NAVAL RESEARCH

REVIEWS

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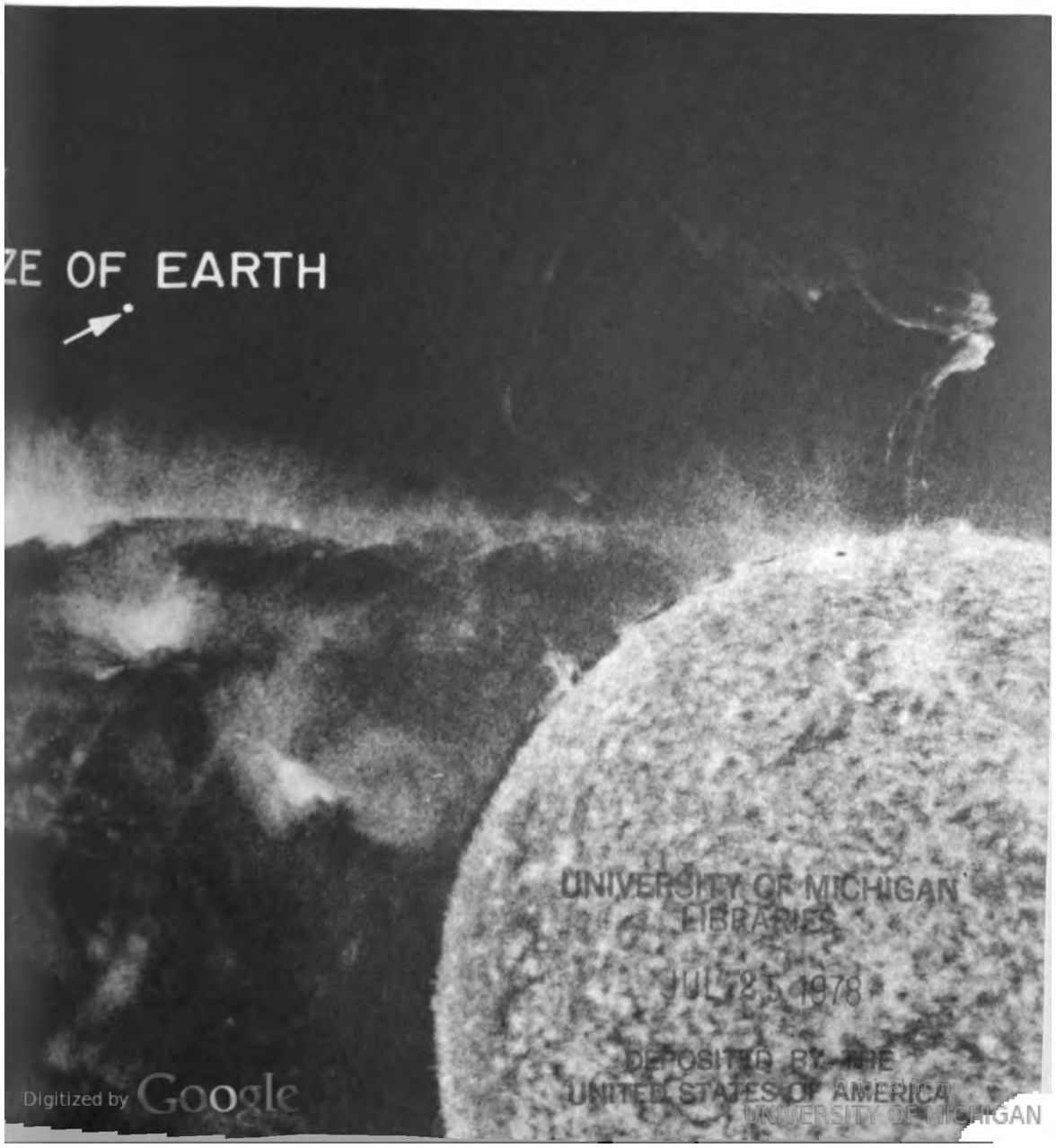

PROFILES IN SCIENCE

Dr. Gerald B. Whitham

Dr. Gerald B. Whitham is Professor and Chairman of the Department of Applied Mathematics at the California Institute of Technology. Professor Whitham, who has been an Office of Naval Research contractor since 1965, has made many outstanding contributions to mathematical theories of fluid mechanics and waves. His research in the area of waves includes: formulas for strength of sonic booms, theories of shock wave propagation and diffraction, variational methods for general study of wave phenomena, and introduction of nonlinear group velocity and related concepts for dispersive waves. Much of this work, which was supported by the Office of Naval Research, is presented in his widely acclaimed book, "Linear and Nonlinear Waves." His recent nonlinear analysis of waves on beaches has answered many signifiant questions concerning the formation of edge waves.

He is a fellow of the Royal Society and a Fellow of the American Academy of Arts and Sciences.

Lasers in Chemistry

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Introduction

Over the past decade lasers have moved very quickly from the development laboratories of atomic and optical physics to the point that they are widely used as tools in physical chemistry laboratories, in engineering and industrial applications, in medicine, weapons, electronics applications and information storage and processing and many other widely diversified areas of science and industry. The acronym laser is used to denote a very wide range of devices ranging from $75 low-power optical alignment, bench-top sources, to surgical instruments, to $20 million development devices which are designed to carry out fusion reactions related to nuclear generation of electrical power. All of these laser devices are characterized by common specialized properties not found in conventional radiation sources. Laser light emission is concentrated into a high-power beam of low divergence, with a high degree of lateral and longitudinal coherence and very narrow spectral band width. In addition, many lasers operating in a pulsed mode are capable of emitting light in bursts of very short duration — in some cases less than 10^{-12} seconds, i.e. one millionth of a millionth of a second. This is on the time scale of a molecular vibration or, looked at in another way, it is the time required for light to travel less than one millimeter in vacuum. It is hardly surprising that such powerful new radiation sources have quickly found applications in many established fields of science and industry.

Laser Technology and Laser Sources

The science and art of laser technology development, even after fifteen years of intense productivity, is continuing to produce major new discoveries on an almost monthly time scale. For many years, pulsed and continuous laser sources have been available at many different wavelengths in the vibrational and rotational infrared regions

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of the spectrum. Line tunable infrared sources are available as laboratory research instruments. For instance, scientists in NRL's Chemistry Division are currently using CO_2 lasers near 10 μm of $\sim$ 200 watts continuous power and pulsed sources of up to $\sim$ 10 joules/pulse. Visible and ultraviolet laser sources of many different types are available depending upon application. Gas laser line sources exist at a variety of ultraviolet and visible wavelengths between 3371 and $\sim$ 7000A. These lasers include both pulsed systems producing up to 1 megawatt peak power and continuously operating types up to several watts in continuous power. A number of solid state laser devices are also available as specific line source laboratory instruments. These pulsed laser sources (ruby, Nd-YAG, etc.) are amenable, because of their coherence properties, to higher order frequency generation by nonlinear, birefringent optical crystals. By use of these techniques, laser wavelengths between 2660A and $\sim$ 1.35 μm can be easily generated. These pulsed sources have peak powers up to several megawatts at selected wavelengths.

Probably the most versatile lasers available to the experimental chemist are the tunable dye lasers. This type of laser source can be pumped by a variety of techniques; i.e., flash lamps, gas lasers, discharge lasers or solid state lasers. Tunable dye lasers with appropriate nonlinear, frequency generation crystals serve as experimental laboratory sources between $\sim$ 2150A and $\sim$ 1.0 μmeters. They can be operated as continuous, very narrow band width sources or as very short pulse length (< 1 picosecond) research instruments. The powers of these devices vary tremendously as a function of pumping technique and particular application.

Recently a new generation of pulsed laser devices has become available to the experimenter. These are the rare gas dimer and rare gas-halogen excimer discharge lasers. They offer great promise because of their high electrical efficiency and because of the new wavelength regions covered. For instance, an ArF laser from a commercial vendor produces $\sim$ 50 mjoule pulses at 1930A at a repetition rate of a few hertz. These sources are particularly intriguing to the experimental photochemist and spectroscopist because the laser emission occurs in a wavelength region which is in resonance with many organic and biological chemical systems. The use of this type of system should, in the next few years, provide the means for study of many photochemical events important to upper atmosphere photochemical reactions, isotope separation, combustion reactions, biochemical reactions and other, as yet undefined, fields such as ultraviolet multiphoton reaction chemistry.

Nonchemical Applications of Lasers

Although lasers are still in their infancy in the context of historic development of new radiation sources, they have found use in and have developed many new areas of science and technology. Many of these

applications, which are of obvious importance to the Navy and the Department of Defense, will not be covered in this review of laser applications in chemistry. However, a list of these areas and application, which are currently in use or are being developed, would include the following:

- Medicine — Optical diagnostic techniques and microsurgery.
- Cutting, Shaping and Welding — Materials range from cloth to thick sheet steel.
- Engineering — Surveying, holography and micromachining.
- Communications — Fiber optic telephone lines, outer space and satellite communications.
- Weapons — Target designators, high-energy defensive weapons.
- Electronics — Optical scanners at grocery store checkout counters, computer data storage and processing.
- Nuclear Chemistry — This year in the U.S. more than twenty million dollars is being spent in the development of lasers for nuclear fusion research for power generation applications.

Subject Matter in this Review

In this review, the discussion has been limited to areas in which lasers have impacted fields which are usually considered to be chemistry from a disciplinary point of view. In some instances, the subject matter will overlap into closely allied areas such as atomic and molecular physics (chemical physics), reaction dynamics and analysis and diagnostics (analytical chemistry). Our objective is to provide a picture of the current state-of-the-art in these areas, and we will draw strongly from research projects in the NRL Chemistry Division for specific experimental techniques and results. The review is not intended to be exhaustive but to demonstrate typical, modern applications of lasers to the solution of chemical problems. We will begin by discussing some new diagnostic and analytical applications of lasers to chemical systems. This will be followed by a discussion to demonstrate some of the areas in which lasers have impacted on experimental chemical physics in the study of the dynamics of fast chemical and physical processes, and a relatively new and expanding field referred to as Laser Induced Chemistry. This will include the discusision of laser initiated reactions and state selective laser induced photochemistry.

Analytical and Diagnostic Applications of Lasers

The field of analytical chemistry is a very fertile area for the application of laser techniques because the discipline traditionally has relied heavily on optical techniques for both remote sensing and for laboratory analytical procedures. The high brightness, monochromaticity and

tunability of laser sources, and the short pulse capabilities of lasers have all been exploited in specific analytical applications. In this section, we will discuss atmospheric sensing and combustion diagnostics, which have experienced rapid development, and laboratory and clinical applications of lasers, an area which shows great promise for development.

Laser Techniques Applied to Atmospheric Analysis

There are several relatively new laser techniques and modifications of older techniques which are currently being applied to analysis of the atmosphere for both global and regional monitoring of ambient concentrations of low-level contaminants and for localized measurements of pollutants associated with industrial and nonindustrial sources.

Long path length infrared absorption. Resonance absorption is probably the most sensitive monitoring technique to provide average pollutant concentrations over long path lengths. These measurements require double ended experiments in which the laser is separated from the detector or has a retro-reflector at some distance away. This does not present a problem, however, for homogeneous atmospheres over path lengths as long as several kilometers. Fixed frequency lasers have been used for several years in such experiments.[1,2] A new, more versatile and sensitive variation of this technique employs tunable infrared diode lasers in a similar application. With this technique, one can multiplex the detection on and off resonances to null out scatter, refractive index gradients and competition from interfering species. In addition, the tunable diode lasers are amenable to measuring many more species than fixed frequency lasers.[3] The current state-of-the-art puts the detection limit for selected species in the part per billion range for path lengths on the order of one kilometer.

Differential Absorption Lidar Techniques. More often than not, one wishes to remotely monitor pollutant concentrations with single ended experiments in association with pseudo point source emitters such as smoke stacks, etc. Under these circumstances, long path length absorption experiments are impractical. Several laser light scattering techniques have been developed which show considerable sensitivity in this area. One such technique is differential absorption Lidar, which uses a tunable laser tuned to an absorption peak of interest. The return signal is provided by back scattering of the laser beam by atmospheric molecules, particulates, and aerosols and its intensity is dependent on the concentration of the absorbing gas. Using a pulsed laser source and time discrimination in the return scattered signal (essentially laser radar techniques), sensitive ranging experiments can also be carried out. In this way, pollutant concentration can be measured as a function of distance from the point source emitter and from the laser-detector system.

Systems such as these are still under development. However, the following are typical reported results. NO_2 has been measured at 0.20 ppm concentrations at ranges of up to 3.5 km from stack gas effluents

with commercially available dye lasers.[4] SO_2 concentrations on the order of 0.10 ppm have been measured in association with power plant stack gas effluents[5] with the same laser. Dispersal in plant plumes can easily be mapped at distances up to ~ 3 km from a single fixed sight monitoring station.

Resonance Scattering and Fluorescence Techniques. In these techniques the laser beam impinges upon the gas sample and either the red shifted Raman signal or resonance fluorescence (also red shifted from the laser frequency) is detected. For low-level measurements, the resonance fluorescence techniques are more applicable because resonance events have optical cross-sections that are orders of magnitude higher.[6] The radical OH has long been postulated as a low-level species in the atmosphere which is intimately involved in chemical reactions relating to photochemical smog production. The measurements of these extremely low-level concentrations have been achieved with the use of laser-induced fluorescence techniques in the ultraviolet region of the spectrum.[7,8] Diurnal variations between 10^6 and 10^8 OH/cm^3 in field tests confirm these postulations.

A laser-induced fluorescence technique has been developed by workers at NRL for the atmospheric measurement of a radioactive isotope of iodine in backgrounds of other iodine isotopes.[9] In this work, a $^3He-^{22}Ne$ neon laser is used because the particular isotope of neon lases only at wavelengths which are absorbed by the $^{129}I_2$ isotopic species. A block diagram of the typical experimental arrangement is shown in Figure 1, and Figure 2 shows a plot of the resulting $^{129}I_2$

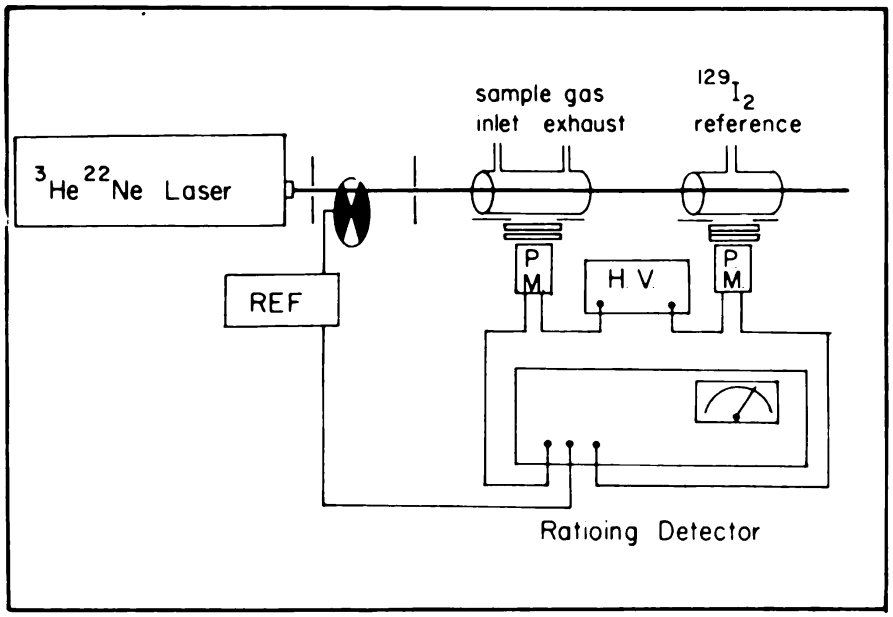

Figure 1 — A block diagram of a laser fluorescence detector to measure airborne concentrations of a radioactive nuclear isotope, $^{129}I_2$. This isotope is a daughter product of the nuclear generation of electrical power.

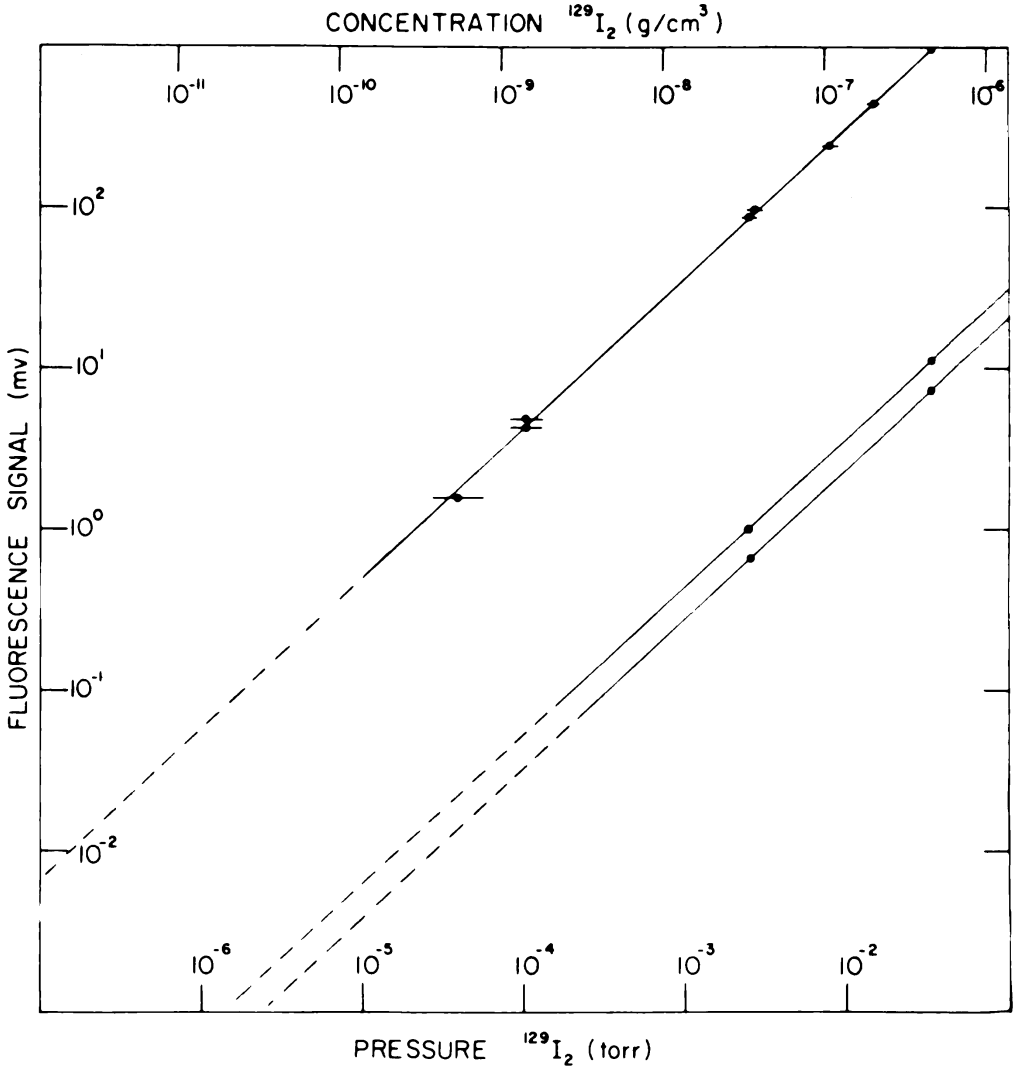

Figure 2 — A plot of laser-induced fluorescence signal as a function of the concentration of $^{129}I_2$ radioisotope. The top curve represents the signal from $^{129}I_2$ in the absence of other gases; the center line is in the presence of one atmosphere of argon; the bottom line is the signal for the airborne iodine isotope.

fluorescence signal as a function of the $^{129}I_2$ concentration. The laboratory model of this detector has a sensitivity for $^{129}I_2$ detection of <100 picograms/cm^3 of iodine in air (1 picogram = 10^{-12} grams). Field hardened prototype commercial instrumentation based upon this design is currently being constructed for use at nuclear facilities where spent nuclear fuel reprocessing operations are being carried out.

Combustion Systems, Plasmas and Discharges

In combustion systems and in plasmas or discharges, typical sampling and physical probing techniques such as gas chromatography, mass spectrometry and final product analysis techniques, are often impractical because the species which one wishes to monitor are often

transient or highly reactive in nature. Classical optical techniques, such as absorption spectroscopy and chemiluminescence, are also often impractical because instantaneous measurements may be required, long path lengths are not available, or the systems are fraught with chemical and spectroscopic interferences. For these reasons, several laser optical diagnostic techniques have been developed for application to these difficult experimental environments. We will review a few of the newest of these experimental techniques which show significant promise as optical diagnostics.

Intercavity Laser Spoiling Techniques. In laboratory scale combustion devices, it has been possible to actually include the flame within the cavity of a dye laser. At frequencies where resonance absorption takes place, the gain of the laser is suppressed and the laser action is quenched. This inverse amplification process increases the sensitivity of these absorption processes by at least a factor of 10^2. Measurements have been reported for numerous atomic species,[10] for several atomic ions[11] (Pr^{3+}, Eu^{3+}, and Ho^{3+}) and for several molecular systems[10a,12] (I_2, NH_2, HCO, NO_2, O_2 and HCl). Theoretical treatments which yield a quantitative description of this intracavity absorption technique have been reported.[13]

Raman Spectroscopic Techniques. The field of Raman Spectroscopy has undergone a substantial revitalization with the inclusion of narrow band, high intensity lasers for excitation sources. Because the spontaneous Raman process is very inefficient, this technique has found only limited utility as a diagnostic tool in flame and discharge applications, however. For relatively high concentration components ($> 1\%$) in systems where fluorescence and scattering are not severe, spontaneous Raman spectroscopy has been successfully employed as an optical analytical device. The major utility is realized for measurement of fuel, oxidizer, carrier gas and major combustion product components, i.e. CH_4, H_2, O_2, CO, CO_2, etc. Such studies are also valuable because measurements of rotational state populations via the Raman spectrum can provide accurate temperature evaluation. Optical temperature probes are a valuable asset because physical measurements of temperature often are not possible or practical.

The use of giant pulsed lasers has opened up the development of several new fields of Raman spectroscopy based upon nonlinear Raman effects; i.e., stimulated Raman emission, inverse Raman effect, Raman-induced Kerr Effect and Coherent Anti-Stokes Raman Spectroscopy (CARS). The CARS technique seems to offer the greatest potential of these new techniques for develpment as a combustion analytical tool. In the CARS technique, two laser beams of different frequencies ω_1 and ω_2 are collinearly focused into the active region to be probed. Because of the nonlinear dielectric properties of the materials, a new coherent beam at the anti-stokes frequency, $\omega_{as} = 2\omega_1 - \omega_2$, is generated. This new laser-like beam (ω_{as}) can be analyzed to obtain qualitative

and quantitative measurements of the components of the gases present.[14] Figure 3 shows a block diagram of a CARS system in use at NRL. Figure 4 shows a CARS spectrum of D_2 gas in a laboratory electrical discharge instrument. Spectra such as these can be used to obtain concentration data and the rotational and vibrational "temperatures" of the medium. Although CARS is much more sensitive than spontaneous Raman spectroscopy in most instances, its ultimate sensitivity is limited by interference effects and by nonresonant CARS generation by background gases. Analytically, applications of CARS techniques in combustion systems can provide measurements of major components at concentrations down to ~ 0.1%, i.e. in the 1000 ppm range.

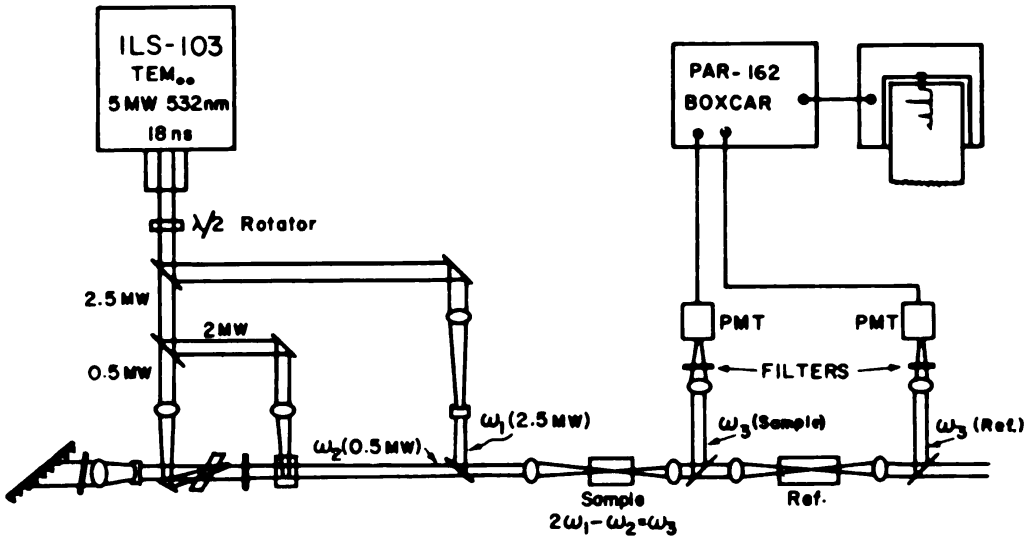

Figure 3 — Apparatus used at NRL to record CARS spectra of gases. The YAG laser has a line width of 0.03 cm^{-1} *and a repetition rate of 10 pps. The dye laser with grating and telescope has a line width of* ~ *0.3* cm^{-1}. *With an added etalon the width narrows to* ~ *0.03* cm^{-1}. *High power from the dye laser is achieved with the amplifier, pumped by 2 MW of 532 nm laser light.*

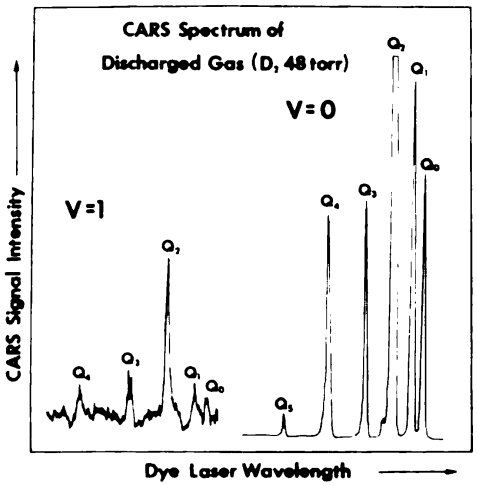

Figure 4 — The CARS spectrum of D_2 *in an electrical discharge taken with the apparatus described in Figure 3 with no etalon in the dye laser and no reference cell. The vibrational temperature calculated from these spectra is* ~ *1050°K, while the rotational temperature is* ~ *400°K. The Q's denote a particular type of transition with the rotational level indicated by the subscript and the vibrational level v = 0 or 1.*

Laser-Induced Fluorescence.. In the last few years, it has been shown that several minor constituents in flames can be detected by laser-induced fluorescence techniques. Atomic species, small molecules, and fragments have been probed by experimental techniques such as that shown in the block diagram in Figure 5 as used at NRL. By scanning the dye laser frequency across molecular resonances, one can profile flames for relative specie concentrations.[15] Such a scan is shown in Figure 6 for C_2 in an oxy-acetylene flame. Spectra such as these can also be used to measure vibrational and rotational "temperatures" of the flame.

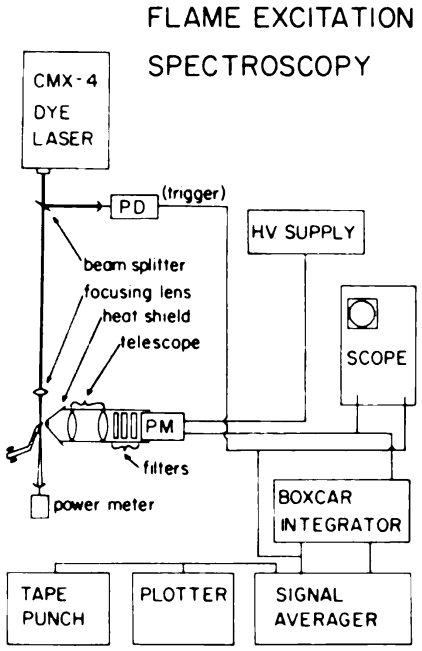

Figure 5 — A block diagram of a laboratory device used to measure low concentration constituents in combustion sources by laser-induced fluorescence. P.D. is a triggering photodiode, and P.M. is the photomultiplier detector.

By tightly focusing the laser beam in the flame, one can saturate the optical absorption for selected species in the combustion region. Theoretical models for those conditions have been developed at NRL which allow one to make absolute concentration measurements for the molecules being studied.[16] To make quantitative determinations, one measures the fluorescence signal as a function of the laser power used to probe the molecules. The resulting experimental data such as shown in Figure 7, then yield absolute concentration measurements[15] for a probed flame volume of $\sim 10^{-5}$ cm^3. While this new field is still under development, it appears that concentration measurements for selected species such as CH, OH, C_2, NH, and atomic species can be carried out at less than 1 ppm. Such techniques should aid in the improvement of burner efficiencies and in complex field of modeling basic combustion reactions.

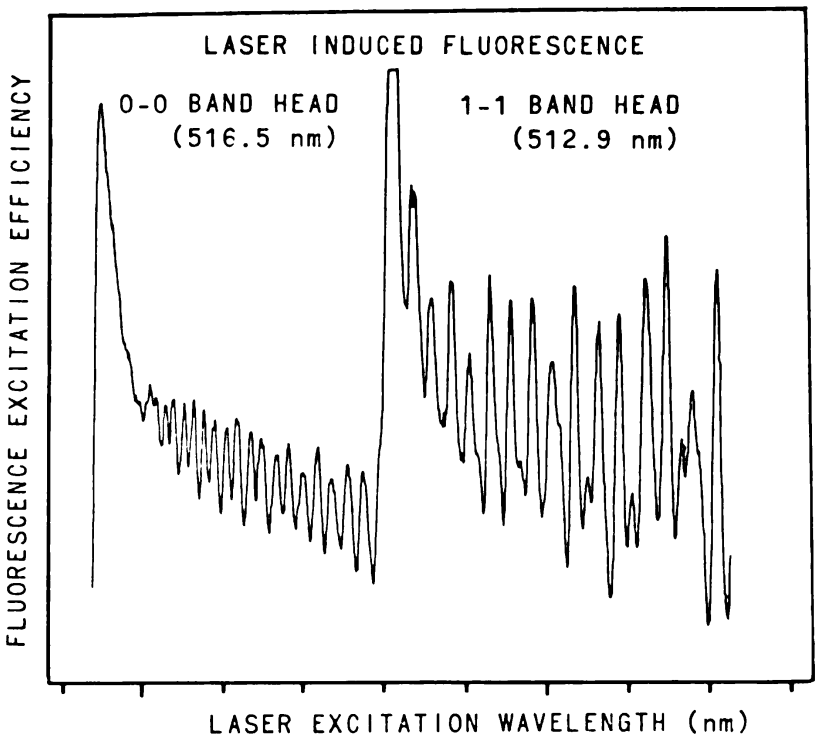

Figure 6 — The laser-induced fluorescence excitation spectrum of a radical transient C_2 in an oxygen-acetylene torch.

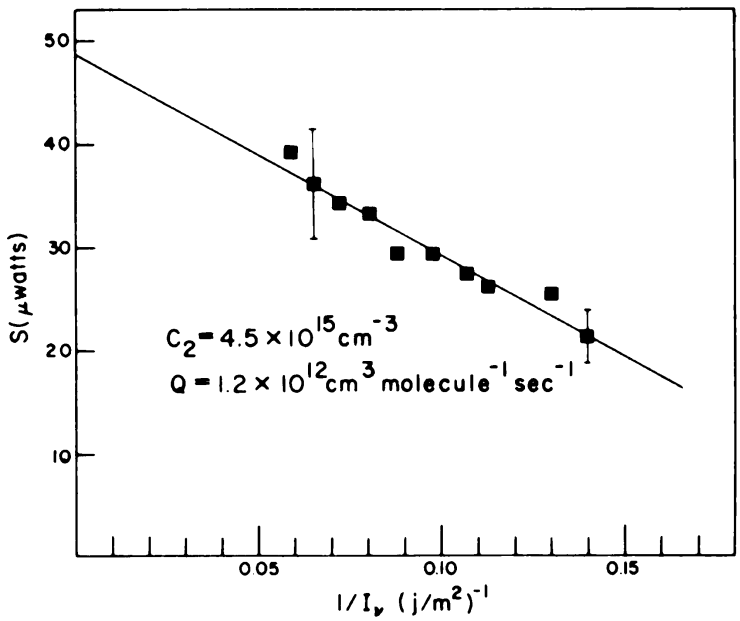

Figure 7 — A plot of the experimental laser-induced fluoresence signal (s) in an oxy-acetylene flame as a function of laser power (1_ν). The intercept of the experimental data yields a measurement of the C_2 concentration in the flame. Q is the rate of depletion of the state excited by the laser and is proportional to the slope of the line.

Analytical Chemical and Biochemical Instrumentation

Essentially, all optical and spectroscopic methods used in analytical chemistry can be improved by the introduction of laser sources. In many cases, the monochromator section in the instrumentation can be replaced by high brightness tunable, narrow bandwidth laser sources. The spectral brightness of lasers (intensity per unit frequency interval), is many orders of magnitude higher than that available from any conventional light sources. In the discussions of analytical applications of lasers to trace detection, the emphasis was on instrumentation configured to make measurements under adverse conditions, such as in flames or field measurements. Analytical laboratory instrumentation can typically be much more sensitive. Routine analytical measurements using direct absorption techniques can measure concentrations below the 1 ppb level[17] and even greater sensitivity is available in fluorometric techniques. Laboratory model fluorometers have been developed for routine analysis at concentrations below the 1 part per billion level.[18] These detection limits correspond to less than 10^4 molecules/cm^3 in 1 torr gas samples, or less than 1 nanogram (10^{-9} gram) detection in solution. For instance, measurements of $\leqslant$ 0.2 nanograms of Aflatoxins on silica gel chromatographic plates by a laser fluorescence technique have been reported.[19]

Unfortunately, most of these extremely sensitive analytical procedures have not progressed to the point of commercial development into anlytical instrumentation. The gain to be realized in analytical and medical laboratories certainly justifies the large capital investment required to start new product lines and the commercial costs of the new instrumentation.

Laser Chemical Processes

Thus far, we have discussed the impact of lasers upon chemistry from an analytical chemistry and optical diagnostic point of view. While the introduction of laser devices to these fields has been important, their impact upon the fields of molecular dynamics and kinetics has been even more profound. Lasers have become important laboratory tools in essentially all experimental physical chemistry laboratories in the U.S. in the last decade.

Molecular Dynamics and Chemical Kinetics

Almost from their inception, lasers have been used to study the dynamics of fast chemical events such as energy migration, relaxation of excited states, fast chemical reactions, and photodissociation processes. The range of laser applications is much too broad to cover here. We will limit discussion to a few topics which will illustrate some of the specialized uses of lasers in physical chemistry laboratories.

Ultrafast Processes. The term ultrafast processes refers to chemical dynamical events which occur on a picosecond and subpicosecond time scale. Most primary photochemical processes in the condensed phase occur on this time scale. These include orientational processes in liquids, decay processes in highly excited molecules, nearest neighbor energy transfer processses and many solid state reaction processes. Mode-locked solid state lasers and dye lasers produce optical pulses to create these events on a *time scale short enough* to leave the systems in the optically prepared state. For the most part, electronic detection devices with which one normally probes such processes have response times which are too slow to resolve subsequent relaxation processes. The most sophisticated experiments in this area use the picosecond exciting pulse to create a secondary probing pulse with which the intially prepared state can be interrogated. The secondary probing pulses usually monitor the excited state absorption processes or induced relaxation events in the initially prepared states. To date, most picosecond measurements have been carried out on large organic molecules (particularly dye molecules) and on biochemically important molecular reactions.[20] This field is still in its infancy, and another decade will probably be required to determine the most important applications and discoveries to be made by these techniques.

Energy Transfer Reactions. Researchers at NRL have been studying electronic to vibrational energy transfer reactions via laser excitiation and infrared laser probing techniques to investigate theoretical mechanisms controlling this type of relaxation phenomenon. Hsu and Lin[21] report the results of a study of the E-V transfer process: $Na(3^2P) + CO(X^1\Sigma^+, v = 0)$ $Na(3^2S) + CO(X^1\Sigma^+, v = 0 - 8)$. The electronically excited sodium atoms are produced with a flash-lamp-pumped dye laser. The resulting vibrational excitation in CO is probed with a stabilized CO infrared laser. In this work it was determined that the CO molecules become excited up to the limits of energy available from the excited sodium. Figure 8 shows a plot of the experimental energy distributions[21] and confirms the appropriate theoretical mechanism.

Photofragmentation Reactions. By the use of pulsed lasers, it is now possible to probe the internal energy states (electronic, vibrational and rotational) of the primary products of photodissociation reactions in the absence of collisions. Determinations such as these are important because the internal energy of reactant species can often influence the rates and mechanisms of secondary reaction processes. Workers[22] at NRL have recently reported the results of a study of the dissociation process

$$ICN \xrightarrow[2660A]{hv(laser)} I + CN .$$

Chemiluminescence measurements have shown that $\sim 60\%$ of the iodine atoms are created in their electronically excited state, $(^2P_{1/2})$,

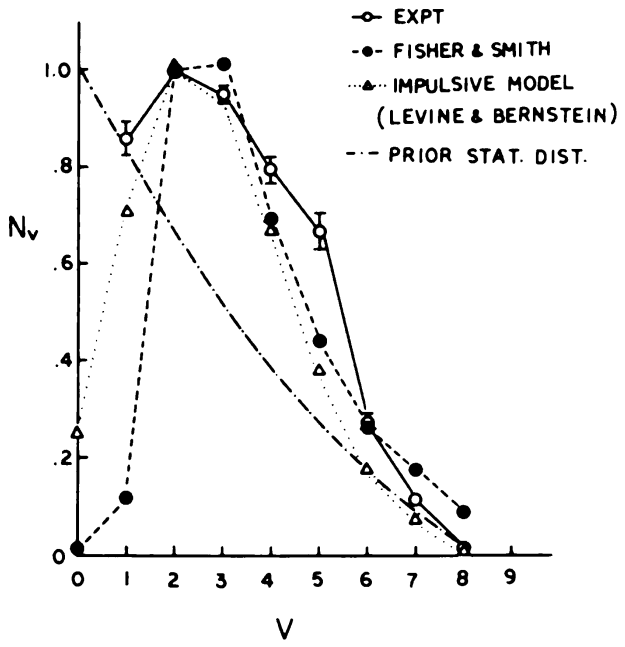

Figure 8 — A plot of the vibrational population in CO *produced by energy transfer from laser excited sodium atoms.*

while the other 40% are in the lowest energy state. Contrary to previous conclusions, it was shown that the CN fragment is created entirely in its electronic ground state. By synchronizing a second tunable laser pulse with the photolysis pulse, the vibrational and rotational energy of the CN fragment can be probed. Figure 9 shows a fluorescence excitation spectrum of the CN fragment which can be analyzed for rotational and vibrational distributions.[22] The CN fragment was shown to have a vibrational "temperature" of ~750°C and a rotational "temperature" of ~3500°C. These measurements have then been used to completely determine the flow of the total energy available in this photodissociation process. These experiments have generated several new theoretical analyses to account for the observations.

Laser Synthesis

It has been the dream of laser scientists for more than a decade to apply lasers as the driving force for laser-induced photochemical synthesis on an industrial scale. Considerable prudence must be used in considering such processes because the laser photons must be considered as one of the reactants. The cost of one mole of laser photons varies widely; from about five cents for CO_2 lasers to several dollars for ultraviolet laser photons. These are operating costs and do not include the capital investment required to set up a new plant operation. It is generally agreed at this point that laser synthesis of chemicals now costing less than a few dollars per pound will be impractical. Nevertheless,

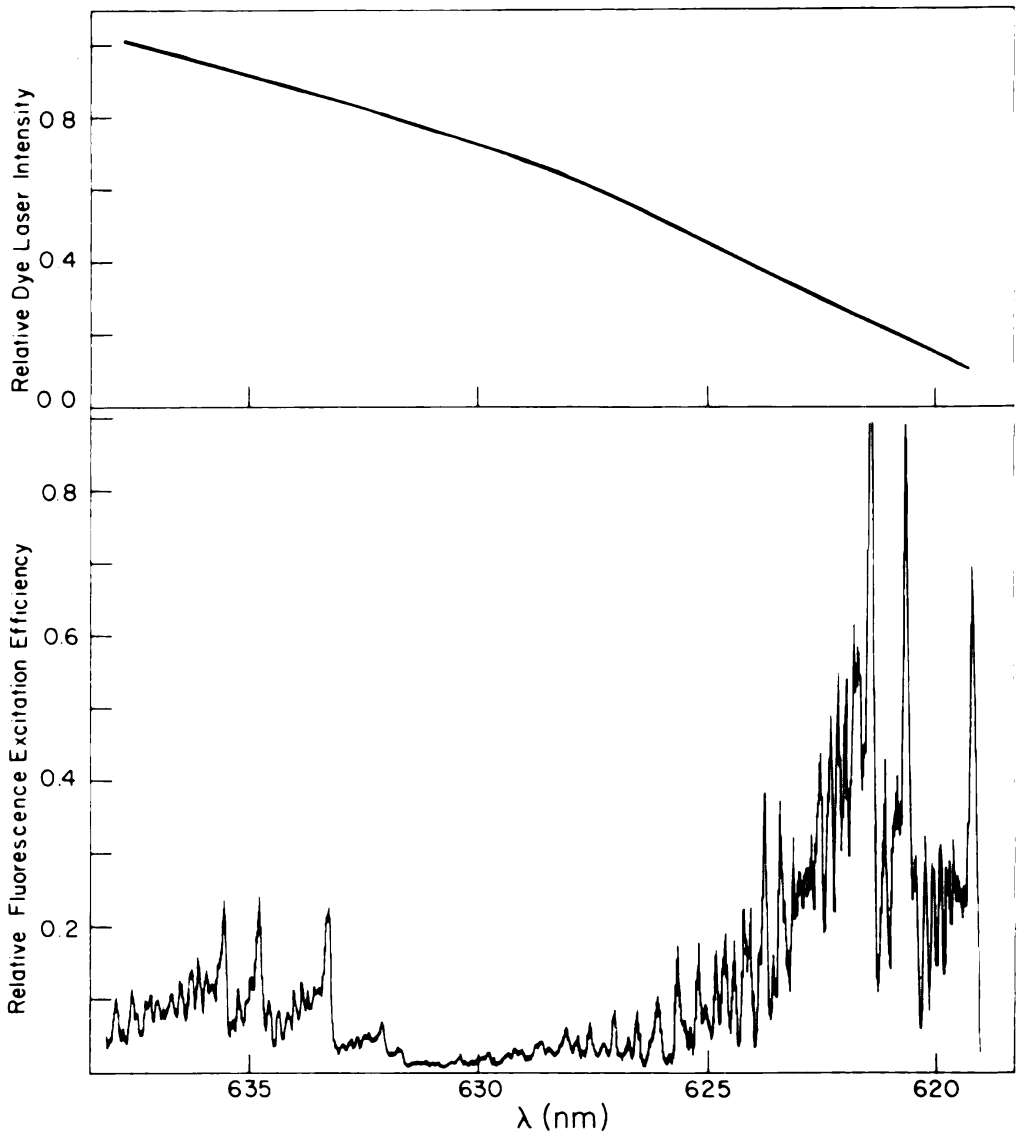

Figure 9 — The laser-induced fluorescence excitation spectrum of the CN *fragments produced in the laser photodissociation of* ICN. *The concetration of* CN *fragments is ~ 1 μtorr or about* 10^{10} *radicals/*cm^3.

several governmental laboratories, and at least two industrial laboratories, have large research efforts dedicated to the development of potentially economic laser synthesis processes. The general areas where laser synthesis has the highest probability of commercial success have been closely scrutinized by several groups, both from a chemical and an economic point of view. The following lists some of the research areas currently being pursued by one or more laboratories now carrying out laser synthesis studies:

- Synthesis of very expensive chemicals where the cost of laser photons can be overcome.
- Preparation of exotic or specialty chemicals which cannot be easily made by traditional thermal chemistry techniques.

- Separation and purification of atmoic isotopes of both light atoms such as H, N, B, C, O, Li, etc. and heavy isotopes, particularly the radioactive species such as unranium and plutonium.
- Destruction or conversion of small concentrations of impurities in batch process or plant streams.
- Chain reaction events such as polymerizations where one can initiate many chemical events with a single photon.
- Specialty applications such as microscopic photochemical applications in microcircuits, fast writing processes, photochemical printing, photochemical coagulation, etc.
- Photochemical separations of molecular components of radioactive nuclear wastes.

As we have already seen in several examples, the study of laser-induced chemical reactions can lead to a better understanding of reaction mechanisms and chemical kinetics. These studies probably will likely also suggest new areas of application for laser processes and serve as a guide for the design of practical reaction systems. In all cases, basic studies will procede applications of laser chemistry for economic development. Invariably, the dissemination of information is impeded by security classification of sensitive processes, as is the case with heavy metal separations in some laboratories. Industrial classification of potentially important economic processes prior to patenting procedures may also delay the general knowledge of breakthroughs in the synthesis field. For the most part, however, there is an openness among workers in this field with respect to the processes being studied, even though it may not include detailed experimental results or measured spectroscopic information, etc. We will briefly review a few of the current experimental results in the field and new experimental techniques which are being developed.

Multiphoton Dissociation Reactions. The field of vibrationally-induced photochemistry is in a high state of development and expanding rapidly. In a typical experiment transversly excited atmospheric (TEA) CO_2 laser emission (with energies of one to a few joules/pulse and durations of $\sim$100 nanoseconds) is focused into infrared absorbing gases at low pressure. The laser is tuned to a particular absorption feature of the sample. Because of the intensity of the pumping source, many infrared photons can be either simultaneously or sequentially absorbed, often raising the internal energy of the molecule sufficiently to overcome the activation energy for unimolecular reaction. Even though it is thought that an essentially instantaneous intramolecular randomization of vibrational energy occurs, the pumping rates are often fast enough to drive several dissociation channels simultaneously. Considerable controversy still exists as to the exact pumping mechanisms and the randomization of the internal energy, which further experiments will doubtless

resolve. At present, this is the most viable method for enrichment of molecular isomers. Spectaular enrichment factors for some specific photoreactions have been reported. For instance, $^{34}SF_6$ concentrations have been increased from 4% to greater than 99% in residual photolyzed gases,[23] and Carbon-13 separation in CF_3I has been attained[24] with separation factors as high as 600. These techniques[25] have been successful for enrichment of various oher isotopes also; i.e., ^{11}B, ^{12}C, ^{28}Si and ^{32}S. Although the separation factors can be very impressive, many photons are required ($\sim 10^8$/molecule) to carry out the reactions.

The concept of state-selective, multiphoton, laser-induced chemistry is being applied to many new systems, and a tremendous amount of new information is being generated which will add to our understanding of this class of fundamental photoprocesses.

Isotope Enrichment Processes. The need for ^{235}U as a fission fuel in light water nuclear reactors has been a powerful economic incentive for investigation of many types of laser-driven isotopic separation schemes. It has been predicted[26,27] that the use of an efficient laser isotope process for nuclear fuel enrichment represents a potential savings of the order of 100 billion dollars over the next 25 years. In addition, there is an important market for lighter isotopes such as D, ^6Li, ^{10}B, ^{13}C, ^{15}N, ^{17}O and ^{18}O in connection with energy production and in other fields such as nonradioactive tracers in analytical, medical and environmental studies.

The major bottleneck in laser isotope enrichment, in general, lies not in selective and efficient pumping of the isomers, but in the extraction technique which must act preferentially with the excited species before relaxation, energy transfer or isotopic scrambling can take place. Various magnetic, electrical, optical and thermal techniques are being used for the extraction processes. However, chemical reaction or molecular isomerization techniques offer the greatest promise for high throughput and economy of extraction. These schemes involving laser-initiated chemical reactions involve a high level of application of photochemistry techniques and require a different solution for each particular atomic isotope to be purified. However, important progress has been reported for the selective enrichment of several isotopic species such as ^{13}C, $^{17,18}O$, B, deuterium and the halogens. In particular, the development of processes for deuterium enrichment is at an advanced state and is apparently proceding into pilot plant separation.

Chemical Separations and Molecular Synthesis. The field of laser enhanced chemistry outside the area of isotopic enrichment processes has developed more slowly because the economic incentives are somewhat less well defined. In a related area, scientists at NRL are attacking problems in the chemical separation of the components in spent nuclear fuel wastes. These wastes must be reduced to tractable volumes for handling and storage. Moreover, they represent a source for important

chemicals if they can be successfully removed from the host materials. Some success has been reported on a laboratory scale for laser-induced chemical separations of selected lanthanide mixtures occurring in these wastes.[27]

A series of laser-induced chemical reactions involving the synthesis of metastable $NH(^1\Delta)$ addition products with organic and inorganic species have been reported.[28] Reactions of this type, as studied at NRL, have importance in combustion processes, upper atmosphere chemistry and in the chemistry of planetary atmospheres and comets.[29] These reactions are difficult to study because they involve the $NH(^1\Delta)$ species which is electronically excited and has only a transient existence. This radical is produced in a laser photodissociation reaction,

$$HN_3 \xrightarrow{h\nu\ 2660\text{Å}} NH(^1\Delta,\ v = 0) + N_2(^1\Sigma^+).$$

Subsequent reactions such as

$$HN(^1\Delta) + HN_3 \rightarrow NH_2(^2A_1) + N_3$$

$$NH(^1\Delta) + c\text{–}C_6H_{12} \rightarrow c\text{–}C_6H_{11}NH_2,\ \text{etc.},$$

are monitored by a chemiluminescence technique.[29] In this work, the reaction rate constants of six NH addition reactions have been measured, and important determinations concerning the reaction mechanisms have been inferred. The synthesis of cyclohexylamine in the liquid phase by the above process has been demonstrated and occurs with high overall efficiency.

Summary

In the past decade, laser sources have progressed from curiosities in optical laboratories to applications in essentially all fields of science and industry. In this short review, we have attempted to give the casual reader a feeling for the wide spread areas of science, engineering and industry which have come to rely on lasers as tools. While focussed on chemistry, there are many other areas such as medicine, engineering applications and weapons and communications technology in which lasers have had considerable impact.

We have covered three areas of chemistry and physics in which laser applications have created somewhat of a revolution of ideas and have generated new applications. The first of these areas involved the analytical and diagnostic applications of lasers to the applied fields of (1) atmospheric chemistry, (2) high temperature combustion, plasmas and discharges, and (3) laboratory analytical chemistry. In the second, we have reviewed some of the modern applications of lasers to the study of basic chemical processes, such as molecular dyamics and chemical

kinetics. And in the third areas, we discussed one of the new fields of application of lasers to chemistry — the use of lasers for separation and purification processes and for carrying out synthetic chemistry by laser-induced reactions.

Finally, we would like to leave the reader with the understanding that lasers are not only extensions of Buck Rogers' Ray Gun, but they are truly a new source of optical radiation with new and special properties which insure that they will have an increasing impact on many facets of science and industry and on our daily lives.

The interested reader is referred to several more "in depth" review articles which are currently available.[31–36]

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Advanced Optical Viewing System

The potential for better and faster sea floor search and mapping capability is at hand with the recently tested Real Time Optical Mapping System (ROMS) developed by Naval Ocean Systems Center (NOSC), San Diego.

ROMS, an advanced optical viewing system, recently completed its first in-ocean test at San Clemente Island. The test results indicate high optical resolution covering a large swath width with a readout showing real time optical pictures of the ocean bottom.

The test shows that the gap between existing acoustic systems which provide long range and real time operation but are limited by low resolution and photographic systems which offer high resolution but are not capable of real time operation has been successfully bridged.

ROMS reduces the detrimental effects of backscatter through the use of the volume scanning principle. The system consists of a flying spot scanner in an underwater transparent acrylic housing. Light source is an argon ion laser which is mechanically scanned to illuminate a 120-degree fan beam. The system provides real time optical pictures of the sea floor from a 120-foot height with a 400-foot swath width. ROMS can be towed at speeds from zero to five knots to provide the vertical sweep.

System capabilities depend on a set of rotating, three-faceted mirrors mounted on a single shaft. The first mirror sweeps the laser beam across a 120-degree angle; the second, synchronized with the first, receives a portion of the beam returned from the sea floor and reflects it through a focusing system to a photomultiplier. The photomultiplier signal is preamplified and processed before it is transmitted to the surface. At the surface it is further processed so as to be compatible with the cathode ray tube display.

The operator is able to control the display and adjust its contrast or zoom in on an object or area of interest.

The receiving mirror is mounted in a water filled acrylic housing to reduce light losses at the water-window-air interface, and its field of view is limited to a region near the sea floor to minimize backscatter.

ROMS applications include also close range classification and inspection, extension of vision to remote undersea work systems, mapping of the ocean floor for geological purposes and salvage operations.

Sun and Weather

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Introduction

Much of the flavor of sun-weather investigations at present is caught in an exchange that occurred at a meeting of the Royal Astronomical Society at Exeter in March 1975 (1).

D. R. DAVIES: I am very sceptical of this Sun-weather business. One needs to be very careful in the interpretation of the sort of statistics used by King. It is no good saying there are correlations without suggesting realistic mechanisms.

J. W. KING: That is just the sort of reaction I have come to expect from some professional meteorologists. There is little doubt that the correlations are real. Even if meteorologists refuse to research possible mechanisms, geophysicists surely will.

For well over 100 years some geophysicists have been attempting to convince meteorologists that the changing sun may cause changes in our weather and climate. We must define what we mean by "changing sun." Everyone agrees that the almost-constant radiant energy at visible wavelengths drives the weather machine and, indeed, is the ultimate energy source for almost all activities on earth. On the other hand, the possibility that changes in the sun may cause changes in weather and climate has been a controversial and sometimes emotional issue.

Several decades ago the "changing sun" in this context would have meant small changes in the radiant energy output of the sun (the so-called solar constant). Charles Greeley Abbot, the former secretary of the Smithsonian Institution, devoted much of his life to this question. He lived to the age of 101 years, and a few months before his death in 1974 he addressed a Symposium on this subject at Goddard Space Flight Center.

Nowadays, we can consider some other aspects of the "changing sun" that may influence weather and climate. A solar wind flows away

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from the sun in all directions, carrying with it the sun's magnetic field and taking about four days to reach the earth. Large solar flares can send shock waves out into the solar wind that reach the earth in one or two days. These shock waves, and also some quasi-stationary structures in the solar wind, considerably influence the intensity at the earth of cosmic rays from the galaxy and of high-energy protons and electrons from the sun.

The rotation period of the sun as seen from the earth is about 27 days. Observations show that, at least in certain wavelengths such as the ultraviolet, the intensity of the solar radiation received at the earth varies with a 27-day period, corresponding to the presence of quasi-stationary large-scale structures on the sun. These solar structures are the source of similar structures in the solar wind that are known to influence several terrestrial effects, such as radio-communication outrages, power-line outages, and high radiation levels in airplanes and spacecraft.

The subject of this paper is the question of whether one (or perhaps several) of these aspects of the "changing sun" may influence weather and climate on the earth. The size of such an influence, if indeed one exists, could be anywhere from a real but very small influence whose practical importance might lie mainly in improving our understanding of meteorological processes to a substantial influence that might have direct significance for forecasting. Much additional work will be needed to establish a firm answer to these questions. The Office of Naval Research is one of the leading sponsors of work in this field.

The Scientific Problem

The principal scientific problem at present is to establish the reality, or lack thereof, of sun-weather influences. As the reality becomes more likely, increasing numbers of scientists and increasing amounts of support are involved in the investigations.

A comprehensive description of observational and theoretical investigations is available in the *Proceedings of a Symposium on Possible Relationships Between Solar Activity and Meteorological Phenomena* held at Goddard Space Flight Center in November 1973 (2) and in recent reviews by King (3) and Wilcox (4). I will not attempt a further review of these reviews and symposium proceedings but rather refer the interested reader to them for technical details. I will concentrate on a discussion of the reality of the sun-weather investigation with which I am most familiar and will supplement this discussion with some recent results that became available after the reviews and proceedings were published.

Some Recent Work

I will first describe some recent work involving the cooperative efforts of several scientists at several institutions (5). For a decade or

more, W. O. Roberts at the National Center for Atmospheric Research and the University of Colorado in Boulder has been a leading American worker on the subject of sun-weather interactions. Some recent work by Roberts and Olson (6) (7) studies days on which geomagetic activity had a sizable increase, which was assumed to have a solar cause. They also studied the history of low-pressure troughs (cyclones) from the Gulf of Alaska as they moved across the continental United States and found that the troughs associated with geomagnetic activity were significantly larger on the average than troughs associated with intervals of quiet geomagnetic conditions. The vorticity area index, a measure of the size of low-pressure troughs devied by Roberts and Olson, has been used in several subsequent investigations.

A low-pressure trough is a large rotary wind system, leaving a diameter of a few thousand kilometers, that is usually associated with clouds, rain, or snow. Although the formation and structure of low-pressure troughs have been studied in some detail, it is not possible in general to predict the time and place at which a trough will form. This is one reason why the skill in short-range weather prediction becomes small (that is, little better than a prediction of average properties) within two or three days (8). The vorticity area devised by Roberts and Olson can be computed from maps of the height of constant-pressure (300-mbar) surfaces by using the geostrophic wind approximation. These maps are prepared twice a day, at 0 and at 12 universal time (UT), by the National Weather Service. The circulation of the air mass in a trough is defined as the line integral of the velocity of the air around a closed path. Vorticity is defined as the circulation per unit area. In our use of the vorticity area index, it is computed for the portion of the northern hemisphere north of 20°N. The index is now defined as the sum of all areas in which the vorticity exceeds a certain threshold, which is chosen so that all well-formed troughs are included. Once the threshold level ($20 \times 10^{-5}\,\mathrm{sec}^{-1}$ in our work) has been chosen, the computation of the vorticity area index is completely objective.

The results of the investigations to be described in this chapter will be presented in terms of graphs in which the meteorological input to the investigation is plotted on the ordinate and the solar input is plotted on the abscissa. The meteorological input is the vorticity area index just described. Now we must consider what the solar input will be.

Roberts and Olson (6) (7) assumed that the increases in geomagnetic activity used in their analysis were caused by the changing sun. This assumption was challenged by Hines (9), who suggested that some geomagnetic activity may be caused by current systems induced by motions of the lower atmosphere. To the extent that this assumption is correct, the assumed chain "sun → geomagnetic increase → weather change" would be replaced by a "weather change → geomagnetic activity → weather change." In my opinion, such an influence on the investiga-

tions of Roberts and Olson (6) (7) can probably be neglected. Nevertheless, it is clearly an advantage in this situation if a structure that is clearly of solar origin can be used for the solar input in the investigation.

For this purpose, we consider the solar sector structure, which is a fundamental large-scale property of the sun. A description of several solar, interplanetary, and terrestrial properties of this structure is available (10). The structure is readily perceived in observations by spacecraft magnetometers of the interplanetary magnetic field that is swept past the earth by the solar wind. For several consecutive days, this interplanetary field will be observed to have a polarity directed away from the sun. For the next several days, it will be observed to have a polarity directed toward the sun. These two sectors are separated by a thin boundary that typically is swept past the earth during an interval measured in tens of minutes.

In the investigations described here, the time at which a sector boundary is observed to sweep past the earth is used as a zero-phase reference. This sharply defined time is very convenient for the analysis, but it must be emphasized that the sector boundary itself is probably not an important influence on the weather. Furthermore, the large-scale sector pattern of the interplanetary magnetic field (and associated structures in the solar wind) is not necessarily a physical influence on the weather. The solar influence (if there is one) described in this chapter could be related to variations in the solar ultraviolet emission in the solar "constant," in some manifestation of the changing solar magnetic field such as energetic particle emission in an influence of the extended solar magnetic field on galactic cosmic rays incident at the earth, or in some other unknown factor. In any event, the extended solar sector structure as observed with spacecraft in the interplanetary magnetic field near the earth is clearly a solar structure that is not influenced by terrestrial weather. We now consider further the possibility that some aspect of the solar structure may influence the weather.

Extension of Earlier Investigations

Our group at Stanford joined forces with Roberts and Olson to extend their original investigations. The first results (11) (12) of this collaboration are shown in Figure 1, where the average change in the vorticity area index is plotted against days from sector boundary as the sector structure is swept past the earth by the solar wind. Day zero represents the time at which a sector boundary passed the earth. We see in Figure 1 that on the average the vorticity area index reaches a minimum approximately one day after the boundary passage. The amplitude of the effect from the minimum to the adjacent maximum is about 10 percent. When we consider that weather usually consists of relatively small changes about climate (the average properties), this represents a sizable and important change. I repeat the warning that the sector boundary passage, although very convenient as a precise tim-

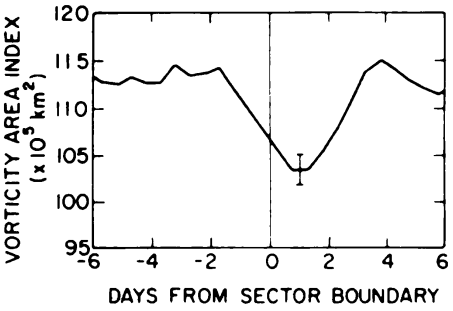

Figure 1 — Average response of the vorticity area index (the area of all the low-pressure troughs in the northern hemisphere) about times when solar magnetic sector boundaries were carried past the earth by the solar wind. Sector boundaries were carried past the earth by the solar wind on day 0. The analysis includes 54 boundaries during the winter months November to March in the years 1964 to 1970. The standard error of the mean (error bar) was calculated after subtracting a 27-day mean centered on each sector boundary, to remove long-term trends. The deviations corresponding to the individual boundaries are consistent with a normal distribution about the mean.

ing mark, almost surely does not have an important physical influence on the weather. The large-scale sectors in the interplanetary magnetic field also may not have a direct causal influence on the weather but may merely delineate some solar structure that does. Figure 1 is computed for 300 millibar, but similar results are found for 200, 500, and 700 mbar.

The result shown in Figure 1 is prominent only during the winter months (13). This may be related to the fact that this is the season in which the equator-to-pole temperature difference is largest, producting the largest stresses on the earth's atmospheric circulation.

Significance and Reality of the Results

The original work shown in Figure 1 used 54 sector boundary crossing times observed with spacecraft orbiting the earth. The evidence for the significance and reality of the claimed effect rested on the size of the standard error of the mean (the error bar shown in Figure 1) and on the result shown in Figure 2 that the effect persisted when the list of

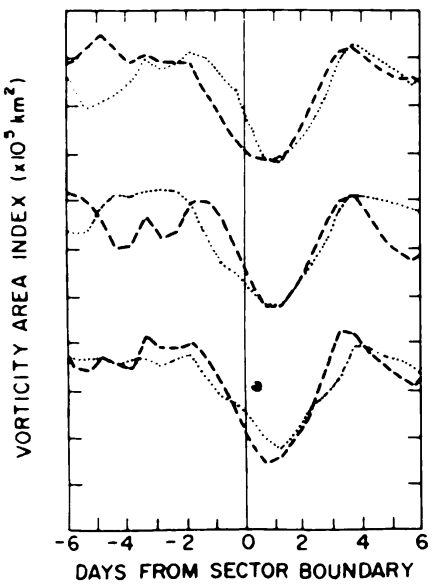

Figure 2 — Same format as Figure 1; the list of boundaries used in Figure 1 was divided into two parts according to (a) the magnetic polarity change at the boundary, (b) the first or last half of the winter, and (c) the yearly invervals 1964 to 1966 and 1967 to 1970. (a) The dotted curve represents 24 boundaries in which the interplanetary magnetic field polarity changed from toward the sun to away, and the dashed curve 29 boundaries in which the polarity changed from away to toward. (b) The dotted curve represents 31 boundaries in the interval November 1 to January 15, and the dashed curve 22 boundaries in the interval January 16 to March 31. (c) The dotted curve represents 26 boundaries in the interval 1964 to 1966, and the dashed curve 27 boundaries in the interval 1967 to 1970. The curves have been arbitrarily displaced in the vertical direction, but the scale of the ordinate is the same as in Figure 1; that is, each interval is 5 × $10^5 km^2$.

boundaries used in Figure 1 was divided into two parts according to (a) the magnetic polarity change at the boundary, (b) the first or last half of the winter, and (c) the yearly intervals 1964 to 1966 and 1967 to 1970. There has been some discussion of the appropriate way to compute the error bar in Figure 1. We believe that the correct method was used, but in any case we describe some independent tests of reality.

A further test of significance is to inquire if the effect persists in new observations (14). Figure 3(a) shows our original analysis while Figure 3(b) shows the same analysis performed with a list of 81 new boundary passage times, none of which is included in the analysis of Figure 3(a). The new boundary passage times used in Figure 3(b) were obtained by increasing the interval examined to 1963 to 1973 and by supplementing spacecraft observations of the interplanetary magnetic-field polarity with inferred polarities of the interplanetary field obtained from analysis of polar geomagnetic variations (15), (16), (17), and (18).

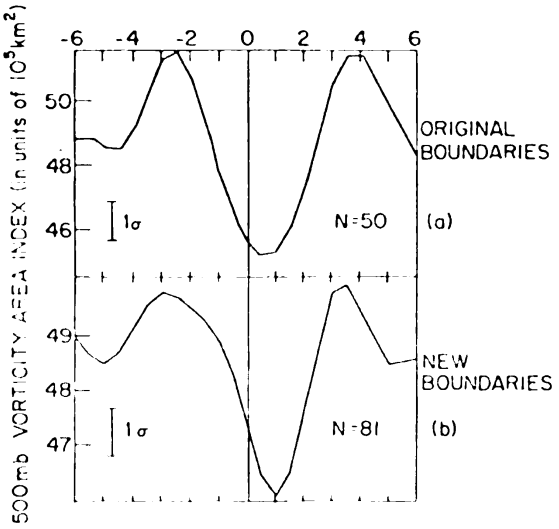

Figure 3 — Same format as Figure 1; for (a) 50 of the boundaries used in the original work and (b) 81 new boundary passages not included in the original analysis.

The most important test of the significance of the results claimed in Figure 1 was made by Hines and Halevy who stated, "Reports of short-term Sun-weather correlations have been greeted with skepticism by many" (19). They subjected the data used in preparing Figure 1 to a variety of statistical tests and requested the analysis of new data shown in Figure 3. They concluded that "We find ourselves obliged, however, to accept the validity of the claim by Wilcox *et al.*, and to seek a physical explanation."

What does one conclude from all of the above? The results of the past century suggest that a certain caution would be very appropriate. The one statement that I would make with complete conviction is that

this appears to be an interesting subject that should be vigorously pursued.

Societal Concerns, Need for Predictions, and Prospects for Improvement

An understanding of the physical mechanisms of an influence of the changing sun on weather could well yield an improvement in the forecasting of climate, to the extent that the factors influencing climate represent longer-term averages of the transient factors influencing weather. We may come first to an understanding of the factors influencing weather, since in a given interval, say 10 years, there are many more repetitions of weather changes than of climate changes.

The needs of society for improved forecasting of weather and of climate are obvious and do not need to be examined in detail here. The suffering and deaths caused by recent droughts in the Sahel and the large international purchases of wheat following crop failures in the Soviet Untion are recent examples.

We cannot quantify possible societal benefits from the understanding of sun-weather effects until we are sure that such effects exist and that we understand the magnitude of the effects. If sun-weather effects turn out to be real but of very small magnitude, the resulting increase in our understanding of meteorological processes may still improve forecasting of weather and climate, with resulting societal benefits. If sun-weather effects should turn out to have a significant magnitude, then they may become a direct part of such forecasting.

Comparison of Sun → Weather and Sun → Geomagnetic Activity

In trying to assess the status of sun-weather investigations at present it is useful to compare with investigations of the influence of the changing sun on geomagnetic activity, i.e., changes in the earth's magnetic field on a time scale of tens of minutes. For about 100 years, some geophysicists have been claiming that variations in the earth's magnetic field are caused by the changing sun. In the early years this viewpoint was quite controversial. In his famous Presidential Address in 1892 to the Royal Society, Lord Kelvin had some firm comments for such geophysicists. He considered the amount of energy involved in geomagnetic activity and concluded, "This result, it seems to me, is *absolutely conclusive* against the supposition that terrestrial magnetic storms are due to magnetic action of the sun; or to any kind of dynamical action taking place within the sun, or in connection with hurricanes in his atmosphere, or anywhere near the sun outside" (20). In spite of these strictures, some geophysicists and astronomers proceeded with their investigations, and today it is universally accepted that the changing sun is the cause of many variations in the earth's magnetic field.

Evaluation of Sun → Weather at Present

What are the prospects for improvement of our understanding of the sun-weather situation in comparison with this description of the sun-geomagnetic activity situation? Sun-weather investigations are at an early point on the time scale of sun-geomagnetic activity investigations, perhaps not long after Lord Kelvin admonished the geophysicists and astronomers. Does this then mean that we will have to wait for 75 years until we can give a fairly complete and concise summary of the physical conditions related to sun-weather? Almost surely not, because spacecraft and modern observational and computational tools have given us a much more powerful handle on the problem.

The meteorological system is much more complex than the geomagnetic field. In meteorology we have to deal with many complex internal processes and with exchanges of energy with large reservoirs such as the oceans. If this complexity of the meteorological system prevents or at least delays an understanding comparable with what we now have of the simpler geomagnetic field, it may still be possible to utilize correlations between the changing sun and meteorological phenomena on an empirical basis, if such correlations can be shown to be real and of sufficient magnitude. Of course, an understanding of the basic physical processes would be much more satisfying from both the practical and the intellectual viewpoints.

A further important point to consider in the analogy between sun-geomagnetic activity and sun-weather investigations is the quantitative way in which the terrrestrial system (the geomagnetic field or meteorological processes) is described. The concise description of geomagnetic activity became possible only when the classical and widely used index of geomagnetic activity (Bartel's index Kp) was set aside and a newer and more descriptive index (Mayaud's index am) was used. There is no way in which this concise description could have been obtained using the older index. Similarly, it is not at all clear that present investigations of sun-weather effects have used an optimum quantitative description of meteorological processes. Indeed, it is very likely that they have not. The search for the optimum quantitative description of meteorologial processes is one of the most important parts of future sun-weather investigations. Here we can take heart in the improved possibilities offered by spacecraft and by modern observational and computational techniques.

An important element in the prospects for improvement of sun-weather investigations is the increasing number of scientists who have become interested in this subject. This is both a cause and a result of several recent symposia and organizational activities. A landmark was the symposium on "Possible Relationships Between Solar Activity and Meteorological Phenomena" held at Goddard Space Flight Center in November 1973 (2). A joint meeting on this subject was held by the

American Meteorological Society and the Solar Physics Division of the American Astronomical Society in January 1975 in Denver. A workshop, "The Solar Constant and the Earth's Atmosphere," was held at Big Bear Solar Observatory in May 1975 (21). A symposium on the subject was held at the General Assembly of the International Union of Geodesy and Geophysics in Grenoble in August 1975.

The Special Commmitee for Solar-Terrestrial Physics of the International Council of Scientific Unions has established a working group on Solar-Terrestrial Physics and Meteorology. A publication, *Solar-Terrestrial Physics and Meteorology: A Working Document*, including a selected bibliography, an address list of recent authors, selected key dates and data, and selected contemporary reviews is available from the Special Committee for Solar-Terrestrial Physics, % National Academy of Sciences, 2101 Constitution Avenue, Washington, D.C. 20418. A joint U.S.A./U.S.S.R. Working Group of Influence of Solar Activity on Climate has held several meetings in the United States and the Soviet Union. The National Aeronautics and Space Administration has established an Advisory Committee on Sun-Weather Investigations.

Recommendations

Since the view of an interdisciplinary committee may carry greater weight than the view of an individual, this section is excerpted from the Report (22) of a Committee* to advise NASA Headquarters on the Relationship Between Solar Activity and Terrestrial Weather:

1. We have studied the literature and we conclude that there is a *prima facie* case for influence of the sun on terrestrial weather on a time scale of a few days.

2. We advocate a careful and extended statistical study of selected indicators of solar and terrestrial phenomena with a view of (a) confirming or disproving the present apparent relationship; (b) determining the reality or otherwise of proposed 11-year and 22-year associations; and (c) searching for a causal chain responsible for any such association.

3. We advocate a program of theoretical research with a view to searching for possible causal chains between the sun and the earth's lower atmosphere and examining proposals in terms of physical processes and meteorological models.

Concerning recommendation 2(a) above, we suggest that there be a study of the morphology of the apparent influence of the solar and interplanetary sector structure on the vorticity area index, tropospheric

*The composition of the Committee is as follows: Peter A. Sturrock, Stanford University, Chairman; Guenter E. Brueckner, Naval Research Laboratory; Robert E. Dickinson, National Center for Atmospheric Research; Norihiko Fukuta, University of Denver; Louis J. Lanzerotti, Bell Laboratories; Richard S. Lindzen, Harvard University; Chung G. Park, Stanford University; and John M. Wilcox, Stanford University.

variations, the zonal index, and other meteorological variables. In addition, high priority should be given to completely new studies (involving different variables and different methods of analysis and possibly different scientists), which may either confirm or negate the results of recent studies.

Concerning item 2(c) above, the Committee recomends searching for correlations between pairs of variables listed in Table 1, as exemplified by the questions listed in Table 2. Some of the questions

Table 1
Variables Possibly Relevant to Casual Chain Relating the Sun to Terrestrial Weather

Sun	Interplanetary Medium	Magnetosphere	Ionosphere	Ground Level
Rotation	Solar-wind speed, Density, temperature, composition	Trapped-particle distribution	Size of auroral electrojet (A_e index)	Rainfall
Sunspot number	Magnetic fields		$n_e(h)$	Winds, ground Winds, 500 mb
Flare activity	Particle flux (solar, galactic)		Total electron content	Pressure
Large-scale magnetic fields				Thunderstorms (global)
10-cm radio emission				Electric fields Magnetic fields Cloud cover Ozone content Tree-ring history

Table 2
Outstanding Questions[a]

A Priority

1. Relation of ionospheric and ground-level electric fields (D, T)
2. Ionization of stratosphere by galactic cosmic rays (D, T)
3. Change of conductivity of atmosphere by cosmic-ray flux (D, T)
4. Effect of ultraviolet and charged-particle fluxes on ozone and nitric oxide (D, M)
5. Effect of ozone and nitric oxide on climate models (T, M)
6. Effect of fair-weather electric fields on thunderstroms and precipitation (D, T)

B Priority

7. Effect of sector magnetic field on solar particle flux (D, T)
8. Effect of stratospheric ionization on formation of condensation nuclei (D, T)
9. Criteria for rainfall and influence on meteorological models (T, M)
10. Modulation of galactic cosmic rays by solar magnetic fields (D, T)
11. Solar-wind velocity and density as a function of sector structure (D, T)
12. Coupling of solar magnetic fields to magnetosphere (D, T)
13. Charge generation in thunderstorms (T)

[a]D, data processing, T, theoretical analysis, M, modeling

listed in Table 2 are susceptible also to theoretical analysis and to model analysis and are therefore specific examples of the general point made in recommednations 3 above.

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Radiometers Detect Inversion-Layer Waves

Dr. Charles I. Beard and Mr. Lee U. Martin of the Naval Research Laboratory report the development of a potential shipboard method to locate atmospheric inversion layers which can cause difficulties in Naval operations. This research was sponsored by the Office of Naval Research.

Atmospheric inversion layers can become radio/radar "ducts" and cause fading or even loss of communications, reduced height-finding accuracy, false targets, and radio/radar "holes." Duct-causing inversion layers possess rapid temperature increases and sharp humidity decreases with increasing height.

The principal investigators in this research observed wave motion on the inversion layer for the first time using 22-GHz microwave radiometers. The researchers then determined the layer height by giving the radiometers a height-finding capability and by measuring the "time of flight" of these waves as they travel between two crossed radiometer beams.

The passage of the waves changes the altitude of the inversion layer and thus the thickness of the column of water vapor below the wave. Since water vapor emits natural radiation at 22 GHz, the height changes of the water vapor column are detected by the upward-looking 22-GHz radiometers.

Through application of this potential method operators would be alerted to the problem and could take corrective action. This new NRL passive technique could also be of tactical use in radio silence conditions.

Devices Measure and Evaluate Sulfur Pollutants

Two highly sensitive x-ray spectrometers, one to measure sulfur pollution in the air, the other to determine whether the source of the sulfur presents a health hazard have been developed at the Naval Research Laboratory.

The Environmental Protection Agency (EPA) called on NRL to help devise sensitive instruments to monitor sulfur and primary sulfate pollution in the atmosphere. Concern for sulfur pollution as a health hazard is increasing because some recent supplies of oil contained impurities which catalyze the production of primary sulfates, and because of the eventual need to burn high-sulfur coal for electric-power production.

The principal investigators for the project, LaVerne Birks and John Gilfrich, developed the x-ray spectrometers for the measurements. One of the instruments is a transportable unit which can be taken to the vicinity of power plants or other suspected sources. It can detect less than five parts per billion of sulfur-containing particles in the atmosphere by filtering a cubic meter of air.

The other instrument is an attachment to existing laboratory units. It is specifically designed to measure the valence state of sulfur, and provide a replacement channel for the multiple-crystal spectrometer instrument used by the EPA for routine analysis.

It is important to distinguish the valence state of sulfur because if the component detected is a sulfate, it more likely represents sulfur which started as sulfur dioxide (SO_2), a primary health hazard. On the other hand, sulfides, say Birks and Gilfrich, are likely to represent mineral dusts, and are not regarded as specific health hazards.

Specific areas where sulfur pollution is more likely are in electric power plants where coal has replaced oil, thus increasing the likelihood of sulfur emission, and where catalytic converters on automobiles are used to minimize carbon monoxide and hydrocarbon emissions. These converters produce enough SO_2 to form up to 0.5 ml of H_2SO_4 for each liter of gasoline burned.

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IN THIS ISSUE

VOL. XXXI, NO. 4

Cover Caption

A complex eruptive prominence on the sun photographed in helium^{+} 304 Å by the Naval Research Laboratory's Spectroheliograph aboard Skylab on August 9, 1973. *(See article on page 21.)*

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