NASA MULTIDISCIPLINARY RESEARCH GRANT
NLG 26-008-006
Final Report
FINAL REPORT

NASA MULTIDISCIPLINARY RESEARCH GRANT

NLG 26-008-006

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I. INTRODUCTION

The NASA Multidisciplinary Research Program at Washington University

Washington University first requested NASA Sustaining University Program Research funds in a proposal dated July 29, 1963. Since that time $1,600,000 of SUP Research funds have been provided by NASA in support of our Multidisciplinary Research Program (MRP).

In the original 1963 application, Provost George Pake requested the funds in order to strengthen the physical sciences and engineering and in order to encourage the University tradition of inter-disciplinary cooperation. Over the years our specific program goals have included: the training of students, the increase of our space-related activities, the increase of multidisciplinary activities and the development of programs connecting technical science and social problems. Some principal features of our pursuit of these goals will be summarized in the following sections of this report. The MRP work has been directed to four major areas: Space and Planetary Science; Materials and Radiation; Systems, Instrumentation and Structures; Technology and Man. Each will be discussed in turn.

In the present section, we wish to present a brief summary and some statistical information designed to place the multidisciplinary program in perspective at Washington University.
Since the NASA MRP grant was awarded in 1964, $1,600,000 MRP funds have been received and expended (Fig. 1). During this same interval the total external funds expenditures for the University (exclusive of the medical school) has exceeded $51,000,000; so the MRP funds have represented about 3% of the externally funded work during the interval. Nevertheless, the NASA Multidisciplinary Research Program has had a major impact on the University; an impact far out of proportion to the amount of the MRP funds provided.

This enhanced impact has come about principally because of the flexibility of the program, which arose mainly from the local management feature of the program. The Provost, or Vice Chancellor, with the help of the Space Science Council, could adjust support to take advantage of new opportunities.

It has been possible to support individuals and coalitions who wanted to enter new fields or who had not yet established the reputations necessary to attract project support. Thus the MRP funds have served as a form of venture capital and have been used to initiate a number of new enterprises, many of which have succeeded admirably.

For example, in the first year of the program considerable support was given to developing the Engineering Computer Laboratory. Once that was in place, support was shifted to faculty who could make best use of the Laboratory and had been stimulated by working with its people.
FIGURE 1

MRP EXPENDITURES AND TOTAL EXTERNAL FUNDS EXPENDITURES (EXCLUSIVE OF THE MEDICAL SCHOOL), BY FISCAL YEAR
In another case the investment of limited funds in an alpha-particle track detection scheme have resulted in a larger program which now has led to an experiment scheduled to fly to the moon on Apollo 16 (Sec. IV).

Some of the faculty members receiving support under the MRP have established close working relationships with NASA Laboratories and have served on various NASA panels. Professor Barbara Shrauner, who works in the field of space plasma theory, collaborates with NASA personnel at Ames Research Center and Goddard Space Flight Center. Professor Robert Walker serves on the NASA Lunar Sample Review Board.

The 1963 proposal set forth the criteria for the support of projects: relevance of the work to the understanding and exploration of space, quality of the proposed research, potential of the proposed program for further development, promise of the principal scientists for growth and accomplishment.

A listing of the titles of the various projects supported is given in Appendix A and the work on each is summarized in Appendix D.

During the course of the MRP, the program has benefitted from the participation of:

- 52 faculty members
- 98 graduate students
- 24 undergraduate students
The MRP support has been instrumental in the production of

57 doctoral degrees (Ph.D. and D.Sc.)

88 publications.

Additional degrees and publications will result from work presently in progress and from the research capabilities established under MRP support. A listing of publications is given in Appendix B and major equipment purchases are tabulated in Appendix C.

Some of the MRP work has been conducted within the Laboratory for Space Physics, which is located in the upper floors of Compton Laboratory, whose construction was supported by a NASA SUP Facilities Grant. Other work, for example that within the Interdepartmental Optics Laboratory, has been performed in space freed for the work by the opening of Compton Laboratory in the fall of 1965.
II. MAJOR ACCOMPLISHMENTS OF THE MULTIDISCIPLINARY RESEARCH PROGRAM

Appendix D presents a detailed recitation of the multitude of accomplishments under MRP support. It is difficult to select the major accomplishments from such a diverse and excellent array. Nevertheless, the following brief listing identifies a few of those accomplishments which clearly are of superior significance:

A. Space and Planetary Science

1. The development of an alpha-recoil track method of absolute age dating (from a joint Earth Science-Physics project) has led to an Apollo 16 experiment and promises to permit significant advances in archeological dating. (R. Walker, page D89).

2. The design and flights of an infrared telescope (M. W. Friedlander) which has led to the discovery of several localized infrared sources in space. It is notable that this work has involved the work of a NASA trainee and also cooperation with another university. (page D70).

B. Materials and Radiation

1. The establishment of the highly successful Thermodynamics Research Laboratory was greatly facilitated by MRP funds (p. D3).

2. The research initiation support for a group of young chemists has led to significant results on reaction rates (Kurz, p. D15), semiconductor radiation detectors (Sarantites, p. D22), and the theoretical analysis of time-dependent systems (Yaris, p. D24).

C. Systems, Instrumentation and Structures

1. Research on the Gunn effect and its application to microwave generation and detection (Rosenbaum, p. D58) has led to a novel microwave swept frequency oscillator and to improvements in understanding noise, modulation and oscillations in Gunn devices. The work has involved close cooperation with local industry.

2. The work on quantum electronics (Chang, p. D43) and on semiclassical radiation theory (Jaynes, p. D71) have led to a successful joint interdepartmental effort (now supported by the AFOSR) on quantum optics. The significant results include work on mode-locking of multiple transitions in lasers and the successful advances of semiclassical radiation theory to yield important new results and predictions.
D. Technology and Man

The most important accomplishment in this area has been the imitation of the program on the Application of Satellite Communication to Educational Development. This effective interdisciplinary activity continues to be a vigorous and socially-significant project (Morgan, p. D1).
III. IMPACT OF THE MULTIDISCIPLINARY RESEARCH PROGRAM

In Section I we cited some numerical data as rough measures of the effectiveness of the MRP: 57 doctoral degrees, 88 publications, etc. However, in a larger sense, these indicate only a part of the impact of the program. Particularly in the area of broadly interdisciplinary activities, the MRP needs to be viewed within the framework of the many broadly-based efforts at Washington University.

The University has a long and substantial record of interdisciplinary research activities and community involvement. These effective and successful activities have been based, for the most part, on the teaching and research of individuals within the various disciplines and departments. For example, the Social Science Institute joins social scientists, law faculty, architects, medical faculty, and engineers in joint attacks on community problems through research. In the Medical Care Research Center, social scientists, medical clinicians, and engineers combine to study the impact of medical culture on the hospital care of the sick. The Dean of the School of Social Work headed the St. Louis Human Development Corporation in the critical first year of its operation, when policies and programs for utilizing federal and local money were being established.
The Computer Research Laboratory and the Biomedical Computer Laboratory join computer scientists, electrical engineers and medical scientists and technicians in applying computer techniques and capabilities to the novel solution of critical medical problems. The Center for the Biology of Natural Systems was started in February, 1966. It has joined staff from the St. Louis Zoo and the Missouri Botanical Gardens with Washington University faculty in the physical and biological sciences, medicine, and sanitary and environmental engineering to do research on plants, or animals viewed as systems or sub-systems. The Center's program is specifically designed to help repair some of the inadequacies in the present relationships between basic research and the practical problems of environmental biology and health.

The Institute for Urban and Regional Studies, established in 1961, provides a focus for expanding cooperative approaches to urban problems by faculty members and students from architecture, law, economics, sociology, political science, applied mathematics and computer science, education, and anthropology. Research on the effect of public transportation on ghetto area unemployment, on the determinants of the spatial form and performance of the city, and an analysis of developmental benefits of water resources investments are some of its recent research programs.
The Laboratory for Space Physics is directed by Professor R. M. Walker, the McDonnell Professor of Physics. A broad program of space studies is carried out involving close cooperation among personnel from physics, chemistry, and earth science. Current projects include several novel experiments on particle tracks in solids: studies of fossil particle tracks in terrestrial samples, meteorites and the lunar surface, and the use of solid state track detectors for cosmic ray studies. Laboratory personnel collaborate in a program in sub-millimeter astronomy and in an HEAO satellite-borne cosmic gamma ray experiment.

The Center for Development Technology has been established in response to the need for creative efforts on the part of developed countries to help the less affluent nations utilize science and technology for the benefit of their people. World peace and mutual understanding among peoples depend heavily on whether the gap in well-being between the "have" and "have not" nations of the world can be narrowed.

The major functions of the Center for Development Technology include research and development, education, and demonstration. The Center draws most of its present research support from the broad NASA program on the Application of Satellite Communications to Educational Development, which program was initiated under NASA MRP support.
Most of these interdisciplinary programs, and many others, have been carried out, in part, by some faculty and students who also participated in the NASA Multidisciplinary Research Program. The interchange of personnel is known to be a highly-effective mode of information transfer. Thus the participation of MRP personnel in other broad-gauged activities has represented a valuable cross-flow within the University. The MRP proposal submitted to NASA in December 1968 was prepared following many lively meetings of a multi-disciplinary advisory council which included faculty members from a variety of disciplines:

W.S.C. Chang (Electrical Engineering)
R. E. Norberg (Physics)
S. Sutera (Mechanical and Aerospace Science)
D. Lipkin (Chemistry)
R. Boguslaw (Sociology)
M. Weidenbaum (Economics)
R. Salisbury (Political Science)
G. Whitaker (Business Administration)
R. Walker (Physics)

One principal result of these efforts was the initiation of our highly successful NASA-supported research effort on "The Application of Satellite Communication to Educational Development". The educational satellite program is summarized
in Appendix IV D. 1, but it should be emphasized here that
the satellite program is one of the outstanding examples
of the continuing impact of the NASA Multidisciplinary
Research Program at Washington University.

Other examples of new activities in the University
in which the impact of the NASA Multidisciplinary Research
Program can be perceived include:

1. The new masters degree programs, in Engineering
   and in Arts and Sciences, in Technology and
   Human Affairs.

2. A number of new multidisciplinary General Studies
   Courses taught by MRP personnel, e.g.:

   GeSt. 245  Energy and the environment
              (Klarmann and Morgan)
   GeSt. 246  The conversion of military-oriented research and
t              development to civilian uses
              (Walker, Morgan and Hochmuth)
   GeSt. 260  Science and man's self-image
              (Shrauner)
   GeSt. 276  Technology, Urbanization and
              International Development
              (Falconer and Morgan)
   GeSt. 408  Research in the university
              (Pake and Pittman).
Finally it should be pointed out that the MRP funds provided a research start in new areas for a number of young faculty members. Their continuing work and the research facilities established will provide a continuing impact in years to come. The feature of the MRP support essential for these research initiation efforts has been the flexibility of the MRP support resulting from the local management feature of the program.
IV. PARTICIPATION IN SPACE FLIGHT EXPERIMENTS

The MRP support has led to a number of instances of direct Washington University participation in space flight experiments. Among these are:

1. **Apollo 16 Experiment**

   As a result of the MRP work of R. M. Walker (page D89) an experiment has been developed for Apollo 16. Mica detectors will be flown to the moon in order to measure the flux of heavy particles in the solar wind.

2. **HEAO-A Experiment on Extremely Heavy Nuclei in Cosmic Rays**

   M. H. Israel is principal investigator of a joint experiment (with the California Institute of Technology and the University of Minnesota) on extremely heavy nuclei in cosmic radiation. Our participation in the experiment is an indirect result of MRP support of research in the Laboratory of Space Physics (Friedlander: Submillimeter and Far Infrared Astronomy; Walker and Johns: Alpha-Recoil Track Method) and of the NASA Facilities Grant in support of the Laboratory of Space Physics portion of Compton Laboratory in which the HEAO experiment is being developed.

   It is probable that other space-flight experiments will follow from other work now in progress.
APPENDIX A

RESEARCH PROJECTS SUPPORTED UNDER NASA -

NSG-581-26-008-006

I. SPACE AND PLANETARY SCIENCE

II. MATERIALS AND RADIATION

III. SYSTEMS, INSTRUMENTATION AND STRUCTURE

IV. TECHNOLOGY AND MAN
I. PROJECTS IN SPACE AND PLANETARY SCIENCE

L. Scharon and E. Mateker (Earth Sciences)
Methods in Geo-Physical Exploration

W. Johns (Earth Sciences)
a) Geochemistry of Ce, F, and B in Terrestrial Rocks
b) Geochemistry of F, Cl, and B in Argillaceous Sediments
c) Amino Acids in Ancient Sediments

W. Johns (Earth Sciences) and R. Walker (Physics)
Development of Non-Destructive Neutron Activation Methods for Chemical Analysis of Terrestrial and Extra-Terrestrial Rock Samples

K. Condie (Earth Sciences)
a) Geochemical and Structural Evolution of the 2.5 - 2.7 Billion Year Old Wyoming Crust
b) Partitioning of Elements between Co-Existing Phases in Granitic Batholiths
c) Rates of Chemical Differentiation of the Earth as Inferred from Basalts

H. Potratz (Chemistry) and K. Condie (Earth Sciences)
Geochemical Studies of Ultramafic Rocks and the Earth Upper Mantle (Thorium and Uranium Contents)

H. Potratz (Chemistry)
Thorium and Uranium Content of Ultramafic Rocks

L. Scharon (Earth Sciences)
a) Magnetic Properties of Ultrabasic and Associate Alkali Rocks
b) Magnetic Properties of Ultrabasic Rocks and Associated Alkali Igneous Complexes
N. Katz and E. Rodin (Applied Mathematics and Computer Science)
A New Approach to Axisymmetric Nonlinear Wave
Propagation in Thermoviscous Media

B. Shrauner (Electrical Engineering)
Collisionless Blast Waves in a Plasma with Anistropic Pressure

M. Friedlander (Physics)
a) Sub-Milimeter Astronomy
b) Far Infared Astronomy

P. Phillips (Physics)
a) Anomalous Spin Interactions
b) Search for a Preferred Frame of Reference
c) Modern Analog of the Michelson-Morley Experiment

J. Brice and W. Johns (Earth Sciences)
Amino Acids in Recent Sediments

J. Brice and K. Condie (Earth Sciences)
Petrochemistry of An Ultramafic Body
II. PROJECTS IN MATERIALS AND RADIATION

M. Wittels (Earth Sciences, Physics)
Studies of Radiation Damage in Crystals

M. Muller (Electrical Engineering) and D. I. Bolef (Physics)
Rare Earth Fluorides

P. Gaspar (Chemistry)
  a) Mechanistic Organic Electrochemistry: Oxidative Decarboxylation of Malonate Ions and Oxidation of Oximes
  b) Reaction Studies of Hot Silicon Radicals
  c) Reactions of Divalent Carbon, Silicon and Germanium Species

B. Smith (Chemical Engineering)
Extension of Molecular Corresponding States Theory to Non-Random Liquid Mixtures

B. Smith, A. DiBenedetto and E. Bagley (Chemical Engineering)
Thermodynamic Laboratory for Research on the Behavior of Liquids and Liquid Mixtures

J. L. Kurz (Chemistry)
Methods of Transition State Characterization

D. Sarantites (Chemistry)
Semi-Conductor Studies and Nuclear Spectroscopic Studies

L. Helmholz (Chemistry)
  a) Investigation of Complex ions
  b) Investigation of Electronic Structure of Transition Metal Complex Ions
  c) Investigation of Complex Ions: Comparison of Optical and Electron Spin Resonance Spectroscopy of Inorganic Complex Ions
A. Hortmann (Chemistry)
   Synthesis of Unknown Strained Ring Systems

R. Yaris (Chemistry)
   Use of Time Dependent Methods in Atomic and Molecular Quantum Mechanics

A. Wahl (Chemistry)
   Short Lived Fission Products

D. Gutsche (Chemistry)
   Mechanism of the Carbene C-H Insertion Reaction

R. Berg (Chemistry)
   a) Spectroscopic Studies of Metal Halide Vapors
   b) Spectroscopic Studies of High Temperature Gaseous Species and Long Range Order in Dye Polymer Systems
   c) Spectroscopic Studies of High Temperature Gaseous Species
III. PROJECTS IN SYSTEMS, INSTRUMENTATION AND STRUCTURES

K. Hohenemser (Mechanical and Aerospace Engineering)
   a) Lifting Rotor Research
   b) Wave Interaction in Supersonic Ejection

J. Zaborszky (Mechanical and Aerospace Engineering)
   a) Systems Identification
   b) Systems and Automatic Control
   c) Application of State Variable Techniques to the Solution of Control Engineering Problems
   d) Sensitivity of Functional Analysis for Control Systems

J. Zaborszky and Chidambara (Mechanical and Aerospace Engineering)
   Systems and Automatic Control

W.S.C. Chang, H. Guckel, F. Rosenbaum, M. Muller (Electrical Engineering)
   a) Investigation of Submillimeter Waves via Gas Laser Techniques
   b) Studies of Coherence Properties of Extremely Short-Pulsed Lasers
   c) Solid State and Quantum Electronics Research

D. Wann (Electrical Engineering)
   Engineering Computer Lab

R. Gregory (Electrical Engineering)
   A Method of Temperature Measurement

F. Rosenbaum and Tsai (Electrical Engineering)
   Gunn Effect Oscillators and Their Microminiaturization
E. Weger (Chemical Engineering)
  a) Momentum and Heat Transfer Characteristics of Circular Turbulent Impinging Jets with Large Temperature Gradients
  b) Char Densification and Ablative Materials

Tomich and Weger (Chemical Engineering)
  Velocity and Temperature Profiles in Compressible Turbulent Free Jets

R. Sundfors (Physics)
  Technique of Coupling Short Pulses of Acoustic Energy to Nuclear Spin Systems

D. Bolef and J. Burgess (Physics)
  Acoustic Spectrum of Solids

E. T. Jaynes (Physics)
  Noise Reduction in Lasers and Masers

B. Pate (Chemistry)
  Semi-Conductor Gamma Detectors

K. Luszczynski and R. Norberg (Physics)
  Cryogenic Detectors

E. Mateker (Earth Sciences)
  Development of an Analog-to-Digital Conversion System

L. Cooper (Applied Mathematics Computer Science)
  a) Mathematical Programming
  b) Non-Linear and Combinatorial Optimization

R. Cook (Applied Mathematics Computer Science)
  a) Integer Programming
  b) Integer Linear Programming
IV. PROJECTS IN TECHNOLOGY AND MAN

R. Morgan (International Development Technology Center)
Application of Satellite Communication to Educational Development

A. Przeworski (Political Science)
Impact of the Information about the State of the Political System on the Economic Decisions.
APPENDIX B

LIST OF PUBLICATIONS


Guernsey, R. W., W. C. Mitchel and K. Luszczynski, "Negative Fluctuations in Temperature Generated by Heat Pulses in He4 at 1°K", Cryogenics 1, 110 (1967).


"Excitations Radiated from a Thermal Source in Helium II below 0.3°K", Phys. Rev. 3, 1052 (1971).


APPENDIX C
MAJOR EQUIPMENT PURCHASED

Equipment Over $1000

Spectra-Physics Model 130 Gas Laser $1,525
Tektronix Type 454 Oscilloscope $2,550
CVC Evaporator System $5,636
Frequency Counter $1,498
Mossbauer Effect Spectrometer $3,380
Component Electronic parts
One Oscilloscope Tektronix 547 $1,875
One Electronic Monometer: GGS 1014 $1,050
One Oscilloscope Tektronix: 535A $1,400
Tektronix 453 Oscilloscope $1,017
Chart Recorder, Electronik 16 (Honeywell) $1,465
Three Heliflux Null Detectors (Schonstedt) $1,305
Oscilloscope and Camera, Type 454 (Tektronix) $3,158
10 Mc/s Scaler (Transistor Specialties, In.) $2,151
Model RRA-5 Amplifier $1,650
Recorder #19301 $1,995
Model 1200A Oscilloscope with Test Mobile $1,998
Tektronix Model 491 Spectrum Analyzer $3,900
Photo-resist Spinner $1,233
Laminar Flow Bench $1,475
High Vacuum System $7,000
Reichart Microscope $4,719
RIDL Designer Series Equipment $2,246
- case and power supply, high voltage
- power supply amplifier, preamplifier,
- scaler and rate meter
Servo-Riter Recorder $1,805
Fisher Isotemp Water Bath, Conductivity Bridge and Conductivity Cell $2,210
Proton Stabilization Conversion Kit for DP60 Spectrometer $8,500
Bridgeport Milling Machine and Accessories $3,463
Spectrometer and Decoupler $4,066
Nuclear Digital Printer $2,725
Jarrel Ash Recording Electronics 82-110 $1,200
Ozonater and Ozone Meter $2,413
Preset Interval Timer and Internal Clock Pulse Generator $1,168
Hewlett Packard Meter and Bridge $1,008
Varial Temp. probe for Varian Spec. $1,801
Power Supply, Discriminater, Rate Meter, Scaler, Preamplifier and case for first four items $1,124
Oscilloscope $2,050
Varian Mass Spectrometer $2,000
Jarrel Ash Grating $1,331
No. V-3523A NMR with Cabinet $1,252
MHZ Probe with Sidebands $1,645
Monroe Calculating Machine $1,175
Nuclear Data Polaroid Printer $1,504
Counting Equipment sample charger $2,496
Philips Electronics Co. X-Ray equip. $5,344
Tool Room Lathe $4,280
Xenon Arc Lamp, Power Supply and Control $1,577
Wang Lab Model 320 Electronic Package and Keyboard $2,095
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<th>Equipment Description</th>
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<tr>
<td>One PS 60Aw Pulsed NMR Spectrometer</td>
<td>$9,868</td>
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<tr>
<td>Ortholux Research Microscope - Adlon Instruments</td>
<td>$3,000</td>
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<tr>
<td>Capacitance-Measuring Assembly with Sample Holder</td>
<td>$2,480</td>
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<tr>
<td>Electronik Compact Portable Strip Chart Recorder</td>
<td>$1,100</td>
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<tr>
<td>Universal Reader with Magnetic Reading Heads and Demodulator Boards and Input Boards</td>
<td>$10,968</td>
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<tr>
<td>Leitz Microscope</td>
<td>$3,000</td>
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<tr>
<td>Labolux-Pol Microscope</td>
<td>$2,043</td>
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<tr>
<td>Nuclear Diodes GE(Ll) Detector System</td>
<td>$9,100</td>
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<td>1024 $10^6$ Channel Analyzer</td>
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<td>Disc Integrator</td>
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<td>Medistor Micro-Voltmeter Model A75</td>
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<td>Hewlett Packard Electronic Counter Model 5246L Option 06</td>
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<td>Hewlett Packard Signal Generator Model 606B</td>
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<td>Artronix Temperature Controller Model 5301</td>
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<tr>
<td>Electronic Associates T48 Analog Computer</td>
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APPENDIX D

DEPARTMENTAL REPORTS

1. CENTER FOR DEVELOPMENT TECHNOLOGY
2. CHEMICAL ENGINEERING
3. CHEMISTRY
4. EARTH SCIENCES
5. ELECTRICAL ENGINEERING
6. MECHANICAL AND AEROSPACE ENGINEERING
7. PHYSICS
APPENDIX D

DEPARTMENTAL REPORT

CENTER FOR DEVELOPMENT TECHNOLOGY
Application of Satellite Communication to Educational Development

(NSG 581-26-008-006)

In the summer of 1969, a research effort was initiated on the application of satellite communication to educational development. Funds were used primarily to support specific research within the subject of interest. However, a second, more long-range accomplishment was the development of an interdisciplinary team of faculty members and students from a variety of disciplines which form the basis for a new and expanded, NASA-supported research effort on the use of satellites for education. The support derived from the NASA Multidisciplinary Research Grant provided crucial seed money for the expanded research program.

During the summer of 1969, three students were supported from the grant. Robert S. Woodward, a graduate student in economics, carried out a background study on the economics of communications and education, and developed some preliminary ideas concerning the development of models for choosing between alternative educational systems. Particular attention was paid to the role of instructional television and communication satellites. Although no formal publication resulted, an unpublished working paper served as useful background material for future investigators at the University.

Mr. James R. DuMolin, an undergraduate student majoring in Latin American Studies, initiated research in two areas: a) background studies on the use of media in education and b) impact of satellite-distributed instruction on Brazilian education and society. This work was useful in helping to define the "software" problems associated with the use of satellite technology in education.

Mr. Amadou Sene, a graduate student in Electrical Engineering, initiated a study of satellite communications and education in West Africa, concentrating on both hardware and software aspects. During the course of the summer, Mr. Sene became interested in hardware research related to low-cost microwave receiver design and went on to do an M.S. thesis in that area.

Another important aspect of the work was that the three research assistants met on a regular weekly basis with a group of faculty members to review background information and develop ideas for an expanded interdisciplinary research effort related to satellites for education. Participating were professors in engineering, physics, law, education and economics. Out of work initiated during the summer came a proposal for a program which is currently being funded by NASA. Two of the three summer student participants and many of the participating faculty members have gone on to play key roles.
APPENDIX D

DEPARTMENTAL REPORT

CHEMICAL ENGINEERING
The expanded program is described in a recent paper presented at an International Conference on Educational Satellites in Nice, France.* This program represents a successful effort to carry out broad-gauged, interdisciplinary, socially-oriented research within a university setting which is directly related to the use and assessment of NASA-derived technology for helping to meet societal needs. It constitutes a major portion of the support for Washington University's Center for Development Technology and has helped spawn a new M.S./M.A. program in Technology and Human Affairs, sponsored jointly by Arts and Sciences and Engineering. It therefore is directly related to the long-range goals of the Sustaining University Program which provided the seed money to get it started.

FACULTY SUPPORTED: NONE

STUDENTS SUPPORTED:

JAMES R. DUMOLIN (B.A.)
Communications Analyst, Center for Development Technology, Washington University

AMADOU SENE (M.S.)
Trainee, African American Institute,
Currently at M.I.T.

ROBERT S. WOODWARD (M.A.)
Currently Ph.D. Candidate in Economics,
Washington University

* Program on Application of Communications Satellites to Educational Development
Robert P. Morgan
Jai P. Singh
Herbert M. Ohlman
James R. DuMolin

This paper was prepared for presentation at the COLLOQUE INTERNATIONAL - LES SATELLITES D'EDUCATION, CENTRE NATIONAL D'ETUDES SPATIALES, Nice, France, May 3-7, 1971.
B. Smith, A. DiBenedetto, and E. Bagley—Thermodynamic Laboratory for Research on the Behavior of Liquids and Liquid Mixtures

B. Smith—Extension of Molecular Corresponding States Theory to Non-Random Liquid Mixtures

The projects listed above will be described together since the second one was a rather small study carried out as part of the larger program in thermodynamics research.

1. The objective of the program supported by the first-listed grant was the establishment of a graduate research facility for research on the thermodynamic properties of liquid mixtures. The facility was established and named the Thermodynamics Research Laboratory in 1967, with Dr. Buford Smith as Director. The NASA funds were used to establish a facility which has since attracted a large number of graduate students and a considerable amount of support from both government and industry sources.

The second project listed above used $2,000 of NASA support to study the applicability of conformal solution theory to liquid mixtures of engineering interest. The funds were used for computer charges. It was found that the theory formalism could be modified to provide an effective correlation for the simultaneous correlation of vapor-liquid equilibrium, heat of mixing, and volume change of mixing data.

Since the initial NASA grant award was made in 1966, the principal investigators in the Laboratory have obtained a total of $171,000 in National Science Foundation Grants to support graduate research in the Laboratory and $155,000 has been obtained from industrial sources. Seven students have completed doctoral dissertations in the Laboratory and, as of June 30, 1971, eleven students were working on graduate research projects. Seven participating companies are now providing $5,000 per year each for general support of the Laboratory program. The Laboratory has begun to attract attention as a major source of new technology in its area of operation and is now generating written publications at the rate of about six to eight papers per year.

2. The NASA support was instrumental in the preliminary work, planning, renovation, and equipping of the Thermodynamics Research Laboratory. Since these funds could be used for this purpose, the provided a very important head-start that got the Laboratory underway much sooner than would have otherwise been possible.
3. The Laboratory has provided an effective interface between the academic graduate research program and engineering practitioners in industry. Each company participating in the Laboratory program names one of its experts in thermodynamics as an advisor to serve on the Laboratory's Industrial Advisory Board. This Board has been an effective mechanism for keeping the Laboratory's research program relevant to real problems. A one-day review meeting is held each year for the advisors, and all graduate student committees have one industrial advisor as a member.

The Laboratory's function is to fill the gap between the engineering practitioner in industry and the theoretical physicists and chemists doing research in the structure of liquids. Industrial advisors provide contact with the engineering practitioners. Professor Ronald Lovett of the Chemistry Department at Washington University provides contact with the theorists. Professor Lovett is a theoretical chemist interested in radial distribution function theory. He sits on most of the graduate student committees and is essentially directing the dissertation project of one doctoral student who is investigating the potential long range usefulness of radial distribution function theory as an engineering tool.

4. The following students received some direct support from the NASA Grant in either stipends or tuition payments:

William J. Calvin (D.Sc.-1969)—presently employed by Esso Engineering at Linden, New Jersey

J. J. Houng (D.Sc.-1970)—present whereabouts are not known.


Two equipment items costing more than $1,000 were purchased with the NASA funds. These were a fume hood ($1,215) and a gas chromatography unit ($4,753).
The two supported projects listed above will be discussed together for purposes of this description since they were part of a single project. The discussion will follow, insofar as possible, the five headings which were given in the June 2 memo requesting information for the final report on NASA Multidisciplinary Grant.

1. The objective of this study was to obtain information on heat and momentum transfer in jets of heated air which were impinging normally on a plain surface. The air was heated sufficiently so that it could be considered a compressible fluid. The work was undertaken because a gap has existed in the heat transfer literature on this phenomena, which is of wide spread practical importance.

Some examples that might be cited of applications of the results of this work include heat transfer to a rocket launching pad from a rocket which is firing on the pad, fluid mechanics of ground effect vehicles, the temperature and velocity field in the vicinity of the engines of vertical takeoff aircraft, and effects encountered in a variety of drying operations where the drying is carried out with blasts of heated air.

The work was divided into two parts. The first part dealt with the structure of the free jet, that is, before it encounters the impingement surface, the second part dealt with the characteristics of the flow over the surface.

For the free jet, the jet Mach number and jet temperature ratio have been found to be the only two initial jet properties which are necessary to characterize the dimensionless velocity and temperature variations in this type of jet. Modifications of dynamic eddy transfer coefficients given in the literature were used in the solution. An experimental program was carried out to obtain data on free jet velocity and temperature variation at high initial jet temperatures and high subsonic Mach numbers where there was a lack of experimental data. The numerical solutions of the time-averaged conservation equations were shown to agree well with the experimental data of this study.
For the wall jet part of the study finite difference techniques were used for the calculation of velocity and temperature profiles. Comparison with experimental data showed that the eddy transfer coefficients which had to be used were functions of the distance from the plate throughout the flow field of the wall jet. Nozzle exit Mach numbers ranged up to 0.85 and nozzle exit temperatures up to 1500° F. The applicability of the calculation method was thoroughly checked for regions of flow extending up to 12 nozzle diameters from the axis of symmetry. The use of the empirical eddy transfer coefficients developed in the study makes it possible to calculate temperature and velocity profiles at any point in the wall jet flow field if the starting profiles are known or given.
E. Weger—Char Densification and Ablative Materials

1. The work done under this grant was part of a larger project, most of which had been supported by the Ballistic Systems Division of the U.S. Air Force. It involved a study of the carbon deposition process which takes place in charred ablative materials during reentry maneuvers. This carbon deposition changes the internal structure of the char and affects the flow of gases and pressure drop through the char during the reentry process. It is therefore important to be able to predict the rate at which carbon deposition occurs and how it affects the structure of the char.

The chars used in the experiments were produced by charring high performance carbon cloth phenolic deposits in a plasma jet. Gas mixtures typical of the decomposition products of phenolic resins (a typical ablative material) were caused to flow through the chars at temperatures comparable to that of reentry which were induced by an induction device. Data on the structural characteristics and permeabilities of the chars, and the changes which occurred in those properties during transpiration, were obtained. With the aid of kinetic data from the literature a calculational program was developed for predicting the change in permeability of and pressure drop across a growing char.

2. Because of budgetary limitations which were imposed on BSD, they were unable to support the final year of this work. The grant of NASA funds enabled one graduate student, Mr. Jere Brew, to complete his doctoral work on this project.

3. Dr. Jere Brew obtained his Doctor of Science degree in 1968 and is now employed by the Shell Oil Company in Houston, Texas.

The results of the work on the project were described in two reports:


1. Major Areas of Research Effort Support by Grant in Department of Chemistry

Inasmuch as the NASA grant was provided not only to certain specific individuals in the department but to the department in its entirety through the Common Facilities portion, all of the members of the department are listed in this section. In each case an account of their general research interests is provided (taken from the departmental brochure on graduate study), and in those instances where specific NASA support was received an account of the research receiving this support is given.

Berg, Robert A. (Physical Chemistry) (left University June, 1970)

Overall Research Program: A wide range of experimental techniques is being used to study the electronic properties of a particular group of linear dyes, the cyanine dyes. In this category of dyes there are several homologous series within which there is a regular increase, from molecule to molecule, of the conjugated π-electron chain length. Absorption spectroscopy, flash photolysis, and ESR are being used to investigate the ground and excited singlet states, the triplet (phosphorescent) states and the doublet (one unpaired electron) states. The aim of this work is a general description of the electronic distribution in each molecule, and of the trends within each series as the conjugated chain length increases.

Alkali halide molecules have been model systems in many physicochemical investigations because they provide the classical example of ionic chemical bonding. However, relatively little information is available concerning some properties of these molecules in the gas phase, in particular the quantitative nature of the potential energy curves for the ground electronic state as well as excited states, the symmetries of the electronic wave-functions, and the differences of electron distributions between the several states. Such data can be obtained only by gas-phase electronic spectroscopy. Vaporizing these molecules requires temperatures in the range of 500° to 1000°C.

NASA-Supported Work: Work progressed in two areas (a) spectroscopic studies of high-temperature gaseous species and (b) long range order in dye polymer systems. The first of these involved investigations of the electronic spectrum of sodium iodide vapor in the region 4000-4300 Å, of interest because it is the only discrete spectrum among the alkyl halides; all other known spectra are continuous. The appearance of the spectrum proves the existence of bound excited states, a fact known in the 1930's but ignored in the recent literature. The second area included an investigation of the electron spin resonance that was detected
in the starch-iodine complex, and this observation has been interpreted in terms of the "metallic" nature of the system.

De Roos, J. Barry (inorganic chemistry) (left University June, 1971)

Overall Research Program: Complexes of the d\(^8\) transition metals (Ni\(^{2+}\), Pd\(^{2+}\), Pt\(^{2+}\), etc.) provide a large variety of structures (square planer, tetrahedral, trigonalbipyrimadal, etc.) to study the effects of ligands and electronic properties on reaction pathways. Recent research has shown that II bonding ligands (RP\(_3\), CO, CN\(^-\), etc.) will stabilize hydride and zero valent complexes of these metals, but the pathways for the formation of these complexes are uncertain. In the platinum system, the reaction of platinum II phosphines with hydrazine results in both platinum II hydrides and platinum zero compounds. Since both these complexes are produced, several competing pathways must be operative in the reaction. Currently detailed investigations of this and other reactions of the d\(^8\) metals are in progress in these laboratories.

Related research on the structural parameters of metal hydride complexes is also being investigated by nuclear magnetic resonance spectroscopy. The metal to hydrogen bond lengths can be determined by analysis of the resonance spectrum of the complexes dissolved in an oriented solvent (nematic liquid crystal).

NASA-Supported Work: The focal point of research was the chemistry of platinum-II phosphine complexes, particularly in reactions with reducing agents that produce platinum hydride complexes. It has been shown that the initial reaction of cis-PtCl\(_2\)(P\(_3\))\(_2\) with hydrazine is the substitution of a Cl\(^-\) by hydrazine to form the [cis-PtCl\((\text{N}_2\text{H}_4)\)(P\(_3\))\(_2\)]\(^+\)Cl\(^-\) complex. The hydrazine then reacts with a stoichiometric amount of hydrazine to give a complex of the two electron oxidation product of the complexed hydrazine, with the following structure.
This initially formed product can then react by two (or more) pathways, one involving oxidation of the hydrazine ligand to form a platinum hydride complex (and nitrogen) and the other involving reduction at the metal to yield zero-valent platinum compounds. Cyclic voltammetry in acetonitrile solution showed that the reduction potential of platinum (II) in these complexes is high (-1.50V). Coordination of the hydrazine ligand lowers the oxidation potential and provides a low energy pathway for the oxidation of the hydrazine and the eventual production of the platinum hydride. Thus, the product of the reaction appears to be dependent on the strength of the oxidizing or reducing agent in the solution. The PtCl₂(ΦCH₂CH₂Φ₂) complex has been prepared and compared with the hydrazine complex. The results show that no detectable amounts of PtHCl(Φ₂CH₂CH₂Φ₂) complex is formed, and the only products isolated were a bridged di-imido complex, analogous to that observed for the cis-PtCl₂(ΦΦ₃)₂ system.

Gaspar, Peter Paul (organic chemistry)

**Overall Research Program:** The goal of physical-organic chemistry is an intimate understanding of the paths of organic reactions. Relationships between structure and reactivity are conveniently studied by building exotic molecules incorporating specific structural features and investigating their spectral and chemical properties. Reactive species are being synthesized in order to determine their "choice" between competing and divergent reaction paths. New methods for the production of certain reactive intermediates such as carbenes are being developed with the goal of studying these species at different energies under widely varying reaction conditions.

Of great interest are the competitive modes of energy dissipation of an excited molecule. That excess energy leads to unusual chemistry is demonstrated by the behavior of carbenes generated by photolysis and pyrolysis. The mechanisms of carbone reactions, whose novelty is virtually unparalleled in organic chemistry, remain a challenge to the physical-organic chemist and are being actively explored in this laboratory. The precise form of excitation responsible for a given chemical change can be studied by varying the source of excitation, by obtaining spectra of the intermediates, and by changing the reaction substrates. Excited molecules can be produced by chemical reaction and by irradiation with visible and ultraviolet light, but the most energetic species available to chemists are atoms recoiling from nuclear reactions. The interaction of "hot" atoms with organic molecules gives promise of new reactions as well as needed information about the energy dependence of mechanisms of known reactions.

**NASA-Supported Work:** Work under this grant has concentrated on the development of a kinetic method for the study of the reactions of ground state triplet carbenes. The goal of the project is to develop an understanding of the detailed transition state structure.
for carbene reactions through direct kinetic measurements. The parameters derived from these rate studies should provide the desired information. Until now carbene reactions have been studied principally by determining the effects of reaction parameters on product yields. The high reactivity and short lifetime of most carbenes have hindered direct kinetic studies.

Two kinetic techniques are being developed for the study of carbene reactions. The first is a flash photolysis-ESR apparatus for the direct monitoring of carbene concentrations by ESR spectroscopy. The second is also an ESR technique employing scavenger molecules as 'spin traps' to convert carbenes to longer-lived free radicals. Progress is being made with both techniques. The most promising spin trap system is the following:

\[
\begin{align*}
\text{N=O} & \quad \text{t}_1/2 \sim 5 \text{ min}
\end{align*}
\]

Gutsche, Carl David (organic chemistry)

Overall Research Program: One of the major areas of investigation in organic chemistry concerns the discovery of methods for the synthesis of organic molecules. Of the numerous classes of organic compounds, the alicyclics have interested chemists for several decades, partly because many important natural products are members of this group and partly because these compounds have provided good test systems for new theories and methods. Particular attention has been given in this laboratory to the development of procedures for the synthesis of alicyclics containing seven-membered rings, bridged rings, and macrocyclic rings. Pertinent to this work are the studies of the reactions of diazoalkanes with ketones, investigations of the chemistry of bivalent carbon (carbenes), and applications of the methods of preparative photolysis.

As the field of organic chemistry has developed, the methods for synthesis have become increasingly refined, and the rationale for a synthesis has become more sophisticated. Among the most delicate and precise organic syntheses are those carried out by living systems under the influence of the enzymes. In the hope of further refining the methods of synthesis available to the chemist, investigations of "enzyme models" are being undertaken. These studies start with the choice of a suitable reaction system (e.g., the condensation of glyceraldehyde with dihydroxyacetone to form fructose, the cyclization of farnesol to terpenes, the
condensation of amino acids to peptides, etc.), continue with an investigation of the mechanism of the reaction, and culminate in the synthesis of a polyfunctional organic compound which catalyzes the reaction in a fashion comparable to that of an enzyme. Through the utility of the techniques of physical organic chemistry, through the use of the modern instrumental methods of structure elucidation, and through the application of "classical" methods of organic synthesis, it is hoped that new approaches to organic synthesis may unfold.

**NASA-Supported Work:** The photo-induced decomposition of pyridine N-oxides is being studied as a means for introducing an oxygen function into unactivated methylene groups. As a part of this study the rearrangement reactions of pyridine-N-oxides under various conditions of irradiation, including intramolecular energy transfer, are being explored. By a careful work-up of the reaction mixture from the photolysis of 2,6-dimethylpyridine-N-oxide the initially-formed 1,2-oxazepin product has been isolated, the first example of this to be achieved although such compounds have been suggested as reaction intermediates in previously-reported photolyses of pyridine-N-oxides.

**Helmholz, Lindsay (physical chemistry)**

**Overall Research Program:** Investigation of the structures of molecules and solids is being carried on by means of several techniques. The diffraction of X-rays by crystalline solids gives information concerning the relative positions of the atoms and molecules making up the solids. Investigations of absorption and fluorescence spectra give information concerning the electronic structure of the molecules or ions; that is, the arrangement of the electrons about the nuclei. Paramagnetic resonance studies of molecules containing unpaired electrons supply information concerning the distribution of these electrons in the molecules. Measurements such as the above may be used to check the results of calculations based on theories of the chemical bond and often suggest necessary corrections or additions to the theory.

The determination of the structure of the solid triamminochromium tetroxide is an example of application of the X-ray technique. Evidence of the degree of covalency in the hexafluoroferrate (III) ion has been obtained from measurements of the magnetic resonance of the paramagnetic ion.

**NASA-Supported Work:** The electron spin resonance spectrum of the ion Cr(CN)$_6^{3-}$ has been observed in a dilute solution in the solid Cs$_2$LiCo(CN)$_6$ in which the site symmetry at the chromium atom in O$_2$. The values of the parameters which are derived from the spectra are in reasonable agreement with those of Rogos and Kaska. The large discrepancy between ratios of $A_p/A_S$ for C in Cr(CN)$_6^{3-}$ and F in CrF$_6^{3-}$ is discussed. Some evidence is presented for a value of $A_S$ for nitrogen in the neighborhood of 0.5 gauss.
The chlorine ligand hyperfine structure has been observed in the EPR spectrum of the octahedral complex ion \((\text{MnCl}_6)^{4-}\), in dilute solution in a single crystal of \(\text{K}_4\text{CdCl}_6\) at room temperature. From isotropic and anisotropic components of the spectrum, it is estimated that \(f_s = 0.40\%\), and \((f_a - f_s) = 3.9\%\), respectively. No chlorine ligand hyperfine structure is observed in tetrahedral complex ion, \((\text{MnCl}_3)^{2-}\), introduced as an impurity in either \((\text{N(CH}_3)_4)_2\text{ZnCl}_4\) or \((\text{C}_6\text{H}_5)_3\text{CH}_3\text{As})_2\text{ZnCl}_4\). A substantial reduction in the manganese nuclear hyperfine coupling constant, \(A_{\text{Mn}}\), is observed in both cases, however, \(A_{\text{Mn}}\) having the value \(-79.50 \pm 0.50\) gauss for \((\text{N(CH}_3)_4)_2\text{ZnCl}_4\), and \(-79.30 \pm 0.50\) gauss for \((\text{C}_6\text{H}_5)_3\text{CH}_3\text{As})_2\text{ZnCl}_4\) compared to \(-86.40 \pm 0.40\) gauss found for \(\text{K}_4\text{CdCl}_6\). The failure to observe ligand hyperfine interactions in the tetrahedral ion is discussed in terms of the larger s-overlaps in the four coordinated compound \((A_s(C1)\approx 0)\) and the increased importance of \(\pi\)-bonding \((A_p(C1)\approx 0)\).

Holtzer, Alfred Melvin (physical chemistry)

**Overall Research Program:** One very large branch of physical chemistry deals with the determination of molecular structure. Since the macroscopic properties of compounds depend on the structure of their constituent molecules, elucidation of molecular structure reveals the underlying basis for the observed behavior of substances and sometimes leads to predictions about properties not yet investigated.

Many substances important in biology are made up of large molecules. Clarification of the relationship of observable biological properties to the molecular constitution of the system thus requires determination of the structures of these large molecules.

Over the years, physical techniques have been developed that make possible the measurement of the molecular weight, size, and shape of macromolecules, and these methods are being employed in this laboratory in examining proteins and polypeptides. For example, recently completed measurements of light scattering, viscosity, and sedimentation in the ultracentrifuge show that the protein para-myosin, which is a major constituent of certain muscles, is made up of rod-like molecules that are 1330 Å long, 20 Å wide and have a molecular weight of 200,000.

As this kind of knowledge accumulates, it becomes fruitful to investigate the molecular structure in greater detail in order to determine the coiling of individual polypeptide chains in the protein and the nature of the intramolecular forces that hold the molecule in its native conformation. Such insight can often be gained by physical studies on simpler, macromolecular substances of synthetic origin that are related to proteins. In this connection, physical studies are also in progress on the molecular structures of simple polypeptides in the presence of various additives.
Overall Research Program: In recent years, interesting and plausible biosynthetic pathways have been proposed for the formation of a variety of naturally-occurring compounds. In addition to providing a powerful guide in the elucidation of the structure of newly discovered natural products, these speculations have also been a contributing factor in the correction of a number of previously established structures and in the correct prediction of the stereochemistry in several compounds.

The interest in the synthesis of natural products in this laboratory centers on those examples which (a) may yield new information regarding the stereochemistry of the system and (b) may lead to the development of new preparative methods. Of particular interest is the development of biogenetically-patterned approaches to these substances. This involves the synthesis of probable biological precursors followed by studies of the conversion of these compounds, by ordinary chemical means, to substances of known structure. In connection with this phase of the work it is contemplated that isotopically-labelled precursors will also be prepared as a means of proving or disproving various new biosynthetic speculations. Several of the projects currently under way involve the application of new photochemical methods to synthesis and the use of spectroscopic techniques to the determination of structure of compounds of the terpene series. An examination of monoterpene biosynthesis in selected plant systems is also in progress.

Another study, unrelated to those described above, involves the development of preparative methods for the synthesis of novel nitrogen and sulfur-containing heterocycles which are of theoretical interest from the standpoint of their chemical bonding. Investigations of the chemistry and spectroscopic properties of two such systems which have been synthesized recently, viz. thiabenzen-1-oxides and 1-azabicyclo(-)butanes, are presently being pursued.

NASA-Supported Work: The object of the work originally proposed was to determine the feasibility of application of newly discovered ylidylic reagents to the synthesis of several strained ring systems which are either unknown or obtainable only with difficulty. The projects were to be exploratory in nature and to provide the basis for further investigations as to the scope and utility of the reactions involved.

Two notable achievements have resulted from this program: (a) The reaction of dimethylsulfoxonium methyldide with acetylenic ketones was found to yield a novel heterocyclic system, the thiabenzen-1-oxide system, rather than the strained bicyclo[1.1.0]butane system which was expected on the basis of the normal pathway followed in reactions of this ylide with olefinic ketones. Since the original publication of the 1-oxide synthesis (Hortmann, J. Am. Chem. Soc., 87, 4972 (1965)) this synthesis has been extended to prepare additional 1-oxides\(^2,3\), and one of these has been converted into the parent thiabenzen system. The chemical bonding of sulfur in
these systems is a subject of theoretical interest and work in this area is continuing. (b) The reaction of dimethylsulfonium methylide with 2-phenylazirines has been found to be a general reaction leading to the 3-phenyl-1-azabicyclobutane system. The 1-azabicyclic system is of theoretical interest from the point of view of the relationship of its bonding structure to that of its carbocyclic analog, and a comparison study of the chemical properties of both systems has evolved from some initial observations made with the support of this Grant.

From a practical point of view, highly strained azabicyclobutane systems, as well as their carbon analogs, should be capable of release of far more energy than their acyclic counterparts on combustion, and could, if even more practical syntheses of these systems can be developed, serve as potential rocket fuels. It is notable that hydrazines incorporating strained rings (e.g., $\text{>N-NH}_2$, $\text{>N-N}$) have already been tested for this purpose.

**Kurz, Joseph L. (organic chemistry)**

**Overall Research Program**: One of the primary tasks of chemical research is the determination of the mechanisms by which chemical reactions take place. According to the transition state theory of reaction rates, the mechanism of a reaction is completely specified by a detailed description of the molecular structures corresponding to the maxima and minima in a plot of the potential energy of a reacting constellation of molecules as a function of the reaction coordinate. The minima correspond to relatively stable structures (reactants, intermediates, and products) which are, in principle, directly observable. In contrast, the structures of the "activated complexes" in the "transition states" corresponding to the maxima in the curve are not directly observable and can be inferred only from the kinetics of the reaction.

Various approaches to the detailed characterization of transition state structure based on the changes in reaction rates as functions of different variables have been used. Two such approaches which remain relatively untested and unexploited are under current investigation in this laboratory. One of these involves the measurement of the rates of corresponding catalyzed and uncatalyzed reactions and the calculation from these rates of the virtual equilibrium constant for dissociation of the catalyst from the transition state. This constant can then be used to calculate extents of bond making and breaking in the transition state. The other approach is based on the measurement of the heat capacity of activation through a precise determination of the temperature dependence of the rate, and the use of this parameter as a measure of transition state solvation.

**NASA-Supported Work**: The continuation of the project, initially supported with NASA funds, has produced several significant results. Among them are: (a) evidence that the rate-determining step in
the H$_3$O$^+$-catalyzed hydration of aldehydes is proton-transfer and not nucleophilic addition, (b) evidence that contributions to observed $\Delta$G$^\neq$ values from covalent bond formation are negligible in aqueous solution, (c) proof that the high dissociation constants of acids such as trichloroacetic are due to unexpectedly low values of $\Delta$S$^\circ$ for their ionization, (d) development of a theory which predicts substituent effects on activated complex structures in $S_n$2 reactions, (e) evidence that the rate-determining process in solvolyses of organic halides is solvent reorganization and not a change in internal structure, and (f) development of a completely new theoretical description of proton-transfer reactions. Although almost all of these results have been obtained after termination of NASA support, it was the NASA grant which allowed the research to be started.

Lin, Tien-sung Tom (physical chemistry)

**Overall Research Program:** Spectroscopy has provided us a doorway to understanding the nature of both the ground and excited vibrational and electronic states of molecules. When molecules are in the crystalline form, the description of the system is modified by various forms of interactions. It is known that most organic solids are in the category of molecular crystals which are defined as having low binding energies. The simplicity of organic crystal symmetry provides us the opportunity to study not just the molecular properties but also various interactions within the crystal. For instance, the vibronic coupling, spin-spin coupling, etc. in molecular crystals can be deduced from such studies. The propagation of excitation energy in molecular crystals imposes a dynamic aspect of intermolecular interactions which can be examined thoroughly via spectroscopic studies. The triplet exciton is the most important and yet the less understood one. The importance of the triplet exciton arises from the fact that the excitation energy into the allowed singled manifold usually intersystem crosses over to the lowest forbidden triplet state. Application of external fields—electric and/or magnetic—will facilitate the assignment of exciton states (spatial and spin symmetry), the ordering of spin substates, and the magnitude of electric dipole moment of the excited states, these will give the electronic distribution and the spin polarization of the observed state. Investigation on the whole exciton band (k dispersion curve) can be made by optical spectroscopy and also by electron paramagnetic resonance (conventional or optical detection technique) on a mixed crystal system. Linewidth studies will also give information on various interactions and rate processes in the excitation of molecular crystals.

The infrared and Raman spectroscopic studies on the ground vibrational exciton states in molecular crystals will yield useful information on intermolecular interaction, phonon states, and the interaction between exciton and phonon. Infrared studies on hydrogen bonding will reveal some details of molecular structure and orientations in vapor, liquid and solid phases. The strength of hydrogen bonding will enable one to explain some extra-ordinary physical and chemical phenomena.
Lipkin, David (organic chemistry)

Overall Research Program: Nucleic acids are currently of great interest because of their unique significance in biological systems. It is recognized that genes are merely specific regions in the enormously complex macromolecules known as the deoxyribonucleic acids. Thus, the whole phenomenon of heredity depends on the molecular structure of these chemical compounds. Furthermore, closely related macromolecules known as ribonucleic acids are intimately involved in the synthesis of proteins in vivo. In this laboratory, work is in progress on the chemical properties of these two distinctively important compounds. The investigations are divided into two parts. Experiments are in progress on the organic chemistry of the macromolecules themselves. These include studies of methods for determining end groups and nucleotide sequences in these naturally occurring polymers, as well as methods of chemically modifying their structure. In addition, work is under way on the chemistry of relatively small molecules (nucleosides and nucleotides) related to the nucleic acids. Recently, this latter line of investigation has led to the synthesis of some interesting naturally-occurring compounds, two of which function as vital coenzymes in living organisms.

Another type of research, entirely unrelated to the work on nucleic acids, deals with synthetic applications of aromatic hydrocarbon free radical anions. An already-completed study demonstrated the use of these compounds as reducing agents of graded oxidation-reduction potentials. Experiments now in progress with these radical anion species are aimed at the hydroaromatic hydrocarbons.

NASA-Supported Work: Electrochemical reactions of anthracene with 1,3-dichloropropane, 1,4-dichlorobutane and 1,4-diiodobutane have been investigated. Dimethylformamide and tetramethylurea were used as solvents, and lithium chloride and tetramethylammonium hexafluorophosphate were used as supporting electrolytes. The products obtained, determined in large part by the supporting electrolyte which was used, were 1,2-propano-1,2-dihydroanthracene, 9,10-propano-9,10-dihydroanthracene, 9-(3-chloropropyl)-9,10-dihydroanthracene, 9-allyl-9,10-dihydroanthracene, 1,2-butano-1,2-dihydroanthracene, 9,10-butano-9,10-dihydroanthracene, 9-(4-chlorobutyl)-9,10-dihydroanthracene and 9,9-butano-9,10-dihydroanthracene.

Lovett, Ronald Allyn (theoretical chemistry)

Overall Research Program: One of the fundamental scientific theories underlying modern chemistry is the kinetic theory of matter. According to this theory the observed properties of matter in the bulk are to be understood as the consequences of a large assembly of fundamental "molecules" acting out the laws of mechanics. The principles and techniques used to quantitatively relate the properties of bulk matter to assumed molecular properties and laws of mechanics are called statistical mechanics.
The class of systems to which statistical mechanics is applicable is obviously very large. Research interests, however, have tended to concentrate on phenomena for which there does not even exist a reasonable qualitative description. In what qualitative was, for example, does a liquid differ from a dense gas? This question becomes particularly acute when one must explain why a dense gas condenses into a liquid, and then even more remarkably why it fails to do so above the critical temperature! An explanation for the rate at which the phase transformation comes about is also needed.

Other topical areas of interest are surface phenomena, electrolyte solutions, and the theory of simple unimolecular reactions.

NASA-Supported Work: The objective of this work has been to incorporate into homogeneous nucleation theory the recent advances in the equilibrium theory of inhomogeneous fluids and in the characterization of fluctuations in a fluid.

The surface tension has been expressed as a formally exact functional of the direct correlation function and numerical calculations have been performed with these assumptions: (a) The point function density in the interfacial region is described with an error function; (b) the direct correlation function is approximated by its low density limit; (c) pairs of molecules interact with the Lennard-Jones potential; (d) experimental coexistence densities are used. The calculated surface tension is a function of the thickness assumed for the interfacial region. This thickness has not been measured (except very near the critical point) but it can be calculated from a fluctuation theory of interfacial structure in terms of the surface tension. Solving these two relations simultaneously gives both the surface tension and thickness. As an example, this procedure predicts a surface tension for argon at 90°K 6% above the experimental value and a thickness of 4.8 Å. Hence the surface tension, one example of a free energy associated with an inhomogeneity, can be calculated rather well by starting with the direct correlation function, and it is expected that the free energy in the nucleation problem will be accounted for with the same accuracy.

A variant of zero-angle light scattering has been analyzed with particular emphasis on the use of this technique for measuring chemical reaction rates. The system analyzed consists of a laser oscillator with a reacting sample placed inside the resonant cavity. Fluctuations about equilibrium of the chemical reaction frequency modulate the oscillator and the power spectrum of the modulating signal is Lorentzian with width proportional to the reaction rate. The modulation signal is very weak, but should be detectable with modern techniques.

In a closely related investigation, an analysis has been made of the contribution of the shot noise inherent in the discrete excitation mechanisms used in gaseous lasers to the finite oscillator line widths. The contribution of this line broadening varies as power⁻¹, in contrast with previously analyzed mechanisms varying as power⁻¹.
Macias, Edward S. (nuclear chemistry)

Overall Research Program: In the past few years experimental tools developed to probe the structure of the atomic nucleus have been applied to other systems with great success. An example is the method of angular correlations, i.e., the measurement of the directional dependence of emitted radiations. The experimental techniques have been refined for detecting the angular correlations of α, β and γ rays emitted in radioactive decay and of particles emitted in nuclear reactions. In the past two years the method has been extended to the measurements of the angular correlations of atomic x-rays following radioactive decay using high-resolution semiconductor detectors. These measurements help to characterize the emitted x radiation. In this laboratory the study of the angular correlations of atomic x-rays following radioactive decay will be continued to determine the properties of the emitted x radiation and to examine the effect of forces which may perturb the angular correlations. The angular correlation of x-rays produced via x-ray fluorescence will also be examined. A possible future experiment is the study of the angular correlations of nuonic x-rays. Nuclear problems under investigation include the angular correlations of γ rays following radioactive decay and the effect of physical environment on the measured correlation functions, and the decay properties of cyclotron-produced radioactive nuclides.

Mastin, Stephen H. (inorganic chemistry)

Overall Research Program: As a result of the nearly simultaneous demands of the atomic age and industry for compounds with new and exotic physical properties, e.g., in the areas of high temperature chemistry, semiconductors, and high energy fuels, there has been a renaissance of inorganic chemistry in the last three decades. One rapidly growing area is concerned with the preparation and properties of organometallic compounds, particularly of the transition metals. These compounds have shown increasing application and relevance to most other branches of chemistry, e.g., organic syntheses, and, in addition, have led to a most fruitful hybridization of concepts from both inorganic and physical organic chemistry in an attempt to explain their bonding and reactivity. For example, the concept of multicenter bonds - originally used in borane chemistry - has found application in the discussion of bonding in carbides such as Fe₅(CO)₁₅C and Ru₆(CO)₁₇C (which contain 5- and 6-coordinate carbon, respectively) and, more recently, in metal-catalyzed reactions of cyclopropanes, while the orbital symmetry rules of Woodward and Hoffman - originally developed for organic systems - have conversely been applied to geometric isomerization reactions of inorganic systems and to transition metal-catalyzed organic reactions.

Two kinds of organometallic systems are under current investigation in this laboratory, metal-carbon σ bonds, as in metal-alkyl and -aryl complexes, and metal-carbon π bonds, as in metal-olefin and -acetylene complexes. These systems are being used for the investigation of a wide variety of problems, from the nature of the
metal-carbon bond in relation to theories of retrodative (or "back") bonding or the nature of the trans effect, to the substituent and neighboring group effects of metals on reactions of organic systems. Such problems involve the synthesis of appropriate model compounds, the development of suitable reaction conditions, isolation and identification of reaction products, and study of reaction mechanism by kinetic and other techniques. Other related studies include investigations of the geometric lability of coordination compounds, particularly of optically active complexes, and the photochemical preparation of organometallic compounds.

Potratz, Herbert August (analytical chemistry) (Professor Emeritus, June, 1971)

Overall Research Program: The principal methods that have been applied in absolute age determination lead to the conclusion that the earth's crust was formed approximately 2 billion years ago and that the development of life on the earth covers a period of about 600 million years. These methods are based on radioactive decay. They rest on the premise that a parent element decays at a known and constant rate into a daughter element either directly or in a radioactive chain and that nothing is added or removed in the process.

The various methods that have been developed for dating ancient materials in the range 1 million to 600 million years old now create the possibility of tracing this interval in considerable detail. More recent materials, that is, materials not over 40,000 years old, can often be dated by the $^{14}$C procedure. No methods have been perfected, however, for bridging the gap, 40,000 years to 1 million years ago. The establishment of dating procedures for this interval is prerequisite to our understanding of the course of events during the Pleistocene epoch, one of the most interesting periods in recent earth history.

A number of potential procedures for dating events over the range, 4000 years to 1,500,000 years ago are being investigated. These studies require measurement of the extent of disequilibrium between certain nuclides of the uranium and actinium decay series in pelagic sediments, investigation of the distribution of these nuclides within the sediments, and interpretation of the results obtained in the light of known geologic history of the specimens.

NASA-Supported Work: Work on the development of a procedure for the determination of thorium in silicate rocks in the parts per billion range has been completed. The procedure involves neutron activation followed by isolation and counting of protactinium-233. This procedure has been applied to a number of samples including a rock that has been selected as a potential standard material and has been distributed by the U. S. Geological Survey.

The development of a procedure for uranium at concentrations below the limits that can be reached by known methods was not under-
taken because this would have required more funds than we had at our disposal. Also, additional refinements in uranium and thorium procedures, published during the time our work was in progress, decreased the necessity for additional work in this area. (Wakita, Nagasawa, Uyeda and Kuno, Geochemical Journal 1, 183-198 (1967)).

The practicability of using a nondestructive method involving neutron activation and high resolution gamma-ray spectrometry in analyzing galena (PbS) for certain trace impurities has been demonstrated. Trace amounts of Na, K, Sr, Ba, Sc, La, Eu, Mn, Co, Cu, Ag, Zn, Hg and Sb in galena have been determined by this procedure. It has also been shown that the sensitivity of the method can be improved and its scope can be extended to include a number of other trace elements in this mineral if antimony is removed from the activated sample before making the gamma-ray analysis.

In barite (BaSO₄) and sphalerite (ZnS), most trace impurities are not readily determined by the nondestructive approach because of interference by the Ba and Zn activities that are produced in activation of the minerals. Here chemical procedures must be used to separate the Ba and Zn activities from activities associated with the trace impurities. Such procedures have also been developed.

Reeder, Paul L. (nuclear chemistry) (left University June, 1970)

Overall Research Program: The energy levels of nuclear systems can be determined by measurement of the decay schemes of radioactive nuclei. These energy levels provide experimental data to which the predictions of various theories of nuclear matter can be compared.

In order to extend the study of decay schemes to nuclei which are far from beta stability, it is necessary to develop techniques of producing, isolating, and measuring these isotopes on a very short time scale. The characteristics of isotopes which decay with half-lives ranging from seconds to milliseconds are currently being studied. These isotopes are produced by nuclear reactions induced by energetic He³ and He⁴ ions at the Washington University cyclotron.

Particular emphasis is currently on the spectroscopy of alpha, delayed-proton, and delayed-neutron emitters as well as on the identification of new isotopes in the light mass region. Some of these isotopes can be measured without separation from other reaction products. When collection and separation are necessary, various procedures such as recoil in gas or on catcher foils are used. Future techniques may include the use of a mass spectrometer or automated chemical separations.

NASA-Supported Work: NASA Funds were used to purchase a stabilized power supply for electronic equipment used in the research described above.
Overall Research Program: A great part of our understanding of the properties and structure of the atomic nucleus is based on experimental evidence from nuclear reaction studies and nuclear spectroscopic measurements. Nuclear reactions are known to proceed via one of two mechanisms, namely, a "direct" interaction of the projectile with the target nucleus or the formation of an intermediate "compound-nucleus." Information concerning the mechanism of a nuclear reaction is obtained in scattering experiments involving nuclear reactions.

Kinetic energy spectra of outgoing light particles and spectra of gamma rays emitted in induced nuclear reactions, when measured as a function of projectile energy and angle of emission, give information about spin and parity assignments of low-lying nuclear energy levels and about the number of levels per unit energy interval at higher excitation energies. Such measurements are made at the cyclotron and the data are processed by use of the electronic computer. The results are compared with calculations based on current nuclear reaction theories.

Nuclear spectroscopic studies following radioactive decay involve the study of the types, energies, and intensities of radiations emitted from specific radionuclides with half-lives as short as a few seconds. The techniques employed in these experiments feature rapid handling, chemical purification, and radiation measurement with use of a pneumatic transfer system (between the cyclotron and the radiochemistry laboratory) whenever necessary. The radiations are assayed with scintillation, proportional, or various types of silicon and germanium semiconductor detectors, coupled with amplifiers and pulse-height analysis equipment. Extensive use of large volume lithium-drifted germanium gamma-ray detectors is made in high resolution studies. Time-(coincidence) and angular-correlations between radiations are extensively investigated in order to measure nuclear half-lives as short as a few nsec, spins of nuclear excited states, multipole mixing ratios, etc. The properties of nuclei thus determined are compared with the predictions of current models for nuclear structure.

NASA-Supported Work: Progress has been made on the research program concerning the production of semiconductor radiation detectors and their use in nuclear spectroscopic studies. Employing the method of parallel drifting sensitive volumes in detectors up to a few cubic centimeters have been achieved. Larger volumes of sensitive volume can easily be achieved, however, using the technique of coaxial drifting. Here, the five faces of the ingot are diffused with lithium employing the same methods as before, except that longer diffusion times are employed so that excess of lithium is diffused to depths of about 1 mm. Several methods of different conditions of drifting have been developed. According to one of these high temperatures ~61°C were used at low DC voltages starting from 80 volts and going down to 30 volts with drifting currents.
ranging from 0.3 to 1.5 amperes, respectively. Under these conditions 5–7 mm depletion depths can be obtained in a few weeks. The diodes thus produced need further low temperature drifting, usually \(24\) hours at \(-67^\circ\text{C}\) in order to improve the diode characteristics.

Considerable success has been achieved in maintaining and operating these diodes as gamma-ray spectrometers when commercial cryostat assemblies were purchased and used. Thus two Nuclear Diodes cryostats have been employed and this eliminated all vacuum failures and high liquid N\(_2\) consumption present in the home-made systems. Thus it has been possible to maintain and operate Ge(Li) detectors over periods of several months without any apparent deterioration in the characteristics.

**Wahl, Arthur C. (nuclear chemistry)**

**Overall Research Program:** The methods of radiochemistry are applicable both to problems in chemistry and to problems in nuclear science. The problems in chemistry under investigation in this laboratory concern the rates and mechanisms of oxidation-reduction reactions, especially those which involve the transfer of electrons. Typical reactions are the isotopic exchange reactions between \(\text{Fe(CN)}_6^{4-}\) and \(\text{Fe(CN)}_6^{3-}\) and reactions between large cations of the type \(\text{Os(phen)}_3^{2+}\) and \(\text{Fe(phen)}_3^{3+}\), in which (phen) represents the chelating ligand 1,10-phenanthroline or derivatives of it. Nuclear magnetic resonance and spectrophotometric methods as well as the methods of radiochemistry are used in the investigations.

Problems in nuclear chemistry of current interest concern the short-lived fission products, their yields, genetic relationships, chemical properties, and radioactive decay schemes. Very rapid chemical separation procedures are used in these studies; for example, exchange of fission-product strontium isotopes with strontium in the surface layer of solid strontium carbonate affords in only a few seconds an efficient separation of these isotopes from their precursors, the rubidium isotopes. Typical problems for investigation are the search for undiscovered isotopes of indium, the genetic relationships between indium, tin, and antimony fission products, the independent yields of tin, and antimony, and iodine fission products, the decay schemes of Sr\(_{93}\) and various other fission products, and the influence of mode of formation on the oxidation states of tin and antimony fission products.

**NASA-Supported Work:** The NASA Funds were used to purchase an automatic sample changer and a coupler to the IBM-526 card punch as part of the automatic beta counting system. The system can now measure the radioactivity of a group of samples automatically and repeatedly (e.g., over night) and record the data on punched cards for analysis on the computer. An "Optikin Fast Digital Printer", a photographic device which allows prompt read-out of the multi-parameter analyzer, has also been purchased, in part with NASA funds.
The equipment has been used for investigation of the yields, genetic relationship, gamma-ray spectra, and/or chemical states of short-lived fission products in the mass number range from 125 to 132, where fission yields increase rapidly for reasons not well understood. The information gained in our investigations about nuclear-charge distribution in this mass-number region may help to clarify the reasons for the asymmetric mass and charge distribution in low-energy fission. The information should also be of use for reactor design.

Weissman, Samuel Isaac (physical chemistry)

Overall Research Program: As various forms of spectroscopy have been developed they have been exploited for studies of structure and processes of chemical interest. Magnetic resonance, a form of spectroscopy which measures magnetic responses of electrons and of nuclei, distribution of electrons and rates and mechanisms of processes which carry electrons and nuclei from one distribution to another are accessible to magnetic resonance. The method is characterized by the enormous range of numerical magnitudes which may be measured. Departure from perfect pairing of electron spins of one part in $10^9$ may be measured in nuclear resonance and complete unpairing may be observed in electron resonance.

In kinetic processes a time scale from $10^{-10}$ seconds to 1 second is accessible. Events occurring in this time range in systems in dynamic equilibrium often produce observable effects in the spectra.

NASA-Supported Work: The NASA funds were used to purchase a Nuclear Magnetic Resonance Specialties high power, coherent pulsed, magnetic resonance spectrometer. Using this instrument, successful line narrowing via the Waugh four pulse sequence has been achieved. The instrument is being used for the study of $\text{P}^{31}$ resonance in solids and in relaxation processes accompanying free radical reactions.

Yarig, Robert (theoretical chemistry)

Overall Research Program: The task of theoretical chemistry is to provide a rational framework which can assimilate, both qualitatively and quantitatively, the data of experimental chemistry. The value of the framework is measured by the extent to which it enlarges our understanding of fundamental phenomena and the extent to which it encourages new investigations. A major concern of the theoretical chemist is with methodology, i.e., the methods by which problems are solved. He strives to discover new methods which are not only more precise than previous ones but also more heuristic. It is with this aspect of theoretical chemistry that work in this laboratory is largely concerned, and present investigations in the methodology of quantum chemistry fall into two areas. The first of these involves the use of perturbational methods in the solving of
chemical problems. Here we are mainly concerned with the use of some of the newer and more powerful formulations of perturbation theory that have been developed, such as operator and Green's functions techniques. Applications of these methods both to time-dependent and time-independent systems are being investigated. The second area involves the study of the electronic structure of atoms and molecules with special emphasis on the role of interelectronic interactions (the so-called correlation problem). Application is being made of some of the physical and mathematical methods that have been found to be useful in the fields of many-body and particle physics.

**NASA-Supported Work:** The work in this area has focused on the use of the time-dependent Green's functions as a means for developing variational methods for time-dependent problems. It has been shown that despite the fact that the time-dependent Green's function itself does not satisfy a minimum principle, a minimum condition can be used in its evaluation. This extension of the original formulation allows for a greater flexibility in the choice of variational functions and increases the power of the method. As an outgrowth of this research dealing with time-dependent problems a new method for dealing with a class of time-independent perturbation problems has also been achieved.

One of the areas of application has been concerned with a perturbing foreign gas and its effects on the spectra, especially in the short time limit. Expressions for the susceptibilities appropriate to third harmonic generation, second harmonic generation and the induced Kerr effect are derived using time-ordered time-dependent perturbation theory. These expressions are used to calculate the susceptibilities for atomic hydrogen and helium. Using a six pole trial function we obtain for He:

\[
\lambda = 6943\,\AA, \quad \chi_{zzzz}(-3\omega;\omega,\omega,\omega) = 47.7 \text{ a.u.};
\]

\[
\lambda = 6943\,\AA, \quad \chi_{zzzz}(-2\omega;\omega,\omega,\omega) = 45.2 \text{ a.u.};
\]

\[
\lambda = 6328\,\AA, \quad \chi_{zzzz}(-\omega;\omega,\omega,\omega) = 43.6 \text{ a.u.};
\]

\[
\chi_{zzzz}(\omega;\omega,\omega,\omega) = 42.6 \text{ a.u.}. \quad \text{The experimental value of } \chi_{zzzz}(-\omega;\omega,\omega,\omega), \text{ obtained from Kerr effect measurements, is } 51.6 \pm 8.6 \text{ a.u.} \quad \text{The calculations are checked by the use of a number of sum rules with the largest disagreement being 0.05%}. 
\]
2. Most Significant Results of NASA Support

The funds provided by the NASA grant have been used primarily to support graduate students and to purchase equipment. To a lesser extent they have been used to support non-academic personnel and young faculty members during the summer. Probably the greatest impact of the NASA money has been on the younger members of our staff who gained promotion to the rank of Associate Professor (or, in the case of R. Yaris, to the rank of Full Professor) during the tenure of the grant. With the help of the NASA funds, Gaspar, Hortmann, Kurz, Lovett, Sarantites, and Yaris were able to launch research programs which have now grown to full scale efforts and which in most instances have succeeded in attracting significant external funding (principally from the NSF, AEC, and PRF). Without the impetus provided by the NASA money it is quite certain that some of these programs would have been slower in getting started and, as a consequence, would be in a poorer competitive position today with respect to external funds. How critical this investment would prove to be was probably not realized at the inception of the grant. In today's situation of increasing requests from researchers and dwindling capacities of agencies to handle these requests, however, the importance of the seed money from the NASA grant is fully appreciated. And, its demise is lamented.

To give a balanced assessment of our use of the NASA money, it must be admitted that all of our investments in young men did not pay dividends. Some of the programs that were supported (Berg, DeRoos, Reeder) failed to progress in the anticipated manner. The programs which have succeeded, however, more than counterbalance those that failed, and the middle group of the department has achieved its present strength in a competitive arena.

3. Additional Relevant Information

The Department of Chemistry has interacted to a considerable extent with other departments in the University as well as with certain of the industrial establishments in the community. For many years there has been an unusually close association between the Departments of Chemistry and Physics as a consequence of common interests of people in these two departments in (a) esr and nmr spectroscopy (Weissman), (b) nuclear phenomena (Macias, Sarantites, Wahl), (c) vibrational spectroscopy (Weissman, Lin), (d) quantum theory (Lovett, Yaris). Interaction with the Department of Biology is primarily the result of the research interests of Holtzer in biopolymers and Lipkin in nucleic acids, and, to a lesser extent, those of Gutsche in enzyme models and Hortmann in natural products. As the result of a joint appointment of Professor M. Welch between the Departments of Radiology and Chemistry, there has been an increasing interaction with the Medical School, and one of our graduate students is currently carrying out his Ph.D. research under the direction of Professor Welch. In the same context, a graduate student enrolled in the Medical School in the combined M.D.-Ph.D. program is carrying out his Ph.D. research with Professor Kurz. Relations with the School of Engineering have been fostered through the efforts of Professor Lovett, acting as a consultant to some of the research being conducted by Professor Burford Smith. Professor Yaris, as a participant in the Center for the Study of Biological Systems, has provided a liaison between the department and this campus activity.
For many years a strong link between the Departments of Chemistry and Earth Sciences has existed through the work of Professor Potratz. Relations with the Monsanto Company have been strengthened through collaborative efforts between Professor Yaris and Dr. J. Schaefer and between Professor Hortmann and Dr. J. Bloomfield, and those with the McDonnell Aircraft Corp. have benefitted from Professor Weissman's efforts. Consulting arrangements between Professor Gutsche and the Monsanto and Petrolite Companies have also served to bring industry and the University closer together.

In addition to the collaborative and consulting ventures with the outside community, the department is also exposed to these foreign influences as the result of several seminar programs. Members of the industrial community frequently attend the regular and special seminars sponsored by the Department of Chemistry, and members of the department frequently attend the seminars sponsored by the American Chemical Society. Particularly flourishing in this latter respect are the Organic Group meetings which are often held in the seminar room in the George F. McMillen Laboratory and which bring together a rather diverse array of chemists in the area.

As a general commentary on the benefits of the NASA program it is fair to say that, next to the NSF Centers of Excellence program, it has been most instrumental in fostering a strong department of chemistry on this campus. It is difficult to point to specific research programs that have received support from NASA and cite these as examples of what these funds have accomplished, for in most instances support has come from elsewhere as well. It has been stated above, however, and it is reiterated that the seed money provided by NASA has been invaluable in helping to nourish programs that might have grown more slowly or even died on the vine for lack of those "extra" funds to support the student, to buy the necessary piece of equipment, or to provide the routine supplies that are necessary for chemical research. The situation that the department again finds itself in, therefore, is most unfortunate. Having sampled the nectar of government largess and having discovered what joy there is in being able to carry out research programs in the proper fashion, the pain of reverting to the austere days of old is doubled. To maintain morale within science, to encourage enough young people to enter science, if not to expand, at least to maintain our present strength, and to insure the continued existence of the university as a sanctuary for research, it is hoped that the government will resurrect its programs of institutional support. Although the individual grant programs are a vital necessity and should not, at all cost, be abandoned, the institutional grant allows investments of a different sort and should be considered as a natural and necessary adjunct to the individual grants.
4. Additional Data

a) List of faculty supported in whole or part

- P. P. Caspar - summer salary 1964, 1965, and 1968
- R. J. Lovett - summer salary 1969 and 1970
- F. S. Quiring (visiting professor) - academic year salary 1967-68
- J. B. De Roos - summer salary 1967 and 1971

b) List of graduate students supported in whole or part

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<td>Postdoctoral work at the California Inst. of Tech.</td>
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<td>G. Skewes</td>
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<td>590420</td>
<td>M. (Tio) Ng</td>
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MOST SIGNIFICANT RESULTS OF NASA SUPPORT

The flexibility of the NASA support definitely increased the amount and diversity of research output of this department and it definitely increased interdepartmental collaboration. It increased research output in two ways: (1) by providing funds for young professors to get research programs going; as the research proved fruitful, funds from NSF and other agencies were attracted and the programs were expanded and (2) since the support could be divided into relatively small amounts (say, $1,000 to $4,000) specific investigations that were not large in scope but looked promising could be pursued by faculty and graduate students. Interdepartmental cooperation carried out with Professor Potratz of the Chemistry Department was a highly desirable outcome of the support. The analytical techniques developed by him for the analysis of earth materials are valuable and are of the sort not likely to be developed by earth scientists. Cooperative work with Professor Walker of the Physics Department was fostered by the support, and the use of fission track dating methods and other techniques developed by Professor Walker have proved most valuable in geological investigations. In addition, two Visiting Professors in the Earth Sciences Department (Mark Wittels and Udo Haack) worked almost full time in Walker's space program. Half of Wittel's salary was paid from NASA funds.
PROGRESS TOWARD GOALS OF THE SUSTAINING UNIVERSITY PROGRAM

The NASA Multidisciplinary Research Program provided valuable support and research opportunities for 9 students who have now received their doctoral degrees and taken positions in Universities and in industry. In addition, research facilities were provided for 4 students who have received Master's degrees. While we cannot claim for the Department of Earth Sciences a substantially increased involvement in aeronautics and space research, it is clear that the NASA support has made a significant contribution to the development of analytical methods applicable to both terrestrial and extra-terrestrial materials and to the strengthening of interdepartmental cooperative. The multidisciplinary research was carried out through cooperative work with H. A. Potratz of the Chemistry Department and R. M. Walker of the Physics Department. The geophysical work of Professor Mateker, part of which was support by the program, is directly transferrable to technology, and as a matter of fact, Professor Mateker has recently transferred to industry, to become a Vice President of Western Geophysical Company.
Research projects carried out by faculty and graduate students of the Department of Earth Sciences, in cooperation with members of the Department of Physics, Chemistry and the Engineering Computer Laboratory, are here summarized under the general areas of geophysics and geochemistry:

Geophysics:

An analog-to-digital conversion system for the purpose of converting analog forms of data from film, strip chart, or maps to digital form was developed under the direction of E.J. Mateker and made available for general use in the Engineering Computer Laboratory. The immediate purpose of the system was for the reduction of geophysical data, but it proved to be useful to research groups from other departments. Electrical properties of carbonate rocks were investigated by Mateker and a doctoral student (W. Beckham) with the objective of understanding their dispersion as a function of induced field frequency and temperature. Among the significant results was the demonstration of the effects of clays. Particular types of clay, distribution of clay, and the interaction of "non-liquid" water and/or organic molecules with clay, determined the nature of dispersion of dielectric constant and loss factor in carbonate rocks.
The magnetic properties of ultramafic rocks were investigated by H.L. Scharon, a visiting professor (S. Sasajima), a research associate (H. Soffel), and a doctoral student (S. Sun). Objectives related to the origin of the ultramafics, their possible derivation from the upper mantle, and the possibility that they may record information about the characteristics of the Earth's magnetic field in the geologic past. Magnetic properties were determined for samples of serpentinites, dunites, and olivinites from localities in the eastern U.S. and from Arkansas, Taiwan, and the Philippines. Among the results was a determination of the temperature of serpentinization for serpentinites from eastern U.S., which the data indicate to be below 500°C. For ultramafic rocks generally, the presence of Cr in the lattice structure of the magnetic minerals contributes to such magnetic properties as the Curie point and the coercive force. Intensities of magnetization are directly proportional to percentage of Cr, V, and Ti but inversely proportional to percentages of Mn. Peridotites and norites, associated with gabbros and anorthosites, from the Adirondack region were investigated by a doctoral student (S. Sun). Remanent magnetism and Curie temperatures of the magnetic minerals were determined and uranium content was measured for most mineral species. Fission track ages of 616 m.y. and 198 m.y. were measured on zircon and apatite. Temperature of ore formation was placed at about 700°C from the relation of Fe-Ti oxide pairs. From fission track ages and the uranium content of zircon and apatite, the rate of uplift of the Adirondack anorthosite massif was determined to be 0.04 mm/yr. Other aspects of the ultramafic rock investigation related to the time of inception of continental drift. Results of
analyses of ultramafic rocks from eastern and central U.S. indicate a Cretaceous age. This age is based on samples that show a high magnetic stability and reliability for VGP (virtual pole position) and have K/Ar and/or Rb/Sr radiometric ages. The ages of ultramafic rocks from Arkansas were also determined by the fission track method.
Geochemistry

W.D. Johns, a doctoral student (J.J. Fan) and a post-doctoral collaborator (M. Akiyama) carried out investigations on amino acids in ancient and recent sediments, which relate to the origin of petroleum, and on the geochemistry of Cl, F, and B. The similarity of the average amino acid composition of recent sediments to that of the Pierre Shale of Cretaceous age suggests that stable polymerized organic matter is produced, which then led to the stabilization during diagenesis. Acidic amino acids are highly concentrated in the nonmarine and nearshore facies relative to deep water facies. The absence of allo-isoleucine in recent sediments suggests enhanced stability of isoleucine is the result of protective adsorption by clay mineral constituents of the sediments. Fan investigated the interrelations among n-hydrocarbons, fatty acids, and alcohols as a function of geologic time, and the environmental factors affecting the spatial distribution pattern of these at a particular time, as inferred from comparative analysis of organic matter in samples from the Upper Cretaceous Pierre Shale. The spatial distribution is related to the depositional environment of the sediment, whether marine, nearshore, or nonmarine. The n-hydrocarbons have higher carbon numbers when derived from a nonmarine source and a lower carbon number when derived from marine organisms. Decarboxylation of n-fatty acids does not appear to be the only major petroleum-forming reaction taking place in natural environments. Also important is hydrogenation of n-fatty acids and the reaction of fatty acids and alcohols to form hydrocarbons through an intermediate of aldehyde or ketone. For the geochemistry of Cl, F, and B, samples of Pierre Shale were analyzed. Cl content could be correlated only with the chlorite content in the less than 0.2 micron clay fraction. It
was concluded that the large Cl ions are incorporated into the silicate structures only at the time of formation, that is, during authigenesis. On the other hand, F is adsorbed by simple OH exchange in both authigenic and detrital hydrous silicates, resulting in substantial depletion of F from sea water.
K.C. Condie carried out a series of field and laboratory investigations directed mainly toward the origin and evolution of the earth's crust which, when understood, should permit the construction of more realistic models for the origin and evolution of crusts on other bodies in the solar system. He acquired, mainly with NASA funds, a gamma ray spectrometer for the development of neutron activation geochemical methods to analyze terrestrial and extraterrestrial material for such trace elements as Cr, Co, Sc, La, Sm, Cu, U, and Th. The importance of these methods lies in their rapidity and accuracy for such purposes as evaluating the variation in concentration of a given element in rocks or meteorites. Non-destructive methods for the rapid determination of Co, Sc, Na, and Mn were perfected and computer programs written to calculate the results. Detailed geochemical study of the Laramie Batholith showed a lognormal distribution of chemical elements, with Fe, Na, Sr, Zr, Mn, Ca, Ti, Al, and Mg showing positive skewness and Si, K, Ni, and Rb negative skewness. The batholith is generally uniform in composition and appears to have followed a calc-alkaline differentiation trend. K/Rb and Rb/Sr ratios are interpreted in terms of a crystal-melt equilibria origin both for the batholith and the light, granitic migmatite bands. Collective evidence from field and laboratory studies indicate that the batholith originated by fractional crystallization of an intermediate or mafic magma that was derived by the partial melting of the lower crust or upper mantle.

To infer rates of chemical differentiation from basalts, Condie analyzed 27 samples of Precambrian basaltic (diabase) dikes from ranges in Wyoming and 20 samples of young basalts from the Yellowstone Park area. Two groups of young basalt in the Yellowstone area are indicated, apparently derived from different depths in the earth's mantle. No striking secular changes in the
composition of basalt have occurred in the Wyoming area in the past 2.5 billion years. The Wyoming diabases are relatively enriched in Rb and depleted in Sr, which may be explained by extensive plagioclase crystallization from Ca-Al-rich primary tholeiitic magma. Samples of young basalts of known relative age from a small geographic area in western Utah were analyzed by neutron activation and X-ray fluorescence for major elements and fine trace elements, and chemical trends through time were determined. A decreasing or approximately constant Sr content in fractionating tholeiitic and high-alumina basalt may necessitate the removal of moderate to large amounts of plagioclase. A corollary of such removal is the necessity of some contamination with Sr-poor material to maintain a basaltic composition.

Investigation of the petrochemistry of the Preacher Creek ultramafic body was carried out under Condie's direction by a doctoral student (Mark Potts). Petrographic study of samples collected throughout the body showed accumulative textures characteristic of stratiform complexes. Total rock chemical analyses were made, as well as rare earth elements analyses of total rock and separated minerals. From the chemical and petrographic evidence, it was inferred that the body formed within the earth's crust by fractional crystallization and gravity accumulation of mafic minerals from a gabbroic magma that was differentiating along a tholeiitic trend. Ultramafic intrusions in orogenic zones with chemical, mineralogical, and structural features similar to those of the Preacher Creek body are probably best explained as crystalline accumulates formed in volcanic magma chambers.
Radiation damage in crystals was investigated by a visiting professor, Mark Wittels, who worked with the Physics Department under the direction of R. M. Walker. Radiation effects resulting from heavy charged particle bombardment were studied in feldspars, pyroxenes, olivine, apatite, and quartz. In addition to the effects of direct atomic displacement, striking results of polygonization were observed where argon and neon ions were trapped within the crystal structures. Conventional single crystal X-ray diffraction techniques were employed in conjunction with thermal annealing studies and scanning electron microscopy of track-producing phenomena.
The research projects of H. Potratz were supported jointly by funds allotted to Chemistry and Earth Sciences; and Potratz has submitted a single summary of his results, which is in the Chemistry Department section of this Appendix (page D20).
LIST OF FACULTY SUPPORTED IN WHOLE OR PART

Mark Wittels 9/1/68 - 5/31/69  50% Visiting Professor
Alan Stueber 9/15/65 - 6/15/66  53% Research Associate
Sadao Sasajima 1/1/67 - 9/30/67  100% Visiting Professor

LIST OF STUDENTS SUPPORTED IN WHOLE OR PART

Mark Potts 9/1/70 - 1/15/71  100%
Ph.D. Thesis Title: Petrochemistry of the Preacher Creek Ultramafic Body, Wyoming

Jieun-Jeou Fan 6/30/67 - 9/31/67, 1/16/70 - 5/31/70, and 9/1/70 - 1/15/71
Ph.D. Thesis Title: Organic Geochemical Study of the Upper Cretaceous Pierre Shale

Howard Hunghsin Lo 7/1/69 - 7/31/69
Ph.D. Thesis Title: Geochemistry of Louis Lake Pluton, Southwestern Wyoming

James A. Madison 10/31/64 - 1/30/65, 2/1/65 - 6/15/65, and 7/1/65 - 7/31/65
Ph.D. Thesis Title: Petrology and Geochemistry of the Webster-Addie Ultramafic Body, Jackson County, North Carolina

Ph.D. Thesis Title: Electrical Polarization in Carbonate Rocks

Stanley S. Sun 9/15/66 - 6/15/67, 6/15/67 - 6/15/68, 6/1/68 - 8/31/68, 6/1/70 - 8/31/70, 9/1/70 - 1/15/71, and 6/1/71 - 9/1/71
Ph.D. Thesis Title: Fission Track Study of the Cheney Pond Titaniferous Iron Ore Deposit, Tahawus, New York

Constance Barsky 4/1/71 - 9/1/71
Ph.D. Thesis Title: Petrochemistry of the Basic Volcanics of the Medicine Lake Highland, California
-13-

PRESENT OCCUPATION OF STUDENTS

<table>
<thead>
<tr>
<th>Name</th>
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<tbody>
<tr>
<td>Mark Potts</td>
<td>Postdoctoral, Goettingen, Germany</td>
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<tr>
<td>Jieun-jeou Fan</td>
<td>Research Geochemist, Mobil Research Laboratory, Dallas, Texas</td>
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<tr>
<td>Howard H. Lo</td>
<td>Assistant Professor, Cleveland State University</td>
</tr>
<tr>
<td>James A. Madison</td>
<td>Chairman, Department of Geology, DePauw University</td>
</tr>
<tr>
<td>Wallace Beckham, Jr.</td>
<td>Research Geophysicist - Texaco Oil Company Bellaire, Texas</td>
</tr>
<tr>
<td>Stanley S. Sun</td>
<td>Assistant Professor, Washington University</td>
</tr>
<tr>
<td>Constance Barsky</td>
<td>Instructor, Electron Microprobe, University of Missouri - Columbia, Missouri</td>
</tr>
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APPENDIX D

DEPARTMENTAL REPORT

ELECTRICAL ENGINEERING
INVESTIGATION OF QUANTUM ELECTRONICS INCLUDING GAS LASER TECHNIQUES, STUDIES OF SHORT-PULSED LASERS
FACULTY INVESTIGATOR: W.S.C. Chang

1. Area of Research

Research was carried out first to investigate the coherence of a super-radiant pulsed Argon laser without feedback from resonant cavity. Quantitative calculations and measurements of the improvement in the degree of coherence of the radiation as a function of gain in the laser tube were obtained. These results indicate to us the type of radiation that might be obtained in an ultra short-pulsed laser. An extension of this work led us to experiment with mode locking in a CW Krypton laser. In this case, we have successfully mode-locked a particular transition of a CW Krypton laser through a novel double cavity technique, and measured the effect of this perturbation to the other laser transitions that share either the upper laser level or the lower laser level with this transition. These cross-coupling effects enabled us to understand much better the effects of atomic life time on mode-locking of laser modes, the formation of mode-lock pulses, and competitions in CW ion lasers. A doctoral dissertation by James S. Brookman, Jr. on the experimentation of mode-locking in Krypton lasers will be published in August 1971.

In another area, our interest in laser holographic techniques has led us to apply the holographic techniques to medicine and to perform a detailed analysis of the holographic optical memories in terms of the modern communication theory. Holograms were made to represent the vector cardiogram in 3-dimensions in collaboration with Dr. David Shander, of the Jewish Hospital, for clinical diagnosis applications. Later, a synthesis of 30 holograms from the successive two dimensional views of an object were made to reconstruct a 3 dimensional
photographs. This was also intended to be applied to clinical medicine to reconstruct 3 dimensional views of various organs based on x-ray photographs. On the other hand, a complete theoretical analysis on holographic memories, that will enable us to optimize the design of large scale optical memories, is nearly finished and will be presented as the doctoral dissertation of Bernard T. Sander, Jr. in August 1971.

The program in coherent optics is closely related to the quantum electronics program of Dr. E. T. Jaynes of the Department of Physics. In our study of the short pulses, we also have collaborated closely with the program of Dr. S. I. Weissman of the Department of Chemistry.

The NASA support enabled us to develop the Applied Physics program in Electrical Engineering.

2. Most Significant Results

a. Successful experimentation with mode-locking of multiple transitions in CW Krypton lasers.

b. Theoretical analysis of the optical holographic memories.

3. Interdisciplinary Activities

Because of the NASA support we were able to develop the application of coherent optics to medicine with Dr. David Shander of the Jewish Hospital.

One very important outgrowth is the collaboration of faculty from the Departments of Physics and Electrical Engineering in AFOSR program on "Optimum Detection Techniques", The second one is the collaboration of the Department of Chemistry and Electrical Engineering in the high power pulsed laser work.
4. **Students**

James S. Brookman, Jr., M.S., 1968  
D.Sc., 1971  
(to be granted in August)  

Mr. Brookman will be employed by McDonnell Douglas Corporation.

Bernard T. Sander, Jr., D.Sc., 1971  
(to be granted in August)
A METHOD OF TEMPERATURE MEASUREMENT
FACULTY INVESTIGATOR: R. Gregory

1. Area of Research

This research was an investigation of a novel means of measuring temperature. Specifically, a thermistor if self heated will attain a temperature dependent on the heat input and the thermal conductivity of the thermistor to its surrounding environment. If the thermal conductivity is constant with temperature, then for a given heat input the temperature rise above ambient will be directly proportional to the heat input.

This effect can be used to implement a thermometer as shown in the accompanying figure 1. The thermistor is part of a self-balanced bridge which is brought into balance by the application of a train of voltage pulses to the bridge of constant amplitude and constant width. Since the frequency is controlled by the bridge output, via an amplifier and synchronous detector, the bridge is maintained in balance and the thermistor is held at a constant temperature. As the ambient temperature changes the power required to keep the bridge balanced will vary and consequently the frequency of the pulse train varies accordingly.

If it be assumed that the thermal conductivity of the thermistor is constant then it may be shown that the ambient temperature and the pulse train frequency are linearly related.

This system was built and experimental results obtained. These were, a resolution equal to 0.01°C and a linearity of ±0.3°C over the temperature range 30-90°C. The primary limitation of the method is that the thermal conductivity of ordinary thermistors is not a very constant function of temperature since it is strongly influenced by radiation which is a fourth power function of temperature. It is anticipated that significant improvement could be obtained by optimizing the thermistor for this application but no real effort has been expended in this direction.
NASA support paid the salary of the principal investigator, Robert Gregory, for one month in summer, 1966. It also paid for electronic supplies of approximately $300.

2. Students

Two students wrote their M.S. theses on this topic.

They were:

Joseph A. Volk, Jr., entitled, "Digital Self-Heated Thermistor Thermometer".

Robert K. Underwood, entitled, "A High Resolution Thermistor Thermometer".

Neither of these students had tuition or other support from NASA.

Mr. Volk is presently self-employed in the St. Louis area while Mr. Underwood is a solid-state devices engineer with Monsanto Company, St. Louis, Missouri.
Block diagram of temperature measuring system.

A - Differential Amplifier
B - Synchronous detector
C - Constant amplitude, constant width pulse generator, whose frequency is voltage controlled.
ESTABLISHMENT OF AN INTEGRATED ELECTRON LABORATORY
FACULTY INVESTIGATOR: H. Guckel

1. Area of Research

The purpose of this project was to set up a complete integrated circuits semiconductor laboratory to conduct research in integrated semiconductor devices.

The NASA support was used primarily to secure some of the research equipment during the initial period. Fortunately, additional support was obtained from ARPA which enabled us to set up a complete Integrated Circuits Laboratory. The initiation of the semiconductor laboratory also enabled us to collaborate much closer with both the Biomedical Computer Lab in the School of Medicine and the Computer Systems Lab in the University.

2. Students

Pong Fui Chang, D.Sc., 1968. Dr. Chang is now conducting research in Chung Shang Research Institute, Taiwan, Republic of China.
STUDY OF RARE EARTH FLUORIDES
FACULTY INVESTIGATORS: D. Bolef and M. Muller

1. Area of Research

Lanthanum trifluoride is an important optical material that has been used as a host lattice in the fabrication of lasers. When doped with appropriate ions of other lanthanide-series rare earths, lasing transitions are produced; the wavelengths of which fall in a broad spectrum ranging from the near ultra-violet to the near infrared. With careful selection of the dopant, lasing transitions can be produced at selected frequencies in the far infrared. An understanding of the symmetry of the crystal lattice is essential for predicting the lasing frequencies, especially those in the far infrared, as well as for interpreting the results of magnetic susceptibility, Faraday rotation, NMR, EPR and optical spectroscopy studies.

Thus, considerable interest was aroused when a controversy developed concerning the structure of LaF$_3$. Some workers reported experiments indicating a trigonal lattice symmetry, while others reported findings indicating hexagonal symmetry. The large number of conflicting reports on the crystal structure was reviewed by Bauman and Porto in 1967.

We proposed to provide additional information concerning the crystal structure of LaF$_3$ through a determination of its elastic properties. The two competing crystal classes which had been proposed by various researchers possessed significantly different elastic tensors, so that by determining which tensor best described the elastic properties of the material, one could deduce the basic symmetry of the lattice. The values of the elastic constants, which comprise the elastic tensor, may be calculated from the velocities of sound measured in various directions in the crystal. The velocities of sound are determined by a method which uses the fact that the frequencies at which a material body resonates are determined by the velocity of sound in the body.
In the course of our experiment it became apparent that our sample of LaF$_3$ had large, internal strains. These strains produced a large scatter in the velocity of sound data which precluded the drawing of meaningful conclusions. While awaiting another sample to be fabricated to our specifications, several more experiments pertaining to the structure of LaF$_3$ were reported$^{2,6,7}$ which all supported the conclusion that the lattice had trigonal symmetry.

The confusion over the two structures was found to result from the fact that one of the La ions in each unit cell was displaced from the position required for hexagonal symmetry by 0.0068 lattice unit (0.049Å), thus producing a trigonal structure differing subtly from the proposed hexagonal structure.

Since the deviation from hexagonal symmetry is so small, entropic arguments indicated the possibility that a phase transition from a trigonal to a hexagonal structure might occur as the material was cooled. The arguments held that at a sufficiently reduced temperature, the lower-entropic, hexagonal structure might be favored over the higher-entropic, trigonal structure. Since the entropy difference between the two structures is small, it was expected that if there is a phase transition, it should occur at moderate temperatures (above 100°K). As the material passed through the transition temperature, there should be an abrupt change in the velocity of sound, and/or an abrupt change in the slope of a velocity vs temperature plot.

Thus, on receipt of a new strain-free sample of LaF$_3$, we began an experiment designed to detect any phase transitions that might occur. Measurements of the velocity of sound were made as a function of temperature between 310°K and 70°K. No discontinuities in the velocity nor in the slope of the velocity were found in this region. We therefore concluded that the structure of LaF$_3$ is trigonal, as reported earlier, and that it remains trigonal from above room temperature to below liquid nitrogen temperature.
This study of the rare-earth fluorides was pursued through the joint efforts of the Electrical Engineering and Physics Departments. The Electrical Engineering Department initiated the program, provided the manpower and the bulk of the necessary experimental equipment. The Physics Department, especially the Acoustics group of Professors Bolef, Sundfors and their students, provided experimental space, office space for the Electrical Engineering graduate student involved, unlimited use of existing equipment, and invaluable assistance in technical problems. Students in both groups benefited as they shared their expertise from diverse areas. In addition, both departments benefited as new lines of communication were opened and as each department has made increased use of the other's facilities.

References

1. Optovac Inc., North Brookfield, Massachusetts.

2. Students

R. W. Patterson, M. S. Thesis "Ultrasonic Velocities in LaF₃".
PLASMA STUDIES
NASA MULTIDISCIPLINARY FINAL REPORT ON
NSG 581-26-008-006
Faculty Investigator: B. Shrauner

Summary

We have treated the solar wind and discontinuities in the solar wind using a tensor plasma pressure. A solution for the solar wind with anisotropic pressure has been given. The correct magnitude of the angular momentum carried off from the sun by the solar wind is found which the hydrodynamic and magnetodynamic models could not give. Agreement with experimental data is quite good for this model. A preliminary treatment of heating in the solar wind was done by deriving directly from the fluid equations the macroscopic equations including the quasilinear fluctuation term for the garden-hose instability.

A tangential discontinuity was described by an exact stationary wave solution of the Vlasov equation. This discontinuity is frequently seen in satellite data. Theoretical treatment of blast waves from solar flares revealed that the magnetic moment need not always be conserved across the shock (perpendicular shock) for an adequate number of jump conditions and that the generalized polytrope laws derived by us that give good solar wind solutions did not give the usual similarity solutions in general.

Research Accomplished

Research on models of the solar wind and discontinuities in the solar wind for a tensor pressure plasma has received some support from the NASA Multidisciplinary Grant NSG 581-26-008-006 although the main support was from other sources. The intent of the research was to devise models for the solar wind and the collisionless shock waves that propagate in it by using a collisionless plasma approximation with tensor plasma pressure. Our model for the solar wind agrees better with the experimental data that has been reported in the last few years than the
hydrodynamic or magnetodynamic models.

Mrs. Muser Tan and I calculated a numerical solution for the solar wind using a generalized polytrope law for the anisotropic pressure. The results agree well with the satellite data. The most significant result was the correct value for the azimuthal velocity of the solar wind which could not be explained by hydrodynamic or magnetohydrodynamic equations. The large angular momentum carried off by the solar wind from the sun has important implications for stellar models. The generalized polytrope laws were derived so that heat equation of the solar wind could be dropped. Neither the isothermal nor the Chew-Goldberger-Low equations were adequate for a description of the solar wind.

We also did some special calculations for the propagation of blast waves from solar flares (interplanetary shock waves) but the polytrope laws did not give the usual similarity solution. We did find that the conservation of magnetic moment was not necessary for an additional condition in all cases (perpendicular shock) as had been assumed by Lynn.

The generalized treatment of an exact stationary wave solution of the Vlasov equation was extended to the relativistic case. A tangential discontinuity was explicitly given. The generalization to shock waves should be possible. Fluid equations with quasi-linear fluctuation terms were derived directly in the fluid approximation using moment equations for the garden-hose instability. This is one of the instabilities suggested for the heating of the solar wind; therefore, the equations are relevant to solar wind models.

Program Goals and Outside Collaboration

Our research has increased Washington University's participation in space plasma research from none to a sustained if small theoretical effort. Two students have been trained and another is being trained in theoretical techniques for analyzing space plasma phenomenon. One student was partially supported by this grant.
Collaboration with NASA installations includes the present data sharing of plasma problem data from the Electrodynamics Branch, Dr. John Wolfe, Chief, Ames Research Center and magnetic field data from the Laboratory for Extraterrestrial Physics, Dr. Norman Ness, Chief, Goddard Space Flight Center. We are now on another grant analyzing interplanetary shocks which have never been studied using this set of data. Dr. Joan Hirshberg of the Physics Branch of Ames Research Center is also interested in the observation times of these shocks and the orientation of shock normals for her study of interplanetary shocks.

Support from Grant

Faculty - Barbara Abraham Shrauner
Summer 6/1-8/31/68 100%

Student - Muser Tan
Summer 6/1-8/31/67
6/1-8/31/68 Ph.D. January 1971; applied for post as lecturer at University of Malay
The Engineering Computer Laboratory was established, primarily through use of NASA funds, to satisfy the following requirements:

i) An immediate need for experimental facilities in conjunction with research and instructional programs in the Automatic Control Department. Specifically, a modern hybrid computer, with extensive analog-digital interfacing was desired.

ii) The anticipation that a hybrid computation-data reduction facility would become increasingly important in areas outside engineering such as the biological sciences, radiochemistry, earth sciences, psychology, low temperature physics, etc., many of which would have NASA support.

b) The Laboratory contained a Digital Equipment Corporation PDP-5 central processor with 4K memory, 5 μsecond cycle time, complete with an integrated magnetic tape system. The peripheral equipment, much of it designed and constructed by engineering graduate students, consist of sixteen channels of high speed analog to digital conversion, six channels of digital to analog conversion, scope displays, light pen communication equipment, process interrupt, hardware character generator, etc. Through this very flexible interface, a fully expanded Electronic Associates TR-48 analog computer has been integrated into the system. This has 48 amplifiers, various nonlinear equipment, repetitive mode of operation and is extremely useful in optimization studies.

c) The type and distribution of problems that have been handled represents nearly all divisions of the University:

i) Automatic Optical Line Tracking and Noise Rejection (Electrical Engineering)
ii) Fatigue of Helicopter Pilots (Medical Psychology)

iii) Analysis and Editing of Geophysical Data (Earth Sciences)

iv) Effects of Environmental Factors on Heart Rate (Psychology)

v) Optimization of Fourth Order Sampled Data Systems (Automatic Control)

vi) Enzyme Reaction Model Matching (Biochemistry)

vii) Characteristics of Highway Surfaces (Mechanical Engineering)

viii) Isotope Image Enhancement (Radiology)

Items ii), iii), and v) were NASA supported.

2. The NASA support permitted the development of a computational facility to serve the needs of a variety of research projects, many of which were included in NASA multidisciplinary grant. The Laboratory thus has filled the need for special purpose hybrid types of computation.

This laboratory greatly strengthened the interaction of faculty members between the Engineering school and other divisions of the University including Biology, Psychology, Earth Science, Radiology, and Anatomy. Collaborative projects were undertaken with faculty in each of these areas.

Faculty Supported

Dr. Donald F. Wann, Professor of Electrical Engineering

Students

Mr. Ronald Shamblin, M. S. in Electrical Engineering
Present Occupation: Development Engineer, Shell Oil Company.

Mr. Robert Shanker, D.Sc. in Automatic Control
Present Occupation: Unknown.
SUMMARY OF ACTIVITIES OF THE MICROWAVE LABORATORY
FUNDED UNDER NSG 581-26-008-006
FACULTY INVESTIGATOR: F. J. ROSENBAUM

The Microwave Laboratory of the Department of Electrical Engineering was founded in September, 1965 by Associate Professor Fred J. Rosenbaum. Funding under NSG 581-26-008-006 provided the "seed" money needed to establish new projects in microwave research and to support them until other funding was obtained. The capability developed in this way has provided Washington University with one of the finest graduate microwave research facilities in the United States.

One current program in the laboratory involves the study of low cost microwave ground stations for the reception of satellite transmissions for educational purposes. This is part of a multidisciplinary program sponsored by NASA. Another program recently initiated is examining the interaction of microwaves with biological materials and systems. It was possible for the Microwave Laboratory to participate in these programs in part due to the capability developed with the help of funding under the above contract.

The research program of the Laboratory has followed two related lines.

I. Electromagnetic wave propagation in anisotropic media.
   a) Ferrites
   b) Semiconductor

II. The Gunn effect and its application to microwave generation and amplification.

These topics will be treated individually. Their relationship to each other, to the other areas supported under the grant, and progress toward long and short range goals of the University Sustaining Program will be noted.

I. Electromagnetic Wave Propagation in Anisotropic Media

One of the fundamental tasks of physics has been the understanding of the nature of the interaction between radiation fields and matter. Many advances in the field of microwave engineering have resulted from such understanding. For example, virtually no
modern microwave system could be built without employing non-reciprocal devices utilizing the properties of ferrite materials.

We have been interested and involved with the continuing development of ferrite microwave devices and the concepts underlying their operation. In a program initiated in 1966, we began the study of the propagation of electromagnetic waves in longitudinally magnetized ferrites in a coaxial geometry. This geometry is a practical one for the fabrication of phase shifters, electrically variable attenuators, modulators, tunable filters, etc. We successfully formulated and solved the boundary value problem posed above, and were able to elucidate the electromagnetic behavior of this geometry. Several devices were constructed to validate our results.

This work \(^1,^2\) has proven of value to later workers in the field and has been cited as a useful analog for the characteristics of microstrip devices on ferrite substrates. This problem has not yet been solved satisfactorily and is of great current interest to the microwave community.

The knowledge obtained in this program has been of benefit to local industry. Emerson Electric Company, St. Louis, Missouri, became active in the field of ferrite phase shifters during this period and successfully completed several significant airborne radar programs under Air Force sponsorship, manned in part by personnel trained in the Microwave Laboratory and who participated in some of the ferrite work. It is our belief that both the short and long range goals of the University Sustaining Program were met by the project.

Ferrite work is now being continued in the Microwave Laboratory under the sponsorship of the United States Air Force.

II. The Gunn Effect and its Application to Microwave Generation and Detection

In 1963, J. B. Gunn of IBM, discovered the first direct process for the conversion of dc power to microwave power. The Gunn effect, utilizing the inherent properties of semiconducting GaAs, has moved from the laboratory to the commercial, military, and space market place in a few short years. It has had a tremendous impact on the microwave industry. Many new systems and devices have come into
being as a result of Gunn effect research. System concepts which were previously infeasible can now be achieved.

In 1966, at the request of the Monsanto Company, the leading commercial source of GaAs, Prof. Rosenbaum began to devote some effort in the application of the Gunn effect to the generation of useful microwave power levels in the X-band. A student, Mr. John Bryan and Prof. Rosenbaum, were employed by Monsanto during the summer of 1967, and subsequently developed a program of Gunn effect research on the Washington University campus, partially supported by the University Sustaining Program grant.

During this program, several important results were achieved. A new, inexpensive, microwave swept frequency oscillator was developed which uses a section of ferrite loaded waveguide as the frequency determining element. This device coupled the new Gunn effect oscillator with the ferrite knowledge developed earlier to produce a new device concept.

At the same time we observed and successfully described theoretically and experimentally a limiting feature of the Gunn effect, namely bias circuit oscillations. These are troublesome, low frequency oscillations, which can be excited in the electrical circuit external to the Gunn diode. In some cases, the diode could be destroyed by uncontrolled bias oscillations. This phenomenon is also directly related to the fast rise time turn on characteristics of pulsed Gunn oscillators. Several useful instrument and circuit applications of bias circuit oscillations were conceived during this work including a voltage controlled high power burst generator, and a fast rise time, short (5 ns) microwave pulse generator.

A phenomenological model for the interaction between the Gunn diode and its surrounding microwave circuit was developed during the program. The model was used to predict the oscillation frequency, the tuning range, and the limits of stability of a mechanically tuned oscillator with great accuracy. With the help of this model the modulation characteristics of a Gunn oscillator were studied and explained.

Significant efforts were also devoted to a detailed analysis of the post coupled waveguide oscillator and the harmonic output of this type of Gunn Oscillator.
There was a strong, continuous relationship between the Microwave Laboratory at Washington University and the Microwave Products Group of the Monsanto Company until its recent sale to Microwave Associates. Several of the students trained in the Laboratory were employed at Monsanto and contributed to its rapid growth as a major Gunn Oscillator manufacturer.

Faculty Supported

Fred J. Rosenbaum, Associate Professor

Students


iv) J. G. Bryan, M.S., June, 1970, Microwave Engineer, California Microwave Corporation.

v) Y. S. Wu, M.S., June, 1970, Graduate Student, Washington University

vi) F. Hummel, Graduate Student, Washington University.
APPENDIX D

DEPARTMENTAL REPORT

MECHANICAL AND AEROSPACE ENGINEERING
General

This department first received support from subject grant in Fiscal Year 1970 when the grant entered a two-year phasing-out period. The allocation for FY 1970 was $9000. A second and final allocation of $7377 was made for FY 1971.

Although somewhat nominal in amount, these allocations were intended to aid the department in its efforts to increase its research activity in V/STOL technology and thus "phase in" to the proposed multidisciplinary program "Aeronautics and Space Science and Technology and Its Role in Modern Society". The proposal was subsequently rejected by NASA in favor of a new program in satellite communications to which Mechanical and Aerospace Engineering was not prepared to contribute. This turn of events effectively aborted the department's interest in a broader based research program in aeronautics.

A substantial part of the above-mentioned allocations was intended for support of a new junior faculty member to be recruited for the area of low speed aeronautics. This new faculty member was to have complemented Dr. Kurt Hohenemser in his basic research on helicopter dynamics, looking not only into other aspects of V/STOL technology but also some of the socio-economic problems associated with short haul air transportation. A recruiting effort was initiated but dropped shortly afterward when the termination of the SUP grant became definite. At that point it was decided to use most of the allocation to support graduate research trainees working with Dr. Hohenemser. Part of the funds were applied to cover some of the expenses of their projects.

During FY 1971 $1800 of the allocation was applied partially to support a new faculty member with interests primarily in environmental engineering and science, Dr. Daniel K. Ai. This support was designated to cover Dr. Ai's efforts to
organize a multidisciplinary proposal for a study of future air-transportation needs of the St. Louis region and the potential impact of the transportation system on the environment.

A total surplus of $2400 was also returned for reallocation to other departments resulting in a net allocation to Mechanical and Aerospace Engineering of $13977.

1. Area of Research

A. Lifting Rotor Analysis


B. Experimental Model of Lifting Rotor

A lifting rotor model has been designed and constructed for the low speed wind tunnel. The model will be used to measure blade responses to deterministic and random frequency excitation. The first data are expected during the summer of 1971. One pre-Master's graduate trainee is working on this project.

C. Wave Interaction in Supersonic Ejectors

Analytical and experimental investigations of the interaction of waves in supersonic ejectors, a problem encountered in jet-propulsion systems of a type which may find application in V/STOL technology, is being conducted by a doctoral candidate.
D. Air-Transportation Systems for the St. Louis Region

A large scale multi-disciplinary study is being planned on:

(i) future air-transportation needs of the St. Louis area, both short and long haul;
(ii) impact of successful V/STOL systems on those needs;
(iii) location of future airports for passenger and freight;
(iv) integration of air-transportation system with regional rapid transit (ground) network;
(v) potential effect of transportation systems on the local environment.

A proposal involving faculty of several university departments is in preparation.

Relationship to other areas supported

None of these projects was directly related to the other areas supported.

Progress toward long and short-range goals

Projects A, B and C contribute directly to the short-range objective of increasing the supply of trained manpower in aeronautics. The grant support will have partially subsidized the production of two D.Sc. and one M.Sc. degrees in the aerospace field.

Project D should certainly increase the University's capability for multidisciplinary research on socially relevant problems.
2. **Most Significant Results of NASA Support**

   To date the most significant accomplishment is the completion of the doctoral dissertation by S. K. Yin (project A, above). A number of fundamental papers based on this dissertation will be published in the aeronautical literature.

3. **Faculty Supported**

   D. K. Ai, Professor of Aerospace Engineering, supported 10% from departmental allocation during Academic Year 1970-71.

4. **Students Supported**

   S. K. Yin  
   Received D.Sc. June 1971. Presently appointed as Post Doctoral Fellow at Washington University, working with K. Hohenemser.

   J. L. Porter  
   Doctoral candidate. Presently employed in the propulsion methods group at the McDonnell-Douglas Aircraft Corporation while working part-time to complete his research.

   S. T. Crews  
   Master's candidate.
APPENDIX D

DEPARTMENTAL REPORT

PHYSICS
DAN I. BOLEF
ACOUSTIC SPECTRUM OF SOLIDS

1. Area of Research

The two major areas of research effort were (i) research on the properties of thin films as microwave sonic transducers, and (ii) research on the development of a novel Mössbauer technique and its application to the study of magnetic solids. Under (i) were studied the properties and uses of piezoelectric thin films (e.g., CdS) as well as of pure metal films to be used in acoustic resonators at microwave frequencies. Under (ii) we designed and constructed an acoustic Mössbauer spectrometer, developed the theory necessary to understand its performance, and applied it to the study of Fe$^{57}$ and Cr hyperfine structure.

2. Significant Results

A. Thin Film Piezoelectric Transducers

Development and use of CdS piezoelectric films up to 12 GHz.

B. Acoustic Mössbauer Effect

(i) Development of a variable-frequency ultrasonic spectrometer for investigating Mössbauer spectra;

(ii) Application of the acoustic Mössbauer effect to the study of acoustic properties of thin metal films;

(iii) A theoretical understanding of the interactions of ultrasound with Mössbauer γ-rays.

3. Interdisciplinary Activities and Impact Outside the University

a) Interest was shown by a number of Mössbauer effect physicists in the use of the Acoustic Mössbauer techniques
developed here in velocity calibration; specifically, S. L. Ruby of Argonne National Laboratories exchanged visits with us as part of a considerable interaction between us on this matter.

b) The CdS thin-film transducer work has enabled us to do experiments at microwave frequencies, and has led directly to collaboration between Professor J. G. Miller (of our group) and Professor Tom Lin of the Chemistry Department on a microwave double-resonance experiment on excited triplet states of certain organic radicals.

c) The CdS evaporation facilities developed on this grant have been used extensively by members of the Engineering Department at Washington University.

d) Several NASA Pre-doctoral trainees have worked on the NASA-sponsored projects: J. G. Miller and D. A. Rudy.

4. Faculty
D. I. Bolef, Professor of Physics
J. H. Burgess, Associate Professor of Physics

Students
R. E. Smith, Ph.D., June 1970 - Union Carbide Res. Labs.
R. Lovelace, B. S., June 1964 - Ph.D. Cornell
A. Gara
J. Mishory, Ph.D., June 1969 - Uni-Royal Res. Labs.
(only one fully supported on grant)
R. G. Leisure, Ph.D., September 1967 - Professor Colorado State College
J. G. Miller, Ph.D., August 1969 - Assistant Professor Washington University
D. A. Ruby, Ph.D., June 1969 - Bell Telephone Labs.
JAMES H. BURGESS
ACOUSTIC SPECTRUM OF SOLIDS

1. Area of Research

Work has focussed on the development of techniques for the generation and detection of microwave ultrasound. These techniques were used successfully in attenuation studies in thin films of superconducting mercury and of organic free radicals.

The grant provided funds to obtain vacuum deposition equipment, autocollimator and clean room facilities which are useful to several projects and could not have been obtained easily for any one project alone.

Additional work has been carried out on technique for the growth of single crystals and the vacuum deposition of thin films of organic structure and composition.

3. Interdisciplinary Activities and Impact Outside the University

In the early stages of this work my ideas concerning the explanation for the low temperature magnetic properties of the organic free radicals involved the possibility of coherent states. These ideas also have application to biological macromolecular systems. In order to pursue these applications I joined the Center for the Biology of Natural Systems at Washington University as a Senior Fellow.

4. Personnel

The following people have received substantial research support from this grant.

Faculty
James H. Burgess - Principal Investigator
Students

Richard B. Ferguson - Ph.D. 1967 now at Los Angeles State College.

Edward J. Hill - Ph.D. 1970 now Research Associate in Biophysics at Washington University Medical School.

David Palaith - Ph.D. August 1971.


Vinodh Narayanan - undergraduate assistant.

Ph.D. Theses - partially supported by this grant

"Hypersonic Attenuation in Superconducting Mercury"

"Spin Relaxation Studies in Stable Organic Free Radicals"

"Applications of a Band Model to Crystalline DPPH Benzene"
D. Palaith, August 1971.
1. **Area of Research**

Accomplishments: construction and successful flight operation of infrared telescope system by high altitude balloon. Location of four infrared objects that emit strongly in the wavelength interval 50-250 microns, yet do not appear to correlate with objects known to be strong radiators at other wavelengths (such as visible, near infrared or radio).

Progress towards long-range goals: the sustaining NASA support enabled this program to be started and continued to the stage where independent support has now been obtained, and the program seems to be assured of steady continuation.

2. **Significant Results**

Without NASA support, this program could not have been started. Scientific results described in publication.

3. **Interdisciplinary Activities and Impact Outside the University**

Shall be working with Professors Robert Bell and Ralph Alexander, University of Missouri at Rolla, in design, construction and operation of further experiments. To date, collaboration has consisted of our using their lab facilities for testing our infrared detector and filters.

4. **Faculty**

M. W. Friedlander - Director of Program, but no salary support.

**Students**

L. A. Lissak supported as NASA pre-doctoral trainee while working on infrared astronomy program.
1. Research Effort

This project started in 1964 with the rather limited objective of studying fluctuation or "noise" effects in masers and lasers (which were not well understood at that time), in hope of reducing or eliminating them. This would be of interest, not only for improving detection of weak signals, and in some precision physical measurements possible with highly stable lasers, but also for physical theory in general, since these fluctuation effects are closely related to basic principles of quantum theory and statistical mechanics on which we have as yet very little direct experimental evidence.

In the first experiments, for preliminary orientation, we measured amplitude fluctuations and two-channel correlations in photocurrent generated by laser light from a commercial He-Ne instrument, and confirmed the long coherence length and frequency stability of this light by a Michelson interferometer with one very long leg. We found that there was still essentially 100% fringe visibility when one of the light signals traversed 300 ft of still air, and rapidly moving fringes were still seen easily by a photomultiplier through 1600 feet of turbulent air. By the fringe motion we were able to measure the few megacycles of 120 cycle frequency modulation due to imperfectly filtered power supply. These results were not published, since essentially the same experiments were then being done in many laboratories, and the results were common knowledge to those working in the field.
During this period theoretical work was also underway, studying
the predictions of both quantum electrodynamics (QED) and a form
of semiclassical radiation theory, which we have called the "neo-
classical" theory (NCT), in which the effect of an atom's self-field
is included in the calculations. In particular, the theory of "spon-
taneous emission noise" (which is generally considered to place a
fundamental limit on the stability of laser oscillators and noise
figure of laser amplifiers) was found to be more complicated than
in previous treatments based largely on "Fermi Golden Rule" approxi-
mations of perturbation theory. According to QED there exist certain
correlated initial states of the system (atoms + field) for which
the rate of spontaneous emission can be either greater (superradiant
states) or less than indicated by elementary calculations, with
correspondingly greater or less noise.

NCT, on the other hand, predicts rather different details for
the onset of spontaneous emission, according to which low noise
should be easier to attain, requiring only efficient pumping (i.e.
every pumped atom is left accurately in the excited state of the
lasing transition, and not in some linear combination of upper and
lower states).

In addition, it developed that NCT could account for some
radiation effects usually claimed as requiring QED for their explana-
tion; and it made a number of new predictions, particularly concerning
noise, coherence, and transient behavior in resonance radiation,
which differed from those of QED in ways which were capable of being
tested experimentally. The scope of our investigations then broadened
beyond noise effects, to the question of radiation theory in general,
since these phenomena appeared capable of giving new basic tests
of QED, in areas where we had no experimental evidence. This theoretical work was reported in the theses of Carlos R. Stroud and Michael D. Crisp.

A theoretical and experimental study of photoelectron statistics was also undertaken, culminating in the thesis of Charles E. Tyler, as described at the end of this Section.

Sequence of Noise Experiments. Whereas at radio and microwave frequencies, the ultimate noise level placing a limit on oscillator stability and useful amplification is the Nyquist thermal noise power $kT\Delta v$, where $k$ is Boltzmann's constant, $T$ the Kelvin temperature, and $\Delta v$ the bandwidth, it is generally believed that the fundamental limit at optical frequencies, where $hv \gg kT$, is instead $hv \Delta v$; i.e. a light signal carrying less power than this cannot be amplified to preserve amplitude and phase information. The physical reason for this much higher limitation is variously described in the literature as spontaneous emission, zero-point energy, or the Heisenberg uncertainty principle; elementary calculations based on all of these premises lead to the same result. However, while the Nyquist noise $kT\Delta v$ is a well-established experimental fact, long used by radio engineers in designing the input circuits of sensitive receivers and amplifiers, the "quantum noise" $hv \Delta v$ remains a theoretical prediction without direct experimental verification. If it is indeed a fundamental limitation, then the possibilities of optical communication and information transfer systems are quite restricted; whereas if this noise is avoidable in any way, so that the limiting noise level would be given by the thermal generalization of Nyquist's formula
there would be, in principle, vastly improved prospects for optical signal detection. On an issue as important as this, one should seek direct experimental evidence, particularly since the theory that leads to the $h \nu \Delta \nu$ prediction is known to be unsatisfactory on mathematical and logical grounds, in spite of several experimental successes.

Accordingly, we have planned and initiated a sequence of three experiments designed to check the reality of this "quantum noise" by three successively more detailed measurements, as follows:

I. Laser Decay and Buildup. When an oscillating He-Ne laser is suddenly turned off, the light intensity in the optical cavity decays exponentially, dropping by about a factor of 10 in each microsecond. The cavity has initially a stored energy of about $10^{10} h \nu$, so it requires about 10 microseconds to decay to the zero-point level $\frac{1}{2} h \nu$. If the laser is turned back on in less than 10 microseconds, the radiation level will therefore start to build up (again exponentially, but at a different rate depending on the excitation) from a higher level than $\frac{1}{2} h \nu$; and so it will reach, say, 90% of its final amplitude in a time that depends on how long it was turned off.

Under ideal conditions, the buildup time would be proportional to the off-time if $t_{\text{off}} < 10$ microseconds.

If now the zero-point energy is real and the physical cause of spontaneous emission (as often supposed in theoretical treatments),
then the cavity energy cannot decay below $\frac{1}{2} \hbar \nu$; and so the buildup time should become independent of the off-time when the latter is greater than about 10 microseconds. On the other hand, if the zero-point energy is only fictitious (as also often assumed in theoretical treatments), then nothing in particular should happen at the level $\frac{1}{2} \hbar \nu$, and the buildup time might be expected to continue increasing with the off time beyond 10 microseconds. Eventually, of course, the buildup time must level off at a value determined by the initial rate of radiation from the plasma into the optical cavity mode; according to our calculations this level is usually not far from $\frac{1}{2} \hbar \nu$, but it should depend on the manner of pumping.

After encountering many difficulties, we have succeeded in developing optical and electronic systems capable of doing this experiment; and indeed we can measure not only the off-times and buildup times, but we can follow the entire decay and recovery curve, down to levels $\sim \frac{1}{2} \hbar \nu$. However, we do not yet have sufficiently accurate calibrations of the optical mirrors, attenuators, etc. to get a good absolute measurement of this level so that definite conclusions could be drawn. This difficulty can be overcome in the second phase of the program.

II. The Injection Experiment. Instead of varying the starting level in the optical cavity by variable off-times, one can inject a weak signal of known amplitude from another laser, and investigate both the buildup time and the phase of the resulting high-level oscillations. (This is, in effect, a superregenerative optical amplifier, whose operation is essentially the same as that of the
Armstrong superregenerative receivers used in the early days of
radio. The experiment then consists of determining the lowest
injected power energy $W$ that can influence the buildup of the laser
oscillator. If the usual quantum noise formula is valid, control
must be lost when $W < \frac{1}{2} \hbar \nu$; conversely, if control persists below
this level, the quantum noise formula would be shown to be incor-
rect, or at least misinterpreted. The microwave version of this
experiment was carried out many years ago, at the Naval Research
Laboratory, by E. T. Jaynes. It was found that control of phase
and buildup of a 1 kw, 1 GHz oscillator was maintained right down
to the level $W = kT$ of the injected signal in the tank circuit,
making the arrangement the most sensitive microwave detector then
in existence. A still more direct test is provided by the last
experiment.

III. The Interferometer Experiment. Here we use one laser
as a high-level signal source, the other as a low-level linear
amplifier. If a light attenuater of attenuation D decibels,
followed by an amplifier of gain D decibels are placed in one leg
of a Mach-Zehnder interferometer, we should still obtain stable
fringes of 100% visibility if the amplifier introduces no noises;
but as D is increased the power level at the amplifier input decreases,
and eventually the amplifier noise, of whatever origin, will obscure
the signal. According to the Heisenberg uncertainty principle (or
rather, one common interpretation of it), we should not be able to
determine simultaneously both the phase and amplitude of a weak
light wave; this again leads to the "quantum noise level" $h\nu \Delta\nu$ as the lowest signal power which can be re-amplified. Observing both the position and visibility of the fringes amounts to measuring simultaneously both the phase and amplitude of the input signal; and if one ever sees stable, high visibility fringes when the input power is less than $h\nu \Delta\nu$, the usual interpretation of the uncertainty principle would be disproved.

Work on these three experiments, conducted by Wm. Ladrigan, is continuing under AFOSR support.

**Photoelectron Counting Statistics.** At the beginning of this project, many laboratories were engaged in experiments on photoelectron statistics, but all with the common viewpoint that the nature of the photoelectric effect was well understood, and statistical counting experiments were used to determine properties of lasers near threshold. We took the opposite view of regarding a laser well above threshold as a new research tool, and using it to investigate some things about the photoelectric effect that had been widely assumed, but not experimentally proven.

The first experiment was a search for some kind of regularity in photoelectron emission times using laser light, the thought being that emission of one photoelectron might in some way "paralyze" a small area of the photocathode, rendering emission of another less probable for a short recovery time. This could not be investigated with previous light sources, because all of them had unknown, but presumably large, instantaneous intensity fluctuations which would obscure any paralysis effect. In addition, the coherence of the laser light over a wide cathode area was a condition previously
unattainable except at very small light intensities. If emission of photoelectrons followed the completely random Poisson law, the times between emission of successive photoelectrons should have an exponential distribution, whereas any paralysis effect would shift the peak of the distribution to some finite delay time. In the first crude experiments we thought we saw such an effect, but upon acquisition of a time-to-amplitude converter and 128-channel analyzer so that very large amounts of data could be processed, the "effect" went away.

Next, we repeated the famous old "starting-time" experiment. One of the strongest arguments for the existence of photons has been the claim that when a photocathode is illuminated, the photoelectric effect starts "instantaneously," in a time so short that on the classical wave theory of light there wasn't enough time to deliver the energy equal to the work function of the cathode to an electron. However, a literature search showed that none of the old experiments cited in our elementary textbooks actually had sufficient time resolution to provide a real test of this claim. Indeed, a simple statistical analysis showed that no experiment performed before the days of the photomultiplier and CW laser could possibly have given such a test; but that with modern photocathode efficiencies and fast pulse circuits, an experiment could now be done that had, effectively, eight orders of magnitude better time resolution than previous ones.

In this experiment, carried out by Charles E. Tyler, light from a He-Ne laser was sent through a very fast electro-optical valve developed here using ferroelectric BaTiO$_3$ crystals driven
by avalanche transistors, as the active elements. With this one could turn on a light beam in not more than 2 nanoseconds. This light was then attenuated by a factor of about $10^{10}$ and fell on the cathode of a cooled photomultiplier. The time-to-amplitude converter measured the interval between turn-on of the light and appearance of the first photoelectron. The best measurement, requiring a week of continuous data-taking, showed that light of intensity corresponding to about 1 photon in 30 microseconds, could occasionally eject a photoelectron in not more than 3 nanoseconds after illumination, thus proving for the first time what had been assumed as fact in two generations of textbooks. The details of this experiment are given in Dr. Tyler's thesis.

Finally, we performed an experiment designed to check for the existence of a "threshold effect": i.e. does light have to have a certain minimum amplitude before it can eject photoelectrons? Such threshold effects had been noted in other processes induced by light, particularly the photographic latent image formation, and in biological effects of gamma-rays. We measured counting rates as a function of light intensity, looking for some nonlinearity in very weak light. Again, an effect appeared at first to exist, but on making various improvements, we could detect no departure from (counting rate) $\sim$ (light intensity) at intensities corresponding to less than ten photons per second, for 6328 Å laser light.
2. Most Significant Results

Probably the most significant results completed thus far are in the theoretical work of C. R. Stroud and M. D. Crisp, which have shown that semiclassical radiation theory can account for far more radiation phenomena than previously thought, and have re-opened this issue, stimulating a number of theoretical investigations and several new experiments, in other laboratories.

The photoelectric starting-time experiment of C. Tyler is at least of great pedagogical significance, since for the first time it was proved that certain properties of the effect, commonly assumed without adequate experimental evidence, were actually correct.

The potentially most significant work is the sequence of quantum noise experiments still underway, on which we hope to have a substantial body of results to report at the end of the next school year.
Faculty Supported in Whole or in Part:

E. T. Jaynes, Professor

Students Supported in Whole or in Part:

<table>
<thead>
<tr>
<th>Name</th>
<th>Details</th>
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<tbody>
<tr>
<td>Michael D. Crisp</td>
<td>(Ph.D. 1968; present address: Owens-Illinois Laboratories, Toledo, Ohio)</td>
</tr>
<tr>
<td>Carlos R. Stroud</td>
<td>(Ph.D. 1969; present address: Institute of Optics, University of Rochester, Rochester, N. Y.)</td>
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<tr>
<td>Conilee Kirkpatrick</td>
<td>(experimental work in Summer of 1969).</td>
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<tr>
<td>J. Wm. Ladrigan</td>
<td>(experimental; probably will finish May 1972)</td>
</tr>
<tr>
<td>David Gibbs</td>
<td>(theoretical; probably will finish May 1972)</td>
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K. LUSZCZYNSKI
CRYOGENIC DETECTORS

1. Area of Research

(i) Investigation of excitations radiated from a thermal source into helium II below 0.3°K, with special emphasis on velocity of propagation, dispersion-spectral distribution and angular distribution of the quasiparticle radiation.

(ii) Investigation of energy transfer from a hot solid surface into helium II under pulsed conditions.

(iii) Cryogenic detectors of hypersonic excitations in helium II.

(iv) Development of He³/He⁴ dilution refrigerator maintaining steady temperatures in the region of 0.1°K.

(v) Trapped magnetic fields in superconducting arrays of cylinders and rings.

(vi) Flux quantizations and Josephson tunneling.

Research accomplishments: the projects described above have been for the most part completed and described in publications and internal reports.

2. Significant Results

This grant has supported in part the work of two graduate students who have completed their Ph.D. research work.

In addition it has provided training and research experience for another graduate student and two undergraduates.

The research work supported in part by this grant has led to new results which provide important new insights into the properties of quasiparticle radiation in helium II. Also, valuable experience has been obtained in the development, and use of sensitive detectors of hypersonic phonons in liquid helium.
Equipment which was bought or built with the aid of this grant has increased the capability of the laboratory for efficient and accurate collection of experimental data.

3. **Interdisciplinary Activities and Impact Outside the University**

The research work described here has overlapping interests with other areas supported by this grant, especially the areas of submillimeter astronomy and acoustic spectrum of solids.

4. **Faculty**

K. Luszczynski - Associate Professor

**Students**

C. Pfeifer - has completed Ph.D. research; thesis in preparation; presently employed as an instructor in the Department of Physics, University of Wisconsin.

Mr. William Ladrigan (CBNS Fellow) - graduate (Ph.D. 1971) now Research Assistant, Washington University.

Dr. Robert Guernsey, (NSF Fellow, predoctoral) (Ph.D. 1969) now Assistant Professor, Columbia University, New York.

Dr. Donald Cowgill (NASA Trainee) (Ph.D. January 1971) now Research Associate, Washington University.

Mr. Fred Weinhaus (undergraduate) - now Research Assistant, Duke University.

Mr. Edwin Nothdurft, (undergraduate) - now graduate student, Washington University.

**Theses**


"Energy Transfer from a Pulsed Thermal Source to He II below 0.3°K", C. D. Pfeifer, Ph.D. (in preparation).

Reports


PETER R. PHILLIPS
SEARCH FOR A PREFERRED FRAME OF REFERENCE

1. Area of Research

We have concentrated almost entirely on a search for a preferred frame of reference. We assume that this will result in an additional term in the Hamiltonian of the form $G \mathbf{\hat{\sigma}} \cdot \mathbf{\hat{v}}$ where $\mathbf{\hat{\sigma}}$ is the spin of a particle and $\mathbf{\hat{v}}$ its velocity in the preferred frame. The aim is then to set a limit on the magnitude of $G$. A second program, on possible superconductivity in organic molecules, was initiated but never carried far in view of the pessimistic theoretical assessments which were soon made.

Research accomplishments have all been made possible by the combined support of NSF and NASA

1. Theoretical work on a possible physical framework underlying a preferred frame, and its compatibility with previous knowledge (Phys. Rev. 139B, 491 (1965)).

2. Experimental search for anomalous torques on the neutron, using suitable nuclei, first D and the C$^{13}$ (Phys. Rev. 180, 1331 (1969)).

3. Experimental search for anomalous torques on the electron, using a torsion pendulum at room temperature, (Nuovo Cimento 64B, 8 (1969)).

4. Continuation of this search using a pendulum at liquid helium temperature.

In the course of this research we have established a laboratory at Tyson Valley, 20 miles from St. Louis, which will be suitable in the future for any other experiments requiring a quiet environment.

Short range goal: training of personnel, Dorothy Woolum earned her Ph.D., went on to work with Professor Walker in the Space Physics Laboratory and is now working with Professor Wasserburg at Cal. Tech.
2. **Significant Results**

Lorentz invariance has been checked in a new way, in two separate experiments, and found to be still valid even in this previously unexplored region.

3. **Interdisciplinary Activities and Impact Outside the University**

The investigation of anomalous torques on the neutron involved collaborations with Dr. Driscoll, at the National Bureau of Standards, and with Professor David Grant, of the University of Utah.
RONALD K. SUNDFORS

TECHNIQUE OF COUPLING SHORT PULSES OF ACOUSTIC ENERGY TO NUCLEAR SPIN SYSTEMS

1. Area of Research

The original research proposal was in the area of experimental research using ultrasonic techniques to study basic properties of solids. Specifically, it was proposed to explore the possibility of using the coupling of short pulses of resonant acoustic energy to nuclear spin systems in solids.

To carry out this proposal, a pulse spectrometer similar to a nuclear magnetic resonance spectrometer was designed and many of the components constructed, assembled, and tested.

During the experimental study of solid samples to be used for this investigation, a very weak but measurable coupling between acoustic waves and the charge carriers in InSb was observed. A particular InSb sample was p-type with average acceptor concentration of \(1.45 \times 10^{16} \text{ cm}^{-3}\). This grant helped to support the initial research which identified this interaction as due to two different acoustic phonon-charge carrier couplings:

(i) deformation potential coupling;
(ii) piezoelectric coupling.

These interactions were studied and the constants characterizing the interactions measured.

This grant also helped support two other investigations related to the main proposal. The energy density of acoustic radiation from a cylindrical quartz transducer bonded to one of two parallel faces of an InSb single crystal was measured. For long acoustic pulses or for continuous wave acoustic radiation the acoustic radiation was found to lie in the beam defined by the radiating area and to fall off rapidly for radii outside the radiating area. These results were
in excellent agreement, for the same radiating diameter to wavelength ratio, with the electromagnetic radiation laser results of Fox and Li of Bell Laboratories.

The grant also supported research to be able to characterize and make absolute measurements of the acoustic properties of a mechanical resonator consisting of a transducer bonding material, and crystal with two flat, parallel faces.

2. **Significant Results**

NASA support are the study of the piezoelectric and deformation potential coupling in InSb, the opportunity to pursue experimental ultrasonic investigations related to the main proposal. The opportunity for support and research training of graduate students.

3. **Interdisciplinary Activities and Impact Outside the University**

This grant helped to support the research of Dr. W. D. Smith during the period that he had an NASA Pre-doctoral training fellowship.

4. **Faculty**

Professor R. K. Sundfors was supported in part.

**Students**

- Mr. Len Fennell, M.S. June 1969 - U.S. Navy
- Mr. C. Myles, M.S. June 1971 - graduate student, W. U.
- Mr. L. Davis, M. S. June 1971 - graduate student, W. U.
- Mr. T. H. Wang - graduate student, W. U.
ROBERT M. WALKER
DEVELOPMENT OF AN ALPHA-RECOIL TRACK METHOD
OF ABSOLUTE AGE DATING

1. Area of Research

The initial support allowed us to explore quickly an interesting new idea and to prove that further work along these lines was worthwhile. We subsequently filed a research proposal with the N.S.F. to undertake further development of this idea as well as several other geologically oriented projects. This research proposal was accepted and we have now been funded for over three years.

2. Significant Results

Interestingly, one outgrowth of this work on alpha-recoil tracks has been the acceptance by NASA of a flight experiment for Apollo 16. Sometime after starting our work on alpha-recoil tracks we realized that their existence implied that extremely heavy solar wind particles should also give tracks. Mica detectors will be flown to the moon in order to measure the flux of such particles.

Part of the work supported under the grant was directed to developing a new method for measuring Th-U ratios on a microscopic scale. These techniques were subsequently utilized by us in our studies of moon samples where we showed that the Th-U ratios of uranium-bearing minerals varied by over a factor of twenty depending on the type of mineral. This has important implications for the chronological studies of moon samples by the Pb isotope dating method and also for the interpretation of extinct isotope data in meteorites.

3. Interdisciplinary Activities and Impact Outside the University

The NASA grant allowed us to establish an immediate collaboration between the Earth Science Department and the Physics Department on a problem of mutual interest to both - namely the development of a new method of absolute age dating.