.

We investigated the reactivity of $CF_3$ radicals on $SiO_2$ using a gold-coated stainless steel Knudsen cell with a background pressure of $10^{-7}$ Torr. The main conclusion was the complete inertness of $CF_3$ towards $SiO_2$ up to temperatures of 300°C. Rather than reacting with $SiO_2$, $CF_3$ reacted with chemisorbed water (surface hydroxyls) to yield HF and $SiF_4$ among other products. This study showed the importance of $H_2O$ vapor in connection with free radical studies on surfaces and put into question the role of thumb, derived from discharge studies, that fluorocarbon free radicals are mainly responsible for $SiO_2$ etching under conditions where ion-induced chemistry seems to be unimportant (high pressure, high frequency).

The heterogeneous interaction of $CF_3$ radical with single crystal silicon was studied up to temperature of 450° C, and steady state etching was observed, albeit at rates that are not important in a practical etching environment. The initial etching efficiency of $CF_3$ approached that of $F_2$ at higher temperatures, and an Arrhenius plot for the surface reactivity of $CF_3$ on Si was obtained ($E_a$ = 8 kcal/mol). The etching efficiency of $CF_3$ decreased with increasing exposure of $CF_3$ to Si and approached a steady-state value of 10 to 50% of the initial value, depending on experimental conditions. This result implies that etching still continues, even though a $CF_x$ layer forms on the Si surface.

In addition to REMPI of free radicals, we recorded the time dependent density of I and Br atoms in ther presence of stainless steel surfaces. The etching coefficient ($\gamma$) of I on stainless steel at ambient temperature was measured as 0.16, whereas vibrationally highly excited $CF_3I$ was deactivating with $\gamma \geq 0.5$. The vibrational relaxation of highly vibrationally excited $CF_3$ was followed by recording the REMPI signal as a function of time, but quantitative results could not be obtained.

The REMPI spectrum of the non-fluorescing $SiH_2$ radical was found and its kinetic behavior on amorphous hydrogenated silicon surfaces studied. The sticking coefficient for relaxed $SiH_2$ was 9.10K±0.02 depending on experimental conditions, whereas $\gamma$ for highly vibrationally excited $SiH_2$ was found to be ≥0.5 in analogy to $CF_3I$. This means that $SiH_2$ with 7000 $cm^{-1}$ of excess energy is deactivated upon every collision. The fact that $SiH_2$ ionizes via predissociation into $Si(^1D_2) + H_2(X)$ at selected wavelengths is responsible for the excellent dynamic range of the $SiH_2$ and $SiH_2$ density which can be followed over 4 orders of magnitude.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: The Kinetics and Dynamics of Iodine Monofluoride Formation in Gas-Phase Collisions

PRINCIPAL INVESTIGATOR: J. C. Whitehead
Chemistry Department
University of Manchester
Manchester, M13 9PL, U.K.

INCLUSIVE DATES: 1 December 1984 - 31 May 1988

CONTRACT/GRANT NUMBER: AFOSR-85-0039

COST AND FY SOURCE: \$55,517, FY 85; \$8,400, FY 86; \$11,336 FY 87

JUNIOR RESEARCH PERSONNEL:
Helen S. Braynis
Timothy Watkinson
David Raybone
Fiona Winterbottom

PUBLICATIONS:

"Two-photon VUV laser-induced fluorescence detection of $I^*(^2P_{1/2})$ and $I^*(^2P_{1/2})$ from alkyl iodide photodissociation at 248 mm", F. G. Godwin, P. A. Gorry, P. M. Hughes, D. Raybone, T. M. Watkinson, and J. C. Whitehead, *Chem. Phys. Lett.*, *135*, 163, (1987).

"On the role of iodine atoms in the production of $IF(B\ ^3\Pi)$ in fluorine atom/iodide flames", D. Raybone, T. M. Watkinson, and J. C. Whitehead, *Chem. Phys. Lett.*, *135*, 171, (1987).

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"The 248 mm KrF laser excitation of alkyl iodide - flourine mixtures: the production and spectroscopy of $CF_2(\hat{A})$", D. Raybone, T. M. Watkinson, and J. C. Whitehead, *J. Chem. Soc. Faraday Trans. 2* *84*, 483, (1988).

"The characterisation of the mechanism of IF(B) production in fluorine iodide systems", D. Raybone, T. M. Watkinson, and J. C. Whitehead, in Selectivity in Chemical Reactions: Proceedings of the NATO Advanced Research Workshop 7th - 11th September 1987, (J. C. Whitehead, Ed.) Reidel, Dordrecht, 1988.

"The production of IF($B^3\Pi$) in the 248 mm laser photolysis of fluorine alkyl iodide mixtures", D. Raybone, T. M. Watkinson, J. C. Whitehead, and F. Winterbottom, Laser Chem., 8, 2988 (in press).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project has concentrated on the formation of electronically excited iodine monofluoride in its B ($^3\Pi 0^+$) state with the aim of identifying high intensity sources of IF(B) for possible chemical laser work and by understanding the mechanism of IF(B) formation thereby to optimise its production. Three major experiments were undertaken with these aims.

In the first, the visible chemiluminescence (200 - 900 mm) resulting from the reactions of fluorine atoms with various organic iodides were studied in the gas-phase (~0.1 - 1.0 Torr) in a flowing system. In addition to the production of IF(B), it was found that these systems also produced $CH^*$, $HCF^*$, $C_2{}^*$ and vibrationally-excited HF, except for F + $CI_4$, where only IF(B) was the only emitter.

In contrast, the reactions of F atoms with a range of inorganic iodides only produced IF(B) and no electronically-excited metal halides. By measuring the IF(B) vibrational population distribution, it was possible to show that IF(B) was produced by a simular mechanism in all these systems and that its precursors were ground state fluorine atoms and electronically-excited iodine atoms, I($^2P_{1/2}$). This mechanism was confirmed and extended to other fluorine / iodide systems by probing the iodine atoms in the flames using two photo VUV laser-induced fluorescence and by kinetic modelling.

In the final series of experiments, it was found to be possible to generate a high intensity pulse of IF(B) by the 248 mm excimer laser photolysis of a mixture of molecular fluorine, helium and an alkyl iodide. Depending on the identity of the iodide, sustained emission from IF(B) was obtained following the laser pulse for periods between 5 and 770 μs. It is suggested that the precursors of IF(B) are again fluorine atoms and excited iodine atoms, where the fluorine atoms result from the reaction between the photolytically produced alkyl radicals and molecular fluorine and the excited iodine atoms results from the photolysis of the iodide. This method of IF(B) production would seem to hold the most promise for future chemical laser developments.

AFOSR Program Manager: Dr Francis J. Wodarczyk

# COMPLETED PROJECT SUMMARY

TITLE: State to State Collision Induced Dissociation and Gas/Surface Interactions

PRINCIPAL INVESTIGATOR:
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Hanna Reisler
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-0482

INCLUSIVE DATES: 1 October 1985 - 30 September 1988

CONTRACT/GRANT NUMBER: F49620-86-C-0004

COST AND FY SOURCE: \$132,109, FY 85; \$115,952, FY 86; \$114,578, FY 87.

SENIOR RESEARCH PERSONNEL: Marcus Noble, Eli Kolodney

JUNIOR RESEARCH PERSONNEL:
Xuao-Wu Quan
Scott Powers
Lori Iwata
Amy Ogai
Delroy Baugh

PUBLICATIONS:

"The Role of Initial Conditions in Elementary Processes Involving Intermediate 'Complexes'," S. Buelow, M. Noble, G. Radhakrishnan, H. Reisler, C. Wittig, and G. Hancock, J. Phys. Chem., 90, 1015, (1986).

"Photodissociation of Jet-Cooled $(CH_3)_3CNO$: Temporal Separation of Radiationless Transitions and Unimolecular Reactions," M. Noble, C. X. W. Quan, H. Reisler, and C. Wittig, J. Chem. Phys., 84, 3573, (1986).

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"Direct Inelastic Scattering of NO from MgO(100)," E. Kolodney, D. Baugh, P. S. Powers, H. Reisler, and C. Wittig, Chem. Phys. Lett., 145, 177, (1988).

"Photodissociation Dynamics of NOCl: State-Specific $\Lambda$-Doublet Ratios in the $^2P_{1/2}$ and $^2P_{3/2}$ States of NO," A. Ogai, C. X. W. Quan, L. Iwata, and H. Reisler, Chem. Phys. Lett., 146, 367, (1988).

"Molecule Surface Dissociative Scattering of n-$C_3F_7NO$ from MgO(100) at Hyperthermal Energies: Nascent NO($X^2\Pi$)," E. Kolodney, D. Baugh, P. S. Powers, H. Reisler, and C. Wittig, J. Chem. Phys., 90, 3883 (1989).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The main thrust of our contract was directed towards the study of gas-surface interactions and the complementary collisionless photodissociation processes. Our initial experiments were concerned with NO scattering from an insulating MgO(100) single crystal surfaces, and the preliminary results have been published in Chem. Phys. Lett. We are now conducting experiments in which molecules with high kinetic energy are dissociated and/or ionized upon impact on surfaces. Our preliminary results, which are first of their kind since they involve state-resolved detection of the dissociation products, have been accepted as a Communication in the Journal of Chemical Physics. In parallel with these new experiments, we have continued our studies of the photophysics and photodissociation dynamics of molecules which are suitable candidates for the beam/surface and beam/beam experiments. These include detailed studies of the photodissociation dynamics of such molecules as nitrosyl cyanide, nitrosyl chloride, t-BuNO and n- and iso-nitrosopropane.

### 1. Gas Surface Collisions

In the surface experiments, we prepare high kinetic energy species using aerodynamic acceleration in pulsed supersonic expansions and then internally excite these species by photoexcitation followed by a radiationless transition. We then measure the outcomes of the gas/surface interactions under UHV conditions. We find that we can accelerate molecules using supersonic expansions and achieve kinetic energies of several eV with a light carrier gas (e.g. $H_2$) and modest heating. In our system, the accelerated molecules can also be excited internally or dissociated via optical excitation. The surface is contained in a typical UHV chamber ($10^{-10}$Torr) and is characterized by He diffraction. The experimental technique allows us to independently vary the internal and kinetic energies and we detect fragments via 2-frequency 2-photon ionization.

Our first goal in the surface studies was to understand surface induced energy flow in the colliding molecules. Therefore, impulsive collisions on a fairly inert, insulating surface were investigated. We measured angular and internal state distributions for NO molecules scattered from cleaved, single-crystal MgO(100) at several kinetic energies and surface temperatures. We find several intriguing features that are different from those observed in collisions of NO with metal surfaces [i.e., Ag(111)]. For example, we observe no vibrational excitation, which is compatible with the suggestion that such excitation results from electronic interactions with the surface.

Understanding the dynamics of collision induced dissociation of molecules on surfaces is of fundamental importance and interest. We have measured the final state distribution of diatomic fragments (NO) resulting from the collision induced dissociation of a polyatomic molecule ($C_3F_7NO$) scattered from a single crystal MgO(100) surface. A pulsed, supersonic molecular beam of a $C_3F_7NO$ seeded in $H_2$ was accelerated to hyperthermal energies in the range of 1-7eV, and the NO fragments were detected state-selectively. The most striking features in the NO rotational distributions are that (i) the ground $^2\Pi_{1/2}$ and excited $^2\Pi_{3/2}$ spin-orbit states have different rotational distributions, and (ii) spin-orbit excitation is relatively low, with a $[^2\Pi_{3/2}]/[^2\Pi_{1/2}]$ population ratio of approximately 1.35. The dissociation probability depends on incident kinetic energy, being 6 times higher at 5eV than 3eV. The direct inelastic nature of the process is demonstrated by the near-specular angular distribution of scattered species, the strong dependence on incident kinetic energy, and a weak $T_s$ dependence for both absolute intensities and rotational distributions in the range 500-800 K. A dissociation probability of 3 ± 1% at 5.1eV and $T_s = 570$ K was estimated. At this stage, we cannot be certain about the respective roles of the different possible dissociation mechanisms: unimolecular decomposition, mechanical distortion followed by direct bond rupture, intramolecular electronic excitation, electronic processes involving the surface (molecule-surface change transfer), etc. Experiments are in progress in which a wide range of kinetic energies are used.

## 2. Photochemistry and Photophysics of NO Containing Molecules

NCNO is one of the prototypical molecules that will be used in studies of surface-induced dissociation of vibrationally excited molecules. Our most recent studies of NCNO explored two aspects: (i) non-radiative transitions and fluorescence lifetimes and (ii) correlations between the internal energies of the two fragments. The experiments on the fluorescence lifetimes of NCNO are particularly germane to the gas/surface collision studies.

Large polyatomic molecules have many vibrational degrees of freedom, and consequently, their $S_0$ and $T_1$ surfaces have high density of states. This results in a fast radiationless decay of $S_1$ levels, and a slower unimolecular reaction rate on $S_0$. In our experiments on t-BuNO, we find that it is indeed possible to separate in time the radiationless transition rate and the unimolecular reaction rate on $S_0$, and we observe competitive dissociation channels on low surfaces -- $T_1$ and $S_0$. Dissociation on $S_0$ leads to nascent NO distribution which can be closely modelled assuming a totally statistical partitioning of the excess enrgy at a very loose transition state with no barrier. Conversely, above the small barrier (~650 $cm^{-1}$) to triplet surface dissociation, very different, non-statistical behavior is observed. $S_1 \rightarrow T_1 \rightarrow$ products rapidly becomes the dominant reaction mechanism, and NO is produced at a rate three orders of magnitude faster than on the $S_1$ surface at the same energy.

Similar experiments are currently underway on $C_3F_7NO$. Here, we also observe two channels: at low excess energies, the dissociation is slow, and the NO product distributions are well described by a statistical model. Above an excess energy of ~2800 $cm^{-1}$, a faster channel starts to appear. Here the NO($^2\Pi_{1/2}$) distributions can still be simulated by the prior model, while the NO($^2\Pi_{3/2}$) distributions are non-statistical.

The photodissociation dynamics of NOCl was also explored, since NOCl is an excellent candidate for photodissociation on surfaces. Measurements of vector and directional properties (i.e., spatial anisotropies, $\Lambda$-doublet populations, v-J correlations) provide a powerful tool for unravelling the nature of the repulsive states involved in the spectroscopy, and in conjunction with product state distributions, provide detailed information on the photodissociation dynamics.

AFOSR Program Manager: Dr Francis J. Wodarczyk

## RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - CHEMICAL REACTIVITY AND SYNTHESIS

DR ANTHONY J. MATUSZKO

| | |
|---|---|
| New Approaches to the Synthesis of Novel Organosilanes<br>AFOSR-84-0008 | Philip Boudjouk<br>Department of Chemistry<br>North Dakota State University<br>Fargo, ND 58105 |
| Novel Organoboranes as Intermediates for Ceramic Precursors and High-Energy Fuels<br>AFOSR-85-0108 | John J. Eisch<br>Department of Chemistry<br>SUNY at Binghamton<br>Binghamton, New York 13901 |
| Polycondensation Reactions of Electrophilic Benzoquinones<br>AFOSR-87-0104 | H. K. Hall, Jr<br>Department of Chemistry<br>University of Arizona<br>Tucson, AZ 85721 |
| Polysilylatted Unsaturated Molecules<br>AFOSR-83-0244 | Paul R. Jones<br>Department of Chemistry<br>University of North Texas<br>Denton, TX 76203-5068 |
| Synthesis of New Polynitropolyhedranes<br>AFOSR-84-0085 | Alan P. Marchand<br>Department of Chemistry<br>University of North Texas<br>NT Station, Box 5068<br>Denton, TX 76203-5068 |
| Polyazidoesters as Energetic Polymers and Copolymer Components with Fluoro Derivatives<br>AFOSR-85-0024 | Robert M. Moriarty<br>Department of Chemistry<br>University of Illinois<br>at Chicago<br>P.O. Box 4348<br>Chicago, IL 60680 |
| The Chemistry of Precursors to Silicon-Carbide<br>AFOSR-83-0209 | Morey A. Ring<br>Edward O'Neal<br>Department of Chemistry<br>San Diego State University<br>San Diego, CA 92182 |
| Organosilicon Compounds and Polymers and Silicon Ceramics<br>AFOSR-85-0265 | Dietmar Seyferth<br>Department of Chemistry<br>M I T<br>Cambridge, MA 02139 |
| The Reactivity of Transition Metal-Silicon Compounds<br>AFOSR-85-0228 | T. Don Tilley<br>Chemistry Department, D-006<br>La Jolla, CA 92093 |

# RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - CHEMICAL REACTIVITY AND SYNTHESIS

DR ANTHONY J. MATUSZKO

| | |
|---|---|
| Symposium on Microstructure and Properties of Catalysts<br>AFOSR-87-0345 | Michael M. J. Treacy<br>Materials Research Society<br>9800 McKnight Road, Suite 327<br>Pittsburgh, PA 15257 |
| Molecular Dynamics of Materials Possessing High Energy Content<br>AFOSR-84-0040 | Nicholas J. Turro<br>Department of Chemistry<br>Columbia University<br>New York, New York 10027 |
| Powerful Photogenerated Reducing Agents<br>AFOSR-86-0081 | David Tyler<br>Department of Chemistry<br>University of Oregon<br>Eugene, Oregon 97403 |
| Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials<br>F49620-86-C-0010 | Robert West<br>Department of Chemistry<br>University of Wisconsin<br>Madison, WI 53706 |

# COMPLETED PROJECT SUMMARY

TITLE: New Approaches to the Synthesis of Novel Organosilanes

| | | |
|---|---|---|
| PRINCIPAL INVESTIGATOR: | Philip Boudjouk<br>Department of Chemistry<br>North Dakota State University<br>Fargo, ND 58105 | |
| INCLUSIVE DATES: | 1 November 1983 - 30 November 1987 | |
| CONTRACT/GRANT NUMBER: | AFOSR-84-0008 | |
| SENIOR RESEARCH PERSONNEL: | Steven Keller<br>Moon-Kyeu Park | Jerry Chrusciel<br>Mohindra Gupta |
| JUNIOR RESEARCH PERSONNEL: | Steven Bahr<br>Byung-Hee Han<br>Dennis Thompson<br>Jeung-Ho So<br>James Woell<br>Amirthini Rajkumar<br>Eric Black<br>Kevin Anderson<br>Ratnasabapathy Sooriyakumaran | John Jacobsen<br>Upasiri Samaraweera<br>Andrew King<br>Walter Ohrbom<br>Elizabeth Bonderson<br>Rajkumar Kumarathasan<br>Michelle Little |

PUBLICATIONS:

"Organic Sonochemistry. Ultrasonic Acceleration of the Hydrosilation Reaction", B-H. Han and P. Boudjouk, Organometallics, 2, 769 (1983).

"Are the Silacyclopentadienyl Anion and the Silacyclopropenyl Cation Aromatic?", M. S. Gordon, P. Boudjouk and P. Anwari, J. Amer. Chem. Soc., 105, (1983) 4972.

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"Theoretical Studies of Polyvinyl-Substituted Carbenium and Silylenium Ions", T. Trung, M. S. Gordon and P. Boudjouk, Organometallics, 3, 484 (1984).

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"The Synthesis of the First Spiropentasilane, Octamethylspiropentasilane", P. Boudjouk and R. Sooriyakumaran, J. Chem. Soc., Chem. Commun., 777 (1984).

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"Synthesis with Ultrasonic Waves", P. Boudjouk, J. Chem. Ed., 63 427 (1986).

"Organic Sonochemistry. Ultrasonic Acceleration of the Reaction of Dicarbonyls with Trimethylchlorosilane in the Presence of Zinc", P. Boudjouk and J.-H.So, Synth. Commun., 16, 775 (1986).

"Ultrasonic Generation of Metal Powders from Lithium and Metal Halides", P. Boudjouk, D. P. Thompson, W. H. Obrbom and B.-H. Han, Organometallics, 5, 1257 (1986).

"Organic Sonochemistry. New Sonically Accelerated Reactions Involving Lithium", P. Boudjouk, R. Sooriyakumaran and B.-H. Han, J. Org. Chem., 51, 2818 (1986).

"Electrochemical and Sonochemical Routes to Organosilane Precursors", in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, Eds., John Wiley & Sons, Inc., New York, (1986).

"The Acceleration of Synthetically Useful Heterogeneous Reactions Using Ultrasonic Waves", P. Boudjouk, in "High Energy Processes in Organometallic Chemistry", K. S. Suslick, Ed., American Chemical Society Symposium Seeries, American Chemical Society, Wash. DC, (1987).

"Generation and Trapping of Diethylsilanelanone. A Reactive Intermediate with a Silicon-Selenium Double Bond", D. P. Thompson and P. Boudjouk, J. Chem. Soc., Chem. Commun., 1466, (1987).

"A Convenient, Naphthalene-Catalyzed Synthesis of Alkali Metal Selenides and Diselenides in Tetrahydrofuran and the Reactivity Differences Exhibited by These Salts Toward Organic Bromides. Effect of Ultrasound", D. P. Thompson and P. Boudjouk, J. Org. Chem., 53, 2109 (1988).

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"Organosilicon Chemistry - A Brief Overview", with T. J. Barton in Advances in Chemistry, J. Ziegler, Ed., American Chemical Society, Wash. DC, (in press).

"Convenient Routes to Di-t-Butylsilylene: Chemical, Thermal and Photo-Chemical Generation", P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrusciel and K. R. Anderson, Angew. Chem., (in press).

"Reductive Coupling of Carbonyls with Zinc and Trimethylchlorosilane to Produce O-Silylated Pinacols. The Effect of Ultrasound", J.-H. So, M. K. Park and P. Boudjouk, J. Org. Chem., (in press).

"Convenient Synthesis of Hexamethyldisilthiane and Tetramethyldisilthiane", J.-H. So and P. Boudjouk, Synthesis, (in press).

"Cyclosilselenanes. Photochemical and Thermal Precursors of Silaneselones, Reactive Intermediates Containing the Silicon Selenium Bond", P. Boudjouk, D. P. Thompson and S. R. Bahr, Organometallics, (in press).

"A New Catalyst for the Efficient and Selective Beta-Hydrosilation of Acrylonitrile. Effect of Ultrasound", A. B. Rajkumar and P. Boudjouk, Organometallics, (in press).

"Hydride Abstraction from Siloles: Routes to Potentially Anti-Aromatic Species", P. Boudjouk, A. B. Rajkumar, J. Lambert, W. Schilf and M. S. Gordon and K. Nguyen, (submitted).

"Convenient One-Pot Synthesis of Selenolate Anions and Selenoacetals via Alkali Metal Cleavage of Diselenides. Effect of Ultrasound", D. P. Thompson and P. Boudjouk, J. Org. Chem., (submitted).

"Reductive Coupling of Carbonyl Compounds to Give Alkenes and/or Pinacolones in the Presence of Zinc and Trimethylchlorosilane. Effects of Ultrasonic Irradiation", J.-H. So, M-K. Park and P. Boudjouk, J. Org. Chem., (submitted).

"Dehydration of Metal Hydrates with Trimethylchlorosilane. A Simple and Convenient Routed to Anhydrous Complexes. P. Boudjouk and J.-H. So, Inorganic Chemistry, (submitted).

"Hexamethyldisilthiane", J.-H. So, and P. Boudjouk, Inorganic Synthesis, (submitted).

## ABSTRACTS OF OBJECTIVES AND ACCOMPLISHMENTS:

Our main objectives during the tenure of this grant were 1) to develop convenient routes to hindered silylenes, 2) to explore routes to potentially aromatic and antiaromatic silicon ring systems, 3) to prepare highly strained but stable siliranes and silirenes as convenient sources of new silicon-containing reactive intermediates and new silicon-containing ring systems, 4) to continue developing the use of ultrasonic waves as a synthetic tool and 5) to initiate a synthesis program in silicon-selenium, -tellurium chemistry.

The first objective was met by the successful generation of di-t-butylsilylene, the most hindered silylene yet reported, by three different routes. All routes require mild conditions and the silylene can be prepared in 50-85% yields and on scales useful for preparative work. The second goal, making aromatic and antiaromatic silanes, was only partially achieved. We failed to make aromatic silanes but in the process proved that silicon heterocycles that bear a negative charge are not aromatic even though they adhere to Huckel's rule for aromaticity, e.g., the silafluorene anion and silacyclopentadienide anion are shown not to be aromatic by NMR spectroscopy. We were able to prepare a stable 4 pi electron system, the silole cation, a particularly novel species because it is both anti-aromatic by electron count and a trivalent silicenium ion. Objective 3, the preparation of stable highly strained rings was achieved through the synthesis of 1,1-di-t-butyl 2,3-dimethylsilirane and 1,1-di-t-butyl-2,3 bis(trimethylsilyl)silirene in gram quantities. The chemistries of these ring systems were explored utilizing pyrolytic, photolytic and chemical methods.

Ultrasound as a useful source of energy in chemical systems has been further developed during this grant period. Significant rate accelerations and increases in yields for a number of reactions have been effected. Platinum metal catalyzed hydrosilations, lithium promoted deprotonations and halogen exchange reactions, the production of highly activated metal powders and the formation of carbon-carbon bonds by zinc reduction of carbonyls are some key examples.

We have initiated a synthetic program in silicon-selenium, -tellurium chemistry and have prepared novel ring systems containing these elements. Thus far we fully characterized four and six membered rings with alternating silicon and selnium atoms. From these rings we have generated new species containing the silicon-selenium double bond, the first examples of silaselones.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: Novel Organoboranes as Intermediates for Ceramic Precursors and High-Energy Fuels

PRINCIPAL INVESTIGATOR: John J. Eisch
Department of Chemistry
State University of New York
Binghamton, New York 13901

INCLUSIVE DATES: 1 February 1985 - 31 August 1988

CONTRACT/GRANT NUMBER: AFOSR-85-0108

COST AND FY SOURCE: $150,000, FY 85; $70,000, FY 88

SENIOR RESEARCH PERSONNEL: Marek P. Boleslawski

JUNIOR RESEARCH PERSONNEL: Babak Shafii

PUBLICATIONS:

"The Physical and Chemical Consequences of Cyclic Conjugation in Boracyclopolyenes. The Antiaromatic Character of Pentaarylboroles", John J. Eisch, James E. Galle, and Sinpei Kozima, J. Am. Chem. Soc., 108, 379-385, (1986).

"The Di-sigma-Methane-like Photorearrangement of Dimesityl(mesitylethynyl)borane", John J. Eisch, Babak Shafii, and Arnold L. Sheingold, J. Am. Chem. Soc., 109, 2526-2528, (1987).

"Fluoro(dimesityl)borane", John J. Eisch, and Babak Shafii, Organomet. Syn., 4, 465-468, (1988).

"Trimesitylborane", John J. Eisch, and Babak Shafii, Organomet. Syn., 4, 469-471, (1988).

"The Photochemical Generation of the Diphenylborate(I) Anion from Metal Tetraphenylborates(III) in Aprotic Media: Repudiation of a Contravening Claim", John J. Eisch, Marek P. Bolesiawski, and Kohei Tamao, J. Org. Chem., 1989, (in press).

"The Thermal Generation and Transformation of the Borepin Ring System: A Paradigm of Pericyclic Processes", John J. Eisch, James E. Galle, Babak Shafii, and Arnold L. Rheingold, Organometallics, 1989 (in preparation).

"Homoaromaticity and Bond Fluxionality in the 7-Borabicyclo[2.2.1]heptadiene Ring System: Degenerate Sigmatropic and Irreversible Ring-Opening Rearrangements", John J. Eisch, James E. Galle, Marek P. Boleslawski, and Aronold L. Rheingold, J. Am. Chem. Soc., 1989 (in preparation).

"Aromatic Stabilization of the Triarylborirene Ring System by Tricoordinate Boron and Facile Ring-Opening with Tetracoordinate Boron", John J. Eisch, Babak Shafii, and Arnold L. Rheingold, Organometallic, 1989 (in preparation).

"The Photochemical Synthesis of the Sodium Diphenylborate(I)Tris(1,2-dimethoxyethane) Complex", John J. Eisch, Marek P. Boleslawski, and Arnold L. Rheingold, J. Am. Chem. Soc., 1989 (in preparation).

Synthesis of Borirenes via the Photochemical Rearrangement of Ethynylboranes, Babak Shafii, Doctoral Dissertation, State University of New York at Binghamton, pp. 170 (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research project pursued, as its primary goal, the synthesis and structural characterization of cyclic arrays of $sp^2$-hybridized carbon and boron atoms that are of interest in the design of novel high-energy fuels. A secondary objective, to which only limited effort could be committed, has been the preparation of monometallic or bimetallic oxide precursors to novel ceramic materials, especially those involving boron or aluminum.

The following summarizes our accomplishments with cyclic, unsaturated organoboranes as potential high-energy fuels:

1) Through studies of cyclic boranes of the boracyclopropene, boracyclopentadiene and boracycloheptatriene types, it has been shown that cyclic pi-electron delocalization between carbon and boron can profoundly influence the stabilization or energy content of the molecule;

2) Crystalline triarylboracyclopropenes (borirenes) have been synthesized for the first time by a novel photorearrangement of alkynylboranes;

3) X-ray crystallographic analysis of such borirenes has demonstrated, unequivocally, the aromatic stabilization of the ring by pi-electron delocalization;

4) Tricoordinate boron is essential for the aromaticity of borirene, for when the boron is made tetracoordinate, the ring is immediately ruptured;

5) Pentaarylboracyclopentadienes (boroles) have been synthesized for the first time and their high chemical reactivity reveal that delocalization in this system leads not to aromatic stabilization, but to antiaromatic reactivity;

6) The 7-borabicyclo[2.2.1]heptadiene system has been synthesized and structurally characterized for the first time; its chemical and spectral properties reveal the operation of homoaromatic stabilization;

7) A rich array of facile, skeletal rearrangements, commenting with boroles and proceeding via borepins ultimately to 1-boratetrahydronaphthalenes, has been discovered; these rearrangements point to the high energy content of such boron compounds;

8) The borepin nucleus or the heptaarylboracycloheptatriene system has been synthesized and been shown to possess aromatic stabilization, even though it is eventually transformed by skeletal rearrangement into another boracarbocycle;

9) Subvalent boron compounds in the form of sodium diphenylborate(I) systems have been generated as potential carbene precursors from the photochemical rearrangement of sodium tetraphenylborate, and an erroneous report by Wilkey and Schuster has been repudiated;

10) Promising results on the coupling of $R_2BX$ to $R_2B\text{-}BR_2$ (diboranes(4)) have been obtained recently; this augurs well for our efforts to prepare subvalent boron intermediates, either boron(II) or Borate(I) anions, by thermal processes.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: Polycondensation Reactions of Electrophilic Benzoquinones

PRINCIPAL INVESTIGATOR: H.K. Hall, Jr.
Department of Chemistry
University of Arizona
Tucson, AZ 87521

INCLUSIVE DATES: 1 January 1988 - 30 June 1988

GRANT/CONTRACT NUMBER: AFOSR-87-0104

COSTS AND FY SOURCE: $15,000 FY88

JUNIOR RESEARCH PERSONNEL: Masayuki Tomida

PUBLICATIONS:

"Examination of Donor-Acceptor Interactions in Pyrazine Polyimides," M. Tomida and H.K. Hall, Jr., J. Polym. Sci., (submitted).

"Three New Electrophilic Quinones," M. Tomida and H.K. Hall, Jr., J. Chem. Res., (submitted).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to synthesize polymers containing extremely electrophilic units in the backbone. The final aim is to synthesize novel conducting polymers.

(1) The synthesis of pyrazinetetracarboxylic dianhydride was improved and this monomer was used in polycondensation polymerization with various aromatic diamines. The intermediate polyamic acids had inherent viscosities in the 0.45-0.60 dl/g range and were film-forming. The films were then imidized by chemical or thermal methods. Model studies show the moderate electrophilic character of these pyrazine units in the polyimide polymer chain.

(2) Three novel electrophilic quinones were synthesized. Starting from dimethyl 2,5-dichloro-1,4-benzoquinone-3.6-dicarboxylate, the following were synthesized: dimethyl 2,5-dichloro-1,4-benzoquinone-3,6-dicarboxylate, dimethyl 2,5-difluoro-1,4-benzoquinone-3,6-dicarboxylate and dimethyl 2,5-dicyano-1,4-benzoquinone-3,6-dicarboxylate. Cyclic voltammetry showed the latter one to be the most electrophilic. Attempts to incorporate these electrophilic benzoquinones in polymers were unsuccessful. The literature procedure for the synthesis of benzoquinonetetracarboxylic acid dianhydride could not be improved.

AFOSR Program Manager: Dr Anthony J. Matuszko

## COMPLETED PROJECT SUMMARY

TITLE: Polysilylated Unsaturated Molecules

PRINCIPAL INVESTIGATOR: Paul R. Jones
Department of Chemistry
University of North Texas
Denton, TX 76203-5068

INCLUSIVE DATES: 1 September 1983 - 29 February 1988

GRANT/CONTRACT NUMBER: AFOSR-83-0244

COSTS AND FY SOURCE: $46,151, FY83; $50,116, FY84; $61,090, FY85; $93,435, FY86

SENIOR RESEARCH PERSONNEL:
Daniel L. Mattern
Seik Weng Ng
P.C. Jones
Yukiko Iwata

JUNIOR RESEARCH PERSONNEL:
James M. Rozell
Shin-nien Uang
Charles W. Knight
Kyo Dong Jo
Todd R. Smith
Alan S. Goeringer
Gary B. Ward
Todd E. Albanesi
Chung-jeng Lai

PUBLICATIONS:

"Silenes and Silenoids, 9. The Synthesis of Polyfunctional Bis(group 14)-substituted Cyclopentadienes via a Novel Cleavage Reaction of Silicon-Carbon Bonds by Chloride Ion," J.M. Rozell, Jr. and P.R. Jones, Organometallics 4, 2206-2210 (1985).

"The Synthesis and Reactivity of Polysilylacetylenes: Diels Alder Reactions to Give Bis(silyl)benzenes," P.R. Jones, T.E. Albanesi, R.D. Gillespie, P. C. Jones, S.W. Ng, Appl Organomet. Chem., 1, 521-528 (1987).

"Polysilypolyynes, 2. Intramolecular Dimerization of a Cyclic Siloxyydiyne to Give a Novel Trimethylenemethane Complex," P.R. Jones, T.E. Albanesi, A.H. Cowley, and C. Nunn, Organometallics, (submitted).

"Polysilyllated Unsaturated Molecules. An Unusual Iodine Promoted Isomerization of Aryl Silanes," P.R. Jones, P.C. Jones, and R.D. Gillespie, J. Organomet. Chem., (in preparation).

"The Catalytic Conversion of Bis(dimethylsilyl)acetylene to Bis(methoxydimethylsilyl)acetylene," P.R. Jones, T.E. Albanesi, P.C. Jones, and R.D. Gillespie, J. Organomet. Chem., (in preparation).

"Polysilypolyynes 3. Unusual Condensation Reactions of Bis(silyl)acetylenes; A Convenient Synthesis of Cyclic Siloxyalkynes," P.R. Jones, P.R.; Albanesi, T.E.; Smith, T.R.; J. Organomet. Chem., (in preparation).

Polysilypolyynes 4. Thermal and Chemical Redistribution Reactions of Diethynyl sailanes", P.R. Jones, P.C. Jones, G.B. Ward, and K. D. Jo, Organometallics (in preparation).

"Polysilylpolyynes 4. Reaction of Alkyllithium Reagents with Bis(trimethyl-silylethynyl)dimethylsilane: An Unusual Methy Substitution Reaction," P.R. Jones, and K.D. Jo, Organometallics. (in preparation).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A series of functionalized disilyl-substituted acetylenes, cyclic and linear polysilylpolyacetylenes and cyclic polysiloxypolyacetylenes were synthesized and characterized. The disilylacetylanes reacted with a-pyrone to give silico-functional disilylated benzenes which were isomerized to their thermodynamically most stable meta isomers using molecular iodine as the catalyst.

The studies on the oligomeric polysilylpolyacetylenes and the polysiloxypolyacetylenes included:

1. The determination of their spectral and non-linear optical properties,
2. Thermal and photochemical polymerization,
3. Reactions catalyzed by and formation of complexes with transition metal carbonyls,
4. Studies of nucleophilic cleavage reactions aimed at determining suitable reagents and conditions for potential ring-opening polymerization reactions,
5. Preliminary studies of metal catalyzed dehydrocondensation reactions.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: Synthesis of New Polynitropolyhedranes

PRINCIPAL INVESTIGATOR: Alan P. Marchand
Department of Chemistry
University of North Texas
NT Station, Box 5068
Denton, TX 76203-5068

INCLUSIVE DATES: 1 April 1984 - 31 March 1988

CONTRACT/GRANT NUMBER: AFOSR-84-0085

COSTS AND FY SOURCE: \$40,000 FY 84; \$40,000 FY 85; \$40,000 FY 86; \$40,000 FY 87

SENIOR RESEARCH PERSONNEL:
Sanjay Basak
Paritosh R. Dave
Ben-min Gong
G. Madhusudhan Reddy
D. Slvakumar Reddy
Vuligonda Vidyasagar
Balan Chenera
Mahendra N. Deshpande
D. Rajapaksa
S. Pulla Reddy
G. V. Madhava Sharma

JUNIOR RESEARCH PERSONNEL:
Monique Davenport
Dalian Zhao
William D. LaRoe

PUBLICATIONS:

"Heptacyclo[$5.5.1.1^{4,10}.0^{2,6}.0^{3,11}.0^{5,9}.0^{8,12}$]tetradecane-13,14-dione: A Novel, Polycyclic Perpendobiplanar $D_{2d}$ Diketone", A. P. Marchand and A. D. Earlywine, *J. Org. Chem.*, *49*, 1660 (1984).

"Synthesis of 3,5,5-Trinitropentacyclo[$5.3.0.0^{2,6}.0^{3,10}.0^{4,8}$]-decane", A. P. Marchand and S. C. Suri, *J. Org. Chem.*, *49*, 2041 (1984).

"On the Stereochemistry of the Reaction of 7-Substituted Norbornadienes with Iron Carbonyls. II. Reaction of Iron Pentacarbonyl with 7-Phenyl-and 7-*ortho*-Anisylnorbornadiene", A. P. Marchand, D. B. Goodin, M. B. Hossain, and D. van der Helm, *J. Org. Chem.*, *49*, 2897 (1984).

"Studies on the Flash Vacuum Pyrolysis and Anomalous Course of Alkali Metal Promoted Reductions of 8-Methylenepentacyclo[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]-undecan-11-one", G. Mehta, K. S. Rao, A. P. Marchand, and R. Kaya, *J. Org. Chem.*, *49*, 3848 (1984).

"Synthesis of 5,5,9,9-Tetranitropentacyclo[$5.3.0.0^{2,6}.0^{3,10}.0^{4,8}$]-decane", A. P. Marchand and D. S. Reddy, *J. Org. Chem.*, *49*, 4078 (1984).

"Heptacyclo[$5.5.1.1^{4,10}.0^{2,6}.0^{3,11}.0^{5,9}.0^{8,12}$]tetradecane-13,14-bis(spiro-1′-cyclopentane): A New $C_{22}H_{28}$ Nonacyclic Cage Hydro-carbon. Improved Synthesis of Bicyclo[2.2.1]hepta-2,5-diene-7-spiro-1′-cyclopentane", A. P. Marchand and A.-h. Wu, *J. Org. Chem.*, *50*, 396 (1985).

"Base-Promoted Rearrangement of Cage *Alpha*-Haloketones. 3. 3,6-Dibromotetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undecane-2,7-dione", A. P. Marchand and D. S. Reddy, *J. Org. Chem.*, *50*, 724 (1985).

"3,5,5-Trinitropentacyclo[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]decane, $C_{10}H_9(NO_3)_2$", H. L. Ammon, C. S. Choi, O. Sandus, A. P. Marchand, and S. C. Suri, *Acta Crystallogr., Section C*, *41C*, 404 (1985).

"5,5,9,9-Tetranitropentacyclo[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]decane", C. George, R. Gilardi, J. L. Flippen-Anderson, C. S. Choi, A. P. Marchand, and D. S. Reddy, *Acta Crystallogr., Section C*, *41C*, 788 (1985).

"The Molecular Geometry of a Heptacyclotetradecane from Gas-Phase Electron Diffraction", I. Hargittai, J. Brunvoll, S. J. Cyvin, and A. P. Marchand, *J. Mol. Struct.*, *149*, 219 (1986).

"Formation of Solfonium Tetrafluoroborates from Reactions of $\gamma$,$\delta$-Unsaturated Ketones with Thiols in the Presence of Boron Trifluoride Etherate", A. P. Marchand, R. Kaya, S. W. Muchmore, and D. van der Helm, *J. Org. Chem.*, *51*, 825 (1986).

"Facile Stereoselective Recuctions of Enediones and Cage Diketones Using $NaBH_4$-$CeCl_3$", A. P. Marchand, W. D. LaRoe, G. V. M. Sharma, S. C. Suri, and D. S. Reddy, *J. Org. Chem.*, *51*, 1622 (1986).

"Synthesis of New Substituted Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5.9}$]undecanes: A Novel Synthesis of Hexacyclo[6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]dodecane (1,3-Bishomopentaprismane)", A. P. Marchand and A.-h. Wu, *J. Org. Chem.*, *51*, 1897 (1986).

"Synthesis of the Two Epimeric 2-Carbonethoxy-3,7-dimethyl-endo-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-5-ones. Unequivocal Structural Assignment of the 5 - and 5 -Isomers via 2D NMR Spectroscopy", W. B. Smith, A. P. Marchand, S. C. Suri, and P.-w. Jin, *J. Org. Chem.*, *51* 3052 (1986).

"Stereochemistry of the Reaction of 7-Substituted Norbornadienes with Iron Carbonyls. 3. Reaction of $Fe(CO)_5$ with 7-(Benzoyloxy)norbornadiene", A. P. Marchand, A. D. Earlywine and M. J. Heeg, *J. Org. Chem.*, *51*, 4096 (1986).

"3-(*p*-Cyanophenoxy)quadricyclane", W. H. Watson, I. Tavanaiepour, A. P. Marchand, and P. R. Dave, *Acta Crystallogr., Section C*, *C43*, 1356 (1987).

"A New Preparation of Ketenes for Intramolecular Cycloadditions", W. T. Brady, A. P. Marchand, Y. F. Giang, and A.-h. Wu, *Synthesis*, 395 (1987).

"Intramolecular [2 + 2] Cycloadditions of ketenes to Carbonyl Groups. A Novel Synthesis of Substituted Benzofurans", W. T. Brady, Y.-s. F. Giang, A. P. Marchand, and A.-h. Wu, *J. Org. Chem.*, *52*, 3457 (1987).

"Lewis Acid-Promoted Reaction of Pentacyclo[5.4.0.,$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione: A Synthetic Entry into the Pentacyclo-[6.5.0.$0^{4,12}$.$0^{5,10}$.$0^{9,13}$]tridecane Ring Systems", A. P. Marchand, B. E. Arney, Jr., R. Gilardi, and J. L. Flippen-Anderson, *J. Org. Chem.*, *52*, 3455 (1987).

"A Novel Rearrangement in the 1,3-Bishomocubyl Ring System", A. P. Marchand, P.-w. Jim, J. L. Flippen-Anderson, R. Gilardi, and C. George, J. Chem. Soc., Chem. Commun., 1108 (1987).

"3-(p-Cyanophenoxy)quadricyclane and a Redetermination of the Structure of a Hexachloroquadricyclane Dicarboxylate", W. H. Watson, I. Tavanaiepour, A. P. Marchand, and P. R. Dave, Acta Crystallogr., Section C, C43, 1356 (1987).

"Structure of a Novel $C_{11}H_{13}N_2O_3$ Cage Molecule. N-hydroxy-3-nitro-4-azahexacyclo$[5.4.1.0^{2,6}.0^{3,19}.0^{5,9}.0^{8,11}]$-dodecane", W. H. Watson, A. P. Marchand, and P. R. Dave, Acta Crystallogr., Section C, C43, 1569 (1987).

"1,6-Dimethyl-1$\alpha$,4$\alpha$,4a$\alpha$,5$\alpha$,8$\beta$,8a$\alpha$-hexaydro-1,4-methanonaphthalene-5,8-diol, $C_{13}H_{18}O_2$", J. L. Flippen-Anderson, R. Gilardi, C. George, A. P. Marchand, and P.-w. Jin, Acta Crystallogr., Section C, C43, 2151 (1987).

"Syn-8,Syn-13-Bis(benzoyloxy)heptacyclo$[7.6.0.0^{2,7}.0^{4,14}.0^{5,12}.0^{6,10}.0^{11,15}]$Pentadecan-3-one, $C_{29}H_{24}O_5$", J. L. Flippen-Anderson, R. Gilardi, C. George, A. P. Marchand, and A. D. Earlywine, Acta Crystallogr., Section C, C43, 2364 (1987).

"Synthesis of Nitro-Substituted 2,3,4,8-Tetraphenylpentacyclo$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$decanes", A. P. Marchand, G. S. Annapurna, V. Vidyasagar, J. L. Flippen-Anderson, R. Gilardi, C. George and H. L. Annon, J. Org. Chem., 52, 4781 (1987).

"Synthesis of Pentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane-4,8,11-trione, Pentacyclo$[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane-4,7,11-trione ($D_3$-Trishomocubanetrione) and 4,4,7,7,11,11-Hexanitropentacyclo-$[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane ($D_3$-Hexanitrotrishomocubane)", A. P. Marchand, G. V. M. Sharma, G. S. Annapurna, and P. R. Pednekar, J. Org. Chem., 52, 4784 (1987).

"Photoelectron Spectra and Electronic Structures of Substituted Pentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecanes", A. P. Marchand, C. Huang, R. Kaya, A. D. Baker, E. D. Jemmis, and D. A. Dixon, J. Am. Chem. Soc., 109, 7095 (1987).

"Synthesis of 8,8,11,11-Tetranitropentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$-undecane", A. P. Marchand, B. E. Arney, Jr., and P. R. Dave, J. Org. Chem., 53, 443 (1988).

"Synthesis and Chemistry of Novel Polynitropolycyclic Cage Molecules", A. P. Marchand, Tetrahedron 44, 2377 (1988).

"Reductive Amination of Pentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$Undecane-8,11-Dione", A. P. Marchand, P. R. Dave, N. Satyanarayana and B. E. Arney, Jr., J. Org. Chem., 53, 1088 (1988).

"Structure of a Bis( $^{4}$-exocyclic-1,3-diene)Fe(CO)$_3$ Complex", W. H. Watson, A. Nagl, A. P. Marchand, and B. Chenera, Acta Crystallogr., Section C, C44, 806 (1988).

"A Dimer Ketone Formed via $Fe(CO)_5$-Promoted Coupling of 7-Phenoxynorbornadiene to Carbon Monoxide", W. H. Watson, A. P. Marchand, and P. R. Dave, Acta Crystallogr., Section C, C44, 940 (1988).

"Synthesis of Substituted Cyclopentenones via Boron Trifluoride Mediated [4 + 2] Cycloreversion Reactions", A. P. Marchand and V. Vidyasagar, J. Org. Chem., 53, 4412 (1988).

"Transannular Cyclizations in the Pentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$-undecane-8,11-dione System: A Reinvestigation", A. P. Marchand, B. E. Arney, Jr., P. R. Dave, N. Satyanarayana, W. H. Watson, and A. Nagl, J. Org. Chem., 53, 2644 (1988).

"Structural Assignment of a Methylcyclopentadiene-Toluquinone Diels-Alder Cycloadduct. Analysis of the 2D-NMR Spectrum of 1,6-Dimethyl-1 ,4 ,4a ,5 ,- 8 ,8a -hexahydro-1,4-methano- naphthalene-5,8-diol", G. S. Linz, A. S. Zektzer, G. E. Martin, A. P. Marchand, and P.-W. Jin, J. Org. Chem., 53, 2647 (1988).

"Structure of a Novel $C_{22}H_{24}$ Cage Dimer", J. L. Flippen-Anderson, R. Gilardi, C. George, A. P. Marchand, P.-w. Jin, and M. N. Deshpande, Acta Crystallogr., Section C, (in press).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The synthesis and chemistry of novel polynitropolycyclic "cage" systems has been pursued in systematic fashion. Our approach involves the introduction of increasing numbers of nitro substituents into a given cage system by employing a logical progression of increasingly functionalized synthetic intermediates. Thus, the cumulative effects of increasing substitution (particularly nitro-group substitution) upon product stability and upon the relative ease of product-forming reactions can be gauged in a gradual and orderly fashion. Importantly, this approach represents entirely new synthetic methodology for incorporating large numbers of nitro-groups into novel, strained systems.

The following new polynitropolycyclic compounds have been synthesized in the course of these studies:

(i) 6,6,8-Trinitropentacyclo$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$decane (1. a trinitro-1,3-bishomohomocubane)

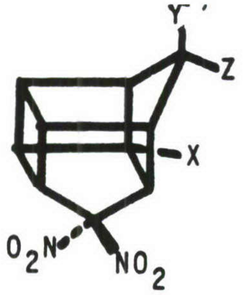
(ii) 6,6,10,10-Tetranitropentacyclo$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$decane (2. a tetranitro-1,3-bishomocubane)

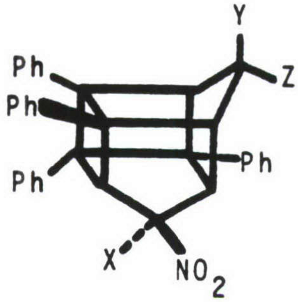
(iii)A series of nitro-substituted 2,3,4,8-tetraphenylpentacyclo-$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$decanes containing two, three, and four $NO_2$ groups, respectively (3a-c)

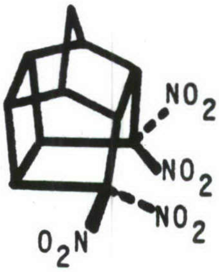
(iv) 8,8,11,11-Tetranitropentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane (4, a tetranitropentacycloundecane)

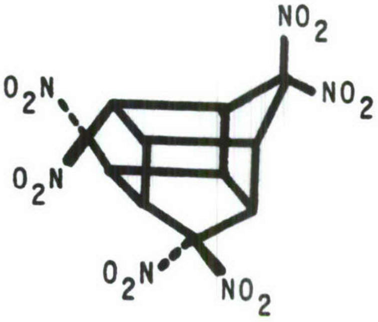
(v) 4,4,7,7,11,11-Hexanitropentacyclo$[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane (5, $D_3$-hexanitrotrishomocubane).

The structures of compounds 1, 2, 3a, 3b, 4, and 5 each have been obtained by single crystal X-ray structural analysis. The thermal behavior and detonation properties of $D_3$-hexanitrotrishomocubane (5) have been studied.









1 ($X = NO_2$, $Y = Z = H$)

2 ($X = H$, $Y = Z = NO_2$)

3a ($X - Y - H$, $Z = NO_2$)

3b ($X = Z = NO_2$, $Y = H$)

3c ($X = Y = Z = NO_2$)

4

5

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: Polyazidoesters as Energetic Polymers and Copolymer Components With Fluoro Derivatives

PRINCIPAL INVESTIGATOR:
Robert M. Moriarty
Department of Chemistry
University of Illinois at Chicago
P.O. Box 4348
Chicago, IL 60680

INCLUSIVE DATES: 1 November 1984 - 31 November 1987

GRANT/CONTRACT NUMBER: AFOSR-85-0024

COSTS AND FY SOURCE $100,000 FY85; $105,000 FY86; $110,000 FY87

| | | |
|---|---|---|
| SENIOR RESEARCH PERSONNEL: | Jaffar Khosrowshahi | Indra Prakash |
| JUNIOR RESEARCH PERSONNEL: | George Kovacevic<br>Michael Duncan | A. Didamenico<br>Tomasz Dalecki |

PUBLICATIONS

"A Versatile Synthesis of Vicinal Diazides Using Hypervalent Iodine", Robertson, Robert M. Moriarty and Jaffar S. Khosrowshahi, Tetrahedron Letters, 27, 2809 (1986).

"Reaction of $\Delta^{5,6}$ Steroids with PhiO/$NaN_3$/$CH_3COOH$, Synthesis of 7 α-Azidosteroids", Robert M. Moriarty, Jaffar S. Khosrowshahi, Synthetic Communications, 17(1), 89-94 (1987).

"P-Azidophenyl Substituted Polyester", Robert M. Moriarty, J.S. Khosrowshahi and G. Kovacevic, 20th Midwest Regional Meeting of the American Chemical Society, SIU Carbondale, November 7, 1985.

"Reactions of $\Delta^{5,6}$ Steroids with PhiO/$NaN_3$/$CH_3COOH$", Robert M. Moriarty and Jaffar S. Khosrowshahi, 20th Midwest Regional Meeting of the American Chemical Society, SIU, Carbondale, November 7, 1985.

"Hypervalent Iodine Oxidation of Alkenes. A Simple Route to Vicinal Diazides and α-Azidoketones", Robert M. Moriarty and J.S. Khosrowshahi, National Meeting of the American Chemical Society, New York City, (1986).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

1. The synthesis of a polyazidopolyester.
2. Synthesize a fluoroazidopolyester
3. Synthesize vicinal and germinal diazides
4. Synthesis a diazoketene.
5. Investigate copolymerization of certain of the above.
6. Synthesize high energy strained polycyclic polyesters.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: The Chemistry of Precursors to Silicon-Carbide

PRINCIPAL INVESTIGATORS:

Morey A. Ring
H. Edward O'Neal
Department of Chemistry
San Diego State University
San Diego, CA 92182

INCLUSIVE DATES: 1 August 1983 - 31 December 1987

GRANT/CONTRACT NUMBER: AFOSR-83-0209

COSTS AND FY SOURCE: $40,000 FY83; $50,000 FY84; $35,055, FY85; $44,945 FY86

JUNIOR RESEARCH PERSONNEL:

Ramon L. Espino-Rios
Barbara A. Sawrey
Jim W. Erwin
Jack G. Martin
Karen A. Nares
Ann P. Dickinson
Rich T. White
Steven A. Rickborn
Dennis S. Rogers
Kathy L. Walker
Mike Harris

PUBLICATIONS:

B.A. Sawrey, H.E. O'Neal, M.A. Ring and D. Coffey, Jr. Int. J. Chem. Kinet., 16, 801 (1984).

S.F. Rickborn, M.A.Ring and H.E. O'Neal, Int. J. Chem. Kinet., 16, 1372 (1984).

R.T. White, R.L. Espino-Rios, D.S. Rogers, M.A. Ring and H.E. O'Neal, Int. J. Chem. Kinet., 17, 1029 (1985).

J.W. Erwin, M.A. Ring and H.E. O'Neal, Int. J. Chem. Kinet., 17, 1067 (1985).

S.F. Rickborn, D.S. Rogers, M.A. Ring and H.E. O'Neal, J. Phys. Chem., 90, 408 (1986).

D.S. Rogers, M.A. Ring and H.E. O'Neal, Organometallics, 5, 1521 (1986).

B.A. Sawrey, H.E. O'Neal and M.A. Ring, Organometallics, 6, 720 (1987).

J.G. Martin, M.A. Ring and H.E. O'Neal, Organometallics, 5, 1228 (1986).

D.S. Rogers, H.E. O'Neal and M.A. Ring, Organometallics, 5, 1467 (1986).

D.S. Rogers, K.L. Waler, M.A. Ring and H.E. O'Neal, Organometallics, 6, 2313 (1987).

A.P. Dickenson, K.E. Nares, M.A. Ring and H.E. O'Neal, Organometallics, 6, 2596 (1987).

H.E. O'Neal and M.A. Ring, Organometallics, 7, April (1988).

K.A. Nares, M.A. Ring, H.E. O'Neal, (in preparation).

K.A. Nares, M.A. Ring, H.E. O'Neal, (to be published).

M. Marris, H.E. O'Neal and M.A. Ring, (to be published).

H.E. O'Neal and M.A. Ring, (in preparation).

G. Licciardi, H.E. O'Neal and M.A. Ring, (to be published).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The research can be divided into 4 main areas

1. Mechanisms and Kinetics of the Decompositions of Silane and Organosubstituted Monosilanes, and of Disilanes.

2. Relative Rate Kinetics of the Trapping Reactions of $SiH_2$ with Ethylene, Acetylene, Butadiene, Methanol, Silane and 1-butene.

3. Mechanisms and Kinetics of Iosmerizations and Decompositions of Organosilylenes.

4. From the above studies, we were able to propose a general reaction mechanism for carbosilane production from the decomposition dimethylsilane.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: Organosilicon Compounds and Polymers and Silicon Ceramics

PRINCIPAL INVESTIGATOR:

Dietmar Seyferth
Department of Chemistry, Room 4-382
Massachusetts Institute of Technology
Cambridge, MA 02139

INCLUSIVE DATES: 1 October 1985 - 31 October 1988

CONTRACT/GRANT NUMBER: AFOSR-85-0265

SENIOR RESEARCH PERSONNEL:

H. Lang
M. J. Michalczyk
T. S. Targos
W. Bernhardt
J. Borm
G. Koppetsch
B. Neumuller

JUNIOR RESEARCH PERSONNEL:

C. A. Sobon
J. L. Robinson
H. J. Tracy
R. C. Hui

PUBLICATIONS:

"The Preparation of Silicon-Containing Ceramics via Polymeric Organosilicon Precursors", D. Seyferth. L'actualite chimique, 71, (March) (1986).

"Organosilicon Polymers as Precursors for Silicon-Containing Ceramics: Recent Developments", D. Seyferth, G. H. Wiseman, C. A. Poutasse, J. M. Schwark, and Y.-F. Yu. Polymer Preprints, 28, 389 (1987).

"Polycarbosilanes: An Overview", D. Seyferth, Chapter in "Inorganic and Organometallic Polymers"(ACS Symposium Series 260), M. Zaddin, K. J. Wynne, and H. R. Allcock, editors, American Chemical Society, Washington, D.C., (1988).

"A Novel Polymeric Organosilazene Precursor to $Si_3N_4$/SiC Ceramics", D. Seyferth, and G. H. Wiseman. In "Science of Ceramic Chemical Processing", L. L. Hench, and D. R. Ulrich, editors, Wiley, New York, Chapter 38, pp. 354-362 (1986).

"The Preceramic Polymer Route to Silicon-Containing Ceramics", D. Seyferth, and Y.-F. Yu. In "Desighn of New Materials", D. L. Cocke, and A. Clearfield, editors, Plenum Press, New York, pp. 79-94 (1987).

"Methyldichlorosilane in the Service of Materials Science", D. Seyferth. In "Ultrastructure Processing of Advanced Ceramics", J. D. Mackenzie, and D. R. Ulrich, editors, Wiley, New York, pp. 33-39 (1988).

"Organosilicon Polymers as Precursors for Silicon-Containing Ceramics. Recent Developments", D. Seyferth, G. H. Wiseman, J. M. Schwark, Y.-F. YU, and C. A. Poutasse. In "Inorganic and Organometallic Polymers" (ACS Symposium Series 360), M. Zeldin, K. J. Wynne, and H. R. Allcock, editors, American Chemical Society, Washington, D.C., pp. 143-155 (1988).

"Applications of Methyldichlorosilane in Preparation of Silicon-Containing Ceramics", D. Seyferth, G. H. Wiseman, Y.-F. Yu, T. S. Targos, C. A. Sobon, T. G. Wood, and G. A. Koppetsch. In "Silicon Chemistry", J. Y. Corey, and P. P. Gaspar, editors, Ellis Horwood, Chichester, pp. 415-424 (1988).

"Organosilicon Polymers as Precursors for Silicon-Containing Ceramics", D. Seyferth. In "Transformation of Organometallics Into Common and Exotic Materials: Design and Activation", (NATO ASI Series E. Applied Sciences, No. 141), R. M. Laine, editor, Martinus Nijhoff Publishers, Dordrecht, pp. 133-154 (1988).

ABSTRACT AND OBJECTIVES AND ACCOMPLISHMENTS

a. The n-BuLi/Me$_3$COK reagent metalates every fourth CH$_2$ group of $[(CH_3)_2SiCh_2)_n$. The metalated polymer was converted to vinyl-containing polycarbosilanes whose reaction with $[(CH_3SiH)_x(CH_3Si)_y]_n$ gave useful preceramic polymers.

b. Cross-linkable $[CH_3(H)SiCH_2]_n$ has been prepared using $[CH_3(Ph)SiCH_2]_n$ as starting material.

c. The reactions of $[(CH_3SiH)_x(CH_3Si)_y]_n$ with Cp$_2$MMe$_2$ (M= Ti, Zr, Hf) gave precursors for SiC/MC blends.

d. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane can be metalated with t-BuLi/TMEDA.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: The Reactivity of Transition Metal-Silicon Compounds

PRINCIPAL INVESTIGATOR:
T. Don Tilley
Chemistry Department, D-006
University of California, San Diego
La Jolla, CA 92093

INCLUSIVE DATES: 1 June 1985 - 31 May 1988

GRANT NUMBER: AFOSR-85-0228

COST AND FY SOURCE: \$100,663 FY85; \$93,128 FY86; \$99,153 FY87

SENIOR RESEARCH PERSONNEL:
Dean M. Roddick
Daniel A. Straus

JUNIOR RESEARCH PERSONNEL:
John Arnold
Brian K. Campion
Frederick H. Elsner
Richard H. Heyn
David N. Shina
Jonathan Falk
Hee-Gwoen Woo
Mary P. Engeler

PUBLICATIONS:

"Ether Cleavage Following Insertion of Carbon Monoxide Into the Tantalum-Silicon Bond of $(n^5\text{-}C_5Me_5)Ta(SiM,e_3)Cl_3$", J. Arnold and T.D. Tilley, J. Am. Chem. Soc., 107, 6409 (1985).

"Tetrahedral Lewis Base Adducts of an Acyl. Preparation and X-ray Structure of the Pyridine Adduct $(n_5\text{-}C_5Me_5)Cl_3Ta(n^2\text{-}OC(SiMe_3)(Nc_5H_5)$", J. Arnold, T.D. Tilley and AlL. Rheingold, J. Am. Chem. Soc., 108, 5355 (1986).

"Preparation and Reaction Chemistry of Trimethylsilyl Derivatives of Tantalum. X-ray Structures of $d^o$ $(n_5\text{-}C_5Me_5)Ta(SiMe_3)Cl_3$ and $d^1(n^5\text{-}C_5Me_5)Ta(SiMe_3)Cl_2$", J. Arnold D.N. Shina, T.D. Tilley and A.M. Arif, Organometallics, 5, 2037 (1986).

"Coordinatively Unsaturated Tris(trimethylsilyl)silyl Complexes of Chromium, Manganese and Iron", D.M. Roddick T.D. Tilley, A.L. Rheingold and S.J. Geib, J. Am. Chem. Soc., 109, 945 (1987).

"Preparation and Reaction Chemistry of Trimethylsilyl Derivatives of Niobium. Redox Chemistry of $(n^5\text{-}C_5H_5)_2Nb(SiMe_3)Cl$ and X-ray Structures of $(n_5\text{-}C_5H_5)_2Nb(SiMe_3)(N^2\text{-}C_2H_4)$ and $(N^5\text{-}C_5H_5)_2Nb(CH_2SiMe_3)Cl)PF_6$", J. Arnold, T.D. Tilley, Al. Rheingold and S.J. Geib, Organometallics, 6, 473 (1987).

"Reactions of Carbon Monoxide with Trimethylsilyl and Tris(trimethylsilyl)silyl Derivatives of Group 4 Metals. Synthesis, Characterization, and Reactivity of Silaacyl Complexes", B.K. Campion, J. Falk and T.D. Tilley, J. Am. Chem. Soc., 109, 2049 (1987).

"Insertion of Organic Carbonyls Into the Tantalum-Silicon Bond of $(n^5\text{-}C_5Me_5)Cl_3$ $TaSiMe_3$. Preparation and Characterization of the a-Silylakoxides $(n^5\text{-}C_5Me_5)Cl_3TaOCRR$ $SiMe_3$", J. Arnold and T.D. Tilley, J. Am. Chem. Soc., 109, 3318 (1987).

"Formation of the Novel Benzophene Sila-acylhydrazonato Complex $(n_5\text{-}C_5Me_5)Cl_3Ta(OC(SiMe_3)NNCPh_2)$ Following Addition of Diphenyldiazomethane to an $n^2$-Sila-acyl Ligand", J. Arnold, T.D. Tilley, A.L. Rheingold and S.J. Geib, J. Chem. Soc. Chem. Commun., 793 (1987).

"Preparation and Characterization of Tris(trimethylsilyl)silyl Derivatives of Zinc, Cadmium and Mercury. X-ray Crystal Structure of $Zn(Si(SiMe_3)_3)_2$", J. Arnold, T.D. Tilley, A.L. Rheingold and S.J. Geib, Inorg Chem., 26, 2106 (1987).

"An Arbuzov-like Reaction in the Trimethylphosphite-$n^2$-Silaacyl Adduct $(n_5\text{-}C_5Me_5)Cl_3Ta(n^2\text{-}OC(SiMe_3)(P(OMe)_3)$", J. Arnold T.D. Tilley, A.L. Rheingold and S.J. Geib, Inorg Chem., 26, 2556 (1987).

"Preparation, Characterization and X-ray Crystal Structure of an Acetonitrile-Complexed Ruthenium Silylene", D.A. Straus, T.D. Tilley, Al. Rheingold and S.J. Geib, J. Am. Chem. Soc., 109, 5372 (1987).

"Preparation of the First Stable Formylsilane, $(Me_3Si)_3SiCHO$, From a Zirconium $n^2$-Silaacyl Complex", F.H. Elsner, H-G Woo and T.D. Tilley, J. Am. Chem Soc., 110, 313 (1988).

"Dimesitylsilyl Derivatives of Zirconium", D.M. Roddick, R.H. Heyn and T.D. Tilley, Organometallics, (in press).

"Reaction of an Early Transition-Metal $n_2$-Silaacyl Complex With Pyridine. Diastereoselectivity in the Formation of a (2-Pyridyl)(silyl)methoxy Ligand", J. Arnold, H-G Woo, T.D. Tilley, A.L. Rheingold and S.J. Geib, Organometallics, (in press).

"Carbonylation Chemistry of the Tantalum Silyl $(n^5\text{-}C_5Me_5)Cl_3TaSiMe_3$. Synthesis, Characterization, and Reaction Chemistry of $(n_5\text{-}C_5Me_5)Cl_3Ta(n^5\text{-}COSiMe_3)$ and Derivatives", J. Arnold, T.D. Tilley, A.L. Rheingold, S.J. Geib and A.M. Arif, J. Am Chem. Soc., (in press).

"Reactions of $(n^5\text{-}C_5H_5)(n^5\text{-}C_5Me_5)Zr(Si(SeMe_3)_3)X(X = Cl, Me)$ Complexes With Carbon Monoxide and the Isocyanide $2,6\text{-}Me_2C_6H_3NC$. Crystal Structure of $(n_5\text{-}C_5H_5)(n^5\text{-}C_5Me_5)$ $Zr(n^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)(Si)\ SiMe_{33})CL$", F.H. Elsner, T.D. Tilley, A.L. Rheingold and S.J. Geib, J. Organometl. Chem., (in press).

"Preparation and Characterization of Tris(trimethylsilyl)silyl and Tris(trimethylsilyl)germyl Derivatives of Zirconium and Hafnium. X-ray Crystal Structures of $(n_5\text{-}C_5Me_5)Cl_2HfSi(SiMe_3)_3$ and $(n^5\text{-}C_5Me_5)Cl_2HfGe(SeMe_3)_3$", J. Arnold, D.M. Roddick, T.D. Tilley, A.L. Rheingold and S.J. Geib, Inorg Chem., (in press).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this work was to synthesize and study early-transition-metal silyl compounds that have the potential to carry out novel chemical transformations and to serve precursors to solid-state materials containing both silicon and an early-transition-metal. Previously this field was quite undeveloped, therefore we surveyed a number of approaches to the synthesis of these new M-Si bonded species.

In the period of this grant, we discovered several routes to new early-transition-metal silyl complexes. These complexes contain $-SiMe_3$, $-Si(SiMe_3)_3$ and $-SiHMes_2$ (Mes = mesityl) silyl groups. These new complexes, of scandium, zirconium, hafnium, niobium and tantalum, have been characterized by a variety of spectroscopic techniques, including X-ray crystallography. Reactivity studies with these new complexes establish basic reactivity patterns toward a range of reactants. Unusual reactions that were discovered for these M-Si bonds include: (1) reductive elimination of silyl groups with chloride, (2) first observation of CO insertion into a transition-metal-silicon bond, (3) routes to the first stable formylsilane, $(Me_3Si)_3SiCHO$, (4) facile ether cleavage following CO/CO coupling by a tantalum-silicon bond, (5) formation of tetrahedral Lewis base adducts of $M(n^2-COSiR_3)$ silaacyl complexes, (6) insertion of organic carbonyls into a tantalum-silicon bond with nucleophilic silyl group transfer, and (7) facile protochemical and thermal insertions of ethylene into metal-silicon bonds.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: Symposium on Microstructure and Properties of Catalysts

PRINCIPAL INVESTIGATOR: Michael J. M. Treacy
Materials Research Society
9800 McKnight Route, Suite 327
Pittsburgh, PA 15257

INCLUSIVE DATES: 01 September 1987 - 28 February 1988

GRANT/CONTRACT NUMBER: AFOSR-87-0345

COSTS AND FY SOURCE: $2,000 FY87

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The symposium was held in Boston, Massachusetts, November 30 - December 3, 1987, and sponsored by the Materials Research Society. The symposium provided a forum for materials scientists, synthesis chemists, physical chemists, chemical engineers, physicists and theorists, to compare and discuss the latest results which establish clear relationships between structure and catalytic properties.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: Molecular Dynamics of Materials Possessing High Energy Content

PRINCIPAL INVESTIGATOR: Nicolas J. Turro
Department of Chemistry
Columbia University
New York, New York 10027

INCLUSIVE DATES: 1 November 1983 - 31 October 1987

GRANT/CONTRACT NUMBER: AFOSR-84-0040

COSTS AND FY SOURCE: \$97,256 FY83; \$133,612 FY84; \$119,248 FY85; \$97,434 FY86

SENIOR RESEARCH PERSONNEL:
I. Gould
C. Kumar
X. Lei
M. Paczkowski
V. Ramamurthy
J. Fehlner
C. Doubleday
P. Kuo
K. Nitsche
K. Cassidy
K. Welsh

JUNIOR RESEARCH PERSONNEL:
P. Hauptman
D. Hessler
N. Han
J. Wang
Z. Zhang
M. Zimmt
Y.Cha

PUBLICATIONS:

"The Observation of CIDEP From the Photodecomposition of Dibenzyl Ketone in Micellar Solution", N.J. Turro, M.A. Paczkowski, M.B. Zimmt and J.K.S. Wan, Chem. Phys. Letts., 114, 561 (1985).

"Time Resolved Flash Spectroscopic Investigations of the Reactions of Singlet Arylhalocarbenes", I.R. Gould, N.J. Turro, J. Butcher, Jr., C. Doubleday, Jr., N.P. Hacker, G.F. Lahr, R.A. Moss, D.P. Cox, W. Guo, R.C. Munjal, L.A. Perez, and M. Fedorynski, Tetrahedron, 41, 1587 (1985).

"The Role of Intersystem Crossing Steps in Singlet Oxygen Chemistry and Photo-oxidations", N.J. Turro, Telrahedron, 41, 2089 (1985).

"Singlet-Triplet Interconversion of Diphenylmethylene Energetics, Dynamics, and Reactivities of Different Spin States", K.B. Eisenthal, N.J. Turro, E.V. Sitzmann, I.R. Gould, G. Hefferon, J. Langan, and Y. Cha, Tetrahedron, 41, 1543 (1985).

"Dynamics of Radical Pair Reactions in Micelles", I.R. Gould, M.B. Zimmt, N.J. Turro, B.H. Baretz, and G.F. Lehr, J. Am. Chem Soc., 107, 4607 (1985).

"Quenching of Pyrene Fluorescence by Cesium Ions in Micellar Systems. Protection by Surface-Active Crown Ethers", I.R. Gould, P.L. Kuo, and N.J. Turro, J. Phys. Chem., 89, 3030 (1985).

"Ketone Photochemistry on Solid Silica. A Diffuse Reflectance Laser Flash Photolysis Study", N.J. Turro, I.R. Gould, M.B. Zimmt and C.C. Cheng, Chem. Phys. Letts., 119, 484 (1985).

"Carbene and Silicon Routes Toward a Simple Nitrile Ylide, Spectroscopic, Kinetic, and Chemical Characterization", N.J. Turro, Y. Cha, I.R. Gould, A. Padwa, J.R. Gasdaska, M. Tomas, J. Org. Chem., 50, 4415 (1985).

"Nanosecond Flash Photolysis Studies of Intersystem Crossing Rate Constants in Biradicals: Structural Effects Brought About by Spin-Orbit Coupling", M.B. Zimmt, C.E. Doubleday, Jr., I.R. Gould, and N.J. Turro, J. Am. Chem Soc., 107, 6724 (1985).

"Magnetic Field Effect on the Intersystem Crossing Rate Constants of Biradicals Measured by Nanosecond Transient UV Absorption", M.B. Zimmt, C.E. Doubleday, Jr. and N.J. Turro, J. Am. Chem. Soc., 107, 6726 (1985).

"Temperature Dependence of the Reactions of Singlet and Triplet Diphenylcarbene, Evidence for Reversible Ylide Formation in the Reaction with Alcohols", N.J. Turro, Y. Cha and I.R. Gould, Tetrahedron Letts., 5951 (1985).

"Modifications of Chemical Reactivity Via Inclusion Complex Formation: Photochemistry of Dibenzyl Ketones and Benzyl Phenylacetates", J. Org Chem., 51, 460 (1986).

"A Fluorescence Probe Investigation of the Effect of Alkali Metal Ions on the Micellar Properties of a Crown Ether Surfactant", N.J. Turro and P.L. Kuo J. Phys. Chem., 90 837 (1986).

"Photosensitization by Reversible Electron Transfer: Theories, Experimental Evidence, and Examples", Chem. Rev., 86, 401 (1986).

"Modification of Chemical Reactivity by Cyclodextrins: Observation of Moderate Effects on Norrish Type I and Type II Photobehavior", S. Singh, G. Usha, C.-H. Tung, N.J. Turro and V. Ramamurthy, J. Org. Chem., 51, 941 (1986).

"Photons in the Service of Understanding Polymer Systems at the Microscopic Level. The Influence of Restricted Reaction Space and Resricted Diffusion on Photophysical and Photochemical Processes", N.J. Turro, Polymer Preprints, 27, 318 (1986).

"Are Phenylhalocarbenes Ambiphilic?" R.A. Moss, W. Lawrynowicz, L.M. Hadel, N.P. Hacker, N.J. Turro, I.R. Gould and Y. Cha, Tetrahedron Letts., 27, 4125 (1986).

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The major objective of this research has been the design and construction of new instrumentation for the investigation of transient high energy materials and the exploration of how the chemistry of transient high energy materials and the dynamics of these reactive species respond to systematic variations in structure, environments and experimental variables. Particular emphasis has been given to investigations of reactions at interfaces provided by micelles, polymers and porous solids. The major accomplishments of this research has been the discovery of numerous novel effects that result when reactive materials are produced by photochemical methods at interfaces. In particular, magnetic isotope effects for isotope separations, magnetic field effects on chemical reactions, and product control by the geometry of interfaces have been developed.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

TITLE: Powerful Photogenerated Reducing Agents

PRINCIPAL INVESTIGATOR: David Tyler
Department of Chemistry
University of Oregon
Eugene, Oregon 97403

INCLUSIVE DATES: 1 April 1986 - 31 March 1988

GRANT/CONTRACT NUMBER: AFOSR-86-0081

COSTS AND FY SOURCE: $40,000 FY86; $40,000 FY87

SENIOR RESEARCH PERSONNEL: Michael Castellani

JUNIOR RESEARCH PERSONNEL:
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Robin Ritter
N.D. Silavwe
Xiong Pan
Cecelia Philbrin

"Photochemical Generation of Nineteen-Electron Organometallic Complexes and Their Use as Reducing Agents in Micellar Systems", D.R. Tyler, V. MacKenzie, and A.S. Goldman Proceedings of the Seventh International Conference on the Photochemistry and and Photophysics of Coordination Complexes: H. Yersin, and A.Vogler, Eds.; Springer-Verlag: New York, pp 263-266 (1987).

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"Water-Soluble Nineteen-Electron Organometallic Complexes", R. Ritter and D.R. Tyler, J. Am. Chem. Soc., (manuscript in preparation).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An investigation of the reducing abilities of photochemically-generated 19-electron complexes was accomplished. The investigation had four primary objectives: (1) study the capabilities and limitations of the 19-electron complexes as reducing agents; (2) synthesize or produce water-soluble 19-electron complexes; (3) recycle the 19-electron reducing agents so as to make these species catalytic reductants; and (4) use the 19-electron reductants to perform chemically interesting transformations. The first two of these objectives were successfully accomplished, and good progress was made on the last two objectives. The 19-electron complexes are generated by reaction of a photogenerated 17-electron organometallic radical (e.g., $Mn(CO)_5$, $CpFe(CO)_2$, $CpMo(CO)_3$; Cp - $\eta^5$-$C_5H_5$) with a ligand. The dominant reactivity of the 19-electron complexes is electron transfer. Our initial studies established that the oxidation potential of the 19-electron complexes is around 1.5 V vs. SCE, depending on the metal and ligand. Substrates that were reduced in non-aqueous solvents including methylviologen, butylviologen, ferricyanide, $Mn_2(CO)_{10}$, cobaltocenium, and butyl pyridinium. In order to reduce substrates with reduction potentials more negative than -1.5 V vs. SCE, we developed a technique for photochemically generating the $W(CO)_5PMe_2Ph^-$ complex ($E < -2.0V$). Using this reductant, we demonstrated the reduction of substrates such as $CO_2$ and acetophenone. The reduction of water-soluble substrates was accomplished by two methods. The first, but least effective, procedure was to use surfactants and generate the 19-electron reductants in an emulsion. The chief drawback to this method is that the concentrations of the reactants must be low so as to prevent separation of the phases. The low concentrations necessarily prevented practical amounts of substrates from being used. The second method involved the synthesis of the $(\eta^5\text{-}C_5H_4COO^-)_2W_2(CO)_6$ complex. This dimeric precursor to the 19-electron complexes is soluble in water, and consequently the 19-electron complexes can be generated directly in aqueous solution. Using this method, a wide variety of water-soluble substrates were reduced. Attempts to recycle the 19-electron complexes were unsuccessful. A scheme involving homolysis of the metal-halide bond in organometallic halide complexes did not work because photochemical reactions reported in the literature could not be reproduced. An investigation of alternative methods for recycling the 19-electron complexes is continuing in our lab. Finally, we are also continuing our study of using the 19-electron complexes as initiators of anionic polymierization reactions.

AFOSR Program Manager: Dr Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

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

PRINCIPAL INVESTIGATOR:
Robert West
Department of Chemistry
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INCLUSIVE DATES: 1 October 1985 - 30 September 1988

CONTRACT/GRANT NUMBER: F49620-86-C-0010

COSTS AND FY SOURCE: $222,397, FY85; $222,658, FY86; $241,093, FY87

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Howard Yokelson
Gregory Gillette
Gail Underiner
Alan Fanta
Tony Millevolte
Scott Archibald

PUBLICATIONS:

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"Trapping of Silylenes by 9,10-Dimethylanthracene: 2,3,5,6-Dibenzo-7-silabicyclo(2.2.1)heptra-2,5-diens." A. Sekiguchi and R. West, Organometallics (In Press).

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"High-Yield Synthesis and Crystal Structure of a Novel Benzene Tris-Annelated With Bicyclo(2.2.2)octene," K. Komatsu, Y. Jinbu, G.R. Gillette and R. West, Chem. letters (Submitted).

"Three-, Four- and Five-Membered Rings From Disilenes," R. West, G.R. Gillette, H.B. Yokelson and A.J. Millevolte, Phosphorus, Sulfur, Silicon and Related Elements (Submitted).

"1,2-Aryl Rearrangement in Tetraaryldisilenes," H.B. Yokelson, D. A. Siegel, A.J. Millevolte, J. Maxka and R. West, J. Am Chem. Soc., (Submitted).

"Organosilane Polymers: Synthesis and Crosslinking of Formable Polymers Containing Phenylsilylene Units," X-H Zhang and R. West, Macromolecules, (Submitted).

"Conformational Energies and Unperturbed Chain Dimensions of Poly-(phenylmethylsilylene) (-SiPhMe-) and Poly(silastyrene) (-SiPhH-SiH2-)," W. J. Welsh, J.R. Damewood, Jr. and R. West, Macromolecules (Submitted).

"Structures of Two Organosilyl Azide," S.S. Zigler, K.J. Haller," R. West and M.S. Gordon, Organometallics (Submitted).

"Tetramesityldisilene," R. West, R.G. Gillette and H.B. Yokelson, Inorg. Synth (Submitted).

"Use of 2-D INEPT-INADEQUATE 29 Si NMR to Determine Structures of Organosilicon Rings," J. Maxka, B.R. Adams and R. West, J. Am. Chem Soc., (Submitted).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

I. Polysilane High Polymers and Oligomers. (a) Light-scattering studies of molecular weight and chain conformations were carried out for six polysilane samples. (b) Silicon-29 NMR spectroscopy was employed to study configurations of polysilane polymers and oligomers. (c) A New class of substances, poly(disilanylene-co-ethynylene) copolymers, were synthesized which show properties indicating $\delta$ $\Pi$electron conjugation.

II. Divalent and Multiply-Bonded Silicon Compounds. (a) Complexes of silylenes, R2Si: with various Lewis bases have been observed spectroscopically. (b) Reactions of disilenes (R2 Si=SiR2) with nitro compounds, nitroso compounds, azides and oxygen have been studied, leading to previously unknown types of cyclic silicon compounds. (c) A new, very stable disilene, 1,2-dimesityl-1,2-bis(1-adamantyl)disilene, was synthesized and investigated. (d) The first silandiimines, RN=Si=NR, have been made and observed at low temperatures. (e) Stable silanamidines, RNH-Si (X)=NR, and silanamidine anions, RN-Si(X)-NR$^-$, have been synthesized and studied.

AFOSR Program Manager: Dr Anthony J. Matuszko

# RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - COMPUTATIONAL CHEMISTRY

LT COL LARRY P. DAVIS, USAF

| | |
|---|---|
| Analytical Methods Using Slater Type Orbitals in Quantum Chemistry<br>AFOSR-86-0149 | Herbert W. Jones<br>Charles A. Weatherford<br>Department of Physics<br>Florida A & M University<br>Tallahassee, Florida |
| Spectroscopic and Light Scattering Instrumentation Proposal<br>AFOSR-85-0096 | John Ross<br>Department of Chemistry<br>Stanford University<br>Stanford, CA 94305 |
| Fundamental Studies of Carbon, NH, and Oxygen Rings and Other High Energy Density Molecular Systems<br>AFOSR-87-0182 | Henry F. Schaefer III<br>Department of Chemistry<br>University of California<br>Berkeley, California 94720 |

## COMPLETED PROJECT SUMMARY

TITLE: Analytical Methods Using Slater-Type Orbitals in Quantum Chemistry

PRINCIPAL INVESTIGATORS: Herbert W. Jones
Charles A. Weatherford
Department of Physics
Florida A&M University
Tallahassee, Florida 32307

INCLUSIVE DATES: October 1986 - October 1988

CONTRACT/GRANT NUMBER: AFOSR-86-0149

PUBLICATIONS:

H.W. Jones, "Computer-Generated Formulas for Exchange Integrals Over Slater-Type Orbitals", International Journal of Quantum Chemistry S19, 157 (1986).

C.A. Weatherford and H.W. Jones, "C-Matrix Formulation of the Coulomb Sturmian Addition Theorem", Bulletin of the American Physical Society 31, 933 (1986).

H.W. Jones, "Exact Formulas for Multipole Moments Using Slater-Type Molecular Orbitals", Physical Review A 33, 2081 (1986).

C.A. Weatherford, "Numerical Study of Some Vectorized Matrix Inverters for the PDE Approach to Electron-Molecule Scattering", Proceedings of the 1986 NSESCC Users Conference, edited by H. Eiserke (Goddard Space Flight Center, 1986).

H.W. Jones, "Computer-Generated Formulas for Four-Center Integrals Over Slater-Type Orbitals", International Journal of Quantum Chemistry 29, 177 (1986).

Contributions in Mathematics and Natural Sciences, edited by H.W. Jones and C.B. Subrahmanyam (FAMU Foundation, Tallahasses, Florida 1986).

H.W. Jones, "C-Matrix Elements to Ordinary Precision and to Exact Precision", in Contributions in Mathematics and Natural Sciences, edited by H.W. Jones and C.B. Subrahmanyam (FAMU Foundation, Tallahassee, Florida 1986).

C.A. Weatherford and A. Poole, "Explicit Derivation of the Associated Legendre Polynomials From the Rodrigues' Formula", in Contributions in Mathematics and Natural Sciences, edited by H.W. Jones and C.B. Subrahmanyam (FAMU Foundation, Tallahassee, Florida 1986).

H.W. Jones, "Exact Formulas and Their Evaluation for Slater-Type Orbital Overlap Integrals with Large Quantum Numbers", Physical Review A 35, 1923 (1987).

C.A. Weatherford, F.B. Brown, and A. Temkin, "Inclusion of Electron Correlation for the Target Wavefunction in Low- to Intermediate-energy e-$N_2$ scattering", Physical Review A 35, 4561 (1987).

C.A. Weatherford, F.B. Brown, and A. Temkin "Target State Correlation in e-$N_2$ Scattering", Proceedings of the Fifteenth International Conference on the Physics of Electronic and Atomic Collisions, Brighton, United Kingdom, edited by M.J. Coggiola, D.L. Huestis, and R.P. Saxon, 268 (1987).

H.W. Jones, B. Bussery and C.A. Weatherford, "An 'E-Matrix' for the Lowdin a Function, Expanded in a Taylor Series: An Analytic Treatment of Molecular Charge Density Near the Origin", International Journal of Quantum Chemistry S21, 693 (1987).

C.A. Weatherford, "An Analytic Method for Three-center Nuclear Attraction Integrals: A Generalization of the Gegenbauer Addition Theorem", International Journal of Quantum Chemistry 33, 19 (1988).

H.W. Jones, B. Etemadi, and C.A. Weatherford,"Analytical Evaluation of the Electrostatic Potential for Diatomic Molecules" International Journal of Quantum Chemistry S22, 297 (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Progress on the Slater-type integral problem has been continuous during the period 1986-88. We have shown how to "project to infinity" and obtain a closed formula for multipole moments. The formula approach using computer algebra has resulted in the best general overlap integral program available. An 'E-matrix' and 'F-matrix' have been developed to deal with small values of parameters in the alpha function. A prototype calculation has been made for electrostatic potentials. The FORTRAN program in single precision and exact precision has been published. The next objective is to make detailed comparisons between a commercial program with Gaussian-type integral packages and the ones we have developed.

In addition, for those multicenter integrals over Slater-type orbitals that cannot be expressed in a closed exponential times terminating polynomial, a factorization technique has been developed. In this technique, the Slater function on an atomic nucleus is factored into a 0-S orbital times a 'evenly loaded' solid harmonic (with at most a single parametric differentiation) such that the harmonic can be translated in finite terms to any other center. The 0-S orbital is then translated using the Gegenbauer addition theorem.

This technique has been programmed for all the integrals required for the traditional configuration interaction (CI) approach for diatomic molecules. The programming for polyatomic molecules is underway. In addition, the application of this technique to explicitly correlated Slater functions is being investigated.

The PDE (partial differential equation) method has been developed and applied to the scattering of electrons by molecular nitrogen. The theory encompasses the fixed nuclei and vibrational close-coupling techniques. The PDE method has proven to be highly vectorizable and extremely stable. The results appear to be best available *ab initio* cross sections in the literature for the 0 to 3.3 eV scattering range. The theoretical generalization to polyatomic targets has been accomplished and is the process of being programmed. The generalization to the discretization of the internuclear separation in diatomic molecules is being programmed.

AFOSR Program Manager: Lt Col Larry P. Davis, USAF

## COMPLETED PROJECT SUMMARY

TITLE: Spectroscopic and Light Scattering Instrumentation Proposal

PRINCIPAL INVESTIGATOR: John Ross
Department of Chemistry
Stanford University
Stanford, CA 94305

INCLUSIVE DATES: 1 January 1985 - 31 December 1987

CONTRACT/GRANT NUMBER: AFOSR-85-0096

| | | |
|---|---|---|
| SENIOR RESEARCH PERSONNEL: | Mark A. Schell | Benjamin Irvin |
| JUNIOR RESEARCH PERSONNEL: | Jean-Marie Bodet<br>Robert H. Harding<br>Mel LeVan<br>Spencer Pugh | Timothy S. Chevalier<br>Jesse Kramer<br>Arnaud Pagola |

PUBLICATIONS:

"Theory of Ostwald Ripening for Open Systems", C.W. Beenakker and John Ross, J. Chem. Phys., 83, 4710 (1985).

"Stabilization of Unstable States, Relaxation, and Critical Slowing Down in a Bistable System", Jesse Kramer and John Ross, J. Chem. Phys., 83, 6234 (1985).

"Propagation of a Chemical Pulse in an Illuminated Thermochemical Bistable System", Jesse Kramer, Johannes Reiter, and John Ross, J. Chem. Phys., 84, 1492 (1986).

"Thermochemical Bistability in an Illuminated Liquid Phase Reaction", Jesse Kramer and John Ros, J. Phys Chem., 90, 923 (1986).

"Monte Carlo Study of a Model of Diffusion-controlled Reactions", C.W.J. Beenakker and John Ross, J. Chem. Phys., 84, 3857 (1986).

"Effects of Periodic Perturbations on the Oscillatory Combustion of Acetaldehyde", Spencer A. Pugh, Mark Schell, and John Ross, J. Chem. Phys., 85, 868 (1986).

"Effects of Two Periodic Perturbations on the Oscillatory Combustion of Acetaldehyde", Spencer A. Pugh, Bruce DeKock, and John Ross, J. Chem. Phys., 85, 879 (1986).

"Measurements of [OH] and ($CH_3CHO$) Oscillations, and Phase Relations in the Combustion of $CH_3CHO$" Spencer A. Pugh, Hyung-Rae Kim, and John Ross, J. Chem. Phys., 86, 776 (1987).

"Effects of Non-Equimolar Reactant Flux on the Oscillatory Oxidation of Acetalydehyde", Spencer A. Pugh and John Ross, J. Phys. Chem., 91, 2178 (1987).

"Experiments on Phase Diffusion Waves", J.M.Bodet, J. Ross, and C. Vidal, J. Chem. Phys., 86, 4418 (1987).

"Measurements and a Hypothesis on Periodic Precipitation Processes", M. LeVan and J. Ross, J. Phys Chem., 91, 6300 (1987).

"Measurement of Dispersion Relation of Chemical Waves in an Oscillatory Reacting Medium", A. Pagola, C. Vidal and J. Ross, J. Phys. Chem., 92, 163 (1988).

"Spectral Kinetics and the Efficiency of (Bio)Chemical Reactions", From Chemical to Biological Organization, S. Pugh, M. Schell, and J. Ross, Springer-Verlag (dedicated to Benno Hess on 65th birthday).

"Explicit Solutions of Normal Form of Driven Oscillatory Systems", G. Tsarouhas and J. Ross, J. Chem. Phys., 87, 6538 (1987).

"Experiments on Bifurcation of Periodic States into Tori for a Periodically Forced Chemcal Oscillator", William Vance and John Ross, J. Chem. Phys., (Submitted for Publication).

"Complex Oscillations in the Combustion of Acetaldehyde", Robert Harding, Hana Sevcikova, and John Ross, J. Chem Phys., (Submitted for Publication).

"Symptoms of Chaos in Observed Oscillations near a Bifurcation with Noise", Robert Harding and John Ross, J. Chem. Phys., (Submitted for Publication).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The equipment purchased on this grant falls into three categories:

The first consists of components for four apparatus systems used for the study of oscillatory reactions and the effects of external periodic perturbations on such reactions. The components include peralstaltic pumps, flow meters, chart recorder, distillation unit, circulation water bath, spectrometer, flow meters. One apparatus has been used extensively for the study of the oscillatory combustion of acetaldehyde with oxygen in which we observed periodic and quasi-periodic responses to external periodic perturbations. We also studied the imposition of two simultaneous periodic perturbations which leads to hysteresis and a variety of responses observed for the first time. In the second apparatus we have studied the response of a liquid phase reaction to external perturbations, have observed a super critical Hopf bifurcation and the generation of an attracting 2-torus from stable limit cycle. In the third apparatus we are studying the efficiency of the combustion of methane with steady and oscillatory input of reactants. In the fourth apparatus we are studying chemical pumps and the thermodynamic efficiency. All these studies lead to enhanced determination of complex reaction mechanisms.

The second category includes generally used instrumentation including a storage oscilloscope, a visible spectrometer, a thermostat bath, an analytical balance, a pH meter and strip chart recorder used in the experiments described in the previous paragraph and, in addition, in the experiments on chemical waves and periodic precipitation processes. We have measured a variety of properties on kinematic waves, trigger waves and phase waves including velocity front profile and dispersion relations. Extensive measurements have been made in periodic precipitation processes by means of absorption and reticon techniques, microscope observation and standard analytical methods in order to obtain the temporal developments of band formation, propagation of the precipitation front, spatial distribution of total precipitate, particle density and variation of average particle radius.

The third category is computers and components including upgrading for laboratory computers on hand, computer networking hardware, computer data acquisition elements (both hardware and software) used in all the experiments as well as theoretical work, associated with the experiments including the study of entrained (periodic) response to periodic perturbations of an oscillatory chemical system, colloidal growth, systems with multiple stationary and the subjects mentioned in the prior paragraphs.

AFOSR Program Manager: Lt Col Larry P. Davis, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Fundamental Studies of Carbon, NH, and Oxygen Rings and Other High Energy Density Molecular Systems

PRINCIPAL INVESTIGATOR: Henry F. Schaefer III
Department of Chemistry
University of California
Berkeley, California 94720

INCLUSIVE DATES: 1 April 1987 - 31 March 1988

CONTRACT/GRANT NUMBER: AFOSR-87-0182

COSTS AND FY SOURCE: $29,671 FY87; $89,001 FY88

SENIOR RESEARCH PERSONNEL: Gustavo E. Scuseria
Yukio Yamaguchi

JUNIOR RESEARCH PERSONNEL: Charles P. Blahous    Edward T. Seidl
Andrew C. Scheiner

PUBLICATIONS:

"Geometrical Structure and Vibrational Frequencies for the Oxygen Analogue of Hexasulfur", C.P. Blahous and H.F. Schaefer, Massimo Simonetta Memorial Issue, J. Phys. Chem., 92, 959 (1988).

"Theoretical Studies of Oxygen Rings: Cyclotetraoxygen $O_4$", E.T. Seidl and H.F. Schaefer, J. Chem. Phys., 88, 7043 (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An analogy is constructed between the known composition of elemental sulfur (principally $S_8$ rings) and the unknown oxygen rings. Due to the weakness of the O-O single bonds, as in hydrogen peroxide, it is hypothesized that oxygen rings are potential high energy density materials. A particularly attractive candidate is the $O_4$ molecule, for which ring strain is expected to provide further destablization relative to two separated $O_2$ molecules. To pursue these qualitative suggestions, ab initio molecular quantum mechanics has been employed. Both self-consistent field (SCF) and configuration interaction including single and double excitations (CISD) methods have been employed in conjuction with double zeta plus polarization basis sets. At the highest level of theory the nonplanar ($D_{2d}$ point group, O-O-O-O torsional angle 25°) equilibrium structure is predicted to lie 2.9 kcal below the planar $D_{4h}$ structure, which is a transition state. The infrared spectrum is predicted at the DZ+P CISD level, as well as lower levels of theory. The $O_4$ minimum is predicted to lie ~ 100 kcal/mol above the asympototic limit of two $O_2$ molecules.

Self-consistent field (SCF) methods with minimum (STO-3G), double zeta (DZ), and double zeta plus polarization (DZP) basis sets predict the $O_6$ ring to assume chair, twist, and boat conformations analogous to similar forms for cyclohexane. All predicted vibrational frequencies for the chair and twist forms are real. Six symmetrically equivalent oxygen atoms are predicted to

comprise the lowest energy chair form, with O-O bond distances of 1.367 A and bond angles of 104.7$^o$ at the DZP SCF level of theory. The boat form is not found to be an energy minimum but rather exhibits one imaginary vibrational frequency which when followed tends toward assumption of the twist form. Energy differences at the DZP SCF level are computed to be 15.9 kcal between the chair and twist forms and 17.5 kcal between the chair and boat. We interpret these results by analogy with cyclohexane and assign the larger energetic discrepancies to shorter bond distances and inherently greater eclipsing effects for adjacent lone electron pairs than those attributed to bonding electron pairs. Homodesmotic and hyperhomodesmotic reactions devised to predict the decomposition exothermicity of the ring gave rather different results, namely, ~ 130 (homodesmotic and ~75 (hyperhomodesmotic) for the heat for formation of $O_6$.

AFOSR Program Manager: Lt Col Larry P. Davis, USAF

## RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - ATMOSPHERIC SCIENCES

LT COL JAMES P. KOERMER
LT COL JAMES I. METCALF (USAF Reserve)

| | |
|---|---|
| Cloud Simulation Chamber Warm Cloud Experiments: Droplet Growth and Aerosol Scavenging<br>AFOSR-85-0071 | John C. Carstens<br>Graduate Center for Cloud Physics Research<br>University of Missouri-Rolla<br>Rolla, MO 65401 |
| Experimental, Theoretical and Numerical Study of Critical Layers<br>F49620-86-C-0015 | Donald P. Delisi<br>Northwest Research Associates<br>P. O. Box 3027<br>Bellevue, WA 98009 |
| Long Term Studies of the Refractive Index Structure Parameter in the Troposphere and Stratosphere<br>AFOSR-86-0049 | C.W. Fairall and D.W. Thomson<br>Department of Meteorology<br>505 Walker Building<br>Pennsylvania State University<br>University Park, PA 16802 |
| Electromechanical Feedback Processes in the Ionosphere<br>AFOSR-85-0048 | Jeffrey M. Forbes<br>Department of Electrical, Computer, and Systems Engineering<br>Boston University<br>Boston, MA 02215 |
| Investigations of the Dynamics and Thermodynamics of the Mesosphere and Upper Thermosphere at the Polar Regions<br>AFOSR-87-0174 | Gonzalo Hernandez<br>Space Physics Research Laboratory<br>University of Michigan<br>2455 Hayward<br>Ann Arbor, MI 48109-2143 |
| A Study of the Identification and Development of Precipitation Using Dual Polarization Radar<br>AFOSR-86-0193 | Anthony J. Illingworth<br>Department of Physics<br>University of Manchester<br>Manchester, M60 1QD, UK |
| Studies of Frontal Zone Dynamics with a High-Resolution Wind Profiling System<br>AFOSR-85-0216 | Miguel F. Larsen<br>Department of Physics and Astronomy<br>Clemson University<br>Clemson, SC 29631 |
| Aircraft Investigation of the Turbulent Transport of Electric Charge Through the Unstable Planetary Boundary Layer<br>F49620-86-C-0013 | Ralph Markson<br>Airborne Research Associates<br>46 Kendal Common Road<br>Weston, MA 02193 |

# RESEARCH EFFORTS COMPLETED IN FY88

## COMPLETED PROJECT SUMMARIES - ATMOSPHERIC SCIENCES

LT COL JAMES P. KOERMER
LT COL JAMES I. METCALF (USAF Reserve)

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| Evaluating Evaporation with<br>Satellite Thermal Data<br>AFOSR-87-0177 | Woodruff Miller<br>Department of Civil<br>Engineering<br>368K CB, BYU<br>Provo, UT 84602 |
| Mesoscale Severe Weather Development<br>Under Orographic Influences<br>F49620-86-C-0080 | Elmar R. Reiter<br>Dept of Atmospheric Sciences<br>Colorado State University<br>Ft Collins, CO 80523 |
| Study of the Continuous/Diffuse<br>Aurora Using Particle Observations<br>from the Dynamics Explorer Satellites<br>F49620-85-C-0029 | James R. Sharber<br>Southwest Research Institute<br>Department of Space Sciences<br>P O Drawer 28510<br>San Antonio, TX 78284 |
| Sensitivity Evaluation Plan<br>for LOWTRAN<br>F49620-87-C-0057 | Ken Tomiyama<br>Dept of Mechanical Engineering<br>Aoyama Gakuin Univ<br>6-16-1 Chitosedai<br>JAPAN<br>(Formerly at<br>Dept of Mechanical Engineering<br>Pennsylvania State University<br>University Park, PA 16802) |
| Infrared and Ionization Structure<br>of the Polar Mesosphere<br>AFOSR-85-0163 | James C. Ulwick<br>Dept of Electrical Eng.<br>Utah State University<br>Logan, UT 84322 |

## COMPLETED PROJECT SUMMARY

TITLE: Cloud Simulation Chamber Warm Cloud Experiments: Droplet Growth and Aerosol Scavenging

PRINCIPAL INVESTIGATOR:
John C. Carstens
Graduate Center for Cloud Physics Research
University of MIssouri-Rolla
Rolla, MO 65401

INCLUSIVE DATES: 1 January 1985 - 31 December 1987

CONTRACT/GRANT NUMBER: AFOSR-85-0071

COSTS AND FY SOURCE: $149,995 FY85; $161,532 FY86; $173,333 FY87

SENIOR RESEARCH PERSONNEL:
Daniel R. White
John L. Schmitt
Donald E. Hagen
Darryl J. Alofs
Sung-Ho Suck Salk

JUNIOR RESEARCH PERSONNEL:
Max B. Trueblood
Max W. Alcorn, Jr
A. Raymond Hopkins

PUBLICATIONS:

"University of Missouri-Rolla cloud simulation facility: Proto II chamber", D.R. White, J.L. Kassner, J.C. Carstens, D.E. Hagen, J.L. Schmitt, D.J. Alofs, A.R. Hopkins, M.B. Trueblood, M.W. Alcorn, and W.L. Walker, Rev. Sci. Instrum., 58, 826-834 (1987).

"UMR cloud simulation studies of droplet growth: investigation of the condensation coefficient", D. Hagen, M. Alcorn, J. Kassner, J. Carstens, R. Hopkins, J. Schmitt, M. Trueblood, W. Walker, and D. White, Preprints, Conf. on Cloud Phys., "Amer. Meteorol. Soc., Boston" C1-C4, (1986).

"Assessment of the input of insoluble and surface active pollutants on fog evolution", J.C. Carstens, J. Podzimek, and H. Andriambeloma, Preprints, Conf. on Cloud Phys., "Amer. Meteorol. Soc., Boston" C32-C35 (1986).

"Measurements of the condensation coefficient of water in the UMR cloud simulation chamber", D.R. White, J.L. Kassner, J.C. Carstens, D.E. Hagen, J.L. Schmitt, D.J. Alofs, A.R. Hopkins, M.B. Trueblood, W.L. Walter, and M.W. Alcorn, Proc. 1987 Conf. on Obscuration and Aerosol Res. Chemical Research and Development, and Engineering Center, Aberdeen, MD 29, (1987).

"Condensation method for humidity measurements in the UMR cloud simulation chamber", D.E. Hagen, D.R. White, and D.J. Alofs, J. Nat. Bureau of Standards, 93, 551 (1988).

"Condensation coefficient measurement for water in the UMR cloud simulation chamber", D.E. Hagen, J.L. Schmitt, M.B. Trueblood, J.C. Carstens, D.R. White, and D. Alofs, J. Atmos. Sci., 46, 803-816 (1989).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objects of this research were to (1) perform a set of experiments to measure the condensation coefficient of water during cloud condensation/evaporation under simulated, well-controlled in-cloud conditions, and (2) measure the phoretic/Brownian scavenging of particles by cloud. These were regarded as shakedown experiments for the newly constructed facility. An attendant objective therefore was to "debug" the facility and establish reliable operational characteristics.

A series of measurements of the condensation coefficient of water revealed a systematic trend of values starting near unity for a newly activated or nucleated cloud drop, and decreasing with time to values in the neighborhood of 0.01. (Experiments were performed using NaCl and carbon particles as nucleants, as well as homogeneously in a fact expansion chamber.) The low values are significant in the broadening of the size distribution of cloud drops.

By matching wall temperature with the gas, cloud motion was suppressed to the extent that measurements could be made on a given portion of cloud throughout a given experimental run. The precision of this dynamical wall-gas temperature tracking is a significant operational feature.

Scavenging experiments were initiated but not completed. Suitable fluorescently tagged scavengeable particles were tested, and a fluorescent particle counter was developed to carry through these delicate experiments.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Experimental, Theoretical, and Numerical Study of Critical Layers

PRINCIPAL INVESTIGATOR: Donald P. Delisi
Northwest Research Associates, Inc.
P.O. Box 3027
Bellevue WA 98009

INCLUSIVE DATES: 1 November 1986 - 30 April 1988

CONTRACT/GRANT NUMBER: F49620-86-C-0015

PUBLICATIONS:

"Laboratory Observations of Gravity Wave Critical-Layer Flows," D. P. Delisi and T. J. Dunkerton, Pure and Applied Geophys., 130 445-461 (1989).

"Laboratory Observations of Turbulent Gravity Wave/Critical Layer Interactions," D. P. Delisi and T. J. Dunkerton, Eighth Symposium on Turbulence and Diffusion, Amer. Meteorol Soc., Boston 70-72 (1988).

"Studies of Internal Wave/Mean Flow Interactions," D. P. Delisi, Final Report, Contract F49620-86-C-0015, AFOSR (1988).

"Laboratory and Numerical Studies of Gravity Wave/Mean Flow Interactions," D. P. Delisi, T. J. Dunkerton, and D. C. Fritts, (in preparation).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The interaction of an internal gravity wave with a critical layer was investigated with a new laboratory facility which was designed and built as part of this study. Limited theoretical and numerical studies were also performed. The objectives were to obtain quantitative laboratory measurements of gravity wave/critical layer interactions over both short and long interaction times. Laboratory measurements included density profiles, instantaneous and mean velocity observations, and shadowgraph visualization. Results were obtained over time periods of several hours, an equivalent of approximately 100 wave cycles.

Results of the project include the following:

a. Early overturning in turbulent critical layer interactions in the laboratory experiments is characterized by Kelvin-Helmholtz instability and not convective overturning.
b. Mean flow modifications for laboratory, early-time, turbulent interactions are qualitatively similar to those predicted by numerical models.
c. The location of early overturning in the laboratory experiments is correlated with mean flow modifications, and the mixing region moves progressively towards the wave source.
d. Late-time interactions in the laboratory experiments are characterized by mixing regions which are not predicted by numerical models.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Long Term Studies of the Refractive Index Structure Parameter In The Troposphere and Stratosphere

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|---|---|
| PRINCIPAL INVESTIGATORS: | C.W. Fairall and D.W. Thomson<br>Department of Meteorology<br>505 Walker Building<br>Pennsylvania State University<br>University Park, PA 16802 |
| INCLUSIVE DATES: | 15 November 1985 - 15 March 1988 |
| GRANT/CONTRACT NUMBER: | AFOSR-86-0049 |
| COSTS AND FY SOURCE: | $146,419 FY86; $111,358 FY87 |
| JUNIOR RESEARCH PERSONNEL: | Robert Peters<br>William Syrett<br>Scott Williams |

PUBLICATIONS:

"An evaluation of errors observed in the measurement of low wind velocities," S.R. Williams, and D.W. Thomas, Handbook for MAP, Vol 20, SCOSTEP Secretariat, Dep. Elec. Comp. Eng., Univ. IL, 256-262 (1986).

"The Penn State Doppler Network Progress Report," S.R. Williams and R. Peters, Handbook for MAP, Vol 20, SCOSTEP Secretariat, Dep. Elec. Comp. Eng., Univ., IL 339-341 (1986).

"Analysis of Temperature and Velocity Microturbulence Parameters from Aircraft Data and Relation to Atmospheric Refractive Index Structure," E.A. Beecher, M.S. Thesis, Pennsylvania State University pp 165 (1987).

"Some Applications of 50 MHz Wind Profiler Data: Detailed Observations of the Jet Stream", W.J. Syrett, M.S. Thesis, Pennsylvania State University, pp 135 (1987).

"A Top-down and Bottom-up Diffusion Model of $C_T^2$ and $C_q^2$ in the Entraining Convective Boundary Layer", C.W. Fairall, J. Atmos. Sci., 44, 1009-1017 (1987).

"Comparison of Wind Profiler Data with NWS RAFS Analyses and Predictions" Reprints 8th Conf. on Numerical Weather Prediction," D.W. Thomson, W.J. Syrett, T.T. Warner, and N.L Seaman, Amer. Meteorol. Soc., p 6 (1988).

"An Aircraft and Radar Study of Temperature and Velocity Microturbulence in the Stably Stratified Free Troposphere," C.W. Fairall, D.W. Thomson and R. Markson, Preprints 8th Symp Turbulence and Diffusion, Amer. Meteorol. Soc., 61-68 (1988).

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project was concerned with the relation of meteorological conditions to parameters and processes that influence the optical propagation properties of the turbulent atmosphere. The approach was centered around the establishment of a climatology of refractive index structure function as measured with a network of Doppler radars. The relation of the atmospheric turbulence profile to the synoptic context and physical models to predict the profile using standard meteorological profile data was also investigated. The study featured two modes of data archiving: (2) continuous archiving of 1-hr average wind profiles and turbulence levels, and (2) high time resolution measurements in association with other measurements (ground-based optical scintillometers, aircraft or radiosondes) in an intensive 'campaign' given the acronym EWAK.

The atmospheric turbulence profiles and resultant optical propagation parameters were found to be strongly influenced by synoptic conditions. In particular, the turbulence is substantially affected by the strength and location of the jet stream. A very strong correlation between wind shear (which is maximum above and below the core of the jet) and pilot reports of turbulence was found. Richardson number gave a much weaker indication, possibly because of the poorer quality of the vertical temperature gradient data. A comparison of five different methods (four measurements and one model) of obtaining optical $C_n^2$ showed average disagreements as large as a factor of three. A study of the ratio of temperature to velocity microturbulence showed that the assumption of a constant mixing efficiency (used in the Van Zandt model) may not be valid for very weak turbulence. The potential for using operational numerical forecast models to compute turbulence estimates from predicted wind and temperature profiles was examined in a preliminary look at the ability of the NMC Nested Grid Model (NGM) to reproduce the wind speed and direction directly measured by the radars. The standard deviation between the radar and model was on the order of 6 m/s for wind speed and 15 degrees for wind direction at the initial analysis time. The uncertainty in wind direction increased to about 25 to 30 degrees for a 48-hr forecast but the uncertainty in wind speed did not change significantly. A systematic difference of several m/s was found during the winter, probably due to over-smoothing of mesoscale features by the model.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

## COMPLETED PROJECT SUMMARY

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|---|---|
| TITLE: | Electromechanical Feedback Processes in the Ionosphere |
| PRINCIPAL INVESTIGATOR: | Jeffrey M. Forbes<br>Department of Electrical, Computer and System Engineering<br>Boston University<br>Boston, MA 02215 |
| INCLUSIVE DATES: | 1 December 1984 - 31 May 1988 |
| GRANT/CONTRACT NUMBER: | AFOSR-85-0048 |
| COSTS AND FY SOURCE: | $150,360 FY84-88 |
| SENIOR RESEARCH PERSONNEL: | P. Batista |
| JUNIOR RESEARCH PERSONNEL: | M. Codrescu<br>A. Bryant<br>T. Hall |

PUBLICATIONS:

"On the Utilization of Ionosonde Data for Analyzing the Latitudinal Penetration of Ionospheric Storm Effects, J.M. Forbes, M. Codrescu, and T.J. Hall, Geophys. Res. Lett., 15, 249-252 (1988).

"Magnetosphere-Thermosphere Coupling: An Experiment in interactive Modeling, J. M. Forbes, M. Harel, J. Geophys. Res., 94 2631-2644 (1989).

"An Analytic/Expirical Model of the Middle and Low-Latitude Ionosphere," J.M. Forbes, D.N. Anderson, M. Codrescu, GL Technical Report GL-TR 89-0096 (1989).

"A Fully Analytic Low and Middle Latitude Ionospheric Model", D.N. Anderson, J.M. Forbes, M. Codrescu, J. Geophys. Res., 94 1520-1524 (1989).

"Thermosphere-Ionosphere Coupling: An Interactive Experiment", J.M. Forbes, R.G. Roble, J. Geophys. Res., 95 201-208 (1990).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The general goals were to provide a better understanding of observed neutral and plasma structures in the upper atmosphere and to define appropriate parameterizations for the neutral-plasma interactions governing these structures in comprehensive numerical models of the thermosphere and ionosphere. A convection model originally developed at Rice University was utilized to investigate the electrodynamic coupling between the magnetosphere and thermosphere, including the effects of neutral winds, and noting the change in electric fields penetrating to low latitudes due to the wind effects. A unique aspect of the study was that the high-latitude convection-driven winds were included self-consistently and interactively; that is, a steady-state wind parameterization was derived analytically in terms of the electric potential, which was in turn included in a closed-loop calculation for the electric potential itself. An analagous study was performed for the thermosphere-ionosphere system, wherein the balance height of the F-layer was expressed analytically in terms of the meridional neutral wind, and the two parameters were allowed to evolve self-consistently within dynamical calculations representing magnetically disturbed and quiet conditions in the thermosphere. In another series of calculations, plasma structures unique to the equatorial ionosphere were modeled analytically and incorporated into a numerical solution of the neutral dynamics to demonstrate the controlling influence of the ionosphere on the equatorial thermosphere. A methodology involving polynomial fitting and color graphics display of global ionosonde data was also developed for analyzing the equatorward penetration of ionosphere-thermosphere coupling signatures during magnetically disturbed periods. This method of analysis is useful in research efforts involving global experimental campaigns and their simulation using numerical models and in the development of operational useful ionospheric empirical models which include the effects of magnetic storms.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

## COMPLETED PROJECT SUMMARY

TITLE: Investigations of the Dynamics and Thermodynamics of the Mesosphere and Upper Thermosphere at the Polar Regions.

PRINCIPAL INVESTIGATOR: Gonzalo Hernandez
Research Scientist
Space Physics Research Laboratory
University of Michigan
2455 Hayward
Ann Arbor, MI 48109-2143

INCLUSIVE DATES: 1 April 1987 - 31 March 1988

GRANT/CONTRACT NUMBER: AFOSR-87-0174

COSTS AND FY SOURCE: $149,482 FY87

SENIOR RESEARCH PERSONNEL:
R.W. Smith
R.J. Sica
R.G. Roble
F.G. McCormack
G.J. Romik

JUNIOR RESEARCH PERSONNEL:
J.E. Schewe
A. Alcock
R. Viereck
J. Conner
J. Minnow

PUBLICATIONS:

"Afocal Coupled Elalons. DEM: A High-Resolution Double-Etalon Modulator Spectrometer", G. Hernandez, Appl Opt., 26, 4857-4869 (1987).

"Afocal Coupled Etalons. Experimental Confirmation of a High-Resolution Double-Etalon Modulator (DEM) Spectrometer", G. Hernandez and F.G. McCormac, Appl Opt., 27, 3492-3495 (1988).

"Global Scale Studies of Thermospheric Dynamics in the CEDAR Program", R.W. Smith, J.W. Meriwether, G. Hernandez, V.B. Wickwar and O. de la Beaujardiere", Trans, Eas. Trans. Am. Geophys. Union. 69, (1988).

"The Control of Auroral Zone Dynamics and Thermodynamics by the Interplanetary Magnetic Field Dawn-Dusk (Y) Component", R.J. Sica, G. Hernandez, B.A. Emery, R.G. Roble, R.W. Smith, M.H. Rees and G.J. Romick, J. Geophys. Res., 94, 11921-11932 (1989).

"Optical Measurements of Winds and Temperatures in the Upper Atmosphere," G. Hernandez and T.L. Killeen, Chapter 5 in COSPAR International Reference Atmosphere" 1988, Adv. Spare Res 8 149-213 (1988).

PRESENTATIONS:

"A Large Amplitude 6-hour Tide in the MALT at Poker Flat." R.W. Smith, G. Hernandez, J. Conner, R. Viereck, G.J. Romick and C.S. Deehr, IAGA/IUGG Assembly, Vancouver, B.C. (1987).

"Fabry-Perot Observations of Winds Near the Mesopause Height at Poker Flat, Alaska," J.Conner, G.J. Romick, R.W. Smith and G. Hernandez, American Geophysical Union Fall Meeting, San Francisco, CA. (1987).

"Very Low Airglow Emission Intensitites in the Auroral Region - Spring 1987", G.J. Romick, A. Alcock, J. Conner, C.S. Deehr, E. Hoch, R.W. Smith, R. Viereck and G. Hernandez, American Geophysical Union, Fall Meeting, San Francisco, CA (1987).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main thrusts of this investigation were the investigation of the dynamical and thermodynamical properties of the mesosphere and the thermosphere. A supporting research program in spectroscopic instrumentation and techniques made it possible to obtain the atmospheric measurements.

The instrumentation was moved to Poker Flat, Alaska because of the increasing light pollution in the Fairbanks area, where the instrument was previously located. The application of Telescience concepts to the automation of the instrumentation made it possible to field the equipment to this unmanned site, yet communication via a telephone link made it possible to interact with the instrument as easily as if the spectrometer were located in the room next door.

The new freedom of operation made it possible to begin an in-depth optical investigation of the dynamical and thermodynamical properties of the mesosphere and lower thermosphere in the polar regions. These studies used the near-infrared emissions of the OH molecule as tracers for the properties of the mesosphere and the visible emission of OI for the lower thermosphere. The use of the OH molecule near-infrared emissions has made it possible to study this nearly unknown region of the upper atmosphere even in the presence of auroral activity, since the OH emissions are specific to this region of the upper atmosphere. The general behavior of the polar mesosphere was determined and, in particular, a mesospheric event (characterized by a decrease of mesospheric and thermospheric emissions by nearly one order of magnitude) lasting from February 20 to April 3, 1987, was monitored. During this period, the typical measured wind field had a variance much larger than its average value although, on a few occasions, the various wind components varied in a coherent way indicating a dominating large scale motion.

The upper thermosphere measurements were continued as the solar activity cycles went from maximum to minimum. The data obtained thus far were used to determine the control of the auroral zone upper thermosphere dynamics and thermodynamics by the interplanetary magnetic field, in particular the y-component. The results show the lowest magnetic latitude at which the classical symmetric two-cell convection is distorted, altering the ion drag forcing of the neutral thermosphere.

Investigation of high-luminosity spectrometers has given rise to the double-etalon modulator (DEM), which has a luminosity increase of nearly a factor of 100 over previously available multiple-beam spectrometers at an arbitrary resolving power. The DEM device, being a compensated device, has a product of luminosity x resolving-power that increases with increasing resolution. This property further shows the advantages of the DEM device, since the typical multiple-beam spectrometers have a constant luminosity x resolving-power product.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

# COMPLETED PROJECT SUMMARY

TITLE: A Study of the Identification and Development of Precipitation Using Dual Polarization Radar

PRINCIPAL INVESTIGATOR: Anthony J. Illingworth
Department of Physics
University of Manchester
Institute of Science and Technology
Manchester M60 1QD, UK

INCLUSIVE DATES: 1 July 1986 - 31 December 1987

CONTRACT/GRANT NUMBER: AFOSR-86-0193

COSTS AND FY SOURCE: $34,020 FY86

JUNIOR RESEARCH PERSONNEL: I. J. Caylor I. R. Frost

PUBLICATIONS:

"Detection of Hail by Dual-Polarication Radar", A.J. Illingworth, J.W.F. Goddard, and S.M. Cherry, Nature 320, 431-433, (1986).

"Observations of the Growth and Evolution of Raindrops Using Dual-Polarization Radar", I.J. Caylor and A.J. Illingworth, 23rd Conf on Radar Meteorol. (Amer. Meteorol. Soc, Boston, R88-R91 (1986).

"Polarization Radar Studies of Precipitation Development in Convective Storms", A.J. Illingworth, J.W.F. Goddard, and S.M. Cherry, Q.J. Roy Met Soc., 113, 469-489 (1987).

"Radar Observations and Modelling of Warm Rain Initiation" Q. J. Roy Met Soc 113, 1171-1191 (1987).

"Polarization Radar Estimates of Raindrop Size Spectra and Rainfall Rates", A.J. Illingworth, I.J. Kaylor, Journal of Atmos and Oceanographic Tech., 6 939-949 (1989).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The polarization properties of radar returns contains much useful information which enable the sizes, types, shapes and concentrations of the precipitation particles to be ascertained. Conventional radars measure only the radar reflectivity, Z, which contains no information as to the types of hydrometeors in the clouds. This study used the Chilbolton radar in Hampshire, England, which, with a 25-m dish, is the largest steerable meteorological radar in the world. It operates at 10 cm so that propagation problems are negligible. It has a quarter-degree beamwidth and because of the unique antenna it is able to make polarization measurements of unrivalled accuracy.

During the period of this grant particular attention was paid to the interpretation of the differential reflectivity - the ratio of the reflectivities measured at vertical and horizontal polarization -- which provides a measure of the mean shape of the precipitation particles. The detection of hail relies on the different shape of hailstones as opposed to raindrops, and appears to be the first reliable method of remotely sensing hail.

When combined with the conventional reflectivity the differential reflectivity measurement of raindrop shape can be used to infer both the size and the concentrations of raindrops. Observations of the growth of raindrops in convective clouds revealed a quite different evolution from the previously accepted picture.

(1) Precipitation development in convective clouds in the absence of ice is far more common than previously believed.

(2) The raindrops first appear as a very low concentration (less than one per cubic meter) of large drops which reach a size of several millimeters. In contrast to this, there are several thousand raindrops per cubic meter in mature clouds.

(3) It was hypothesized that these raindrops first form on ultra-giant nuclei (above 50 micrometer diameter) which are present in the atmosphere in these low concentrations. The previous concept was that many small cloud droplets were produced by condensation, and these small droplets then coalesced to form raindrops; the problem was to explain how such small droplets were able to collide with one another in the time available. The giant nuclei are able to capture cloud droplets and form embryonic raindrops much more easily.

(4) During periods of vigorous growth of convective clouds regions of large supercooled raindrops are found up to two kilometers above the zero degree celsius isotherm. These supercooled raindrops occur in transient vertical columns, approximately circular in cross-section with a diameter of one to two kilometers, and a lifetime of about ten minutes before they glaciate. Their position appears to coincide with the updraft.

The observations described above demonstrate the potential of the new radar technique; it would be difficult or impossible to obtain a sample of such clouds using a penetrating aircraft. During the period of the grant two new radar parameters were implemented on the Chilbolton radar, the linear depolarization ratio, which reflects the fall mode of the particles, and the copolar correlation which reflects the variety of particle shapes present. These parameters promise to provide further information about the characteristics of the ice particles in the clouds and their growth and melting behavior.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

## COMPLETED PROJECT SUMMARY

TITLE: Studies of Frontal Zone Dynamics with a High-Resolution Wind Profiling System

PRINCIPAL INVESTIGATOR: Miguel F. Larsen
Department of Physics & Astronomy
Clemson University
Clemson, SC 29631

INCLUSIVE DATES: May 1, 1985 - September 30, 1988

CONTRACT/GRANT NUMBER: AFOSR-85-0216

COST AND FY SOURCE: $49,429, FY 85; $47,458, FY 86;
$41,729, FY 87

JUNIOR RESEARCH PERSONNEL: James G. Voe T. S. Dennis
M. A. Clerk Tim Marshall

PUBLICATIONS:

"A Review of Synoptic Scale Wave Perturbations in the Equatorial Stratosphere", C. R. Cornish, and M. F. Larsen, J. Atmos. Terr. Phys., 47, 769-780, (1985).

"Observations of Frontal Zone and Tropopause Structures With a VHF Doppler Radar and Radiosondes", M. F. Larsen, and J. Rottger, , Radio Sci., 20, 1223-1232, (1985).

"A Comparison of Thunderstorm Reflectivities Measured at VHF and UHF", M. F. Larsen, and J. Rottger, , J. Atmos. Ocean. Tech., 4, 151-159, (1986).

"Power Spectra of Oblique Velocities in the Troposphere and Lower Stratosphere observed at Arecibo, Puerto Rico," M. F. Larsen, R. F. Woodman, T. Sato, and M. K. Davis, , J. Atmos. Sci., 43, 2230-2240, (1986).

"Direct Measurements of Vertical Velocity Power Spectra With the SOUSY-VHF-Radar Wind Profiler System", M. F. Larsen, J. Rottger, and D. N. Holden, J. Atmos. Sci., 44, 2442-3448, (1987).

"A Comparison of Operational Analysis and VHF Wind Profiler Vertical Velocities", M. F. Larsen, J. Rottger, and T. S. Dennis, Mon. Wea. Rev., 116, 48-59, (1988).

"UHF/VHF Radar Techniques for Atmospheric Research and Wind Profiler Applications", J. Rottger, and M. F. Larsen, Radar in Meteorology, American Meteorological Society, Boston, Chapter 21A, 235-281 (1989).

"A Comparison of Thunderstorm Reflectivities Measured at VHF and UHF", Proceedings of the URSI/SCOSTEP Workshop on Technical Aspects of MST Radare (1985), M. F. Larsen, and J. Rottger, Handbook for MAP, 20, University of Illinois, 279-287, (1986).

"Need for a Subtropical Wind Profiling System", Proceedings of the URSI/SCOSTEP Workship on Technical Aspects of MST Radars (1985), J. Rottg M. F. Larsen, H. M. Ierkic, and T. Hagfors Handbook for MAP, 20, Universi Illinois, 86-89, (1986).

"Observations of Mesoscale Vertical Velocities Around Frontal Zones", Proceedings URSI/SCOSTEP Workshop on Technical Aspects of MST Radars (1985) T. S. Dennis, M. F. Larsen, and J. Rottger, Handbook for MAP, 20, University of Illinois, 35-43, (1986).

"UHF and VHF Observations of Thunderstorms", Proceedings of the URSI/SCOSTEP Workshop on Technical Aspects of MST Radars (1985), D. N. Holden, C. W. Ulbrich, and M. F. Larsen Handbook for MAP, 20, University of Illinois, 288-292, (1986).

"Observations of Vertical Velocity Power Spectra with the SOUSY-VHF-Radar", Proceedings of the URSI/SCOSTEP Workshop on Technical Aspects of MST Radars (1985), M. F. Larsen, J. Rottger, and D. N. Holden, Handbook for MAP, 20, University of Illinois, 231-235, (1986).

"Observations of Thunder with the Arecibo VHF Radar", Proceedings of the URSI/SCOSTEP Workshop on Technical Aspects of MST Radars (1985), D. N. Holden, and M. F. Larsen, Handbook for MAP, 20, University of Illinois, 147-152, (1986).

"Comparison of Vertical Velocities Analyzed by a Numerical Model and Measured by a VHF Radar Over an Eleven Day Period", Proceedings of the URSI/SCOSTEP Workshop on Technical Aspects of MST Radars (1985), M. F. Larsen, J. Rottger, and T. S. Dennis, Handbook for MAP, 20, University of Illinois, 44-47, (1986).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHEMENTS:

Objectives included an analysis of errors in UHF and VHF radar wind profiler measurements of vertical velocities and potential errors associated with tilting of isentropic (specular reflection layers) and scattering from precipitation. Additional goals included the comparison of radar vertical velocities with the operational analysis from the "European Centre for Medium Range Weather Forecasts" and the determination of the vertical circulations around a series of cold fronts, warm fronts, occlusions, and one tropopause fold that passed the SOUSY-VHF-Radar in West Germany.

Results showed that radars operating at frequencies close to 400 MHz, the frequency of the proposed operational network, will be dominated by scattering from precipation even for small rainfall rates. Thus, vertical velocity measurements with 400-MHz systems are essentially impossible when there is precipitation in the environment. Radars operating at frequencies close to 50 MHz have approximately equal contributions from precipitation and turbulent scattering, and the two components can be separated in the frequency spectra. Therefore, 50-MHz systems can measure vertical air motions in virtually all conditions.

The observation of vertical circulations in frontal zones showed a distinctive banded structure that included a strong indirect circulation component in all the warm and cold fronts that passed the radar site. The exceptions included two occlusions that showed no evidence of an indirect circulation. The vertical velocity patterns of ascent and descent were in agreement with expectations in an average sense, but the strongest ascent and descent were highly localized. The variance of the radar data and the vertical velocity from the European Centre's operational analysis agreed well in magnitude. Many of the same features, although not all of the vertical velocity bands, were evident in both time series, but the timing of the passage of the bands varied by as much as 12-24 hr between the two sets of values. The tropopause folding event showed strong descent on each side of the frontal location near the tropopause, in agreement with a model proposed earlier, but the two shafts of strong subsidence were aligned much closer to the vertical than the frontal zone itself. The latter finding is different from the conventional picture of the vertical circulation near tropopause folds and is of interest to the extent that the observation is representative of more cases than the one that occurred over the SOUSY radar.

The tilt of isentropic (specular) surfaces was analyzerd based on the phase information derived from the spaced antennas of the SOUSY system. The results showed surface tilts of 2-3 degrees or less, in general agreement with expectations, but the largest tilts were located in the frontal zones. The tilts imply that a correction needs to be made in VHF vertical velocity measurements due to the contamination of the vertical beam, line-of-sight velocity by the horizontal wind component. The tilt measurements also show the potential of the radars for measurements of the baroclinicity in actively developing frontal zones.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

## COMPLETED PROJECT SUMMARY

TITLE: Aircraft Investigation of the Turbulent Transport of Electric Charge Through the Unstable Planetary Boundary Layer

PRINCIPAL INVESTIGATOR: Ralph Markson
Airborne Research Associates
46 Kendal Common Road
Weston, MA 02193

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|---|---|
| INCLUSIVE DATES: | 15 November 1985 - 14 November 1987 |
| CONTRACT/GRANT NUMBER: | F49620-86-C-0013 |
| TOTAL COST: | $233,120 |
| SENIOR RESEARCH PERSONNEL: | Bruce Anderson<br>Airborne Research Associates |

PUBLICATIONS AND PRESENTATIONS:

"A Field Study of the Electrode Effect and Convection Current Over Land", C. W. Fairall, J. C. Willett, R. Markson, and B. Anderson, Fall Meeting, Amer. Geophys, Union Eos, Trans. Amer. Geophys. Union, 57(44), 891, (1986).

"Electrical Structure in the Marine Boundary Layer", B. Anderson, R. Markson, C. W. Fairall, and J. C. Willett, Eos, Trans. Amer. Geophys. Union, 68(44), 1218, (1987).

"Aircraft Investigation of Electric Charge Flux Over Land and Sea", B. E. Anderson, R. Markson, C. W. Fairall, and J. C. Willett, Proc. VIII Int. Conf. Atmos. Electricity, 782, Uppsala Sweden, (June, 1988), Institute for High Voltage Reserrch at Uppsala University, Sweden, J. Geophys. Res., (to be published (1988).

"Comparison of Ionospheric Potential and Air-Earth Current as Indicators of the Global Circuit Current", R. Markson, Proc. VIII Int. Conf. Atmos. Electricity, 814, Uppsala, Sweden, (June 1988), Insittute of High Voltage Research at Uppsala University, Sweden, J. Geophys. Res., (to be published (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

There were two main objectives to the research:

(1)To examine the strength of the electrode effect charge source over land and sea.

(2)To obtain simultaneous measurements of meteorological and charge fluxes under varying conditions of convection to test predictions of a second order closure model of the turbulent transport of electrode effect space charge through the planetary boundary layer.

Aircraft soundings of electric field, conductivity, temperature, condensation nuclei, dew point, and turbulence structure functions for velocity, temperature and humidity along with surface temperatures and wind speeds were obtained over the desert in southeastern New Mexico and over water in the Bahamas. Sixteen flights were performed in the desert deployment where, in addition, a ground station was operated to obtain simultaneous measurements of wind speed at two heights, air-earth current density, electric field, and turbulence structure functions for temperature and velocity. Eleven flights were carried out over the ocean near Eleuthera, Bahamas.

Our results indicate:

(1) Strong electrode layers form over the ocean but are often inhibited over land. These are attributed to radioactive emanations from the ground which cause ionization close to surface, preventing an accumulation of monopolar ions.

(2) The shape and intensity of convection current profiles are dependent on the electrical relaxation time and turbulence intensity as predicted by the charge transport model.

(3) Vertical electric field measurements, because of their sensitivity to volumes of space charge, are a better indicator of organized oceanic convective structure than humidity or other <u>in situ</u> measurements.

(4) Ionospheric potential is a much better parameter for observing temporal variations in the global electric circuit supply current than air-earth current density because of the latter's sensitivy to changes in columnar resistance and convection current.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Evaluating Evaporation with Satellite Thermal Data

PRINCIPAL INVESTIGATOR: Woodruff Miller
Department of Civil Engineering
368K CB, Brigham Young Univ
Provo, UT 84602

INCLUSIVE DATES: 1 April 1987 - 1 October 1987

GRANT/CONTRACT NUMBER: AFOSR-87-0177

COSTS AND FY SOURCE: $9,944 FY86

JUNIOR RESEARCH PERSONNEL: Eric Millis

PUBLICATIONS:

"Using Thermal Infrared Satellite Imagery to Estimate Evaporation from the Great Salt Lake, Utah", E. Millis Master's Thesis, Brigham Young University (1987).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Water surface temperatures can be obtained from satellite thermal remote sensing. Landsat and other satellites sense emitted thermal infrared radiation on a regular basis over much of the earth's surface. Evaporation is accomplished by the net transport of mass from the water surface to the atmosphere. Energy from the change of state in part comes from the subsurface and passes through the surface conduction layer. Therefore, the latent transfer (evaporation) predominantly determines the water surface temperature. Hence, there should be good correlations between evaporation and surface temperatures.

Previous investigations on Utah Lake with satellite-derived temperatures and pan- and model-derived evaporations have produced good correlations. The relationships which were developed have been applied at other dates on Utah Lake and on Lake Powell and Lake Havasu with some success. However, more study was required with additional satellite data and evaporation measurements for saltwater conditions. The applicability of this method for estimating evaporation on Utah's Great Salt Lake was of particular interest at this time because of the unprecedented rise of this terminal lake and because of the similarities with ocean evaporation.

Satellite thermal data and evaporation data from four different years were obtained for the Great Salt Lake and surrounding region. More than 350 correlation and linear regression analyses were performed on the temperature and evaporation data. These included daily, multiple-day, and monthly values from measurements and modeling for the whole lake and areas within the lake using both day and night observations. The lake salt concentrations were also factored into the analyses in several different ways. The correlation results were generally very good (correlation coefficients of 85%-97%) and a methodology for using satellite-derived water surface temperatures along with

salt concentrations was developed to estimate evaporation. Continuing efforts now include acquiring thermal data at less cost, more frequently and more quickly in order to apply the temperature-evaporation models in near real time to lakes and the ocean.

Evaporation was modeled for monthly and short-term periods of one, two and three days. Most of the better models represent the monthly evaporation. However, there were some which would estimate the evaporation for the short-term very effectively. A climatologically-based model (WREVAP) provided evaporation estimates that correlated very well with the surface temperatures. The output of this model also showed a nearly one-to-one relationship with pan evaporations from the Saltair pan thus confirming its reliability.

A major conclusion drawn from the correlation results was that salinity effects can be successfully factored into the evaporation-temperature relationships. Accurate saltwater lake evaporations are determined by multiplying the results from the equations developed to yield pan evaporations by the appropriate pan and salt coefficients. The results of this study show that the modeling was successful, demonstrating that the evaporation from saline bodies of water can be effectively estimated using remote sensing techniques.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Mesoscale Severe Weather Development Under Orographic Influences

PRINCIPAL INVESTIGATOR: Elmar R. Reiter
Department of Atmospheric Sciences
Colorado State University
Ft Collins, CO 80523

INCLUSIVE DATES: 1 July 1986 - 30 September 1988

CONTRACT/GRANT NUMBER: F49620-86-C-0080

COSTS AND FY SOURCE: 1986/87 $138,469; 1987/88 $139,067

SENIOR RESEARCH PERSONNEL: Bruce C. Macdonald

JUNIOR RESEARCH PERSONNEL: James F. Bresch, John Shaeffer, Marjorie A. Klitch

PUBLICATIONS:

"A Diagnostic Study of Explosive Cyclogenesis in the Lee of the Rocky Mountains" Qi Hu and E. R. Reiter, Meteorol. Atmos. Phys., 36, 161-187 (1987).

"Aspects of Regional-Scale Flows in Mountainous Terrain" J. E. Bossert, J. D. Shaeffer and E. R. Reiter, J. Appl. Meteorol. 28, 590,601 (1989).

"Tibet Revisited - TIPMEX-86" E. R. Reiter, J. D. Shaeffer, J.E. Bossert, E. A. Smith, G. Stone, R. McBeth and Q. Zheng. Bull. Amer. Meteoro. Soc., 68 607-615 (1987).

"ROMPEX - The Rocky Mountain Peaks Experiment of 1985: Preliminary Assessment" E. R. Reiter, J. D. Shaeffer, J. E. Bossert and R. C. Fleming, W. E. Clements, J. T. Lee, S. Barr, J A. Archuleta, and D. E. Hoard, Bull. Amer. Meteoro. Soc., 68, 321-328, (1987).

"Measurements of Surface Energy Budgets in the Rocky Mountains of Colorado" J. D. Shaeffer and E. R. Reiter, J. Geoph. Res. 92, 4145-4162 (1987).

"Urban Climate Effects of Energy Demand for Space Heating" E. R. Reiter, J. D. Shaeffer. Meteorol. Atmos. Phys., 38, 202-214 (1988).

"Modeling Heavy Precipitation in Complex Terrain" D. F. Tucker and E. R. Reiter. Meteorol. Atmos. Phys., 39, 119-131 (1988).

"The Verification of Numerical Models with Multivariate Randomized Block Permutation Procedures" D. F. Tucker, P. W. Mielhe, and E. R. Reiter, 1640, 181-188 Meteorol. Atmos. Phys. (1989).

"Heavy Rainfall in Complex Terrain: Insights from a Numerical Model" D. F. Tucker and E. R. Reiter. 40, 194-210, Meteorol. Atmos. Phys. (1989).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The project had two goals: (1) to study the role of topography in the development of mesoscale convective systems of summer, and (2) to assess the orographic effects on rapid severe weather developments during seasons other than summer.

The first goal entailed several field measurement programs to determine the surface energy budget in complex terrain. Two stations were set up in Tibet at the end of May 1986 and operated until early July 1986, one near Lhasa (3635 above sea level), the other near Nagqu (4500 m) about 300 km north of Lhasa. Data were collected on the downward and upward fluxes of visible, near-infrared, and longwave radiation, the soil heat and moisture budgets, as well as temperature, humidity and wind profiles on 20-m towers. Two NCAR-ADAS sounding stations, one at each location, provided upper-air data. The importance of the latent heat cycle through precipitation and local re-evaporation became evident. Turbidity measurements in Lhasa revealed a high level of particulate aerosol on most days.

Similar measurements were conducted during the summers of 1986 through 1988 at mountain peak and valley locations in Colorado. Strong, quasi-periodic nocturnal wind regimes found earlier to be associated with outflow from collapsing, monsoon-produced convective systems over the Rocky Mountain main range, were tracked along transects of stations and by soundings. Weaker wind regimes, produced by nocturnal radiative cooling, were found to be strongly influenced by terrain details.

Numerical modeling studies concentrated on assessing the sensitivity of heavy precipitation from summertime convective systems to topographic details, synoptic patterns, and various physical processes in the model. It was found that flash floods of seemingly the same type may be quite different in their prominent mechanisms. Experiments in the numerical prediction of rapid and severe cyclogenesis (so-called "bombs") over the eastern U.S. produced encouraging results when "features", such as enhanced vorticity patterns associated with a low-level jet stream, were assimilated into the model at successive time steps. Forecasts of snowstorm conditions in eastern Colorado were markedly improved if jet stream velocities over the U.S. west coast were enhanced by "bogus" soundings. These enhancements were made to produce a region of zero absolute vorticity on the anticyclonic side of strong jet maxima, where wind observations usually are missing, and objective analysis techniques tend to grossly underestimate wind velocities.

AFOSR Program Manager: Lt Col James P. Koermer, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Study of the Continuous/Diffuse Aurora Using Particle Observations from the Dynamics Explorer Satellites

PRINCIPAL INVESTIGATOR:
James R. Sharber
Southwest Research Institute
Department of Space Sciences
P.O. Drawer 28510
San Antonio, TX 78284

INCLUSIVE DATES: 1 January 1985 - 30 September 1988

CONTRACT/GRANT NUMBER: F49620-85-C-0029

SENIOR RESEARCH PERSONNEL:
J. R. Sharber
J. D. Menietti
J. D. Winningham

PUBLICATIONS:

"Dynamics Explorer-2 Measurements During an Isolated Auroral Substorm", J. R. Sharber, and J. D. Winningham, Proceedings of the Third Finnish-American Auroral Workshop (1985), Finnish Academy of Science and Letters, Report No. 45, 36-49, (1986).

"E- and F-Region Study of the Enening Sector Auroral Oval: A Chatanika/Dynamics Explorer-2/NOAA-6 Comparison", C. Senior, J. R. Sharber, O. de la Beaujardiere, R. A. Heelis, D. S. Evans, J. D. Winningham, M. Sughura, and W. R. Hoegy, J. Geophys. Res., 92, 2277-2494, (1987).

"Ionospheric Convection Signatures Observed by DE-2 During Northward IMF", R. A. Heelis, P. H. Reiff, J. D. Winningham, and W. Hanson, J. Geophys. Res., 91, 5817-5830, (1986).

"Ionospheric Convection Signatures and Magnetic Field Topology", W. R. Coley, R. A. Heelis, P. H. Reiff, J. B. Hanson, J. D. Winningham, and J. R. Sharber, J. Geophys. Res., 92, 12352-12363, (1987).

"Simultaneous Density and Electric Field Fluctuation Spectra Associated with Velocity Shears in the Auroral Oval", Sunanda Basu, Santimay Basu, E. MacKenzie, P. F. Fougere, W. R. Coley, R. A. Heelis, N. Maynard, J. D. Winningham, W. B. Hanson, C. S. Lin, W. R. Hoegy, and B. G. Ledley, J. Geophys. Res., 93, 115-136, (1988).

"Coherent Mesoscale Convection Patterns During Northward IMP", H. C. Carlson, R. A. Heelis, E. J. Weber, and J. R. Sharber, J. Geophys. Res. 93, 14501-14514, (1988).

"Plasma Waves Associated with Electron Beams in the Diffuse Auroral Region", J. D. Menletti, J. R. Sharber, J. F. Burch, and D. A. Gurnett, Proceedings of the 1987 Cambridge Workshop on Geoplasma Physics: Ionosphere-Magnetosphere-Solar Wind Coupling SPI conference Proceedings and Reprint Series, 7, editors T. Chang, C. B. Crew, and J. R. Jasperse, Scientific Publishers, Inc., Cambridge, MA (1988).

"Further Boundary Conditions on the Low-Energy Electrons in the Plasmapause Region", J. R. Sharber, J. D. Winningham, J. L. Bunch, W. R. Hoegy, A. M. Persoon, and J. H. Watte, Jr., Proceedings of the 1987 Cambridge Workshop on Geoplasma Physics: Ionosphere-Magnetosphere-Solar Wind Coupling Processes, SPI Conference Proceedings and Reprint Series, 7, editors T. Chang, G. B. Crew, and J. R. Jasperse, Scientific Publishers, Inc., Cambridge, MA (1988).

"Plasma Waves Associated with Diffuse Auroral Electrons at Mid-Altitudes", J. R. Sharber, J. D. Menietti, H. K. wong, J. L. Burch, D. A. Gurnett, J. D. Winningham, and P. J. Tarakanen, Adv. Space Res., 8, (9), 447-452, (1989).

"Modeled F-Region Response to Auroral Dynamics Based Upon Dynamics Explorer Auroral Observations", J. J. Sojka, R. W. Schunk, J. Craven, L. A. Frank, J. R. Sharber, and J. D. Winningham, J. Geophys. Res., 94, 8993-9008 (1989).

"Plasma and Field Properties of Suprathermal Electron Bursts", R. M. Robinson, J. D. Winningham, J. R. Sharber, J. L. Burch, and R. Heelis, J. Geophys. Res., 94 12031-12036 (1989).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research project was an investigation of the continuous/diffuse aurora and related auroral studies using as the primary data observations from instruments on the Dynamics Explorer satellites. These satellites carried particle detection instrumentation referred to as the High Altitude Plasma Instrument (HAPI) on the DE-1 and the Low Altitude Plasma Instrument (LAPI) on DE-2, and together provided high quality spectral and angular measurements of electron and positive ions at altitudes between 500 km and $4R_E$ above the auroral region. The objectives of the research were: (1) to provide a thorough description of the particle populations that produce the quiet and active continuous/diffuse aurora, (2) to determine what mechanisms act within the plasma sheet and on supra-auroral field lines to precipitate the continuouse/diffuse auroral particles, (3) to find a simple and effective way to model the effects of this aurora, and (4) to apply the Dynamics Explorer database to selective investigations of the high-latitude auroral regions.

Objectives (1), (2), and (4) were successfully completed. Objective (3), the modeling objective, was completed to the point of determining spectral shapes typical of the diffuse auroral electron and ion populations, but it was not extended to all local time sectors. The research included a description of quiet and disturbed diffuse auroral particles, a study of particles and waves in the diffuse aurora, an attempt to determine the mechanisms of the precipitation, and studies of polar arcs, ionization, and convection in the high-latitude regions.

The most significant accomplishments are:

(1) Coordinated study of the evening sector aurora and associated ionization. This was a comprehensive investigation involving DE-2, NOAA-6, and Chatanika radar observations that enabled a very thorough description of a moderately active diffuse aurora from the standpoint of particle (electron and ion) precipitation, E and F layer ionization, field aligned current regions, and magnetosphere/ionosphere electrodynamics.

(2) Observation of the electrostatic and electromagnetic waves associated with the diffuse aurora and identification of electron acoustic mode waves associated with upward electron beams in the diffuse auroral region. This resulted from a survey of mid-latitude (DE-1) simultaneously measured particle and wave data. Implications of these and other wave observations to the diffuse auroral electron precipitation mechanism are provided in the Final Tecnical Report.

(3) Investigations of the diffuse auroral region, the trough, and the plasmapause have provided additional boundary conditions associated with the 10 eV electrons in the presence of high energy dumping events seen in the precipitating (>15 KeV) LAPI electron and Geiger counter (>35 keV) fluxes. Results are consistent with Coulomb scattering of ring current $O^+$ ions with plasmaspheric electrons.

(4) The determination of coherent mesoscale convection patterns in the polar cap and their relationship with particle precipitation. The study established the importance during IMF north conditions, of extended, "finger-like" convection patterns in the the polar cap and the one-to-one correspondence of these elongated cells with electron precipitation field aligned currents, and gradients in the plasma (ion) drift veocity where the $V.E < 0$ condition is met. Essential in the study was the combination of the DE-2 observations and the AFGL all-sky photometric images.

AFOSR Program Manager: Lt Col James G. Stobie, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Sensitivity Evaluation Plan for LOWTRAN

PRINCIPAL INVESTIGATOR:
Professor Ken Tomiyama
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Pennsylvania State University
University Park, PA 16802)
(Now at
Department of Mechanical Engineering
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Setagaya, Tokyo 157 JAPAN)

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| INCLUSIVE DATES: | 1 June 1987 - 31 May 1988 |
| CONTRACT/GRANT NUMBER: | F49620-87-C-0057 to Pennsylvania State University |
| SENIOR RESEARCH PERSONNEL: | Ken Tomiyama |
| JUNIOR RESEARCH PERSONNEL: | Michael Hogan |

PUBLICATIONS:

"Sensitivity Analysis of LOWTRAN," K. Tomiyama, presented at the Annual Meeting, Optical Society of America, (1987).

"SENTRAN: LOWTRAN Pre- and Post-Processing Utility," K. Tomiyama, M. Hogan, and G. Anderson, SPIE's 33rd International Symposium, San Diego, (1989).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this project was to develop a systematic sensitivity analysis plan for the LOWTRAN program. The plan was to quantitatively and qualitatively evaluate variations in transmittances and radiances computed by LOWTRAN against perturbations in input climatological conditions. Initial effort was spent on determining the optimal method of presenting the sensitivity. The plan evolved eventually into a computer software, called SENTRAN (Sensitivity analysis plan for LOWTRAN). SENTRAN furnishes an extremely efficient and user-friendly analysis environment for LOWTRAN users. It serves as a universal interface to LOWTRAN, and provides the user with (1) interactive entry of LOWTRAN input parameter values, including perturbations to climatological variables, (2) intelligent generation of corresponding LOWTRAN input deck images, (3) autonomous post-processing of LOWTRAN outputs for data extraction, (4) partial derivative evaluation, (5) 2D and 3D plot generation, and (6) a help utility. Since the capability of SENTRAN greatly exceeded the originally conceived specification for the sensitivity analysis plan, its usefulness is not limited to sensitivity analysis as was original intended. It was shown that massive data generation from LOWTRAN can be performed effortlessly with SENTRAN in a fraction of the time required otherwise. It has become apparent that SENTRAN can revolutionize the way in which LOWTRAN is used and the scope of analyses that can be performed.

AFOSR PROGRAM MANAGER: Lt Col James G. Stobie, USAF

# COMPLETED PROJECT SUMMARY

TITLE: Infrared and Ionization Structure of the Polar Mesosphere

PRINCIPAL INVESTIGATOR:
James C. Ulwick
Department of Electrical Engineering
Utah State University
Logan, UT 84322

INCLUSIVE DATES: 19 March 1985 - 15 May 1988

GRANT NUMBER: AFOSR-85-0163

COST AND FY SOURCE: $109,534, FY 85; $100,231, FY 86; $94,218, FY 87

SENIOR RESEARCH PERSONNEL: Kay D. Baker Michael Kelley

JUNIOR RESEARCH PERSONNEL: Glenn Berg

PUBLICATIONS:

"Mesospheric Minor Species Determinations from Rocket and Ground-Based IR Measurements," J. C. Ulwick, K. D. Baker, D. J. Baker, A. J. Steed, W. R. Pendleton Jr., K. Grossmann, and H. G. Bruckelmann, J Atmos Terr Phys, 49, 855 (1987).

"Measurements of Odd Oxygen in the Polar Region on 10 February 1984 During MAP/WINE," P. H. G. Dickinson, G. Witt, A. Zuber, D. Murtagh, K. U. Grossmann, H. G. Bruckelmann, P. Schwabbauer, K. D. Baker, J. C. Ulwick, and R. J. Thomas, J Atmos Terr Phys, 49, 843 (1987).

"Comparison of Simultaneous MST Radar and Electron Density Probe Measurements During STATE," J. C. Ulwick, K. D. Baker, M. C. Kelley, B. B. Balsley, and W. L. Ecklund, J Geophys Res, 93, 6989 (1988).

"Large and Small Scale Organization of Electrons in the High Latitude Mesosphere: Implications of the STATE Data," M. C. Kelley and J. C. Ulwick," J Geophys Res, 93, (1988).

"Comparison of Simultaneous MST Radar and Electron Density Probe Measurements in the Polar Mesosphere," J. C. Ulwick, SPIE, 874, 260 (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of this project was the investigation of the spatial and temporal structuring and photochemistry of the infrared airglow and the dynamic processes that modify the physical and radiative properties of the polar mesosphere. The approach was to perform measurements with ground-based mesospheric/stratospheric/tropospheric (MST) radar and rocket-borne probes together with other investigations in campaigns to obtain a coordinated data base.

Rockets containing DC probes were launched at Poker Flat, Alaska, in two different campaigns to measure electron density irregularities with high spatial resolution. They were launched at times when the MST radar showed regions of intense backscatter in the mesosphere. Large changes and strong gradients in the electron density profiles in general show different characteristics in the peak scattering region. Spectra of the spatial density fluctuations have been derived from the campaign results. In the region of most intense backscatter, the power is up over the whole frequency range by almost 5 orders of magnitude. A comparison between the measured radar echo power and the calculated echo power based on the in situ rocket measurements gives very good correspondence. Several results from the spectra which are in agreement with present theories for mesospheric dynamics and its interaction with the electron gas are as follows: (1) The electron fluctuation spectrum displayed both a Kolmogorov inertial subrange and a viscous subrange characterized by an inner scale for turbulence; (2) A neutral density fluctuation strength of 1% integrated was estimated over the range from 1 m to 700 m, a result in agreement with other mesospheric observations; (3) The inner scale size for the electron gas varies with the energy dissipation rate in a manner predicted by classical turbulence theory; (4) The 50 MHz scattering signal is in qualitative agreement with the _in situ_ measurements. Some of the more controversial results were: (1) The microscale for turbulence in the electron gas is much smaller than expected; (2) The electrons seem to behave as a passive scalar but one with a large Schmidt number; this in turn may be due to an anomalously high ion mass; (3) The fact that strong high latitude mesospheric scatter occurs at all for a 50 MHz radar is due to the unusual character of the electron spectrum; (4) For weak electron density gradients the electron spectrum has a Kolmogorov form, but for the case of strong gradients, the spectrum is steepened. In addition to these results, evidence was found for an outer vertical scale near 700 m in the large scale organization or electrons by the neutral dynamics just above the mesopause. Imbedded in these large scale electron density oscillations are peaks in the short wavelength fluctuations ($\lambda \approx 3$m) which occur when the electron density is at a local minimum. Analysis of the interaction with the neutral gas shows that the turbulence is strongest when the neutral gas is moving upward, with weaker short scale irregularities found when the perturbation velocity is downwards.

AFOSR Program Manager: Lt Col James P. Koermer, USAF