Naval Research Reviews

Office of Naval Research
Two / 1988
Vol XL

NRL engineers place Vanguard I atop the third stage of the launching vehicle. From left to right are Roger L. Easton, Sandy J. Smith, Robert C. Baumann, and Joseph B. Schwartz.

World's Oldest Orbiting Spacecraft is 30 Years Old

The Naval Research Laboratory's (NRL) Vanguard I satellite celebrated its 30th year in orbit in March. Launched on March 17, 1958 from Cape Canaveral, Florida, Vanguard was the second artificial satellite successfully placed in earth orbit by the United States.

The first solar-powered satellite, Vanguard has the distinction of now being the oldest artificial satellite orbiting the earth. (Its predecessors, Sputniks I and II and Explorer I, have since fallen out of orbit.)

Vanguard I was launched as part of the United States' participation in the International Geophysical Year (July 1957 to December 1958) in a tri-service project with the Army operating the tracking stations and the Air Force providing the launching site. NRL was also responsible for developing the launch vehicles; developing and installing the satellite tracking system; and developing, constructing and testing the satellites in a program headed by NRL's Dr. John Hagen.

Vanguard I is six inches in diameter and weighs about three pounds. Despite its diminutive proportions, Vanguard I provided several important findings. It proved that the earth is pear-shaped, not round; corrected ideas about the atmosphere's density at high altitudes; and improved the accuracy of world maps.

A former NRL scientist who worked on the Vanguard tracking system, remarked that the Vanguard program was significant in that, "it was a purely scientific rocket and spacecraft program," and that it was "most successful in accomplishing its mission."

Although Vanguard I's solar-powered radio transmitter stopped transmitting in 1964, U.S. space surveillance systems still track the spacecraft.

When it was launched 30 years ago, it was estimated that the satellite's life expectancy would be about 200 years. Since then, scientists have extended this estimate to 2000 years. Thus, Vanguard I should be celebrating many more birthdays in space.

Naval Research Reviews

Office of Naval Research
Two / 1988
Vol XL

Articles

Departments

About the Cover

The Guided Missile Destroyer USS Barney, DDG-6, underway during rough seas in the Atlantic Ocean. (See article on page 9.)

Naval Research Reviews publishes articles about research conducted by the laboratories and contractors of the Office of Naval Research and describes important naval experimental activities. Manuscripts submitted for publication, correspondence concerning prospective articles, and changes of address, should be directed to Code OPARI, Office of Naval Research, Arlington, Va. 22217–5000. Requests for subscriptions should be directed to the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. *Naval Research Reviews* is published from appropriated funds by authority of the Office of Naval Research in accordance with Navy Publications and Printing Regulations NAVSO P-35.

REALIZING THE POTENTIAL OF HIGH TEMPERATURE SUPERCONDUCTORS—

Roles of the Federal Government and Industry

by Arden L. Bement
TRW Inc.

Introduction

The following article was given as the dinner speech on February 9, 1988 at the Sheraton Silver Spring, in conjunction with the conference "Superconductivity Research & Development in the U.S. Navy" sponsored by both the Office of the Chief of Naval Research and the National Security Industrial Association. This conference was hosted by Naval Surface Warfare Center's White Oak Laboratory, in Silver Spring, Maryland. This classified briefing included approximately 200 government and industry representatives, of whom some 90 were in attendance at the dinner.

Dr. Arden L. Bement has held the position of Vice President (Technical Resources) since joining TRW Incorporated in 1981. In this capacity he identifies and evaluates emerging technologies and recommends product, material, and process development projects. He also develops special relationships with selected universities and helps recruit key individuals in new technologies of interest to TRW. His previous industrial experience began with his first employment as a research metallurgist and reactor project engineer at General Electric Company at the Hanford Atomic Products Operation in Richland, Washington. He subsequently became manager, metallurgy research department, and later manager, fuels and materials department, at Battelle Memorial Institute.

Dr. Bement received his Engineer of Metallurgy degree in 1954 from the Colorado School of Mines, his M.S. in Metallurgical Engineering from the University of Idaho in 1959, and a Ph.D. from the University of Michigan in 1963. He is a member of the National Academy of Engineering. From 1970–1976 he was Professor of Nuclear Materials, Massachusetts Institute of Technology.

In 1976 Dr. Bement became Director of the Materials Science Office of the Defense Advanced Research Projects Agency (DARPA). From 1979–1980 he was Deputy Under Secretary of Defense (Research and Engineering). On leaving government service he was awarded the Distinguished Civilian Service Award by the Secretary of Defense. Dr. Bement served the Department of Defense as a reserve officer in the U.S. Army Corps of Engineers, retiring as a Lieutenant Colonel.

With Dr. Bement's permission we have included this excellent speech in Naval Research Reviews to give it broad dissemination. We were privileged to have such an honored guest at our conference on superconductivity R&D, where we described our goals as follows:

- ☐ *Keep U.S. companies informed of our quest for successes in superconductivity R&D by describing to them those programs which are in progress and our plans for the future.*
- ☐ *Enlist those industries as partners in our quest by identifying our applications needs and potential areas for their participation.*

Charles H. Craig
Engineering Sciences Directorate
Office of Naval Research

I am honored to be invited to participate in this important conference on Navy research, development and applications of high temperature superconductivity. I would like to reflect with you this evening on the promises, challenges and roles of government and industry in this exciting new field.

Since World War II the Office of Naval Research, the Naval Research Laboratory and the Navy research and development establishment at large have been pioneers in low temperature physics research, the development of superconducting materials and devices, and the applications of superconductivity to Navy needs. The quality of this research has been extraordinarily high and has been responsible for many breakthroughs in electronic devices, magnets, motors, instrumentation, directed energy weapons and magnetic resonance imaging and spectroscopy.

As the Naval Studies Board of the National Research Council has recently concluded:[1] "With the background (in ONR) . . . and the very substantial and excellent in-house superconductivity research being undertaken at the NRL, the Navy is particularly well-positioned to enhance its basic research effort in high-temperature superconductors". The Naval Studies Board went on to recommend that this topic be considered by the ONR as an multidisciplinary Accelerated Research Initiative (ARI), with a broad fundamental approach including theory, chemical synthesis, stability and protective coatings, electronic devices and ceramic processing of bulk and thin-film superconductors. The Board also recommended a focused thrust in thin-film devices, such as Josephson junctions and SQUIDS.

The prospects of achieving room temperature superconductivity; higher field magnets; faster, lower-noise Josephson junctions; higher sensitivity SQUIDS; and high-speed hybrid devices has kindled excitement in nearly every field of science and engineering. Physicists and astronomers together are anticipating new capabilities for advancing the grand unification theory; searching for cosmic relics from the "Big Bang", such as gravitational waves, monopoles and strings; and in measuring the gravitational drag of the earth on the universe. Biophysicists are anticipating greater resolution in imaging the human heart, brain and other organs through magnetic resonance imaging and spectroscopy. They are also interested in probing more deeply into the effects of high magnetic fields on biological processes. Industry is anticipating the emergence of new commercial markets in superconducting electronics, transportation systems, research instrumentation, power machinery, communications, computers and medical diagnostic equipment.

It is interesting to note, however, that nearly all of this excitement has been based on technical concepts that are well understood and have been reduced to practice for some time. Only a few visionaries are beginning to recognize that the unconventional nature and properties of these new superconducting ceramics should lead to new technological concepts not yet fully imagined. I believe such unconventional thinking should be encouraged for long-range Navy applications.

Navy Applications and TRW's Role

The potential of high-temperature superconductivity applications in the Navy span a large spectrum, as you have been discussing at this conference. Large-scale applications include high-field magnets, energy storage systems, fast switches, and superconducting motors and generators for electrical power supply, electrical and MHD propulsion, and directed energy weapons. Small-scale applications include infrared focal plane sensors; antennas; monolithic millimeter wave integrated circuits for space radiometers, communications and missile seekers; SQUID magnetometers and gradiometers for anomaly detectors; and ultra-fast memories, multiplexers and A/D converters for high-performance signal analysis and massive data processing.

TRW has been an industry leader in low temperature superconductive electronics technology for space and defense applications for over 10 years, TRW's program has been led by such veterans of Josephson Junction and SQUID technology as Arnold Silver, who has been in the field since 1964 and who gave the SQUID its name. Under this program, which has involved over $8 million in TRW and contract funding, our team at Space Park has performed a number of advanced technology demonstrations based on niobium and niobium nitride Josephson junction technology; to include:

- ☐ low noise microwave and millimeter-wave amplifiers under NRL sponsorship, and
- ☐ voltage-controlled microwave and millimeter-wave oscillators under ONR sponsorship.

In addition, major current developments include:

- ☐ a monolithic, 100 GHz, low-noise receiver, and a new IR detector for cryogenic focal planes, both under SDI sponsorship, and
- ☐ ultra-low power, ultra-high resolution A/D converters, for which TRW has been awarded two patents and two contract awards, one from ONR.

In January, 1987, TRW began developing a plan for exploiting high temperature superconductivity to address a number of long-term space and defense applications to include magnetic anomaly detectors, millimeter-wave imagers, wide-band signal processors, IR focal plane processors, radar signal processors, millimeter-wave radar, and communication receivers. At present, our Advanced Technology Division is engaged in the first stage of this plan, focused on processing developments and characterization of yttrium and erbium 1:2:3 thin films on strontium titanate, sapphire, and other substrates. We are on the threshold of demonstrating the performance of an RF SQUID made of the yttrium 1:2:3 compound.

In making a strong IR&D commitment to high-temperature superconductivity TRW has envisioned an electronics technology with a number of exciting characteristics:

- ☐ virtually dispersionless transmission lines to 100 GHz,
- ☐ computers with less than half nanosecond cycle times,
- ☐ parallel processing architectures with picosecond gate delays,
- ☐ advanced communication systems and radars with frequencies approaching 1THz, and
- ☐ imaging focal plane receivers and preprocessors with full monolithic array densities operating at fractions of a watt of dissipated power per array.

Compared with conventional superconductors, we foresee that the application of high temperature superconductors will greatly reduce or eliminate cryogenic requirements in space and make available electronic devices and systems with:

- ☐ ten times higher operating frequencies, approaching 10^{13} Hz
- ☐ ten times greater bandwidths, approaching 10^{13} Hz, and
- ☐ ten times faster digital logic, approaching 10^{-14} sec.

For example, a high-temperature superconducting A/D converter would produce more than 3 extra bits resolution or ten times the sampling rate within the same architecture. The ability to operate both superconductor and semiconductor electronic devices at a common 77 K would result in compatible signal levels and efficient hybrid circuits which best utilize the advantageous characteristics of each technology. Furthermore, entirely new device concepts could emerge from such hybridization. If these advances can be realized, they would dramatically improve future capabilities for Navy surveillance systems.

Technology Challenges

While one might speculate about the promises of high-temperature superconductivity, there are a number of formidable technology issues that must be resolved before these promises can be fulfilled. Most of these challenges in the near-term center on materials science and engineering; more specifically materials processing technology.

While one might be fascinated by the elegance of the crystal structure of the perovskite 1:2:3 compounds, these compounds are so difficult to understand and control that no one can yet reproducibly manufacture reliable products from them in either bulk or thin films:

- ☐ The crystalline structure of these compounds has distortions and defects which seem to be important to their properties, but the ro!e of these imperfections is not well understood.
- ☐ The compounds are extremely sensitive to minute variations in treatment, and often no two samples are alike even when the same recipe is followed.
- ☐ The boundaries between grains reduce the current carrying capability by a factor of 100 or more.
- ☐ The crystalline structure is layered as a natural superlattice and the superconducting current prefers to flow within layers and along rows of copper and oxygen atoms and breaks down perpendicular to these layers.
- ☐ The ceramics are not only brittle but deteriorate when exposed to water vapor, CO_2, and other reactive gases.

In addition to these problems, the processing of thin film Josephson junctions, SQUIDS and hybrid circuits have their own special technological problems:

- ☐ The need to heat treat at between 700 and 900°C to develop superconducting properties creates special problems in hybrid circuits involving silicon or gallium arsenide which can tolerate temperatures of only 350°C and 450°C, respectively.
- ☐ Substrates, such as strontium titanate, which permit a useful critical current density at 77 K in thin films are not useful as electronic materials because of their high dielectric constant.
- ☐ The physical and chemical compatibilities of these thin films with today's device processing technologies are not yet well established. However, problems have already been uncovered in the thermal, chemical and particle damage stability of the 1:2:3 compounds with some of these processes.
- ☐ The conducting properties of these materials are sensitive to oxygen content. When heated in a vacuum or reactive gases they can convert from a superconductor to a semiconductor and then to an insulator at low temperatures with the loss of oxygen. The oxygen content must be either maintained during all processing steps or restored at the end of processing. This behavior presents a special problem in the formation of Josephson junctions separated by an oxide layer. New junction configurations or new tunneling barriers may have to be invented to prevent stoichiometry shifts within the 15-20A coherence length of the film free surface or interface.

In spite of these challenges, there are a number of processing developments which give the hope of producing useful devices:

- ☐ Thin films of 1:2:3 compounds with precise control of composition and stoichiometry have been produced by a variety of deposition techniques, to include co-sputtering, electron beam co-evaporation, laser deposition, spin coating and other techniques.
- ☐ Several investigators have reported current densities of 10^4A/cm^2 in micron-thin films. Professor Uchida, University of Tokyo, has claimed $2x10^6$A/cm^2 in the a-b plane for europium 1:2:3 in highly oriented films and the production of single crystals close to 1 mm thick.[2]
- ☐ Highly aligned crystallites with current densities of 1000 A/cm^2 in a 1 Tesla field at 77 K have been produced at AT&T Bell Laboratories by melt textured growth.[2]

However, we must remind ourselves that it took nearly thirty years to develop commercial applications for niobium-titanium, a relatively easy material to fabricate. One shouldn't expect early commercial successes for perovskite compounds, considering their high brittleness and 2-dimensional conducting nature.

While considerable progress in the field is being made, there are also significant impediments to progress. The most important is the lack of a fundamental physical understanding of these new high temperature superconducting materials. Another is the dearth of conceptual studies and systems analyses that demonstrate the advantages of superconductivity at 77 K or above in an applications design context.

Roles of Industry and Government

Clearly a push-pull amplifier is needed to accelerate applications during the early stages. If we are to compress lead time and stake out a competitive position for U.S. industry and our national defense posture we can't wait until all of the early research and science has been completed. The development of applications must be done in concert with the development of the base technology. Defense applications are of such national importance that they warrant special consideration:

- ☐ There is a critical need for more knowledge into the fundamental nature of high-temperature superconducting materials in order to steer technology and indicate possibilities for wholly unique device concepts.
- ☐ More precise measurements are needed to clarify some of the hasty work done to date and to fill critical gaps in knowledge, such as frequency responses into the high GH_z regime.
- ☐ Basic data which will allow evaluating reliability, lifetime, operating margins, and hardness are needed to allow serious applications work to proceed.
- ☐ Technology development programs funded under 6.2 and 6.3A must push to find the highest-leverage opportunities for applicability.
- ☐ Significant efforts are needed to demonstrate on paper those systems performance advantages that will stimulate the resources necessary to develop this new technology.

Strong mission pull is paramount to justifying the substantial R&D investments needed from government and industry to find out if devices and products employing these high temperature superconductors will work. Because of the natural conservatism of designers to introducing new technology on a substitution basis, the technology insertion path must meet several criteria:

- ☐ It must provide significant benefits,
- ☐ It must be modest so that it ensures success, and
- ☐ It must be timely to maintain an aggressive position.

As a start to concept analyses, we might ask:

- ☐ If conventional superconductors could retain their low temperature properties at 77 K what differences would they make?
- ☐ In what ways would Josephson junctions at 77 K dramatically outperform silicon and gallium arsenide devices operating at this same temperature?
- ☐ In what ways could one exploit the lower thermal noise sensitivity, higher magnetic fields and wider dynamic range of high temperature superconductors at low temperatures?
- ☐ Considering the unique superlattice nature of these ceramic superconductors and the close proximity of the coherence length to the repeat distance of the superconducting planes what new device concepts seem feasible?

Such studies should consider the broad spectrum of potential uses, for example:

- ☐ digital and analog electronics,
- ☐ sensors for RF, mm-wave, IR and magnetic fields,
- ☐ electromagnetic shields,
- ☐ power transmission,
- ☐ passive components, and
- ☐ propulsion systems.

The details of processing these extremely difficult materials into circuits must yet be developed. Fortunately, there are many potential routes that can be tried. However, highly innovative techniques yet to be invented will also be needed. The interrelationships between processing and design will be a continuing challenge to materials scientists and engineers, applied physicists, and designers.

Taking all these needs into account, and recognizing that R&D in this field must compete with other urgent priorities, there is a need for a development plan for 1990-1993 and beyond that will address the following questions:

- ☐ Who will define the applications and missions which will uniquely capitalize on the special properties of high temperature superconductors?
- ☐ Who will define the performance requirements for these applications and missions?
- ☐ Who will conduct the demonstrations and pilots of increasing complexity that will serve as the vehicles for technology insertion?

It seems clear to me that industry and the DoD laboratories will have to work in close partnership to find answers to these questions. These answers are the missing elements needed to increase industry's commitment and R&D investment, establish closer linkages between industry and government laboratories, and bring needed focus to the national R&D program.

Defense contractors are currently developing a capability to design and produce devices, subcomponents, and systems involving the use of high temperature superconductors. The U.S. industrial R&D effort is currently estimated at between $50 and $100 million,[2] which is roughly comparable to the Federal government investment. Most of this research currently is focused on materials science and engineering and early processing developments. Much of the progress being made is still awaiting publication pending patent clearing. Objective observers claim that the U.S. is presently doing the best research in terms of versatility and depth. However, the Japanese seem to have the best coordinated effort to achieve the early applications because of their better integrated government-industry joint planning and execution. Furthermore, Japan's ratio of industry to government investment in this field is very much larger.

Applications of superconductivity technology to defense systems in general are still at an early stage. Therefore, it is essential that developments of low temperature superconductivity be continued in order to validate the possible application advantages over alternate technology options. For example, TRW is still sustaining its IR&D investment in low temperature superconductivity developments to strengthen its technology base at the device and systems level necessary to pull through high temperature superconductors as the materials and processing technologies mature. Furthermore, there are still many unknowns about operational feasibility that can be best understood at the circuit and system levels of integration. Continued emphasis on low temperature superconductivity continues to be necessary to develop critical information for future high temperature superconductor designs.

During this early stage of finding out what technological future the U.S. will have in high temperature superconductivity, industry will need to make a concerted effort to link their capabilities with those of universities and Federal laboratories:

- ☐ Industry will depend on universities and Federal laboratories, especially the considerable expertise and special experimental facilities for superconductivity research at NRL, NBS and the national DoE laboratories, to develop a detailed fundamental understanding of these materials.
- ☐ Industry also needs sources of current information of leading scientific and technical developments around the world. The many national and international conferences being sponsored by the Federal agencies and the services of the ONR offices in London and Tokyo are vital in this regard.
- ☐ Industry needs planning guidance from the mission agencies on missions, applications, early demonstration test beds and application requirements in order to formulate their strategic business plans and focus their R&D investments. As early application targets get defined, industry's risk takers will become more visible, commitments will become firmer, and stronger linkages will be forged between industry, universities, government laboratories and program offices.

Even at this early stage, considerable leveraging of technical resources is taking place both in government and industry:

- ☐ Improved coordination of in-house and out-of-house R&D sponsorship is taking place through the Federal Laboratory Consortium, which in turn is seeking closer ties to the Industrial Research Institute. The current Navy Consortium on High Temperature Superconductivity is an excellent example of cooperation among government R&D establishments
- ☐ Industry is establishing closer ties to government laboratories through provisions of the Technology Transfer Act of 1986 and the President's Executive Order on "Facilitating Access to Science and Technology", dated April 10, 1987.
- ☐ Industry is also looking forward to the competitiveness benefits from the President's eleven point superconductivity initiative. The announced shifting of resources to stimulate research on superconductors is of particular interest.
- ☐ National industrial councils and R&D consortiums are springing up to pool common interests and resources to exploit early technological advantages for possible defense applications and commercial markets.

TRW, with its balanced program in both low temperature and high temperature superconductivity based on Josephson junctions, is pursuing close ties with NRL, NBS, JPL, Lawrence Livermore Laboratory, Los Alamos Scientific Laboratory and several other leading research groups at government and university laboratories to augment our knowledge, capabilities and know-how in superconducting electronics. Our program plan places particular emphasis on identifying superior outside sources of technology and tapping these sources by appropriate means to accelerate progress on specific early application developments.

From what I have heard today, the Navy is at the forefront of this exciting new scientific technological enterprise and is rapidly identifying the high-leverage opportunities for future Navy needs. As you begin to formulate your 6.2 and 6.3A initiatives. I would commend to you the recommendations of the National Academy of Sciences' Committee on Science, Engineering and Public Policy (COSEPUP) in the examination of the Federal role in applied research:

- ☐ Define goals modestly.
- ☐ Tailor the program to fit the structure of the target industry.
- ☐ Match the needs of users and the capabilities of research institutions, and
- ☐ Emphasize generic research, leaving product design and commercialization to the private sector.

Of course, being aggressive at this early stage of international competition has a virtue all its own.

In conclusion. I am greatly honored to be a participant in this critically important conference, and look forward to sharing with you the excitement of this new technological adventure.

References

1 *Research Opportunities in Materials Science*, Naval Studies Board, National Research Council, NRC:NSB:025, National Academy Press, Washington, D.C., 1988.

2 *Materials and Processing Report*, Massachusetts Institute of Technology Press, Vol. 2, No. 10, January 1988.

Profiles in Science

Cathleen Synge Morawetz

Dr. Cathleen Synge Morawetz has been the Director of the Courant Institute of Mathematical Sciences, New York University since 1984. For 42 years, Professor Morawetz has been affiliated with the Courant Institute as research assistant, student, and professor. She has often been a principal investigator for the Office of Naval Research beginning in the early 1950's.

Professor Morawetz is nationally known for her work in the applications of partial differential equations particularly as these are used in the analysis of transonic flow and acoustic wave propagation. Another research interest of Professor Morawetz is the mathematics of the scattering of waves. Scattering arises in all sorts of stituations. When a wave which can be electromagnetic, sound, or elastic hits a barrier, it interacts with the barrier. The wave can be reflected, absorbed, or transmitted depending on such things as the wave frequency and the properties of the barrier. The problem in scattering theory is to analyze how the interactions take place and what can be observed from a distance.

Professor Morawetz has twice been a Guggenheim Fellow and in 1980 received the prestigious Lester R. Ford Award from the Mathematical Association of America. Currently a trustee of the Mathematical Association, Morawetz also served for several years as a trustee of Princeton University. She is at present the director of the NCR Corporation (a large computer firm) as well as a trustee of the Alfred P. Sloan Foundation. She is a Fellow of the American Association for the Advancement of Science and the American Academy of Arts and Sciences.

Growth of Winter Storms at Sea

by Carl W. Kreitzberg, Drexel University
Ron Hadlock, Battelle Ocean Sciences

The ERICA Phenomenon

Stormy weather at sea outside of the tropics is predominantly associated with mid-latitude low-pressure systems about 1000 kilometers in diameter that contain most of the strong surface winds and heavy precipitation. Storms form as the result of the horizontal temperature gradient, baroclinity, that develops between cold air masses that form in polar and cold continental or ice-covered regions and warm air masses that form at lower latitudes and over warmer oceans. The temperature gradients become large where the air masses are brought into proximity by the larger-scale planetary circulations. The air masses and planetary circulations evolve over spatial scales of 3000 kilometers and time scales of ten days. The center of gravity of the cold air mass is lowered when the cold air sinks and the warm air rises during storm growth, thereby converting gravitational potential energy into the kinetic energy of the strong winds. The winds in the storms rotate in the direction of the Earth's rotation, cyclonically, so the storms are called cyclones and their development is called cyclogenesis.

Horizontal winds on the scale of 1000 km and larger are determined to a first approximation by the balance of the horizontal pressure gradient force, toward lower pressure, and the Coriolis force due to the Earth's rotation (when viewed in a coordinate system rotating with the Earth) which is to the right of the horizontal wind vector. Exact balance of these forces is called geostrophic balance which can be maintained without any vertical motion even with a large horizontal temperature gradient that does not change with time. This balance is achieved through a thermal wind shear directed normal to the temperature gradient with the warmer air to the right; when warmer air is to the south, the geostrophically balanced wind component toward the east increases at higher levels. The jet stream is the result of the thermal wind shear at those latitudes with the strongest horizontal temperature gradient. Growth of these storms, cyclogenesis, occurs when the temperature gradients change and vertical air motions occur so that the winds can adjust to the new temperature gradients.

The vertical motions associated with storm development require horizontal motions that change the rotation of the air about the vertical axis; this rotation is the vorticity, relative to the coordinate system rotating with the Earth. The absolute vorticity is the sum of the relative vorticity and the vertical component of the Earth's vorticity and is generally positive. Therefore, air converging beneath regions of ascending vertical motion rotates ever more rapidly about the vertical axis nearly in balance with the low pressure system developing at the center of the rotating circulation.

The fundamental mechanism of cyclogenesis is well understood from a half-century of observations by instruments carried aloft over continents on weather balloons. These instruments are called rawinsondes because they radio back data from which pressure, temperature, humidity and wind data are determined; the data are soundings of conditions in the column through which the balloons rise.

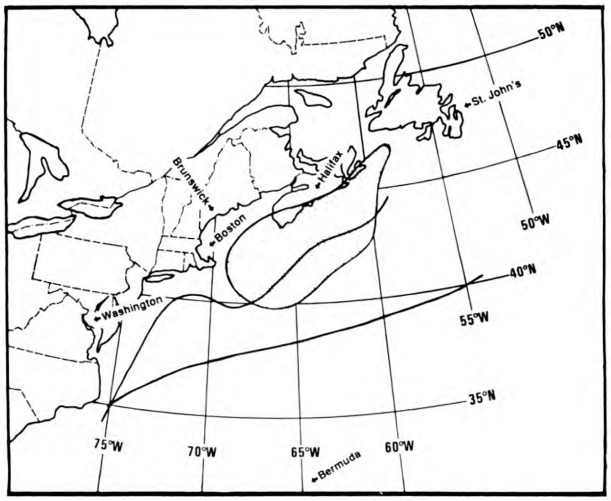
The traditional quasi-geostrophic theory of cyclogenesis outlined above does not explain the rate of growth of many of the winter storms at sea. The Experiment on Rapid Intensification of Cyclones over the Atlantic (ERICA) is a project being conducted to understand why wintertime ocean storm development often is far more rapid than that observed over land. The storms are very dangerous because of their high frequency of occurence, the large size of the region of the gale and hurricane force winds they produce and the damage to ships and coasts produced by the substantial waves and icing. Because of their sudden growth, in about 12 hours, protection from these extreme hazards depends upon confidence in weather forecasts (or else we can plan to not operate in the winter in oceans that are often stormy). Confidence in forecasts of storms as yet unborn is unlikely to be warranted until we understand the physical mechanisms responsible for the growth of these storms and build that information into our weather observing and forecasting system.

ERICA is the larger portion of the Heavy Weather at Sea Accelerated Research Initiative in the Marine Meteorology Program at the Office of Naval Research (ONR). The Department of Defense, through many Navy, Air Force, and Marine Corps organizations, is a major partner with ONR in the ERICA field study. The National Oceanic and Atmospheric Administration (NOAA), through their Office of Aircraft Operations (OAO), National Weather Service (NWS) and National Environmental Satellite and Data Information Service (NESDIS); the Atmospheric Environment Service of Canada (AES) and the Federal Panel on Energy Research and Development (PERD); the National Science Foundation (NSF); and the National Center for Atmospheric Research and the Oceanographer of the Navy are also major partners in the research to be conducted in Winter, 1988-89 over the northwest Atlantic.

The ERICA phenomenon is the abnormally rapid growth of winter cyclones in a remarkably small portion of the northwest Atlantic. This phenomenon has been identified by the highly focused distribution of rapid intensification of

Figure 1

The ERICA region: the stippled area denotes the region of greatest pressure falls in ERICA storms; the smoothed Continental Shelf boundary (100 fathoms) and the smoothed Gulf Stream mean position (to the South) are indicated.



cyclones east of Cape Cod and south of Nova Scotia in Figure 1. The focus of the storm growth region is between the Gulf Stream and Nova Scotia, centered over the Continental Shelf.

A study of NWS surface weather maps during 22 winter seasons identified the tracks of storms that deepened at the ERICA criterion rate (at least 10mb per 6 hours for at least 6 hours). The study was confined to the region from 50 W to the Rocky Mountains and 30 N to 55 N and to the months of December, January and February. Of the 111 storms found to meet the ERICA criterion for rapid development, 104 were maritime cases and 7 were continental cases; therefore the phenomenon is predominantly maritime. The tracks for the maritime storms ar shown in Figure 2. Preliminary studies showed far fewer developments at the ERICA rate outside of these winter months so it is also predominantly a wintertime phenomenon.

To quantify the location of growth for ERICA storms, the pressure deepenings following the centers of the storms during rapid growth were tabulated for each 2 degree latitude, longitude square. These values shown in Figure 3 are the total deepenings in millibars in each square for the 104 maritime cases whose tracks appear in the previous figure. The region with deepenings exceeding 50mb is outlined in Figure 3 and shown by stippling in Figure 1. These storms are typically 10 to 15 degrees latitude in diameter, so for their growth region to be so sharply confined between about 40 deg. N and 45 deg. N. in Figure 3 is truly remarkable. It is also surprising that the growth is more rapid where the Gulf Stream is further from the continent.

Figure 2

Tracks (straight lines drawn between the beginning and ending of rapid development) for 104 ERICA-type maritime storms during 22 winters (1966-1987).

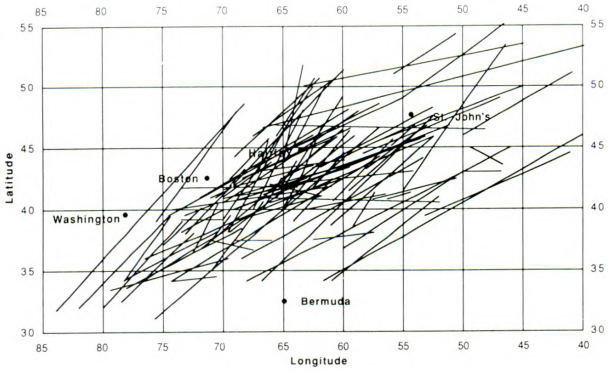


Figure 3

Spatial distribution of pressure falls for 104 ERICA storms during 22 winters (1966-1987). The region of greatest pressure falls is bounded as denoted in Fig. 1.

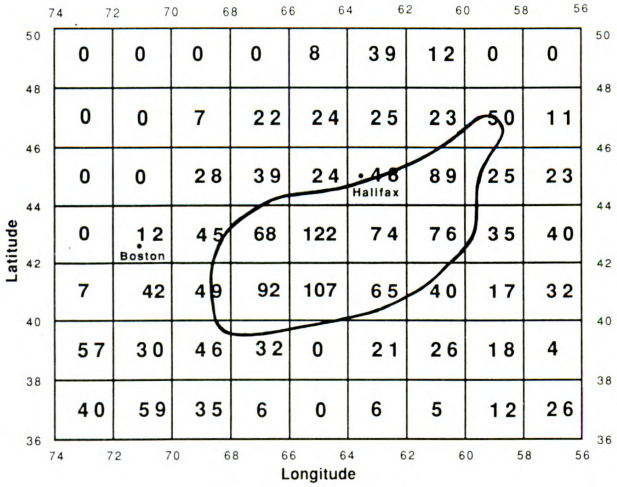
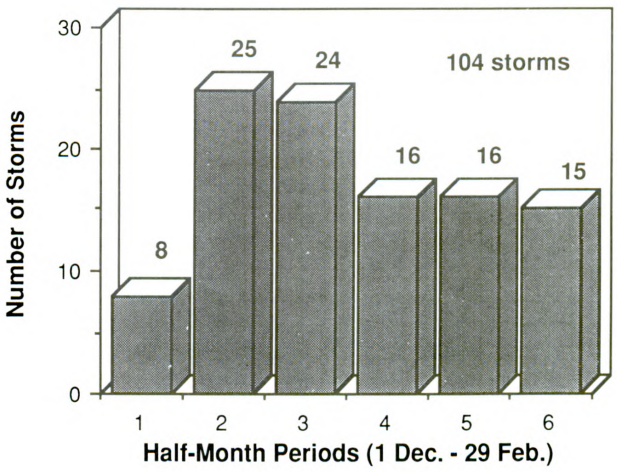


Figure 4 shows the distribution of these storms within the winter months, grouped into biweekly periods. Storm occurence frequently peaks in the last half of December and the first half of January. A comparison of five-day ERICA storm frequency and five day mean surface temperatures over the United States east of the Rockies reveals a gap in the ERICA storm frequency in late January in conjunction with the "January thaw" in the temperature data during these same 22 years. This relation needs further study and is beyond the scope of this paper.

Figure 4

Temporal distribution, in biweekly periods, of 104 ERICA storms during 22 winters (1966-1987).



The ERICA problem, then, is to determine the mechanisms responsible for the remarkable distribution of abnormally rapidly developing winter storms between the Gulf Stream and North America. The practical problem of forecasting these very important storms is one step beyond the basic research problem under study by ONR but is the center of concern of the operational components of the Department of Defense, the NWS and the AES. Until now, it has been impossible to observe the details of these storms because they develop over the ocean in cloudy conditions where conventional observations are inadequate. Therefore, an integral part of the ERICA program has been to find new observing tools that will be adequate to study the interior structure of these storms.

New Tools

Airborne science has developed to the point that reliable aircraft with weather instruments and experienced crews are available to study storms at sea. NOAA/OAO has two Lockheed Orion WP-3D aircraft well equipped for research in ocean storms. These facilities have been used for a number of years to study the internal structure of hurricanes. The National Center for Atmospheric Research, Research Aviation Facility, NCAR/RAF, has an Electra with many of the capabilities of the OAO WP-3Ds. NCAR is sponsored by the National Science Foundation. RAF also has a Sabreliner outfitted for measuring atmospheric properties at flight levels near the jet stream (8 to 10 kilometers) and above the operational altitude of the WP-3Ds and Electra. The United States Air Force has WC-130s equipped for operational weather reconnaissance. These USAF aircraft locate hurricanes in the summer and operate in the winter under the National Winter Storms Operations Plan, NWSOP, in conjunction with the NWS National Meteorological Center, NMC, and can gather data over large regions in and around ERICA-type storms.

All of these aircraft operated in the Genesis of Atlantic Lows Experiment, GALE, January-March, 1986, a project that was led by NSF with many oceanic observations being funded by the Heavy Weather at Sea Initiative at ONR. GALE set the stage for ERICA in many ways; it focused on the initial formation of cyclones off the Carolina coast some of which developed into ERICA-type storms as they moved further north and out to sea. Coincident with GALE, the AES conducted the Canadian Atlantic Storms Project, CASP, that studied many of the GALE storms as they crossed Nova Scotia and Newfoundland Island.

One of the most important data sources for studies of cyclogenesis are the sounding instruments carried upward on weather balloons, called rawinsondes, or dropped from aircraft on parachutes and called dropwindsondes. Current operational dropwindsondes used in GALE and on the USAF NWSOP missions are called Omega Dropwindsondes, ODWs, because they use Omega navigation signals to determine winds. These instruments have several limitations. The aircraft equipment and the sondes are rather expensive, the sondes are so heavy that they can only be used over the ocean when there are no aircraft beneath the launching aircraft and the vertical resolution of the wind data in the atmospheric boundary layer (the lowest kilometer) is too coarse for many purposes.

The NCAR Surface and Sounding Systems Facility, SSSF, has developed a Loran-C dropwindsonde system, with support from ONR, that will be used in ERICA. These instruments are called Le Sondes, for Lally and Lauritsen (the principal engineers) and Loran, and model e (for ERICA). The aircraft data system and the LeSondes are less expensive and have the desired vertical resolution in the boundary layer; the cross-chain Loran-C navigation system is used to determine the winds. Most importantly, LeSondes are so light that they are safe to use over land and sea regardless of air traffic below.

The fundamental measure of storm growth rate is the pressure fall following the center of the storm. Because the ERICA storms develop so rapidly in a region known for violent storms, routine surface ship observations are too sparse for ERICA research; an enhanced surface observing network with about 50 sites is desired. Drifting buoys are more practical for such a large network if both the buoys and the means used for their deployment are also practical. Relatively low-cost buoys that can be deployed from any aircraft with conventional sonobuoy launching capability are required. These buoys need to report surface air temperature and sea-surface temperature as well as surface pressure back through the ARGOS satellite system in essentially real time. Such a buoy has undergone tests by the Naval Ocean Research and Development Activity, NORDA, with supporting services by the U.S. Coast Guard and in collaboration with ERICA. 100 of these will be used in ERICA; 50 for initial seeding of the region and another 50 for reseeding and deployment ahead of forcasted storms.

It is likely that the development of ERICA storms is strongly influenced by the release of latent heat in the precipitating region in the ascending air ahead of the storms where the surface pressure is falling rapidly. Since precipitation has large spatial variation, weather radar is the natural tool for quantifying the spatial distribution of latent heat release. Airborne Doppler radars currently are available on the two NOAA/OAO WP-3Ds, in addition to a conventional airborne weather radar. The Doppler data reveal the velocity of the precipitation so the horizontal winds and strong vertical air motions can be determined. This information will be critically important in evaluation of mechanisms that can link together low-level and upper-level circulations of the horizontal wind.

Land-based soundings southwest of the region of storm development and over Atlantic Canada will be vital for input to numerical weather prediction models that will be used to simulate and predict development of these storms. Additional sounding sites will be established on the U.S. East Coast and in Nova Scotia to make observations at 3-hour intervals during the storms, using the Cross-chain Loran-C Atomspheric Sounding System, CLASS, developed for GALE by NCAR/SSSF. The United States CLASS sites will be operated by: Air Force Geophysics Laboratories, Bedford, MA; Brookhaven National Laboratory, Long Island, NY; and the Naval Eastern Oceanography Command, Norfolk, VA.

The operational NWS and AES sounding system over eastern North America will make soundings at 6-hour intervals instead of the normal 12-hour intervals. To record nearly continuous wind soundings in these ERICA storms, one or more radar wind profilers will be established in the Nova Scotia area by the Pennsylvania State University, PSU, and AES.

A major advance in meteorological data coverage is possible by using the Aeronautical Communications Addressing and Reporting System, ACARS. Data from this source will be available during ERICA, for research purposes only, from the Program for Regional Observing and Forecasting Services, PROFS, operated by the NOAA Environmental Research Laboratories, ERL.

To test as many of the new tools and operating procedures as possible, a pre-ERICA field test was conducted during January 1988. Measurements by aircraft were made on a rapidly-intensifying northwestern Atlantic winter storm, generally in and near the region over which ERICA field study measurements will occur during Winter 1988-89. The East Coast snowstorm, 25-26 January 1988, was observed on special aircraft flights: two NOAA/OAO WP-3D research missions, with the airplane temporarily based at the Brunswick, Maine, Naval Air Station, and three USAF WC-130 NWSOP missions.

The NWSOP flights provided valuable flight-level data and dropsonde data for short-term storm forecasting and nowcasting as well as for understanding the pre-conditioning of air entering the storm. Air traffic control presented no serious problems even when the WP-3D aircraft was operating in the congested Boston area in the middle of the storm. We will have to explain to Boston Air Traffic Control why we want to do that which we request of them before the field research program begins again next winter.

The storm structure was studied from Cape Cod across the Gulf of Maine to Nova Scotia, and thence across the Gulf of St. Lawrence to Newfoundland Island. The WP-3D flights, which incorporated successful tests of the new LeSonde system, concentrated on precipitating regions that cause storm growth. Also, the storm center was examined at three stages: beginning, during, and ending of extreme deepening. This activity is the first time that the complete cycle of extreme oceanic storm development has been observed by the same scientific personnel within the storm interior.

Some preliminary general findings of the Pre-ERICA storm observations are: Bermuda-type air was present off Cape Cod and just south of Newfoundland that resulted in the extreme temperature gradient which permitted the rapid storm growth; a strong temperature inversion in the first 150 meters isolated the atmosphere from the lower boundary layer thereby creating a free slip lower boundary condition for the storm; widespread intense turbulence was found in the center of the mature storm which had no precipitation; and a change was observed in the Gulf of St. Lawrence's surface, from ice-covered before the storm to open water with high waves in the storm. The storm completely developed within 24 hours, moved at 45 knots and had wind speeds of 150 knots at 5.8 km, well below the jet stream that probably had speeds close to 225 knots. For contrast, hurricanes are far less frequent in any given location, form over a period of many days and generally travel at about 15 knots.

The Pre-ERICA test phase also includes deployment and data quality tests on drifting buoys to be utilized in the ERICA field phase; these tests are being conducted by NORDA in Gulf of Mexico and northwestern Atlantic waters. Some fishy data were received but the explanation is that a shrimper had recovered a buoy and placed it in the ship's hold.

Having looked at the observing tools that make it possible to study the ERICA phenomena where the development is occurring, attention now will return to the phenomena and the issues and hypotheses that need to be examined in the ERICA Field Study.

Issues and Hypotheses

A number of issues and hypotheses regarding the ERICA phenomenon have been discussed at scientific workshops held for this purpose.*

Some of this material is included here to show the nature of the scientific questions being addressed in ERICA.

It is widely believed that, for rapid cyclogenesis to occur, favorable conditions are required in the lower troposhere (surface to 3 kilometers) along with forcing from a mobile disturbance in the middle or upper troposhpere (4 to 10 kilometers). The wintertime maximum of the phenomenon reinforces the belief that a very strong horizontal temperature gradient is necessary for ERICA cyclogenesis. Because ERICA storms are primarily a maritime phenomenon, latent heat released during ascent of moist air ahead of the storm is likely to be very important, if not essential, in growth at these large rates of fall of storm central pressure. Because the growth rate is faster when static stability and inertial stability in the air that ascends ahead of the storm is low, low stability is expected to be essential for ERICA storm development.

* For details, see the ERICA Overview Document, March, 1987 and the ERICA Field Implementation Plan, November, 1987. These reports can be obtained from Dr. Ron Hadlock, ERICA Project Office, Battelle Ocean Sciences, 429 Snyder Road, Richland, WA 99352.

Since these storms have yet to be observed in detail, these general beliefs remain to be quantified and verified. The observations during ERICA will be extensive in about eight Intensive Observation Periods, IOPs. Nevertheless, the complex dynamical interactions will only be clearly understood when they can be reproduced numerically in dynamic models, based on the physical (primitive) equations of motion and conservation of mass, moisture and energy.

To a certain extent most scientists agree on what generally is required for cyclones to grow at the ERICA rate, in spite of or because of the lack of data. Yet the relative importance of different factors, the reason for the spatial distribution of the phenomenon and the predictability of timing and growth rate are not agreed upon.

One hypothesis is that the abnormal growth is the normal response to abnormally strong forcing, for example very strong horizontal temperature gradients through a substantial depth of the troposphere. The counter hypothesis is that the abnormal growth is the result of normal forcing but abnormally low stability, that is, low resistance to growth. Most probably the answer is the combination of strong forcing and low stability.

Another consideration is the relative importance of lower tropospheric conditions (surface to 3 kilometers) and upper tropospheric forcing (8 to 12 kilometers). The fact that the phenomenon is focused in such a small geographic area and that it rarely occurs over continents is very strong evidence that the lower tropospheric conditions must be of paramount importance. On the other hand, upper tropospheric forcing almost always triggers development of the oceanic storms, as it does for continental storms. It is doubtful that the abnormal growth rate is due to abnormal conditions in the upper troposphere.

The role of latent heat release in the oceanic storms is the center of considerable controversy, and the answer could have significant importance in determining what numerical weather prediction model might do best. If deep cumulus convection, for example thunderstorms, is of central importance to cyclone growth rate, then the details of the treatment of the convection process could be very important. Probably there are both kinds of ERICA storms, those with and those without significant deep cumulus convection. Therefore a model that does little to handle convection properly, may do well in forecasting some storms and poorly in forecasting other storms. Since protection from these extremely hazardous storms requires confidence in forecasts, it may be essential to properly treat convection even if it is important in only a fraction of the cases.

Another hypothesis is that the organization of the latent heat release is critically important; more so than the total magnitude. This question is very difficult to address because any particular organization may be the cause of or be caused by the rapidly growing storm. It will probably require in-depth diagnostic studies of numerical model simulations of storm growth to resolve this chicken/egg controversy if any particular organization of latent heat release (precipitation) is found in ERICA IOPs with high growth rate storms.

There are some lines of evidence that the precipitation ahead of oceanic storms (with the warm front) is much more extensive and important than the precipitation behind the storms (with the cold front), in contrast to conditions in continental cyclones. This predominance of warm frontal precipitation may be the result of destabilization of the air in the lower troposphere ahead of the storm. That air could have been drawn out from the cold continent over the cool water south of Nova Scotia and even the warm water south of the Gulf Stream by the preceding storm. The fluxes of heat and moisture from the ocean into the lower troposphere could lower the stability so that the next storm that feeds on this preconditioned air grows abnormally rapidly.

The sparse evidence we do have is enough that the possibility that there is a single explanation for the ERICA phenomenon is remote. Even preliminary examination of data from the storm of 25-26 January 1988 is enough to conclude that the ocean surface was isolated from the storm circulation by the large stable layer between the cool water on the continental shelf and the warm air being drawn northward ahead of the rapidly intensifying cyclone. However, the situation may have been different in the first few hours of the rapid intensification; the dominant mechanism could change from stage to stage within a single storm's growth period.

Field Program

The ERICA Field Study will be conducted during December, 1988 and January, February, 1989 in the region between the Gulf Stream and North America. It is expected that about eight storms will be examined during Intensive Observation Periods, IOPs. It is hoped that half of the cases will develop rapidly, meeting the ERICA criteria, and half of the cases will develop at the more modest rate typical of cyclones over land.

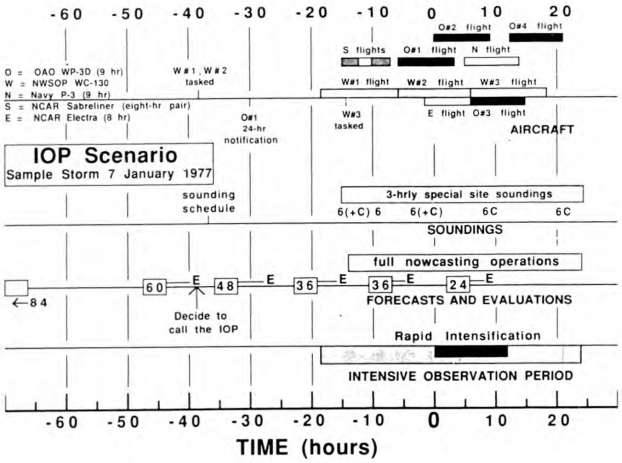
The primary special observing systems will be the aircraft with dropwindsondes and Doppler radar, the air-deployed drifting buoys, and the land-based soundings and wind profilers. The conventional surface, upper-air and satellite data are used to predict the storms, initiate the IOPs and guide the aircraft into the storms.

The design scenario for an ERICA IOP is shown in Figure 5. Time in hours increases to the right across the diagram. Activities are shown along four time lines: aircraft operations at the top, sounding activities next, with forecast activities below. The bottom time line shows the storm activity, with time 0 being defined as the beginning of the period of rapid intensification; the period lasted for 12 hours in this sample storm.

This diagram shows that the activity schedule is relatively simple once the start of rapid intensification, time 0, is specified. Then the aircraft operations can be scheduled. First the NWSOP flights are scheduled as they are the least sensitive to last minute changes in time 0 and storm track and could use the most advance warning. Then the Sabreliner and OAO WP-3D missions are scheduled. Finally, the Electra and Navy P-3 missions are scheduled; the operational P-3 will have the primary responsibility of drifting buoy deployment and will also deploy LeSondes at the peak of the Storm development.

Figure 5

Intensive Observation Period (IOP) scenario: time lines of: aircraft activity; sounding activity; forecasts and evaluations; storm development activity. Time 0 indicates the beginning of rapid intensification.



Special soundings at conventional stations would be taken over a 40-hour period with sites to the West starting first and those in northeast Canada ending last (on the time line, both Canadian and U.S. six-hrly soundings are indicated). Some sites will take three-hrly soundings also. In general these conventional sites need 12 to 24 hour advance notice, depending upon time of day and day of week. The map of Figure 6 shows the conventional and special sounding sites for the ERICA field phase. Eight special CLASS sites, with three-hrly or more frequent soundings, will be used. The CLASS sites are located to give best coverage in Nova Scotia and southeast New England for calculations, from the data, of meteorological quantities, e.g., vorticity, divergence etc.

Figure 6

Map of the ERICA sounding sites. Circles and squares are regular and Canadian sounding sites. Open circles indicate those sites at which six-hrly soundings may sometimes be requested. The closed circles are the U.S. and Canadian regular sites at which supplementary soundings are usually taken at six-hrly intervals. Sites at which three-hrly soundings are usually taken are indicated by closed squares, and the open squares are two sites at which three-hrly soundings are sometimes requested. Eight stars are CLASS sites.

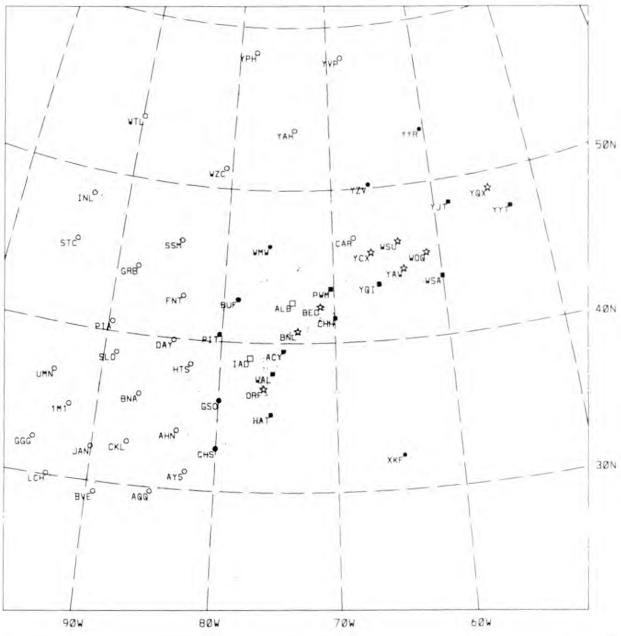
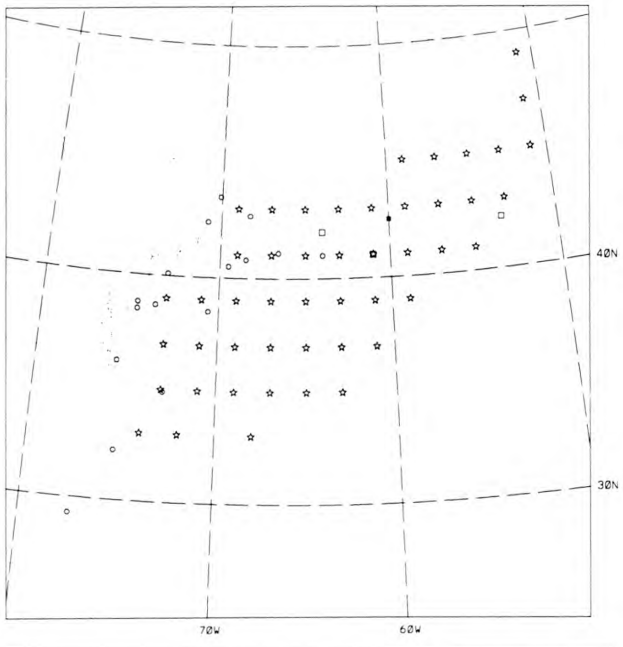


Figure 7 shows the locations of the Meteorological buoys that will provide data during the ERICA field phase. Three-hrly mapping of surface atmospheric pressure and temperature will contribute vital information for the forecasting of the oceanic storms.

Figure 7

Map of the ERICA buoy pattern. Stars are the planned initial deployment array of 48 drifting buoys (about 200km spacing). The circles are existing moored buoys, primarily in coastal waters and lakes. Four deep-water moored buoys are also located by squares: (AES—open squares at 41N, 61W; 42N, 64W; and 42.2N, 53.3W), and (WHOI—closed square at 42.5N, 60.0W).



The forecast and evaluation schedule line of Figure 5 shows the forecast period that needs to be evaluated as time 0 approaches. The 84 hour and 72 hour outlooks are used to advise participants when they might be called. These are not reliable enough to make it worth while to alert many of the participants beyond the NWSOP crews that are called upon to take the earliest action. At time 0 minus 40 hours, the major decision is made to call the IOP based on the 60 hour forecast. The IOP can be cancelled up to 20 hours before time 0 without great loss of resources.

It can be seen that the ERICA IOP activities have been kept fairly simple so that they can be conducted, with a minimum of operations staff, over a 3-month period, regardless of day of week or time of day except for a five-day break at Christmas. In the ideal season, there would be a dozen IOPs of up to three days each in the 90 day period. Four of the IOPs would be aborted before major expenditures of resources, four storms would grow at normal rates and four storms would grow at the abnormally high ERICA rates. If we are very fortunate indeed, we will find no more than two very different mechanisms responsible for the ERICA growth rates in those four storms; therefore, four ERICA-type storm IOPs will make a successful field study.

The forecast and operations scheduling activities were tested extensively in Winter, 1987-88. The Field Director (Ron Hadlock) and the Chief Forecaster (Greg Forbes from PSU) spent three weeks at the NESDIS and NMC offices in the World Weather Building. During the balance of the winter, forecasts and operation schedules were exchanged in real time through electronic mail. Richard Reed and Mark Albright participated in the forecasting from the University of Washington, Carl Kreitzberg participated in the operations scheduling and Jim McFadden from NOAA/OAO evaluated the feasibility of meeting the operations schedules.

Besides being very informative, these exercises demonstrated that forecast skill is capable of meeting the requirements of operations scheduling. There was very little change in the forecast position and growth period within 36 hours of that period. The growth rate could be estimated qualitatively but the magnitude of the growth was difficult to specify; that is, whether it would deepen somewhat more rapidly or less rapidly than the ERICA criteria could be expressed only as a probability.

The 72 hr to 84 hr outlooks were sometimes excellent and other times they were wrong, so reliability could not be achieved much beyond 36 hours. In this problem the timing is not the difficulty as much as is the geographical location. At 84 hours the outlook had difficulty determining whether the cyclone would track through the ERICA region, or pass northward or rapidly across to the southeast of the region that would favor rapid development.

There were about twice the normal number of ERICA storms in the Winter, 1987-88 season, so if we had IOPs whenever the rapid development probability reached 50% we would have reached our quota of storms half way through the season, an excellent situation. However, variation of ERICA storm activity both within and between seasons is very large in the 22 year study so conditions that will be encountered in the 1988-89 Field Study cannot be estimated with much precision and reliability at this time.

In conclusion we are convinced from the Pre-ERICA experiments that the Field Study can be conducted with a minimum of operational personnel so that it will be practical to operate anytime in the three month period that ERICA storms will occur. Moreover, the forecast/operation scheduling system will be capable of getting observations in the planned places in a timely manner. Much work remains to ensure that we know when and where in the storm we should be planning to take observations.

Future Possibilities

Because the ERICA phenomenon is so strong, it is likely that the field study results and numerical simulations will document the interior structure of the storms and clarify most of the physical mechanisms that control their growth rate. The numerical prediction models that incorporate the scientific findings should then be capable of anticipating rapidly intensifying storms in this region up to 36 hours in advance

with considerable reliability. This optimism is based on the belief that the critical initial conditions needed to make the predictions will exist over North America and the western Atlantic where land-based observations, drifting buoys and NWSOP aircraft observations would be adequate, particularly when the ACARS data from the commercial aircraft are made available for use in forecasting.

The progress anticipated above deals with forecasting storm central pressure and circulation on scales greater than 100 kilometers. This does not mean that detailed information on airport terminal weather, snowfall distribution and the timing and location of the rain, snow and icing zones will be adequate for many of the weather sensitive activities along the coast. Such details on scales of tens of kilometers and one hour will not be known more than a few hours before they occur and such forecasts will rely heavily on new land-based Doppler radars to be installed in the United States over the next few years by the National Weather Service, the Federal Aviation Administration and the Department of Defense. Most probably, a field study directed at such details will be conducted in the northeastern United States in the mid-1990s.

The question of extreme importance to ships is the sea-state, icing and wind conditions at the deck level during rapidly developing storms. Work on this important practical problem is only beginning to be addressed but it will be a vital follow-on to the ERICA problem. Typical wind speed increases of 40 knots in 12 hours (in storm coordinates) over areas several hundred kilometers wide are to be expected in these storms. Since the storms move very fast (80 km/hr or 45 knots), a ship can encounter speed increases of 40 knots in a couple of hours from a storm that was first observed less than a day before. The sea-state created by this type of rapidly developing and moving storm is yet to be studied to our knowledge. We certainly would hope that sea-state measurements could be made from remote sensors on the ERICA research aircraft, but such plans have yet to be made.

Oceanic storm forecasting can be expected to improve during the 1990s to the extent that observations of atmospheric conditions over the oceans are improved. Such improvements are likely because the technology is available, as exemplified by the air-deployed drifting buoys and dropwindsondes. Conversion of the dropwindsondes from Loran-C to Global Positioning System, GPS, technology in the early 1990s will provide this system with world-wide capability. Deployment of dropwindsondes from routine commercial airlines overflying oceanic storms will compensate for the inability of satellite remote sensing systems to obtain the data necessary for improved large-scale weather prediction.

Extending the predictability of winter storms in the northwest Atlantic from 36 hours to several days with reliability will depend upon reliable observations over the Pacific Ocean. Since weather forecasts over all of North America would benefit substantially from improved observations over the Pacific, one would expect to see efforts made to improve observations over that ocean early in 1990s.

Once observations are improved also over the oceans in the southern hemisphere, significant improvements in the five to ten day forecasts of winter storms are possible throughout the world. Thus, the main reason for optimism that the available technologies will be applied to get the data over the oceans needed to forecast oceanic winter storms, is the need for such data to extend the time period of reliable weather predictions over the continents.

Biographies

Carl W. Kreitzberg, Ph.D has been studying storm structure, primarily on the mesoscale (scales about 100 km) since receiving his Ph.D. degree at the University of Washington in 1963. He worked at the Air Force Geophysics Laboratory in the mid-1960s and taught at The Pennsylvania State University in the late 1960s. He has been at Drexel University since 1970 developing one of the first mesoscale numerical weather prediction systems and participating in the SESAME, GALE and ERICA field studies. He is currently serving as Director of the ONR's Heavy Weather at Sea Accelerated Research Initiative and is the Scientific Coordinator of Research Aircraft Operations for ERICA.

Ron Hadlock received his Ph.D degree in meteorology, with emphasis on laboratory hurricane modeling, at the Florida State University in 1966. He has worked in field measurement programs including BOMEX, micrometeorological studies on the heat and moisture transfer from thermally hot ponds, GALE, and CASP. He was jointly appointed to the faculties of FSU's Meteorology and Oceanography Departments and was a member of the Geophysical Fluid Dynamics Institute. In 1973 he joined Battelle Pacific Northwest Laboratories at Richland, Washington and was Manager of the Applied Meteorology and Emissions Assessment Section of the Atmospheric Sciences Department for several years. Presently, with Battelle Ocean Sciences, Duxbury, Massachusetts (but with his offices at Richland), he is ERICA Field Director.

MOLECULAR BEAM STUDIES OF ELEMENTARY CHEMICAL PROCESSES*

by Yuan Tseh Lee
University of California, Berkeley

Chemistry is the study of material transformations. Yet a knowledge of the rate, or time dependence, of chemical change is of critical importance for the successful synthesis of new materials and for the utilization of the energy generated by a reaction. During the past century it has become clear that all macroscopic chemical processes consist of many elementary chemical reactions that are themselves simply a series of encounters between atomic or molecular species. In order to understand the time dependence of chemical reactions, chemical kineticists have traditionally focused on sorting out all of the elementary chemical reactions involved in a macroscopic chemical process and determining their respective rates.

Our basic understanding of the relation between reactive molecular encounters and rates of reactions (formulated in terms of activation energies, E_a, and pre-exponential factors, A, as elucidated by Arrhenius in his rate constant expression, $k = A\exp(-E_a/kT)$), was deepened some fifty years ago following the discovery of quantum mechanics. Since a chemical reaction is fundamentally a mechanical event, involving the rearrangement of atoms and molecules during a collision, detailed information on the dynamics of simple chemical reactions could be obtained by first carrying out extensive quantum mechanical calculations of the interaction potential as a function of interatomic distances and then computing classical trajectories based on this potential energy surface.[1] Although these initial theoretical studies were only qualitative, they heralded a new era in the field of chemical kinetics; the chemist could now, in principle, predict the dynamical course of a chemical reaction.

During the past three decades, with the development of many sophisticated experimental techniques, it has become possible to study the dynamics of elementary chemical reactions in the laboratory. For example, detailed information on the nascent quantum state distributions of simple products for some chemical reactions can be derived from the chemiluminescence spectra of reaction products obtained under single collision conditions,[2] the analysis of the threshold operating conditions of a chemical laser,[3] or the spectra obtained using various linear or non-linear laser spectroscopic techniques.[4,5] However, when one desires to (1) control the energies of the reagents, (2) understand the dependence of chemical reactivity on molecular orientation, (3) explore the nature of reaction intermediates and their subsequent decay dynamics, and (4) identify complex reaction mechanisms involving polyatomic radical products, the crossed molecular beams technique is most suitable.[6,7]

Information derived from the measurements of angular and velocity distributions of reaction products played a crucial role in the advancement of our understanding of the dynamics of elementary chemical reactions. This and the more general investigations of chemical reactions under single collision conditions in crossed molecular beams will be the subject of this lecture.

---

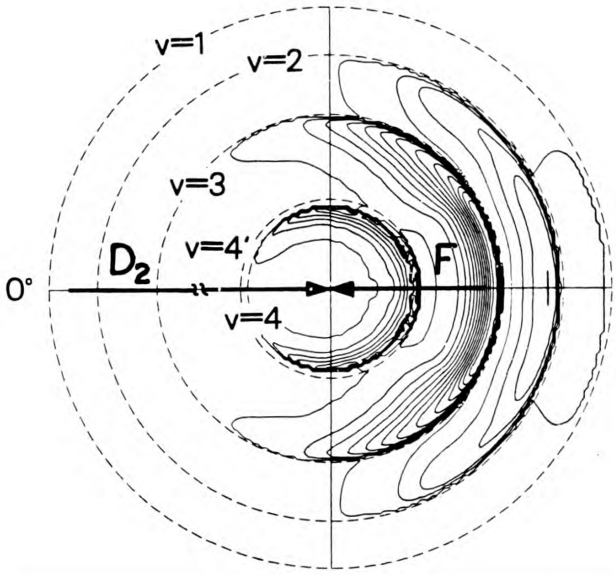
* *Professor Lee presented this paper in Stockholm in 1986 when he received the Nobel Prize in chemistry. The paper describes some of his important research accomplishments which were supported by the Office of Naval Research.*

Crossed Molecular Beams Experiments: Measurements of Angular and Velocity Distributions of Products

If the motion of individual atoms were observable during reactive collisions between molecules, it would be possible to understand exactly how a chemical reaction takes place by just following the motion of these atoms. Unfortunately, despite recent advances in microscope technology that allow us to observe the static arrangement of atoms in a solid, we are still far from being able to follow the motion of atoms in the gas phase in real time. The idea of crossed molecular beams experiments is in a sense to "visualize" the details of a chemical reaction by tracing the trajectories of the reaction products. This is done by first defining the velocities, approach angle, and other initial conditions of the reactants, and then measuring the velocity and angular distributions of the products. For example, in the investigation of the $F + D_2 \rightarrow DF + D$ reaction,[8] if we let F atoms and D_2 molecules collide at a relative energy of 1.82 kcal/mol and then measure the angular and velocity distributions of DF products, we will obtain the results shown in Figure 1. This contour map shows the probability of DF products appearing at specific angles and velocities and reveals a great deal about the dynamics of the reaction. 0° corresponds to the initial direction of the F atom beam and the distance between any point and the center is the center-of-mass velocity. The strong backward peaking of DF products with respect to the initial direction of F atoms indicates that not all the collisions between F atoms and D_2 molecules produce DF product. Only those collisions in which the F atom and the two D atoms are nearly linear will react and produce DF. Apparently, if an F atom collides with a D_2 molecule from a direction perpendicular to the molecular axis of the D_2, the F atom will only bounce off elastically. The appearance of DF in several velocity bands is due to the fact that DF molecules are produced in several vibrational states with different recoil velocities as indicated in the figure. Since the total energy released in every reactive encounter between F and D_2 is the same, the maximum energy available for translational motion will depend on the vibrational quantum state of DF. Because the rotational energy spread of DF products is less than the spacings of the vibrational energy levels, the recoil velocities of various vibrational states of DF products are well separated and can be identified easily.

Figure 1

Center-of-mass velocity flux contour map for the $F + D_2 \rightarrow DF + D$ reaction. F atoms and D_2 molecules move towards each other at a collision energy of 1.82 kcal/mol, with the F atoms moving from right to left.



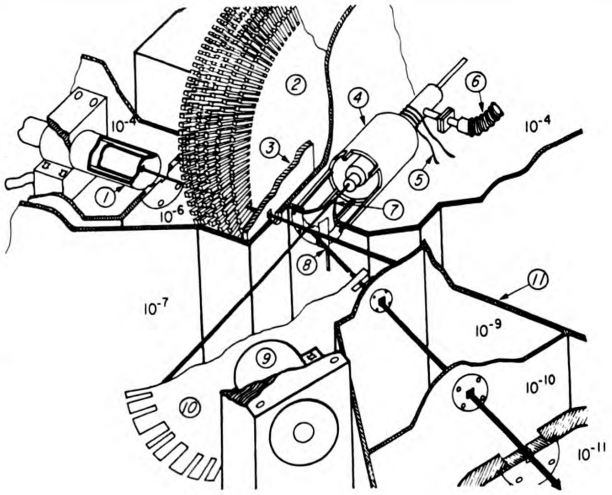
If a crossed molecular beams study of the $F + D_2 \rightarrow DF + D$ reaction is carried using the experimental arrangement shown in Figure 2, the rate of production of DF products, dN_{DF}/dt, in the scattering volume defined by the crossing of two beams can be estimated from the following equation:

$$\frac{dN_{DF}}{dt} = n_F n_{D_2} \sigma g \Delta V$$

where n_f and n_{D_2} are the number densities of F atoms and D_2 molecules in the scattering region, σ, g, and ΔV are the reaction cross section, the relative velocity between F and D_2 and the scattering volume, respectively. In an experiment using a velocity selected effusive F atom source and a supersonic beam of D_2, the values of n_F, n_{D_2}, and ΔV are typically 10^{10} molecules/cc, and 10^{12} molecules/cc, and 10^{-2} cc. If the relative velocity between F and D_2 is 10^5 cm/sec and the reactive cross section is 10^{-15} cm^2, then dN_{HF}/dt will have a value of 10^{10} molecules/sec. These DF products with various recoil velocities will scatter into a range of laboratory angles. If the DF is scattered fairly evenly within 1 steradian of solid angle in the laboratory and if the movable detector which scans the anqular distribution has an acceptance solid angle of 1/3000 steradian (approximately an angular width of 1° in both directions from the detector axis), the detector will receive ~3 x 10^6 DF molecules per second.

Figure 2

Experimental arrangement for $F + D_2 \rightarrow DF + D$ and $F + H_2 \rightarrow HF + H$ reactive scattering. Pressures (in torr) for each region are indicated. Components shown by numbers are: (1) effusive F atom beam source made of nickel, resistively heated; (2) velocity selector; (3) liquid nitrogen cooled cold trap; (4) D_2 or H_2 beam source, supersonic expansion, (5) heater, (6) liquid nitrogen feed line, (7) skimmer, (8) tuning fork chopper, (9) synchoronous motor, (10) cross correlation chopper for time-of-flight velocity analysis, (11) ultrahigh vacuum, triply differentially pumped, mass spectrometric detector chamber.



This would certainly constitute a large product signal, assuming we were able to count all of these molecules. Indeed, in a reactive scattering experiment using a beam of alkali atoms, surface ionization could be used to detect the alkali containing product with nearly 100 percent efficiency and with high specificity. Therefore, even in the presence of a billion times more background molecules very good signal to noise ratios can be obtained in a short time.

To detect the DF products, however, first it is necessary to ionize DF to DF^+ by electron bombardment. The product ion can then be mass filtered and counted. The typical ionization efficiency for a molecule during the short transit time through the ionizer is about 10^{-4}. 3 x 10^6 DF/sec reaching the detector will yield only 300 DF^+ ions/sec. However, this is a large enough number to allow reliable measurements of angular and velocity distributions in a relatively short time if the background count rate is not much greater. Indeed, the success of a crossed molecular beams study of such a chemical reaction depends entirely on whether the background in the mass spectrometric detector can be reduced sufficiently.[9]

There are two sources of background molecules in the detector that one has to deal with in a crossed molecular beams experiment: the inherent background in the detector chamber and the background caused by the effusion of molecules from the collision chamber into the detector when the beams are on. The former is mainly due to outgassing from the materials used for the construction of the chamber and to limitations imposed by the performance of the ultrahigh vacuum pumping equipment. Reduction of the latter requires many stages of differential pumping using buffer chambers. 3 x 10^6 molecules/sec entering the detector with a speed of 10^5 cm/sec through a 0.3 cm^2 aperture will establish a steady state density of only 100 molecules/cc, which is equivalent to a DF pressure of about 3 x 10^{-15} torr. This is four orders of magnitude lower than the pressure attainable using conventional ultrahigh vacuum techniques. Since none of the chemical compounds found in a vacuum system give ions with a mass-to-charge ratio (m/e) of 21 (DF^+) in the ionization process, inherent background will not be a problem for the investigation of the $F + D_2 \rightarrow DF + D$ reaction even if the ultimate pressure of the detector chamber is around 10^{-11} torr.

Suppose the partial pressure of DF background molecules in the collision chamber after the introduction of beams of F atoms and D_2 molecules reaches $\sim 10^{-9}$ torr. Then three stages of differential pumping will be required to obtain a partial pressure of $\sim 10^{-15}$ in the ionizer chamber if the partial pressure of DF is reduced by a factor of 100 in each separately pumped buffer chamber. As long as the inherent background in the detector does not contain the species to be detected, extensive differential pumping appears to be the only thing needed to make reactive scattering experiments feasible. This conclusion is unfortunately not quite correct. In order to detect the scattered products, the defining apertures, which are located on the walls of the buffer chambers of the detector, must be perfectly aligned. This limits the reduction of background that would be possible through many stages of differential pumping since some of the DF molecules in the main chamber moving along the axis of the detector will pass straight through all the defining apertures and into the detector chamber. It is important to understand that no matter how many stages of differential pumping are arranged between the collision chamber and the detector chamber, the number of these "straight through" molecules can not be reduced.

If all the apertures on the walls of the buffer chambers and the detector chamber have the same area, A, the steady state density of "straight through" molecules in the detector chamber, n′, at a distance d from the entrance aperture of the first buffer chamber can be calculated from the following relation

$$n' = \frac{nA}{4\pi d^2}$$

where n is the number density of background molecules in the collision chamber. If d is 20 cm and A is 0.3 cm^2

$$n' = \frac{0.3}{4\pi \cdot (20)^2} \quad n \approx 6 \times 10^{-5} n .$$

If the partial pressure of DF background molecules in the collision chamber is 10^{-9} torr, the "straight through" molecules will create a steady state density of 6×10^{-14} torr, which is 60 times larger than what one hopes to accomplish with 3 stages of differential pumping. Of course, reduction of the partial pressure of DF molecules in the collision chamber will also reduce the "straight through" background, but increasing the pumping speed in the collision chamber to reduce the partial pressure of DF by several orders of magnitude is simply not a practical solution.

Fortunately there is a way to reduce this background without substantially increasing the pumping speed in the collision chamber. Recognizing that at a pressure of 10^{-7} torr the mean free path between molecular collisions in the collision chamber is more than 100 meters, which is two orders of magnitude larger than the size of a typical scattering apparatus, one realizes that almost all of the "straight through" background will come from those molecules that bounce off the surface which is in the line-of-sight of the detector, and not from gas phase collisions that occur in the viewing window of the detector. Installing a small liquid helium cooled surface opposite the detector and behind the collision region, such that the detector line-of-sight always faces a cold surface, will help to eliminate this background since the surface will trap essentially all condensable molecules that impinge on it.

Since the mid-1960's, many "universal" crossed molecular beams apparati have been constructed in various laboratories. Since ultrahigh vacuum equipment available twenty years ago could attain an ultimate pressure of only $\sim 10^{-10}$ torr, and only two stages of differential pumping were needed to reduce the pressure from 10^{-7} torr in the collision chamber to 10^{-10} torr in the detector chamber, almost all mass spectrometric detectors with electron impact ionization were constructed with no more than two stages of differential pumping, the principal exceptions being those built in our laboratory.[10] The failure to recognize that for many chemical species the partial pressure in the detector chamber could be reduced well below the ultimate total pressure through additional differential pumping was part of the reason why many of these apparatuses did not perform optimally.

Direct Experimental Probing of Potential Energy Surfaces

For gaseous rare gas systems, if the interaction potentials between the atoms are accurately known, all bulk properties and transport phenomena can be predicted theoretically. Similarly, for a simple atom-molecule reaction, the potential energy surface, which describes the interaction potential as a function of the coordinates of the atoms, will be the basis for the understanding of the detailed dynamics of a chemical reaction.

One of the systems which has attracted extensive attention in both experimental and theoretical efforts during the last fifteen years is the reaction of $F + H_2 \rightarrow HF + H$. In the early 1970's, using quasi-classical trajectory calculations, Muckerman derived a semiempirical potential energy surface, known as the Muckerman V surface, which gave results in agreement with all experimental data available at that time.[11] These results included rate constants, vibrational-rotational state distributions obtained from chemical laser and chemiluminescence experiments, as well as product angular distributions obtained from $F + D_2 \rightarrow DF + D$ experiments as shown in Figure 1. The potential energy surface obtained from the ab initio quantum mechanical calculations[12] was still rather limited at that time, but it did show many important features which were in good qualitative agreement with the Muckerman V surface.

If the Muckerman V surface were sufficiently accurate, it would be possible to carry out scattering calculations using this surface under conditions which could not be easily arranged in the laboratory. This would significantly expand the scope of our understanding of the dynamics of this system. However, the accuracy of the Muckerman V surface depends not only on the reliability of the experimental input used in the derivation of the surface, but also on the applicability of classical mechanics in treating the $F + H_2 \rightarrow HF + H$ reaction. This is certainly a major concern for an H atom transfer reaction.

One dimensional quantum calculations on the $F + H_2$ reaction, although not necessarily realistic, had in fact shown the inadequacy of classical mechanics in handling this reaction.[13,14] Quantum effects were, indeed, very important, and in all these calculations strong "resonances" were found in the dependence of reaction probability on collision energy.[15] These resonances were later shown to be due to the formation of "quasi-bound" states in the F-H-H reaction intermediate.[16,17] The $F + H_2$ surface has a barrier in the entrance channel, but there is no attractive well in the intimate region near the transition state. The quasi-bound states in the $F + H_2$ reaction are entirely dynamical in nature. Loosely speaking, the first dynamic resonance is due to the formation of a bound state which is a superposition of $F + H_2(v=0)$ and $HF(v=3) + H$ in the intimate region of chemical interaction.

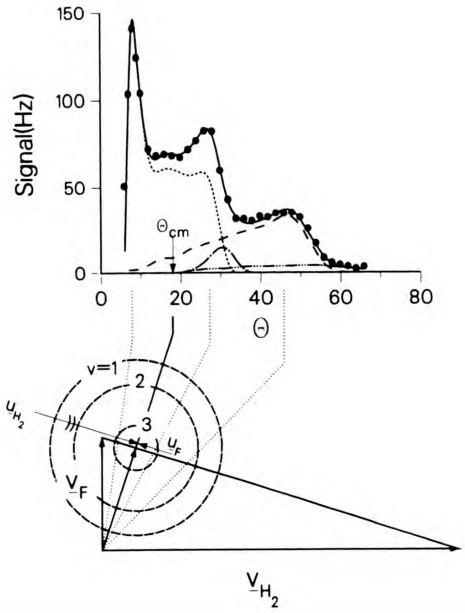
The discovery of dynamical resonances in the collinear quantal calculations of the F + H_2 system provided new possibilities for probing the critical region of the potential energy surface more directly. In contrast to most other microscopic experiments, in which the influence of the potential energy surface on the final distribution of products is assessed, the experimental observation of resonances is almost equivalent to carrying out vibrational spectroscopy directly on the reaction intermediate. Thus it should offer a more stringent test of the details of the calculated potential energy surface.[16]

In a three dimensional Quantum scattering calculation of F + H_2 on the Muckerman V surface, Wyatt et al.[18] have shown that as the collision energy is increased beyond the one dimensional resonance energy, the resonance does not just disappear but occurs at increasingly larger impact parameters. Consequently, resonances cannot be observed in an experiment in which the reaction cross section is measured as a function of collision energy. On the other hand, if the experiment is carried out at a fixed collision energy, and if the reaction probability is measured as a function of impact parameter, the resonance should be observable. Unfortunately, one has no hope of controlling or measuring the impact parameter in a scattering experiment. But, for F + H_2 → HF + H, in which the collinear configuration dominates the reactive scattering at lower collision energies, the scattering angle of HF should depend on the impact parameter. In particular, when a quasi-bound state is formed, if the average lifetime of the F-H-H intermediate is an appreciable fraction of its rotational period, HF produced from the decay of the F-H-H quasi-bound state is expected to scatter in a more forward direction compared to the strongly backward peaked HF produced by direct reaction. One of the unique and most important aspects of the measurement of product angular distributions is that one can use the rotational period of the reaction intermediate, typically $10^{-12} - 10^{-13}$ sec to judge the lifetime of the reaction intermediate.[6] If the average lifetime of the intermediate is much longer than the rotational period, the angular distribution of products will show forward-backward symmetry. On the other hand, if the lifetime is much shorter, the asymmetric angular distribution reveals the preferred molecular orientation for the chemical reaction to occur.

Experimental measurements of the laboratory angular distribution and time-of-flight velocity distributions of HF products at a collision energy of 1.84 kcal/mole, using the experimental arrangement shown in Figure 2, are shown in Figures 3 and 4. The velocity and angular distributions in the center-of-mass coordinate system derived from these experimental results are shown in Figure 5.[19] The enhanced forward peaking in the angular distribution of HF in v = 3 is a strong indication that quasi-bound states are indeed formed in the F + H_2 → HF + H reaction at this energy, and that they seem to decay exclusively into HF in the v = 3 state.

Figure 3

Laboratory angular distribution for F + para-H_2, 1.84 kcal/mol, velocity diagram shown below. Both the data and calculated laboratory distributions are shown (• data, _____ total calculated, _____. . ._____ v = 1, _____ _____ _____ v = 2, - - - - - - v = 3, _____._____ v = 3' (from H_2(J = ').



For the reaction of F + HD → HF + D, quantal collinear calculations give a very striking result. There is a sharp spike in the HF(v = 2) reaction probability near threshold and virtually no other product is formed at higher collision energies up to 0.2 eV. The collinear calculations therefore indicate that the formation of HF in this reaction is dominated by resonant scattering while the DF product is formed by direct scattering. As shown in Figure 6, the product angular distribution of HF measured at a collision energy of 1.98 kcal/mol indeed shows that most of the signal is in the forward direction as expected, in strong contrast to the DF signal which is formed through direct scattering and is therefore mainly scattered in the backward direction. Again, the forward peaked HF products are found to be in the v = 3 state, rather than v = 2, as was observed in the quantal calculations on F + H_2 → HF + F. This disagreement is certainly due to the shortcoming in the M5 surface. These vibrationally state specific angular distributions obtained at various collision energies for F + H_2, HD and D_2 reactions provide a very stringent test for the ever improving potential energy surfaces obtained from ab initio quantum mechanical calculations.

Figure 4

Time-of-flight spectra for F + para-H_2, 1.84 kcal/mol. (Δ data, _____ total calculated, _____..._____ v = 1, _____ _____ _____ v = 2, - - - - - - v = 3, _____._____ v = 3′.

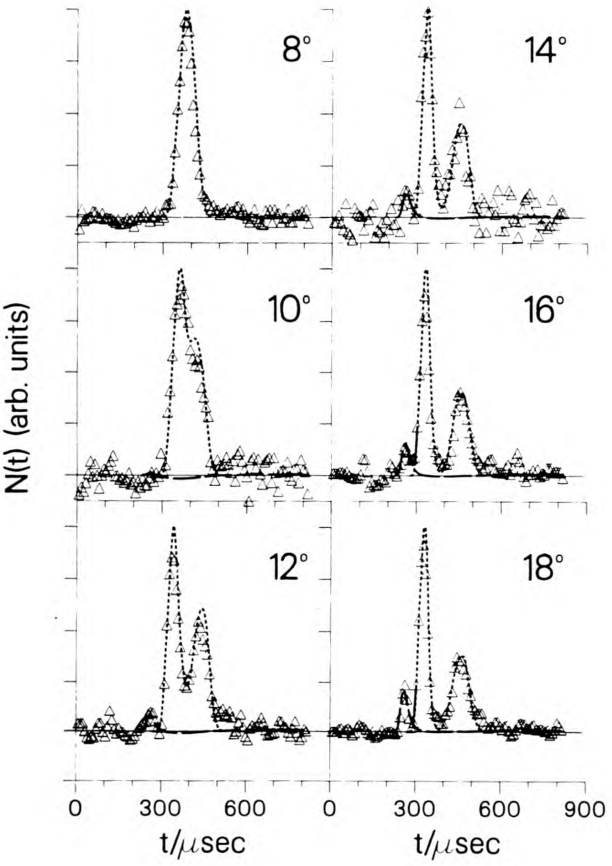
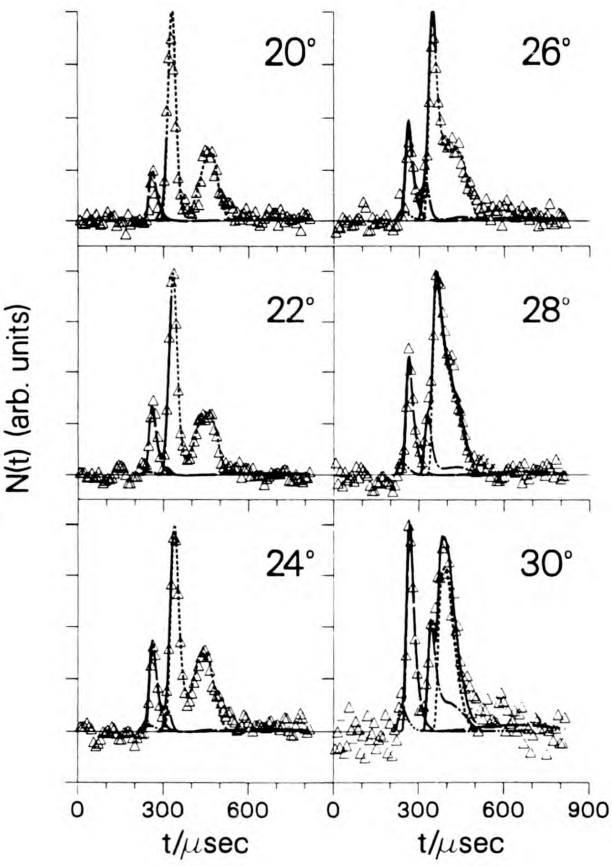


Figure 4

Time-of-flight spectra for F + para-H_2, 1.84 kcal/mol. (Δ data, _____ total calculated, _____..._____ v = 1, _____ _____ _____ v = 2, - - - - - - v = 3, _____._____ v = 3′.



There is no doubt that through meaningful comparisons with experimental results, more sophisticated and reliable ab initio quantum mechanical calculation techniques will emerge. In the near future, ab initio calculations of potential energy surfaces and exact scattering calculations on these systems will likely provide more detailed and accurate information on simple reactive systems such as $F + H_2$ than one could possibly learn in the laboratory. The fruitful interplay of theory and experiment will then extend to more complicated systems, making chemistry a more exact science.

Figure 4

Time-of-flight spectra for F + para-H_2, 1.84 kcal/mol. (Δ data, _____ total calculated, _____..._____ v = 1, _____ _____ _____ v = 2, - - - - - - v = 3, _____._____ v = 3'.

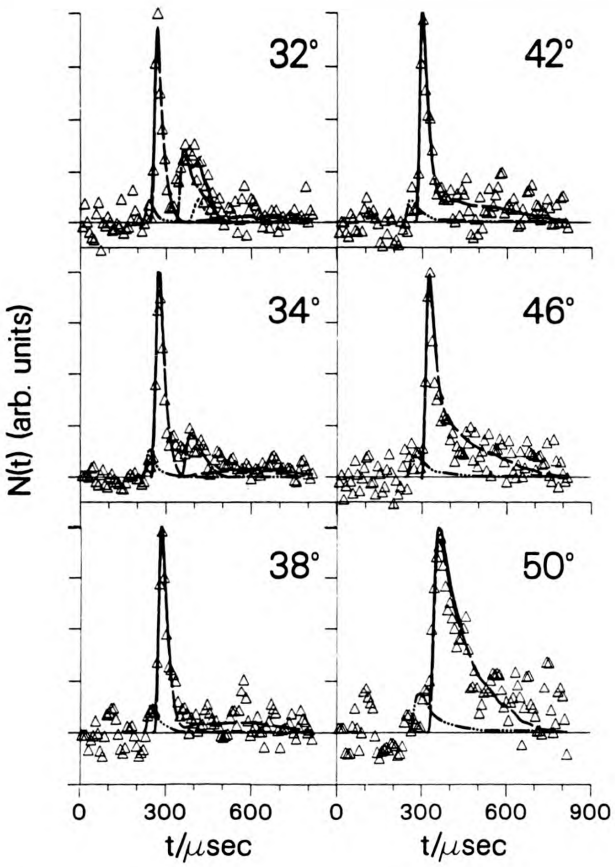


Figure 5

Center-of-mass velocity flux contour map for F + para-H_2, 1.84 kcal/mol, shown in three-dimensional perspective.

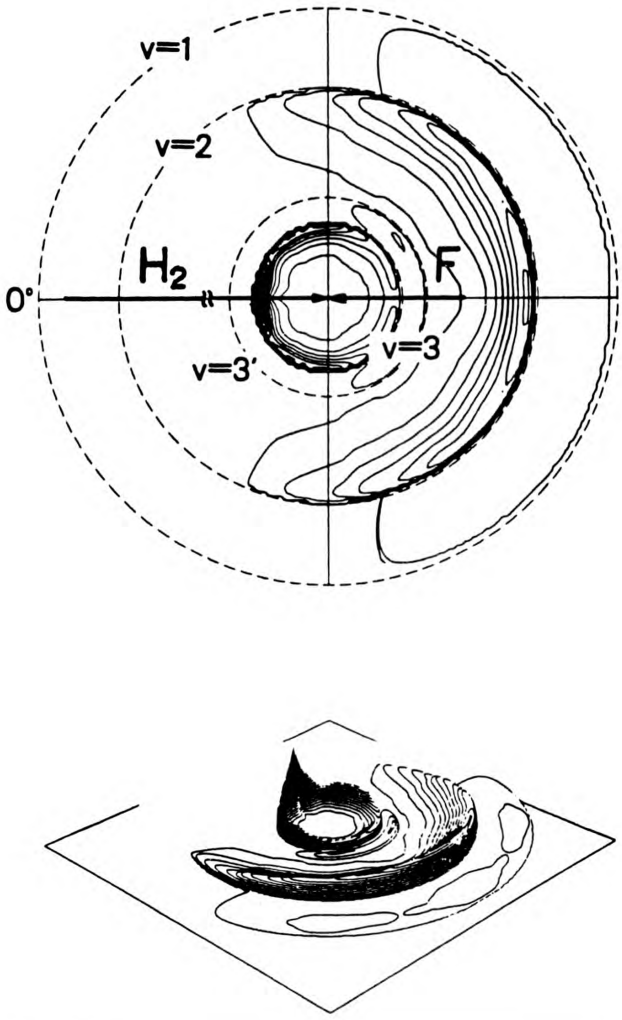
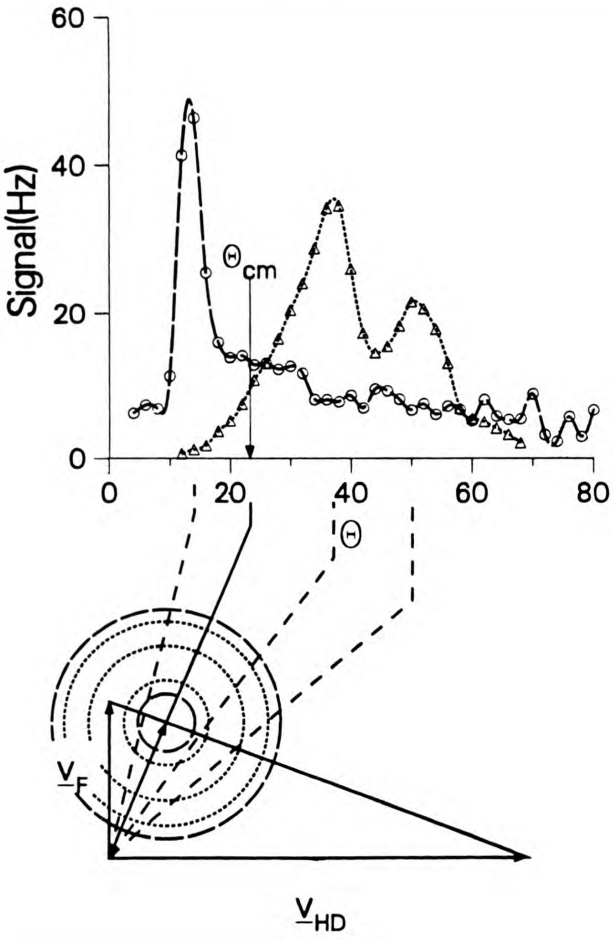


Figure 6

Laboratory angular distribution for F + HD, at a collision energy of 1.98 kcal/mol (- - - O - - - O - - - HF product, ...Δ....Δ.... DF product). The Newton circles corresponding to HF and DF product are drawn with the same texture as the lines in the angular distributions. The HF(v=3) and v=2 circles are shown, as are the v=4, 3, and 2 circles for DF.



Exploration of New Chemistry Under Single Collision Conditions

There are many mysterious phenomena in nature which have thus far defied explanation. The mystery is often due to the fact that a certain phenomenon cannot be understood based on our established knowledge or common sense.

The ease with which F_2 and I_2 react to produce electronically excited IF molecules which relax through photon emission was a mystery a dozen years ago.[20] A molecule-molecule reaction is supposed to have a high energy barrier and the four-center reaction producing two IF molecules, with either both in the ground state or one of them in an excited state, is a symmetry forbidden process. The text book mechanism has either I_2 or F_2 molecules first dissociating into atoms followed by the radical chain reactions $F + I_2 \rightarrow IF + I$ and $I + F_2 \rightarrow IF + F$. However, neither of these reactions is exothermic enough to produce electronically excited IF.

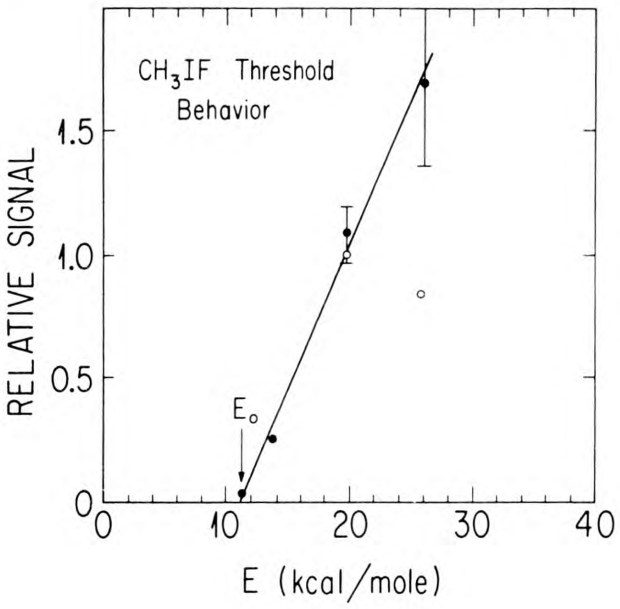
The clue that something new might be happening in this reaction was actually discovered in a crossed molecular beams study of the $F + CH_3I \rightarrow IF + CH_3$ reaction.[21] When we found that this reaction proceeded through the formation of a long lived complex, we began to increase the collision energy to see whether it was possible to shorten the lifetime enough to make it comparable to the rotational period of the CH_3IF complex. If we could estimate the lifetime of the collision complex using the rotational period as a clock, it would be possible to evaluate the stability of this reaction intermediate using statistical theories for the unimolecular decomposition rate constants. At higher collision energies, the angular distribution of products monitored at m/e = 146 (IF^+) showed a peculiar feature which could not possibly be due to IF produced from the $F + CH_3I$ reaction. This was later shown to be from stable CH_3IF produced in the collision volume of the two beams which yielded additional IF^+ signal after dissociative ionization. The stable CH_3IF was in fact formed by the reaction of undissociated F_2 in our F atom beam with CH_3I:

$$CH_3I + F_2 \rightarrow CH_3IF + F.$$

The threshold for this reaction was found to be 11 kcal/mol as shown in Figure 7. The product angular distribution measured at a collision energy of 25.1 kcal/mol is shown in Figure 8. Since the dissociation energy of F_2 is 37 kcal/mole, the dissociation energy of $CH_3IF \rightarrow CH_3I + F$ could be as high as 26 kcal/mol (Figure 9). This was certainly a surprising result and was entirely unsuspected.

Figure 7

The kinetic energy dependence of the production of CH_3IF in the $F_2 + CH_3I \rightarrow CH_3IF + F$ reaction.



In the reaction of I_2 and F_2, it was not surprising that the stability of the I_2F radical is the driving force for the reaction

$$I_2 + F_2 \rightarrow I_2F + F$$

to proceed. But, what amazed us most was that this reaction had a threshold of only 4 kcal/mol, and that at 7 kcal/mol the reaction

$$I_2 + F_2 \rightarrow I + IF + F$$

was observed.[22] The production of I and IF in this reaction is most likely through the secondary decomposition of vibrationally excited I_2F radicals. Later, a careful investigation showed that the threshold energy for producing electronically excited iodofluoride, IF*,[23]

$$I_2 + F_2 \rightarrow IF^* + IF$$

is identical to that for $I_2F + F$ formation. However, the formation of electronically excited IF* is only a minor channel compared to $I_2F + F$ formation. Apparently, it is a secondary encounter between the departing F atom and the terminal I atom in I_2F which produces IF*. A relatively rare sequential process during a binary collision between F_2 and I_2 is responsible for the production of electronically excited IF, not the symmetry forbidden four-center reaction which breaks and forms two bonds simultaneously.

Figure 8

CH_3IF angular distribution, obtained in the reaction of $F_2 + CH_3I \rightarrow CH_3IF + F$ at a collision energy of 25.1 kcal/mol.

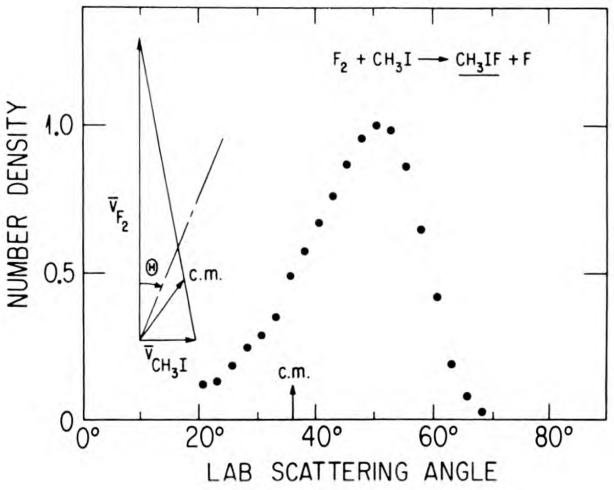
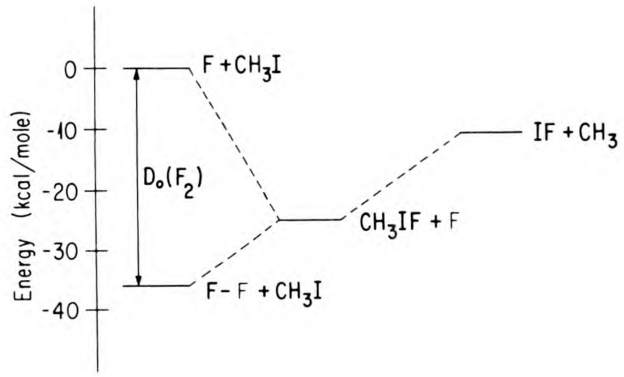


Figure 9

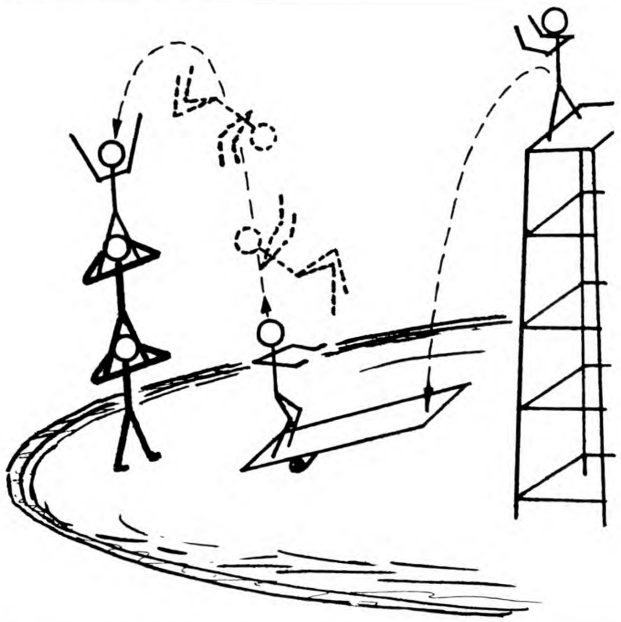
Energy diagram showing the relative energy CH_3IF intermediate in the reaction of $F + CH_3I \rightarrow CH_3 + IF$ and as a product of the endothermic $F_2 + CH_3I \rightarrow CH_3IF + F$ reaction.



The fact that one can control kinetic energy precisely and carry out a synthetic study of delicate new radicals through endothermic reactions is certainly among the most dramatic features of crossed molecular beams experiments. Successful studies of the stabilities of a series of I-F containing radicals such as HIF, ClIF and I_2F were carried out by transferring the correct amount of kinetic energy into potential energy, just like an acrobatic performance in a circus in which an acrobat is bounced off of a plank and lands gently on the shoulder of a second acrobat who is standing on top of a third to form a fragile three acrobat formation (Figure 10).

Figure 10

An acrobat bounced off the plank converts his kinetic energy into potential energy on his way to forming a delicate three-man formation. Many delicate radicals which can not be synthesized through exothermic channels were synthesized by this method.



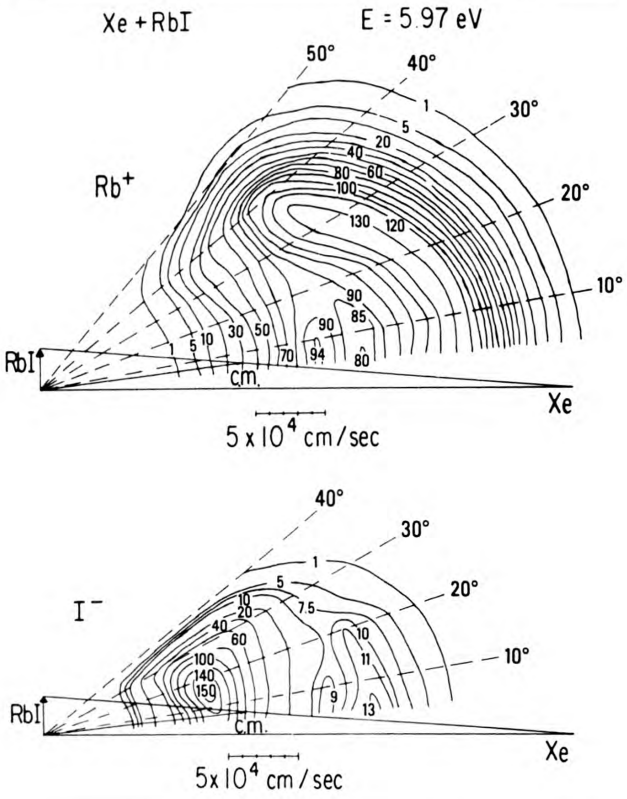
The development of the seeded supersonic beam source has been largely responsible for making crossed molecular beams experiments at higher collision energies possible.[24] If a gaseous mixture is expanded into a vacuum chamber through a small nozzle with a sufficiently high stagnation pressure, all molecules, regardless of their molecular weights, attain the same average terminal speed. Consequently, the kinetic energies of molecules in the beam will be proportional to their molecular weights, and for heavier atoms or molecules a very high kinetic energy can be obtained by seeding a small fraction of heavy particles in a very light carrier gas.

Using this aerodynamic acceleration for heavier particles many interesting experiments have been carried out in our laboratory. In the collision induced dissociation of alkali halides by rare gas atoms,[25] it was found from classical trajectory simulations of velocity and angular distributions of the products that for most dissociative collisions at energies near the dissociation threshold, the most efficient means of transferring translational energy into internal energy is through initial bond compression in near collinear collisions. The experimental angular and velocity distributions of Rb^+ and I^- from the reaction $Xe + RbI \rightarrow Xe + Rb^+ + I^-$ at a collision energy of 5.97 eV is shown in Figure 11. The amount of energy transferred as measured from the final translational energy distributions of dissociated atoms agrees with the estimated initial momentum transfer to one of the atoms in the diatomic molecule using the impulse approximation.

In a recent series of investigations of substantially endothermic reactions of Br atoms with ortho-, meta- and para-chlorotoluenes, a beam of energetic Br atoms was used to study of reactivity and dynamics of Cl atom substitution by Br atoms.[26] The intermediates of these reactions are expected to have potential wells which are much shallower than the endothermicity of reaction. From the measurements of the translational energy dependence of the reaction cross sections and the product translational energy distributions, the extent of energy randomization among various vibrational degrees of freedom was found to be rather limited. Despite the fact that ortho- and para-chlorotoluenes react easily, no substitution was observed for meta-chlorotoluene indicating that the electron density distribution on the benzene ring strongly influences the reactivity, even though dynamic factors are expected to be more important in endothermic substitution reactions.

Figure 11

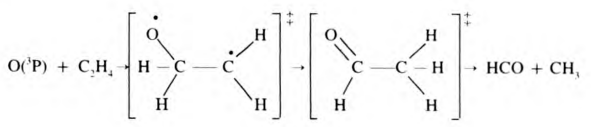
Cartesian contour map of Rb^+ and I^- angular and velocity distributions resulting from dissociative Xe + RbI collisions at a most probable relative collision energy of 5.97 eV.



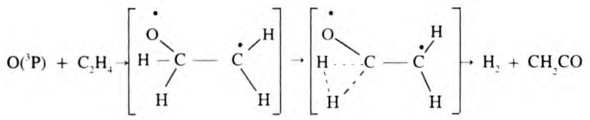
Elucidation of Reaction Mechanisms from Product Angular and Velocity Distributions.

In elementary chemical reactions involving complicated polyatomic molecules, the unravelling of the reaction mechanism is often the most important issue. Without the positive identification of primary products, it is not possible to discuss reaction dynamics in a meaningful way. In bulk experiments, the identification of primary products has often been complicated by fast secondary reactions of primary products. Recently, advances in sensitive detection methods and time resolved laser techniques have allowed single collision experiments to become possible even in the bulk, and complications caused by secondary collisions can be avoided. However, the positive identification of internally excited polyatomic radicals produced under single collision conditions is still a very difficult problem. Spectroscopic techniques which are so powerful in providing state resolved detection of atoms or diatomic molecules are often not very useful, either because of the lack of spectroscopic information or simply because huge numbers of states are involved. The more general mass spectrometric technique, which depends heavily on "fingerprints" of fragment ions for positive identification, also suffers from the fact that fragmentation patterns for vibrationally excited polyatomic radical products in electron bombardment ionization are not known. This problem is especially serious because many radicals do not yield parent ions. Even if stable molecules are formed as products, the change in fragmentation patterns with increasing internal energy can be so drastic that erroneous conclusions are often reached. For example, at room temperature both ethanol (C_2H_5OH) and acetaldehyde (CH_3CHO) will yield $CH_2H_5OH^+$ and CH_3CHO^+, respectively, as major ions by electron bombardment ionization. However, since both these ions contain a very weak bond and most of the vibrational energy is retained in the ionization process, when highly vibrationally excited C_2H_5OH and CH_3CHO are ionized, even if parent ions are initially produced, they will further dissociate into $C_2H_5O^+$ and CH_3CO^+ by ejecting an H atom.[27]

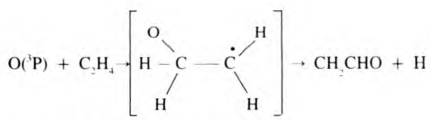
The problem of product identification caused by the fragmentation of primary products during the ionization process can be overcome if product angular and velocity distributions are measured carefully in high resolution crossed molecular beams experiments. For example, the reaction between $O(^3P)$ and C_2H_4 under single collision conditions using a mass spectrometer to detect the products generates signal at m/e = 43,42,29,27, and 15. The fact that m/e = 15 (CH_3^+) and 29 (HCO^+) are the most intense signals suggests that CH_3 + HCO is the major reaction channel. This conclusion is in agreement with previous studies of the reaction of $O(^3P)$ with C_2H_4 carried out by Cvetanovic,[28] Pruss et al.,[29] and Blumenberg et al.[30] From the analysis of final products in a bulk experiment using photoionization detection of products with hydrogen Lyman-α (10.2 eV) radiation and electron bombardment ionization mass spectrometry, it was concluded that formation of CH_3 and HCO, resulting from 1,2 migration of a hydrogen atom in the reaction intermediate and subsequent C-C rupture, as shown below, provides 90 percent of the products.



The remaining 10 percent is ketene formed by a three center elimination of an H_2 molecule from the reaction intermediate.



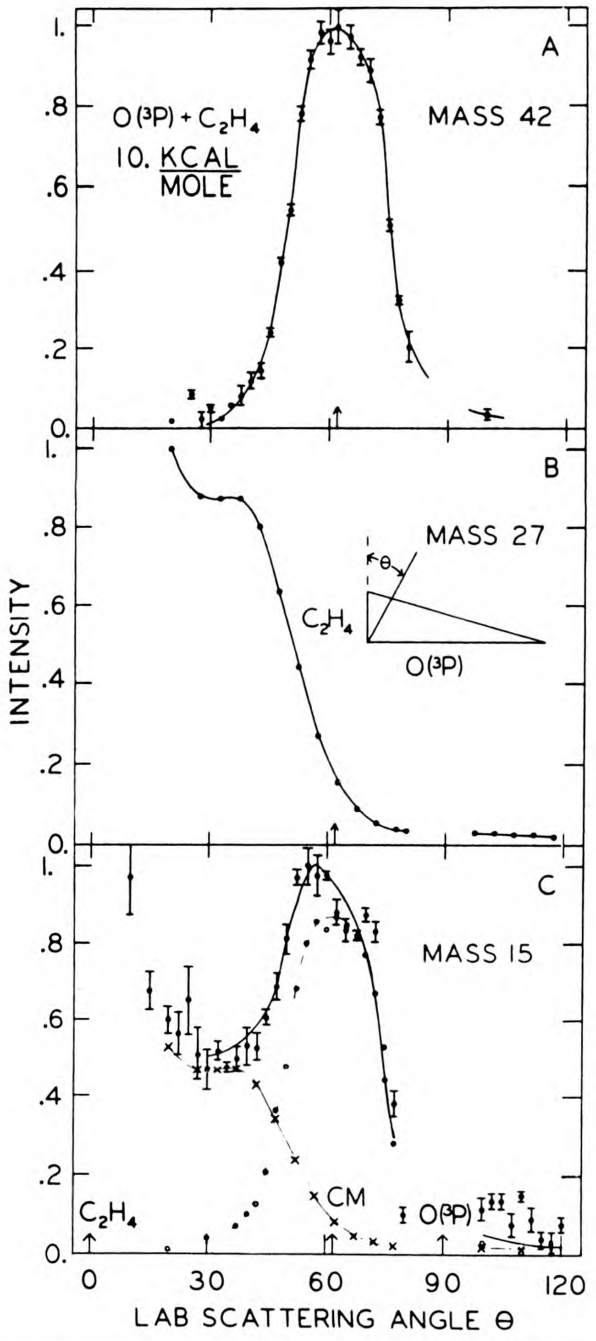
The measurements of product angular distributions in a crossed molecular beams experiment,[31] as shown in Figure 12, gave strong evidence that the above conclusion was not quite correct. The fact that the intense m/e = 42 signal and the weak m/e = 43 signal (not shown) have the same angular distributions indicates that the substitution reaction forming vinyloxy radical, CH_2CHO + H, occurs. The m/e = 42 signal ($C_2H_2O^+$) results from dissociative ionization of CH_2CHO product rather than from the formation of CH_2CO and H_2. The formation of CH_2CO through the three center elimination of a hydrogen molecule is expected to release a larger amount of recoil energy and the fact that CH_2CO is recoiling from H_2 rather than from an H atom will cause the laboratory angular distribution of CH_2CO to be much broader than that of CH_2CHO. The m/e = 15 (CH_3^+) angular distribution clearly shows that in addition to reaction products, elastically scattered C_2H_4 molecules also produce CH_3^+ ions during ionization. The angular distribution of scattered C_2H_4 can be unambiguously measured at m/e = 27 ($C_2H_3^+$). After substracting the contribution from elastically scattered C_2H_4 from the angular distribution at m/e = 15, it is quite clear that the residual angular distribution of reactively scattered CH_3^+ has an identical angular distribution to that measured at m/e 43 and 42. Apparently, most of the CH_3^+ from reactive scattering are also daughter ions of vinyloxy radicals, CH_3CHO. If the product channel CH_3 + HCO were dominant the angular distribution of CH_3^+ would be much broader. Without the measurement of product angular or velocity distributions which reveal the parent-daughter relations one would not have suspected that the simple substitution reaction forming vinyloxy radical



is in fact the major channel.

Figure 12

Angular distributions from the reaction O + C_2H_4 at 10.7 kcal/mol collision energy. (A) CH_2CHO product, (B) elastic scattering of C_2H_4 monitored at m/e = 27 ($C_2H_3^+$), (C) m/e = 15 (CH_3^+), contributions from C_2H_4 and CH_2CHO are indicated by x and o respectively.

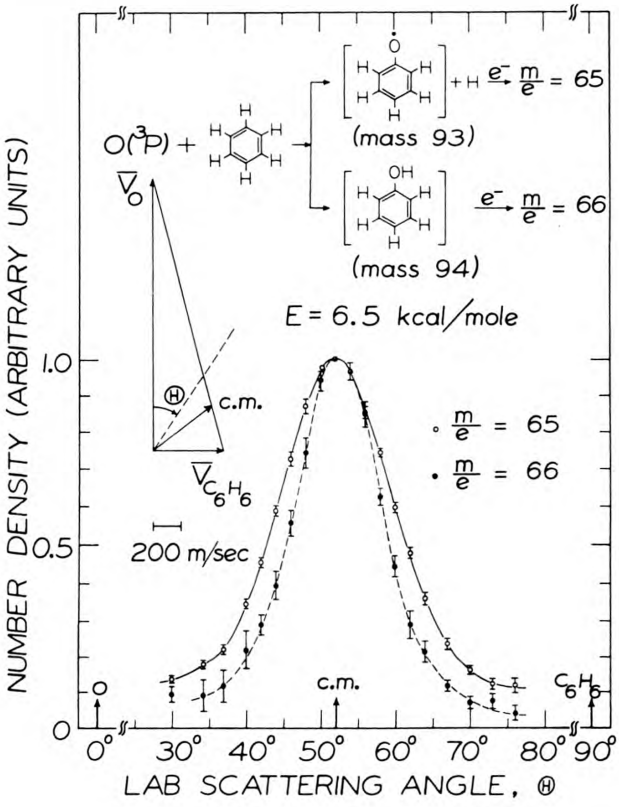


This was certainly a shocking discovery to chemical kineticists, since the reaction mechanism, $O(^3P) + C_2H_4 \rightarrow CH_3 + HCO$, was thought to be well established. The important role played by the $CH_2CHO + H$ channel was never suspected. Several recent bulk studies using various time resolved spectroscopic techniques[32-36] have verified the major role played by the hydrogen substitution channel indicated by the crossed molecular beams experiments. These were not strictly single collision experiments, but all showed that the reaction channel $CH_2CHO + H$ accounted for at least half of the products.

For the reaction of oxygen atoms with benzene the story is quite similar.[37] In earlier mass spectrometric studies of the reaction products under single collision conditions, it was concluded that in addition to the formation of a stable addition product, CO elimination from the reaction intermediate to form C_5H_6 was another major pathway. The CO elimination mechanism was mostly based on the experimental observation that m/e = 66 and 65 ($C_5H_6^+$ and $C_5H_5^+$) were the most intense signals. However, the angular distribution of products monitored at m/e = 66 and 65 in the crossed molecular beams experiments clearly show that they are different from each other but very similar to those monitored at m/e = 94 and 93 [$C_6H_5OH^+$ and $C_6H_5O^+$], respectively. Apparently, $C_5H_5^+$ ions observed are not from neutral C_5H_5 product, but are actually daughter ions of the phenoxy radical C_6H_5O. The fact that the very weak signals at m/e = 94 and 93 have different angular distributions, as also reflected in the angular distributions of m/e = 66 and 65 shown in Figure 13, is convincing evidence that the m/e = 93 signal ($C_6H_5O^+$) is not entirely from the dissociative ionization of the addition product, C_6H_5OH. It is the substitution reaction, in which an oxygen atom replaces a hydrogen atom in the benzene molecule, which causes the angular distribution of the phenoxy product, C_6H5_5O, to be broader than that of the adduct, C_6H_5OH. The benzene ring does not seem to open up after the initial attack of an oxygen atom. The subsequent decomposition of phenoxy radicals appears to be the important ring opening step. Crossed beams studies of substitution reactions of oxygen atoms with a series of halogenated benzenes,[38] indeed showed that very highly vibrationally excited phenoxy radicals, produced by substituting bromine and iodine atoms in bromo- and iodobenzene with oxygen atoms, undergo decomposition to eliminate CO.

Figure 13

Angular distributions from the reaction $O(^3P) + C_6H_6$, at a collision energy of 6.5 kcal/mol. The primary reaction products formed were C_6H_5O and C_6H_5OH, which subsequently fragmented during electron bombardment ionization.



The fact that each product in a crossed molecular beam experiment has a unique angular and velocity distribution and the requirements that total mass number in a chemical reaction be conserved and that a pair of products from a given channel have the ratio of their center-of-mass recoil velocities inversely proportional to their mass ratio in order to conserve linear momentum are three of the main reasons why measurements of product angular and velocity distributions are so useful in the positive identification of reaction products, even in those cases where none of the products yield parent ions in mass spectroelectric detection.[9] In fact, there is no other general method more useful in elucidating complex gas phase reaction mechanisms and providing information on the energetics and dynamics.

Molecular Beam Studies of Photochemical Processes

In the investigation of reaction dynamics, lasers have become increasingly important. Not only are they used extensively for the preparation of reagents and quantum state specific detection of products, but they have also become indispensable for the investigation of the dynamics and mechanisms of photochemical processes.

One of the more exciting application of lasers in crossed molecular beams experiments is the control of the alignment and orientation of electronically excited orbitals before a reactive encounter. For example, in the reaction of Na with O_2,[39, 40] if linearly polarized dye lasers are used to sequentially excite Na atoms from the 3S to 3P to 4D states, the electronically excited 4d orbital can be aligned along the polarization direction of the electric field vector of the lasers. Consequently, the effect of the alignment of the excited orbital on chemical reactivity can be studied in detail by simply rotating the polarization of the lasers with respect to the relative velocity vector.

For many atom-molecule reactions that proceed directly without forming long-lived complexes, for example, $K + CH_3I$, $F + H_2$ and D_2, and $Na(4D) + O_2$, the dependence of chemical reactivity on the molecular orientation can be obtained from measurements of product angular distributions. For symmetric top molecules, control of molecular orientation in the laboratory frame is possible, and careful investigations of the orientation dependence of chemical reactivity have been carried out for many systems. The combination of laser induced alignment of excited atomic orbitals and measurements of product angular distributions provide the first opportunity for the detailed experimental probing of the correlation between the alignment of the excited atomic orbital and the orientation of the molecule in a reactive encounter between an atom and a molecule.

The experimental arrangement for the reactive scattering of electronically excited Na with simple molecules is schematically shown in Figure 14. Because the radiative lifetimes of electronically excited Na are short, excitation and alignment have to be carried out in the intersection region of the two beams.

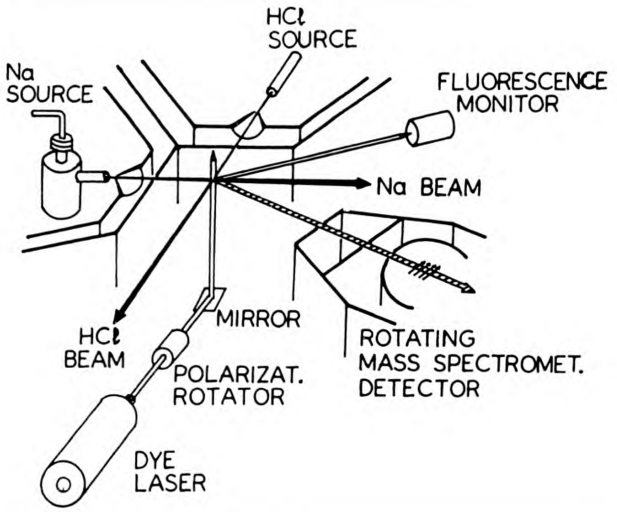
The reaction of ground state Na atoms with O_2

$$Na(3S) + O_2 \rightarrow NaO + O$$

is substantially endothermic. Even if Na is electronically excited to the 3P state, it is still slightly endothermic, and excess translational energy in the reactants was not found to promote NaO formation in our recent experiments. Further excitation of Na from 3P to either the 4D or 5S state, which require comparable excitation energies, makes NaO formation highly exothermic, but only Na(4D) reacts with O_2 and then only at collision energies greater than 18 kcal/mol. The NaO produced is sharply backward peaked with respect to the Na atom beam. As in the low energy reactive scattering of $F + D_2 \rightarrow DF + D$, the Na(4D) and two O atoms must be lined up collinearly in order for chemical reaction to take place. Such a strict entrance channel configuration with a high threshold energy for $Na(4D) + 02 \rightarrow NaO + O$ and the lack of chemical reactivity for Na(5S) are quite astonishing for a system in which electron transfer from Na to O_2 is expected to take place at a relatively large separation.

Figure 14

Cut-out view of the experimental apparatus for the reactive scattering of electronically excited sodium atoms with various molecules.

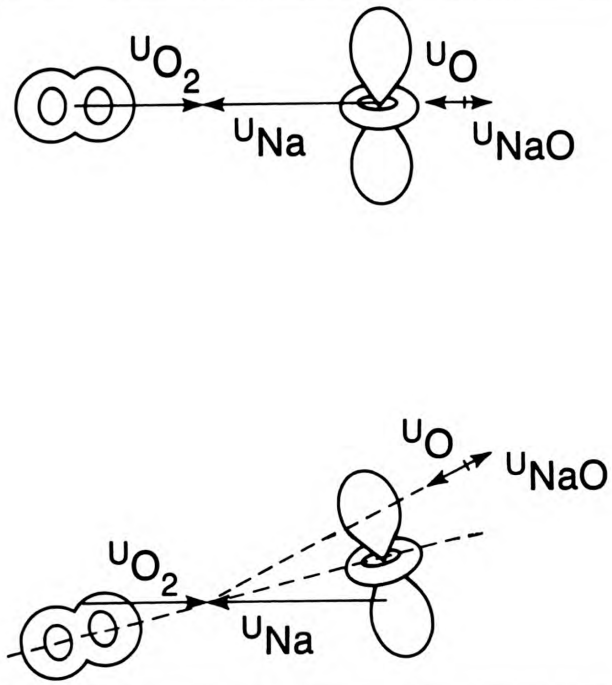


The 4D state of Na prepared by sequential excitation using linearly polarized lasers has an electron density distribution similar to that of the d_{z^2} orbital in a H atom, if we take the laser polarization axis to be the Z-axis. Rotation of this excited 4D orbital with respect to the relative velocity vector was found to cause a strong variation in reactivity. The reactively scattered signal reaches a maximum when the d_{z^2} orbital approaches O_2 perpendicularly to the relative velocity vector as shown in Figure 15. The polarization dependence of products appearing at different scattering angles reflects the strong preference for the d_{z^2} orbital to be aligned perpendicularly to the O_2 molecular axis as shown in the bottom frame of Figure 15.

These experimental observations are contrary to what one would expect from simple theoretical considerations. Because O_2 has a finite electron affinity, the Na(4D)-O_2 potential energy surface is expected to cross the Na^+-O_2^- surface at a relatively large internuclear distance and the long range electron transfer from Na(4D) to O_2, to form a $Na^+O_2^-$ intermediate, should play an important role. If this chemically activated $Na^+O_2^-$ complex is indeed responsible for the formation of an ionic NaO product, the reaction

Figure 15

From the measurements of polarization dependence at various angles, the required geometry for reaction was shown to have the Na-0-0 intermediate collinear, so that with increasing impact parameter, the Na-0-0 axis must be tilted with respect to the relative velocity vector. The Na(4d$_z$2) orbital remains perpendicular to the Na-0-0 axis as shown.



should proceed with a large cross section at low collision energies. Also, because the most stable structure of $Na^+O_2^-$ is an isosceles triangle, the angular distribution of NaO product should show either forward peaking or forward-backward symmetry.

Apparently, this long range electron transfer, in spite of its importance, is not the mechanism by which NaO product is formed, and may lead only to the quenching of electronically excited Na(4D) through an inelastic scattering process. It appears that only those collinear collisions that have the d_{z^2} orbital of Na(4D) aligned perpendicularly to the molecular axis can effectively avoid the long range electron transfer. Then, with this configuration and sufficient collision energy, Na and O_2 could follow a covalent surface to reach a very short Na-O distance where the electron from Na(4D) is transferred to an electronically excited orbital of O_2 after which the complex can separate as Na^+O^- and O.

$Na(4D) + NO_2 \rightarrow NaO + NO$ is a substantially more exothermic reaction, but it has many features which are similar to those found in the $Na(4D) + O_2 \rightarrow NaO + O$ reaction.[41] First of all, the high translational energy requirement, >18 kcal/mol, for NaO product formation again indicates that the entrance channel is very restricted and is likely to be along an O-N bond. If a Na(4D) atom must approach an NO_2 molecule along an O-N bond at a high translational energy in order for a chemical reaction to occur, the orbital angular momentum between Na(4D) and NO_2 will overwhelm the molecular angular momentum of NO_2, coplanar scattering will dominate, and NaO product will be scattered in the plane of the NO_2, which also contains the relative velocity vector. In other words, when Na(4D) approaches NO_2 along the NO bond, all the forces between the interacting atoms will lie in the plane of the NO_2, and the scattered NaO will be confined to that plane. Thus the detector, which rotates in a plane containing both the Na and NO_2 beams, can only detect those NaO products which are produced from NO_2 molecules lying in this plane at the instant when the reactions take place. In contrast to the collinear approach of Na and O_2, there is no cylindrical symmetry about the O-N axis when Na approaches NO_2 along that axis. Because of this, the reaction will depend not only on the d_{z^2} orbital alignment in the plane defined by the beams and the detector, but also on the alignment of the d_{z^2} about the relative velocity vector. This is exactly what we have observed in the laboratory. The reactivity of $Na(4D) + NO_2 \rightarrow NaO + NO$ as a function of the d_{z^2} orbital alignment with respect to the NO_2 molecule is shown in Figure 16. The most favorable approach has the d_{z^2} orbital approaching the O-N axis perpendicularly and lying in the plane of the NO_2. When the alignment of the d_{z^2} orbital is rotated in the plane of the NO_2 the reactivity is reduced as the d_{z^2} orbital comes closer to being collinear with the O-N axis. When the d_{z^2} orbital is rotated out of the NO_2 plane from this collinear configuration, the reactivity decreases further and reaches a minimum when the orbital becomes perpendicular to the NO_2 plane.

The reaction of ground state Na atoms with HCl is endothermic by 5.6 kcal/mol. Figure 17 shows the product NaCl angular distributions for Na(3S,3P,4D) at an average collision energy of 5 kcal/mol. These angular distributions were measured at m/e = 23 because most of the NaCl fragments yield Na^+ in the electron bombardment ionizer. The rising signal at low angles is due to elastically scattered Na atoms. The reactive cross section increases with increasing electronic energy. At the collision energy shown, the Na(3S) ground state atoms react because the high velocity components of each beam just barely overcome the endothermicity of the reaction. For the reaction of the Na(3P) atoms, NaCl product is observed over the full laboratory angular range possible allowing for the conservation of the momentum and total energy of the system. This implies a broad range of product translational energies, a conclusion which is supported by product velocity measurements. The same is not true of the reaction of the Na(4D) and Na(5S) states, in which the NaCl is scattered over a narrower angular range than that produced from the Na(3P) state, indicating less translational energy despite an additional 2 eV of excess

Figure 16

Polarization dependence of NaO signal from the Na(4D) + NO_2 → NaO + NO reaction. As the $4d_z^2$ orbital of Na was rotated in the plane which contains both beams and the detector, the signal was found to reach a maximum when the $4d_z^2$ orbital was perpendicular to the relative velocity vector and reached a minimum when it was parallel.

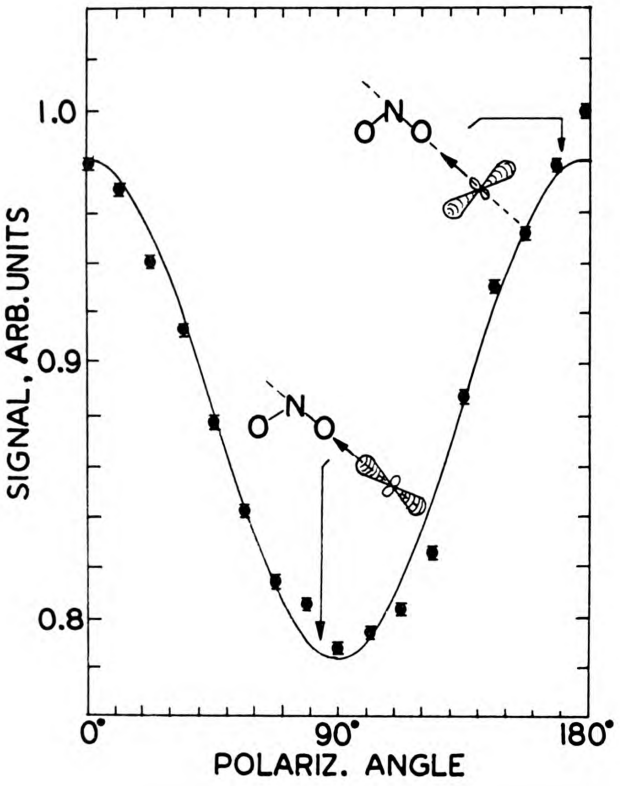
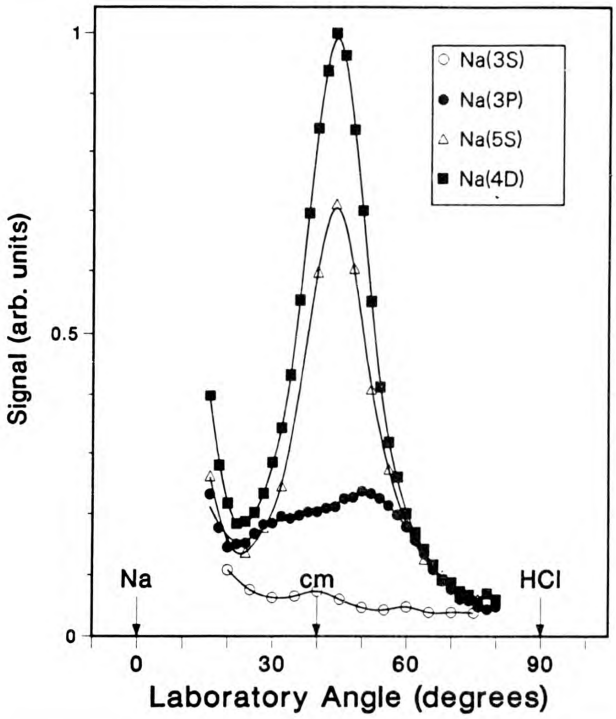


Figure 17

NaCl angular distributions for Na(3S,3P,4D,5S) + HCl at a collision energy of 5.6 kcal/mol.



energy. This is illustrated in Figure 18 in which the Na(3P) and Na(4D) angular distributions from Figure 17 have both been normalized.

These interesting results can be explained by invoking electron transfer followed by repulsion of the H atom and NaCl products. HCl is known to be dissociated by slow electrons, and has a *negative* vertical electron affinity of approximately 1 eV. For the reaction of the Na(3P) atoms this electron transfer becomes energetically possible at 3.5 Å. This is, incidentally, the peak of the Na(3P) orbital density. What the departing H atom feels is the repulsion from the Cl atom of the fully developed closed shell NaCl molecule, and a significant impulse is given to it. In the case of the Na(4D) atoms, the crossing of the neutral and ionic potential curves (the initial point of electron transfer) moves out to 7.7 Å. Thus, an electron transfers over, HCl^- dissociates, the H atom departs and the Na^+ and Cl^- are drawn together. The highly vibrationally excited NaCl cannot get rid of any of its energy as the H atom is already gone. The H atom has only felt the repulsion of the loosely bound or highly vibrationally excited NaCl. This interpretation is borne out by the polarization measurements in which the favored alignment of the Na(4d) orbital for reactive signal at any laboratory detector angle is along the relative velocity vector of the system. This corresponds to pointing the 4d orbital towards the HCl, because at long range the relative velocity vector in the laboratory is from the Na to the HCl.

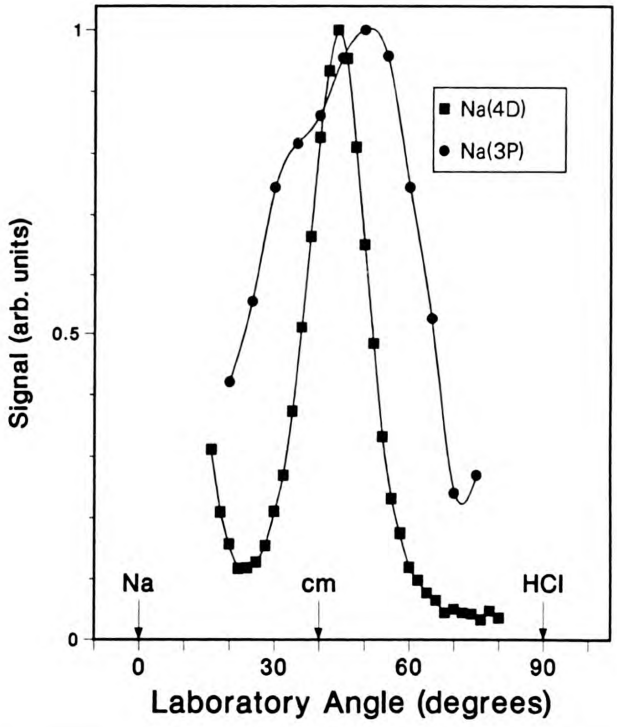
Such a detailed study of the dependence of reactivity on the orbital alignment and the molecular orientation is possible only by combining the crossed molecular beams method with laser excitation.

Concluding Remarks

The experimental investigation of elementary chemical reactions is presently in a very exciting period. The advancement in modern microscopic experimental methods, especially crossed molecular beams and laser technology, has made it possible to explore the dynamics and mechanisms of important elementary chemical reactions in great detail. Through the continued accumulation of detailed and reliable

Figure 18

NaCl angular distributions for Na(3P,4D) + HCl at a collision energy of 5.6 kcal/mol from Figure 17. The peak intensity of the distribution arising from the reaction of Na(3P) is normalized to that arising from Na(4D) allowing comparison of the angular widths of the two distributions.



knowledge about elementary reactions, we will be in a better position to understand, predict and control many time-dependent macroscopic chemical processes which are important in nature or to human society.

In addition, because of recent improvements in the accuracy of theoretical predictions based on large scale ab initio quantum mechanical calculations, meaningful comparisons between theoretical and experimental findings have become possible. In the remaining years of the twentieth century, there is no doubt that the experimental investigation of the dynamics and mechanisms of elementary chemical reactions will play a very important role in bridging the gap between the basic laws of mechanics and the real world of chemistry.

The experimental investigations described in this article would not have been possible without the dedicated efforts of my brilliant and enthusiastic coworkers during the past twenty years. I enjoyed working with them immensely and sharing the excitement of carrying out research together.

I entered the field of reaction dynamics in 1965 as a post-doctoral fellow in the late Bruce Mahan's group at Berkeley, and learned a lot about the art of designing and assembling a complex experimental apparatus from many scientists and supporting staff at the Lawrence Berkeley Laboratory while studying ion-molecule scattering. In February of 1967, I joined Dudley Herschbach's group at Harvard as a post-doctoral fellow. There, I was exposed to the excitement of the crossed molecular beams research and participated in the construction of an universal crossed molecular beams apparatus. Dudley's contagious enthusiasm and spectacular insight motivated not only me, but a whole generation of chemical dynamicists.

Molecular collision dynamics has been a wonderful area of research for all practitioners. This is especially true for those who were following the footsteps of pioneers and leaders of the field twenty years ago. In my early years, I was also inspired by the pioneering research work of Sheldon Datz and Ellison Taylor, Richard Bernstein, John Ross, and Ned Green, as well as the "supersonic" John Fenn. They have been most generous and caring scientists and all of us admire them. Their work is the main reason why the field of molecular beam scattering has attracted many of the best minds in the world and made it a most exciting and rewarding field.

My associations with the University of Chicago (1968-74) and with the University of California, Berkeley (1974-) have been very rewarding. I could not ask for a better environment to pursue an academic career. The stimulating colleagues and excellent facilities as shown in Figure 19 are what made these institutions so wonderful.

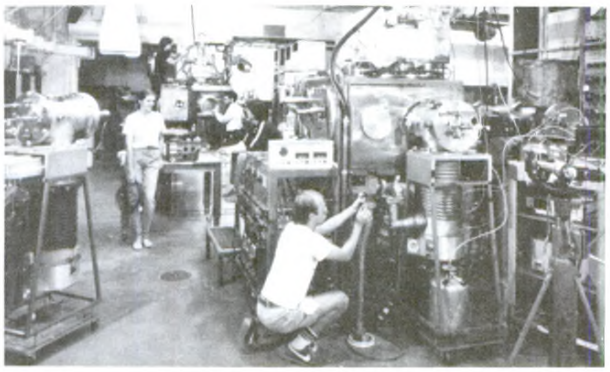
Throughout all these years, my scientific research activities have been supported continuously by the Office of Basic Energy Sciences of the Department of Energy and the Office of Naval Research. The stable and continuing support and the confidence they have shown in my research have been most important and are gratefully appreciated.

Biography

Yuan Tseh Lee, Professor of Chemistry at the University of California, Berkeley, has been a pioneer in the study of chemical reaction dynamics. His development, with Dudley Herschbach, of the universal crossed molecular beams apparatus in 1968 has given chemists an unprecedented view of the mechanisms of numerous chemical reactions. Today, in addition to crossed beams studies of chemical reaction dynamics, Professor Lee's work includes laser photochemistry, unimolecular decomposition, and the structure and dynamics of molecular and ionic clusters. Professor Lee has received numerous awards for his work, the most notable being the Nobel Prize in Chemistry in 1986. He has been a principal investigator for the Office of Naval Research since the early 1970's.

Figure 19

Part of the new molecular beam laboratory at the University of California, Berkeley.



References

1. H. Eyring and M. Polanyi, Z. Phys. Chem. *B12* (1931) 279.

2. J. C. Polanyi and D. C. Tardy, J. Chem. Phys. *51* (1969) 5717.

3. J. H. Parker and G. C. Pimentel, J. Chem. Phys. *51* (1969) 91.

4. H. W. Cruse, P. J. Dagdigian, and R. N. Zare, Faraday Discussion of the Chemical Society, *55* (1973) p. 277.

5. D. P. Gerrity and J. J. Valentini, J. Chem. Phys. *82* (1985) 1323.

6. D. R. Herschbach, in *Les Prix Nobel* 1985, Nobel Foundation, 1987.

7. R. B. Bernstein, *Chemical Dynamics via Molecular Beam and Laser Techniques,* Oxford University Press, 1982.

8. D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobatake, R. K. Sparks, T. P. Schaefer, and Y. T. Lee, J. Chem. Phys. 82 (1985) 3067.

9. Y. T. Lee, in *Atomic and Molecular Beam Method*, edited by G. Scoles and U. Buck, Oxford University Press, 1986.

10. Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, Rev. Sci. Instr. *40* (1969) 1402.

11. J. T. Muckerman, in *Theoretical Chemistry—Advances and Perspectives,* edited by H. Eyring and D. Henderson (Academic Press, New York, 1981), Vol. 6A, 1-77.

12. C. F. Bender, P. K. Pearson, S. V. O'Neill, and H. F. Schaefer, J. Chem. Phys. *56* (1972) 4626; Science, *176* (1972) 1412.

13. D. G. Truhlar and A. Kuppermann, J. Chem. Phys. *52* (1970) 384; *56* (1972) 2232.

14. S-.F. Wu and R. D. Levine, Mol. Phys. *22* (1971) 991.

15. G. C. Schatz, J. M. Bowman, and A. Kuppermann, J. Chem. Phys. *63* (1975) 674.

16. A. Kuppermann, in *Potential Energy Surfaces and Dynamics Calculations,* edited by D. G. Truhlar (Plenum Publishing Corporation, New York, 1981).

17. J. M. Launay and M. LeDourneuf, J. Phys. *B15* (1982) L455.

18. R. E. Wyatt, J. F. McNutt, and M. J. Redmon, Ber. Bunsenges. Phys. Chem. *86* (1982) 437.

19. D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee, J. Chem. Phys. *82* (1985) 3045.

20. J. W. Birks, S. D. Gabelnick, and H. S. Johnston, J. Mol. Spectr. *57* (1975) 23.

21. J. M. Farrar, J. Chem. Phys. *63* (1975) 3639.

22. M. J. Coggiola, J. J. Valentini, and Y. T. Lee, Int. J. Chem. Kin. *8* (1976) 605.

23. C. C. Kahler and Y. T. Lee, J. Chem. Phys. *73* (1980) 5122.

24. R. P. Andres, J. B. Fenn, and D. R. Miller, *Rarefied Gas Dynamics,* Fifth Symposium, 1317-1336 (1967).

25. F. P. Tully, N. H. Cheung, H. Haberland, and Y. T. Lee, J. Chem. Phys. *73* (1980) 4460.

26. G. N. Robinson, R. E. Continetti, and Y. T. Lee, to be published Faraday Disc. Chem. Soc. *84* (1987).

27. F. Huisken, D. Krajnovich, Z. Zhang, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. *78,* 3806 (1983).

28. R. J. Cvetanovic, Can. J. Chem. *33* (1955) 1684.

29. F. J. Pruss, J. R. Slagle, and D. Gutman, J. Phys. Chem. *78* (1974) 663.

30. B. Blumenberg, K. Hoyerman and R. Sievert, Proc. 16th Int. Symp. on Combustion, The Combustion Institute, 1977, p. 841.

31. R. J. Buss, R. J. Baseman, G. He, and Y. T. Lee, J. Photochem. *17* (1981) 389.

32. G. Inoue and H. Akimoto, J. Chem. Phys. *74* (1981) 425.

33. H. E. Hunziker, H. Kneppe, and H. R. Wendt, J. Photochem. *17* (1981) 377.

34. F. Temps and H. G. Wagner, Max Planck Inst. Stromungsforsch. Ber. *18* (1982).

35. U. C. Sridharan and F. Kaufman, Chem. Phys. Lett. *102* (1983) 45.

36. Y. Endo, S. Tsuchiya, C. Yamada, and E. Hirota, J. Chem. Phys. *85,* 1986) 4446.

37. S. J. Sibener, R. J. Buss, P. Casavecchia, T. Hirooka, and Y. T. Lee, J. Chem. Phys. *72* (1980) 4341.

38. R. J. Brudzynski, A. M. Schmoltner, P. Chu, and Y. T. Lee, to be published in J. Chem. Phys. 1987.

39. H. Schmidt, P. S. Weiss, J. M. Mestdagh, M. H. Covinsky, and Y. T. Lee, Chem. Phys. Lett. *118* (1985) 539.

40. P. S. Weiss, Ph.D. Thesis, University of California, 1986.

41. B. A. Balko, H. Schmidt, C. P. Schulz, M. H. Covinsky, J. M. Mestdagh, and Y. T. Lee, to be published J. Chem. Phys. 1987.

Atmospheric Compensation Experiment

The Naval Research Laboratory (NRL) has designed and is completing preparation of the Low-power Atmospheric Compensation Experiment (LACE) satellite system for the Strategic Defense Initiative Organization (SDIO).

LACE is an atmospheric distortion measurement system that is expected to provide proof-of-concept for atmospheric compensation using ground-based lasers as a defense element, says Mr. Robert Palma, head of the SDI office in NRL's Space System Development Department. It has a planned mission life of two and one-half years and is SDIO's first "long-term" experiment.

The LACE satellite, which will be launched into low-Earth orbit in 1989, is the space-borne portion of the system. The satellite will carry the Sensor Array System (SAS), an instrumented target board for atmospheric compensation development.

The system also includes two transportable ground stations (TGSs), which are the command, control and data gathering portion of the ground segment.

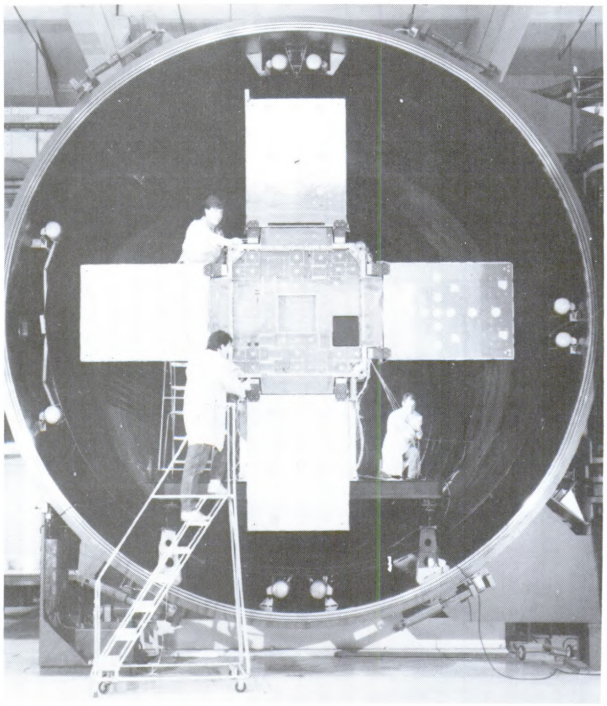
Additionally, there is an optical tracking system within the ground segment that will transmit a laser beam to LACE's SAS target board. The SAS will sample the laser beam cross-sectional power distribution in any one of the infrared, visible or ultraviolet bands.

The SAS will measure laser beam spot size to evaluate effectiveness of atmospheric compensation and acquire significant quantities of data at several wavelengths. Adaptive optics will adjust on a millisecond time scale and the SAS will measure target board spot size and radiometric intensity as the optics achieve and maintain proper compensation. The SAS will provide onscale measurements as the beam goes from completely uncompensated to a fully compensated state.

The SAS will help to determine a real-time scale for dealing with atmospheric compensation. It will also show the size and variability of the isoplanatic patch and determine the problems or advantages attached to certain wavelengths.

LACE will further serve as a test bed for piggy-back experiments. The Ultraviolet Plume Instrument (UVPI), also managed by NRL, is a launch vehicle plume tracking camera system which will obtain plume images and background data required to study plume geometry and radiometrics.

The gravity gradient LACE satellite has a launch weight of 1400 kg. Its main body measures 1.4 m by 1.4 m by 2.4 m, excluding the four sensor panels and three extendable booms.



Scientists performing thermal analysis in space-like environment on LACE satellite model.

Tech Base Notes

Described below is a synopsis of recent technology accomplishments sponsored by the Office of Naval Technology, which is the Navy research and development (R&D) organization responsible for conducting the exploratory development (6.2 category) for the Navy. Exploratory development programs are conducted in industry, academia and in the Navy's own R&D centers.

Filmless X-ray Inspection Technique. Filmless x-ray technique for inspection of aircraft structures onboard aircraft carriers, has been developed by the Naval Air Engineering Center under sponsorship of the Office of Naval Technology. Instead of film, this technique utilizes x-ray solid state sensors and replaces the film cassette with a compatibly-sized electronic memory unit. Benefits of the filmless x-ray technique include reduced inspection time and faster processing of x-ray images.

Physiological Adaptation to Cold Weather. Researchers at the Naval Medical Research Institute have, under Office of Naval Technology sponsorship, demonstrated, that prolonged cold air exposure, either natural or laboratory produced, causes pronounced changes in the quantity and distribution of the thyroid hormone, triiodothyronine (T3), as well as increases in the metabolic rate and the level of serum cholesterol. As Navy people may be deployed to severely cold environments on short notice and without adequate time for predeployment adaptation to the cold, it would be beneficial to develop biomedical therapies which can rapidly effect acclimatization. These findings clearly indicate that the T3 system is central to the human cold weather response and should be a focus for cold therapies development efforts.

Fire-Resistant Hydraulic Fluid. A fire-resistant, nontoxic hydraulic fluid for use in high-pressure systems such as aircraft carrier elevators has been developed under a program of the Office of Naval Technology. The fluid has been developed as a possible replacement for the flammable and highly toxic hydraulic fluids now in use fleet-wide. The new phosphazene-based hydraulic fluid has transitioned to advanced development for testing under full spectrum, at sea, ship operating conditions.

Advanced Rotary Engine. A stratified charge rotary engine has proven successful in an 800-hour demonstration under simulated shipboard conditions. The new engine concept is lighter, has half the moving parts of conventional shipboard diesel power plants and has reduced noise levels. Based on the results of the demonstration, a 350hp rotary engine has been designed for follow-on shipboard testing.

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
ARLINGTON, VA. 22217

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

THIRD-CLASS MAIL
POSTAGE & FEES PAID
USN
PERMIT No. GS-9