7-100-1-6/78

Energy and Technology Review

Lawrence Livermore Laboratory

January 1978

IMAGING
THERMONUCLEAR
BURN

THE COVER

A coded image of the alpha-particle emission from the thermonuclear burn of a laser fusion microtarget; the image is a shadowgraph produced by the passage of the emitted alpha radiation through a Fresnel zone plate (*inset*) onto a thin sheet of cellulose nitrate. Each alpha particle that strikes the thin plastic sheet produces a microscopic pinhole. The pinhole pattern, when appropriately processed, is used to optically reconstruct a real image of the thermonuclear burn distribution within the microtarget. The image is time-integrated over the burn duration (less than 15 ps).

See p. 1 for a discussion of zone-plate coded imaging, a new diagnostic technique for producing high-resolution images of radiation from imploded fusion targets.

ABOUT THE JOURNAL

The Lawrence Livermore Laboratory is operated by the University of California for the United States Department of Energy. The Laboratory is one of two nuclear weapons design laboratories in the United States. Today nearly half of our effort is devoted to programs in magnetic and laser fusion energy, biomedical and environmental research, applied energy technology, and other research activities.

The *Energy and Technology Review* is published monthly to report on accomplishments in this energy and environmental research and on unclassified portions of the weapons program. A companion journal, the *Research Monthly*, reports on weapons research and other classified programs. Selected titles from past issues of the *Energy and Technology Review* are listed opposite the inside back cover.

Rev. 1984

UCRL-52000-78-1
Distribution Category UC-2

January 1978

Energy and Technology Review

Lawrence Livermore Laboratory

Prepared for DOE under contract No. W-7405-Eng-48

MASTER

Scientific Editor:

Henry D. Shay

BRIEF

ii

Cryogenic Forming: Process Evaluation Using High-Purity Nickel.

General Editors:

A. Paul Adye
Richard B. Crawford
Judyth K. Prono
Jane T. Staehle

ZONE-PLATE CODED IMAGING OF THERMONUCLEAR BURN

1

A Fresnel zone-plate imaging technique has been developed that provides high-resolution images of the thermonuclear burn region in laser fusion experiments.

LASER-INDUCED MOLECULAR FLUORESCENCE FOR CHEMICAL ANALYSIS

9

Laser fluorescence technology is improving the sensitivity of chemical analysis by as much as four orders of magnitude.

THE OZONE LAYER: ASSESSING MAN-MADE PERTURBATIONS

17

We are studying how various man-made perturbations may reduce or redistribute stratospheric ozone. These perturbations include engine effluents from high-altitude aircraft, chlorofluoromethanes, and atmospheric nuclear explosions.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISSEMINATION OF THIS DOCUMENT IS UNLIMITED

104

BRIEF

CRYOGENIC FORMING: PROCESS EVALUATION USING HIGH-PURITY NICKEL

Cryogenic forming, or cryoforming, is the process of shaping a material by pressure at cryogenic temperatures. Forming strengthens a material, and our tests indicate that cryoforming strengthens some materials far more than standard room-temperature forming processes. Some materials, such as austenitic stainless steels, are strengthened by phase changes; some, such as pure nickel, are strengthened by working (deformation). Pure nickel is strengthened only by working—rolling, drawing, forming—and responds very well to cryoforming.

For our first evaluation of the cryogenic forming process, we chose high-purity nickel-270 because of its possible interest to LLL programs. We formed a set of nickel samples at liquid-nitrogen temperature (77 K) and another set at room temperature, both at fast strain rates (fast forming). We measured the two sets at room temperature for failure strength, then compared the amount of working strain required to produce that strength. We then formed two sets at slow strain rates (slow forming); again one set was formed at liquid-nitrogen temperature and the other at room temperature. These sets were measured in the same way as those formed at fast strain rates.

Figure 1 compares nickel-270 strengths on the basis of how they were formed and shows that cryoforming produced a 30% higher strength nickel than that produced at room temperature at equal strains and strain rates. Forming-rate effects disappeared as working temperature decreased. Rate-insensitive cryoforming produced a considerably

Fig. 1. Nickel-270 failure curves showing the strength gained by cryoforming (ultimate test stress vs forming strain or elongation). The dashed curve is derived from tests on samples cryoformed at fast and slow strain rates at liquid nitrogen temperature. The two solid curves are derived from tests on samples formed at room temperature, one at a fast strain rate and the other at a slow rate.

stronger room-temperature material than room-temperature forming at high strain rates. Transmission electron microscopy indicated apparent structural differences between cryoformed nickel and nickel formed at room temperature.

Why cryoforming is more effective than room-temperature forming at fast or slow rates is not completely understood; nevertheless, the process is a workable means of gaining high strength for some materials.

Contact David E. Lord (422-1270) for further information on this subject.

Zone-Plate Coded Imaging of Thermonuclear Burn

The first high-resolution, direct images of the region of thermonuclear burn in laser fusion experiments have been produced using a novel, two-step imaging technique called zone-plate coded imaging. This technique is extremely versatile and well suited for the microscopy of laser fusion targets. It has a tomographic capability, which provides three-dimensional images of the source distribution. It is equally useful for imaging x-ray and particle emissions. Since this technique is much more sensitive than competing imaging techniques, it permits us to investigate low-intensity sources.

In the Laboratory's laser fusion program, we are experimenting with thermonuclear explosions on a microscopic scale using focused, high-power laser beams. A typical experiment focuses multiple laser beams onto a spherical glass pellet about $100\text{ }\mu\text{m}$ in diameter that is filled with a high-pressure mixture of deuterium-tritium gas. The incident laser radiation heats and compresses the target, driving it to thermonuclear burn conditions.

To obtain a more detailed understanding of the physical processes involved in laser-driven implosions, advanced diagnostic devices are used to collect and analyze the x-ray and particle emissions from such targets. Recently, a new diagnostic device, a Fresnel zone-plate camera employing coded imaging principles, was used to image the alpha-particle emission (one of the fusion reaction by-products) from imploded fusion targets, and thereby to produce the first high-resolution, direct

images of thermonuclear burn in such experiments.¹ These measurements provide an explicit demonstration that the thermonuclear burn produced by laser-driven implosions does indeed occur within a compressed core of the imploded target.

Use of the zone-plate-coded imaging (ZPCI) technique in laser fusion experiments involves a simple two-step procedure, which is outlined below and illustrated in Fig. 1.

Step 1—Shadowgraph Recording. A Fresnel zone-plate camera views the laser-irradiated target. The zone-plate camera is a simple shadow device containing no lenses or shutters. It uses a Fresnel zone plate—a concentric array of alternately transparent and opaque rings of equal area—as an aperture at the front, an appropriate recording film at the rear, and filter foils to keep unwanted radiation from reaching the film. The radiation emitted from the target casts a geometrical shadow through the transparent rings of the zone plate onto the recording film, producing a shadowgraph. This shadowgraph, also called a coded image, contains all the necessary information about the spatial distribution of the source, but that information is scrambled, or coded.

Step 2—Image Reconstruction. Unscrambling or decoding information that has been recorded in the shadowgraph is accomplished by shining a laser beam through the shadowgraph and viewing the diffracted laser light at the appropriate planes downbeam, much in the same way one would reconstruct an image from a hologram. At each plane, there is a high-resolution, optical, real image of the radiation emitted from the corresponding plane of the target. The simplicity

Contact Natale M. Ceglio (422-8251) for further information on this article.

of the ZPCI optical reconstruction procedure is due to the choice of the Fresnel zone pattern as the aperture on the shadow camera (Fig. 2). No other aperture pattern would permit the use of such a simple optical procedure for image reconstruction.

The Fresnel zone pattern operates in two distinct ways in the two steps of the ZPCI procedure.

In step 1, the radiation passing through the zone plate has wavelengths very much smaller than the minimum zone width. In this case, diffraction effects are negligible, and the zone plate acts merely as a coded aperture for casting shadows. In step 2, the wavelength of the reconstruction laser light is comparable to the minimum zone width so that

Fig. 1. Basic principles of the two-step ZPCI technique. *Step 1:* a zone-plate shadow camera views the imploding target. The emitted radiation—appropriately filtered—casts a shadow through a Fresnel-zone-plate aperture onto a recording film. Each source point will cast a separate shadow onto the recording film, producing a shadowgraph. Each zone-plate shadow uniquely characterizes, by its size and position, the spatial position of its associated point. *Step 2:* the processed shadowgraph transparency is illuminated with a low-power, visible-light laser beam. Each zone-plate shadow focuses the incident laser light to a diffraction-limited spot—the inversely located image of its associated source point.

diffraction effects dominate in image reconstruction. Each individual zone-plate shadow in the coded image acts as a circularly symmetric diffraction grating, focusing the incident laser light.

We can illustrate the significance of the Fresnel zone pattern more fully by considering how the technique works. We choose for illustration a hypothetical, incoherent radiation-source distribution composed of three separated point sources. The points may emit any incoherent radiation—electrons, x rays, alpha particles—that travels in a straight line from the source through the zone-plate aperture to the recording film. Each source point will cast a separate zone-plate shadow onto the film (see Fig. 1). Note that each zone-plate shadow uniquely characterizes, by its size and position, the spatial position of its associated source point. That is, off-axis points cast off-axis

shadows, more distant points cast smaller shadows, and closer points cast larger shadows. Thus, the spatial distribution and size of the zone-plate shadows encode on the shadowgraph the information about the spatial distribution of the source.

The unique focusing properties of the Fresnel zone pattern are used in the image reconstruction. Each zone-plate shadow focuses the incident laser light to a diffraction-limited spot, the image of its associated source point. In this way the three zone-plate shadows focus the incident laser light to a three-point image of the original three-point source. This simple concept of point-by-point reconstruction from zone-plate shadows can be extended to understand how a more complicated source distribution is imaged by the ZPCI two-step technique.

Fig. 2. Micro-Fresnel zone plates. The Fresnel zone plate is a pattern of alternately transparent and opaque, equal-area, annular zones. High-resolution coded imaging requires the use of free-standing, metallic zone plates having zone widths of microscopic size. These are fabricated at LLL using ultraviolet photolithography and microelectroplating techniques.² (a) A free-standing gold zone plate in which the gold zones are supported by a series of radial struts. The zone plate is $5\text{ }\mu\text{m}$ thick, its diameter is 1 mm, the outermost zone is $2.5\text{ }\mu\text{m}$ wide, and the plate has 100 zones. (b) Scanning-electron micrographs of sections of a similar gold zone plate before it was lifted off the substrate on which it was fabricated.

SPECIAL FEATURES OF THE ZPCI TECHNIQUE

Three particular features of the ZPCI technique make it especially attractive for diagnostic measurement of laser fusion plasmas:

- Tomographic capability—it produces three-dimensional images of three-dimensional sources.
- Broad radiation applicability—it can be used to image any incoherent radiation (x rays, electrons, alpha particles, etc.) that travels in straight lines.
- Efficient information collection—it can see small, low-intensity sources better than conventional imaging techniques.

Tomography. ZPCI produces three-dimensional images in much the same way as holography, except that there is no coherence requirement for the source. We record three-dimensional source information on the two-dimensional coded image and then retrieve it by viewing the reconstructed image distribution in separate reconstruction planes (Fig. 3). Ideally, there is a one-to-one correspondence between each reconstruction plane and each source plane. Thus, a complex three-dimensional source distribution can be ideally synthesized plane by plane.

The tomographic capability of ZPCI has been experimentally demonstrated. Shown in Fig. 3 are

Fig. 3. Schematic representation of the tomographic image reconstruction of the x-ray emission from a laser-irradiated, glass-microsphere target. Much like holography, the ZPCI technique can image objects in three dimensions. The information about the spatial distribution of the source is recorded in the superimposed, overlapping zone-plate shadow patterns that form the two-dimensional coded image. The information is retrieved by viewing the reconstructed image distribution in separate reconstruction planes. In this way, a three-dimensional source can be synthesized plane by plane.

reconstructed images of the thermal x-ray emission from a glass microsphere target, irradiated from two opposite directions by a low-power neodymium-glass laser pulse. Because of the low power on target, no compression was achieved. The images show the x-ray emission from the outer glass shell of the target as it is heated by the two laser beams. The three images are contour maps representing the x-ray emission from three separate planes within the target.

There are, of course, practical resolution limits to the tomographic capability of ZPCI. In alpha imaging experiments, for example, the small size of the compressed target core (about $25\text{ }\mu\text{m}$) precluded the possibility of three-dimensional images of the thermonuclear burn region. The zone-plate camera used had an aperture with 100 zones and a tomographic resolution of only $70\text{ }\mu\text{m}$. Since tomographic resolution improves with the number of zones, work is under way to produce a zone-plate camera with a 1000-zone aperture, having a tomographic resolution of about $10\text{ }\mu\text{m}$.

Broad Radiation Applicability. Zone-plate coded imaging is an extremely versatile technique for imaging small x-ray sources³ as well as alpha-particle emission. The attractiveness of ZPCI for x-ray imaging is enhanced by its high-energy x-ray capability. In this application, ZPCI complements the high-resolution capability of the grazing-incidence-reflection x-ray microscope that operates below about 6 keV. The ZPCI technique has been used to image fusion target x-ray emissions in the range 12 to 24 keV. (In these experiments, the high-energy limit was determined by x-ray transmission through the solid zones of the gold zone plate used, and the low-energy limit was set by the x-ray filter foils used.)

Information Collection Efficiency. The zone-plate shadow camera has a very high information collection efficiency that allows it to see small, low-intensity sources with a much greater signal-to-noise ratio than conventional imaging techniques. For example, to improve resolution, a conventional pinhole camera must sacrifice radiation collection by reducing pinhole diameter. The zone-plate camera, on the other hand, can maintain

both high resolution and high collection efficiency by merely increasing the number of zones in its zone-plate aperture.

The radiation collection efficiency of the zone-plate shadow camera has made it particularly well suited for imaging thermonuclear burn in current laser fusion experiments. The thermonuclear burn region has been small (typically less than $25\text{ }\mu\text{m}$ in diameter), and the total alpha emission has been limited. In one of the alpha-imaging experiments to be discussed, the imploded target emitted only 300 million alpha particles. The zone-plate camera collected roughly one-half million alphas and yielded a reconstructed image with resolution of about $3\text{ }\mu\text{m}$. A conventional pinhole camera having the same nominal resolution would have collected only two alpha particles—a number insufficient to produce an image of the burning thermonuclear fuel.

ALPHA-IMAGING TARGET EXPERIMENTS

Imaging thermonuclear burn in laser fusion presented us with three primary challenges: the microscopic dimensions of the source required a high resolution capability; the relatively low yield of current target experiments required efficient collection of the alpha-particle emission; and the very high level of background radiation accompanying the alpha emission required extraordinary radiation discrimination in image recording. We have already seen how the zone-plate shadow camera served to obviate the first two of these requirements. The procedures used to achieve the appropriate radiation discrimination in these experiments are outlined below.

There was approximately 100 000 times more energy in background radiation (x rays, electrons, ions) from the target experiments under discussion than in the alpha-particle emission. We successfully recorded the alpha-particle coded image without interference from the intense radiation background by using a very thin (about $6\text{ }\mu\text{m}$) layer of red plastic (cellulose nitrate) instead of photographic film. The thin plastic layer was placed close behind a beryllium filter foil about

8 μm thick that served to stop all heavy ions from reaching the plastic, while letting the alpha particles through. The cellulose nitrate acted as a highly discriminating alpha-particle recording film. Each alpha incident on the plastic produced a microscopic damage channel, which upon subsequent etching produced a pinhole all the way through the 6- μm layer. None of the other radiation reaching the cellulose nitrate produced pinholes through the film. The final coded image appeared as an array of pinholes—each produced by an alpha-particle track—through the red cellulose nitrate layer. This pinhole pattern was then contact-printed, using green light for maximum contrast, onto a photographic glass plate and optically reconstructed as detailed earlier.

The reconstructed images of the alpha-particle emission from two different target experiments are presented in Fig. 4. Shown are isoemission contour maps of the burn region. Each contour line represents a locus of constant alpha-emission density, time-integrated over the duration of the burn (less than 15 ps). The incremental change in alpha emission is constant between successive contours, with the lowest emission level represented by the outermost contour.

These experiments were conducted using the Argus laser, which produces a dual-beam, multi-terawatt pulse of 1.06- μm light. The laser output was focused onto the target from two opposing, parallel directions by a pair of $f/1$ aspheric lenses. Typical pulse lengths for these experiments were

Table 1. Burning fuel dimensions.

	Shot A	Shot B
Outer dimension, μm	27 $\times$ 26	26 $\times$ 22
FWHM dimension, μm	16 $\times$ 16	18 $\times$ 15
Alpha yield	300 $\times 10^6$	800 $\times 10^6$

25 to 60 ps (full width, half maximum), with 50 to 80 J per beam. Microsphere target diameters ranged from 80 to 100 μm , and the target implosions produced alpha-particle yields ranging from 300 to 800 million.

The images of Fig. 4 show that the burning fuel was compressed into an egg-shaped core at the center of the spherical target. The eccentricity of the oval core was found to increase (core became less spherical) as the laser power on target increased. The dimensions of the burning fuel region are given in Table 1. Nominal image resolution is 10 μm . (Using more advanced procedures, we have recently achieved higher resolution images; see Fig. 5.) From these measurements, we can infer a fuel-volume compression factor of 1.50 and an estimated compressed-core fuel density of 3×10^{22} ions/cm³. Fuel temperature was measured independently at about 7.3 keV.

The alpha-particle images confirm for the first time that the thermonuclear reactions in laser implosion experiments do indeed occur within a compressed core of the target. They provide direct information about thermonuclear burn geometry

Fig. 4. Reconstructed images of the thermonuclear burn region for two representative laser target shots. The images shown are isoemission contour maps of the burn region. The alpha yields for shots A and B were 300 and 800 million, respectively. Nominal planar image resolution is 10 μm . These results show that the thermonuclear burn occurred within a compressed target core about 25 μm in diameter.

that can be compared with complex computer-code calculations. Thus, they provide an important test of the basic physics described in the codes.

RECENT IMPROVEMENTS IN IMAGING CAPABILITIES

We are continuing to improve and extend the imaging capability of the ZPCI technique. Since our primary concern is the microscopy of laser fusion plasmas, our efforts are directed toward improving the planar (two-dimensional) and tomographic (three-dimensional) resolution of the technique and

toward extending its spectral range to higher x-ray energies. The zone-plate coded imaging capability can be improved by increasing the quality of information collection during shadowgraph recording (step 1) and by improving the quality of information extraction during image reconstruction (step 2). We have made significant progress in both areas.

The imaging characteristics of the zone-plate shadow camera are strongly dependent on the dimensions of its zone-plate aperture. The planar resolution of the camera improves as the minimum zone width of the aperture is reduced.⁴

Fig. 5. Image of the thermonuclear burn in a laser fusion target, reconstructed in first and third order. A zone-plate coded image acts as a generalized diffraction grating, focusing incident laser light into multiple, well-separated, reconstructed images—each image a complete, three-dimensional representation of the source. Each separate reconstructed image is designated by an order number, M . Higher order (shorter reconstruction distance) images are reduced in intensity by $1/M^2$ —therefore, reduced signal-to-noise ratio—but their resolution is improved M -fold. A third-order image, having a threefold resolution improvement, allows us to see spatial detail not apparent in a first-order image.

Tomographic resolution improves as zone number increases. The high-energy x-ray capability increases as the x-ray opacity of the solid zones of the zone-plate aperture is increased, that is, thick zone plates of high atomic-number material are required. We are extending the technology of micro-Fresnel zone-plate fabrication to meet these needs. We are currently fabricating zone plates with minimum zone widths of $2.5\text{ }\mu\text{m}$, thicknesses of $10\text{ }\mu\text{m}$ (gold), and 240 zones. We expect soon to be fabricating zone plates having 1000 zones with widths of $1\text{ }\mu\text{m}$ and thicknesses of $20\text{ }\mu\text{m}$.

Significant improvement in image resolution may also be achieved by higher order reconstruction of coded images. A coded image, acting very much like a generalized diffraction grating, will focus the incident laser light into multiple, well-separated reconstructed images (see Fig. 5). Higher order reconstructed images have a reduced intensity (therefore, reduced signal-to-noise ratio) but a higher resolution. The M th order image will have a better resolution by a factor of M (both transverse and tomographic). The M fold improvement in resolution derives from the fact that for the M th order the effective f /number of the coded image is reduced by a factor of M , while image magnification is independent of reconstruction order. This is illustrated in Fig. 5, which shows an image of the

thermonuclear burn in a laser fusion target reconstructed in first and third order. The third-order image, having a threefold resolution improvement, allows us to see spatial detail not apparent in the first-order image.

The improvement in zone-plate fabrication technology along with the use of higher order image reconstruction techniques has extended the ZPCI capability to about $1\text{-}\mu\text{m}$ planar resolution, $10\text{-}\mu\text{m}$ tomographic resolution, and 40-keV x-ray energy.

Key Words: alpha emission; alpha measurements; plasma—diagnostics; radiation—measurements, x-ray emission; x-ray images; zone-plate coded imaging; ZPCI.

NOTES AND REFERENCES

1. N. M. Ceglio and L. W. Coleman, "Spatially Resolved Emission from Laser Fusion Targets," *Phys. Rev. Lett.* **39**, 20 (1977).
2. N. M. Ceglio and H. I. Smith, "Micro-Fresnel Zone Plates for Coded Imaging Applications," *Rev. Sci. Instr.* **49** (January 1978).
3. N. M. Ceglio, D. T. Attwood, and E. V. George, "Zone Plate Coded Imaging of Laser Produced Plasmas," *J. Appl. Phys.* **48**, 1566 (1977).
4. N. M. Ceglio, "Zone Plate Coded Imaging on a Microscopic Scale," *J. Appl. Phys.* **48**, 1563 (1977).

Laser-Induced Molecular Fluorescence for Chemical Analysis

Optical fluorescence, long a tool for chemical analysis, is not sensitive and selective enough to satisfy new and complex requirements in such varied areas as flow cytometry, uranium trace detection, and rainout studies. We are developing laser fluorescence analysis to fill this analytical gap. We have consistently improved the limits of detection for numerous compounds by tenfold to a thousandfold. We have found numerous research and programmatic applications for this newly developed analytical capability.

The ability to monitor or analyze samples non-destructively *in situ* and to acquire and process the data in real time is becoming increasingly important. The need for this ability, together with the increasing demand for sensitivity and selectivity in chemical analysis, has spawned a profusion of new analytical techniques.

Many of these techniques are optical. Light of an appropriate wavelength irradiates the sample, and a quantitative analysis results from measuring a change in the intensity, frequency, or polarization of the light detected. Optical analytical techniques are being used widely because of their high inherent sensitivity and relatively simple instrumentation.

Fluorescence of wavelengths between 200 and 1000 nm is intrinsically the most sensitive and selective of these optical techniques for chemical analysis. Photomultiplier tubes can detect a single photon in this wavelength range and hence can approach the ultimate in sensitivity. Furthermore, in this range the potential ability to excite the molecule

into higher electronic states, coupled with the Stokes shift between excitation into and emission from the lowest electronically excited state, makes spectral discrimination against the excitation light relatively straightforward. Fluorescence analysis therefore has the enormous advantage of detecting a small change against nearly zero background.

The recent development of lasers has multiplied the utility of optical analytical techniques and revolutionized optical instrumentation. Lasers have a much higher spectral intensity (energy per unit frequency), narrower bandwidth, and greater ease of polarization than conventional light sources. Both continuous wave and pulsed lasers are highly collimated, coherent light sources, which permit spatial discrimination in optical analysis. Furthermore, both types of lasers can provide the additional dimension of temporal resolution.

One reason for the great selectivity of laser-induced molecular fluorescence (LIMF) is that the fluorescence spectrum is characterized by three distinct parameters: excitation wavelength, emission or fluorescence wavelength, and fluorescence lifetime. The system can discriminate against background on the basis of any or all of these characteristics. Also, fluorescence lifetimes are much more sensitive to the local molecular environment than are emission and excitation spectra. Thus, temporal discrimination can be used to distinguish fluorescence from scattering, one compound from another, and even one local environment from another for the same compound.

Laser-induced fluorescence analysis is a recent development. Other researchers demonstrated only about two years ago the large increase in sensitivity for gas-phase fluorescence obtainable by using

Contact Jeffery H. Richardson (422-6351) for further information on this article.

lasers as excitation sources. We decided to apply similar methods and to concentrate on studying condensed phases, since most samples requiring analysis are either solids or solutions.

LASERS FOR FLUORESCENCE

The many capabilities offered by laser technology inevitably raise the question: Which laser is most appropriate for a particular application? Linewidth, for example, is a minor consideration for trace detection of compounds in solution, but tunability is a major consideration. Less obvious are the relative merits of excitation-pulse width. A short pulse is desirable for temporal discrimination against background fluorescence, but the significance of temporal resolution will depend on the relative decay times of the laser excitation source, the background fluorescence, and the signal fluorescence. Repetition rate and peak power, on the other hand, are factors that can be treated simultaneously—a relevant parameter is their product. High peak powers entail low repetition rates, and low peak powers entail high repetition rates.

As an example of this latter tradeoff, we compared experimentally the detection limits for rhodamine B with two systems: a nitrogen-pumped dye laser and a cavity-dumped argon-ion laser, both operated with 10-ns pulses.¹ The nitrogen-pumped

dye laser is tunable from 360 to 750 nm and can be effectively frequency-doubled to 258 nm. Although its maximum repetition rate is only 50 Hz, its pulses have a maximum peak power of about 100 kW. The cavity-dumped argon-ion laser (nontunable) has a repetition rate of 1 MHz, but its pulses have a peak power of only 10 W.

We used identical signal-processing equipment to compare the two laser sources, although the comparison was somewhat biased in favor of the argon laser by the choice of rhodamine B for the target molecule. Many other fluorophors can be excited by the tunable light from the nitrogen-pumped dye laser but do not fluoresce in argon-laser light. The detection limits with rhodamine B for the nitrogen and the argon lasers were 1.0 and 0.5 $\mu\text{g}/\text{m}^3$, respectively—more than a hundred times smaller than the best results in previous studies.

Although nearly identical detection limits were achieved with the two lasers, we concluded that the nitrogen-pumped dye laser currently represents the best source for molecular fluorescence analyses. Its slightly less favorable detection limit in this case is more than compensated for by several distinct advantages: its tunability, which extends into the ultraviolet, its large signals, which permit the use of a monochromator for greater spectral discrimination, and its higher peak powers, which make feasible such nonlinear processes as two-photon absorption,

Fig. 1. A schematic drawing of the experimental apparatus used for observing laser-induced molecular fluorescence. A nitrogen laser (10-ns pulses, 1 MW) is used to transversely pump a dye laser (10-ns pulses, 100 kW). The tunable radiation from the dye laser is directed into the sample chamber, where a small portion is absorbed by the species of interest. The resulting fluorescence is viewed at right angles, spectrally defined, and then converted to electrical pulses by a photomultiplier detector tube. A box-car integrator (single-channel analyzer) processes the electrical pulses for recording or display.

Table 1. Limits of detection of biochemicals in water using laser-induced molecular fluorescence (LIMF).

Compound	Excitation wavelength, nm	Fluorescence wavelength, nm	Limits of detection, $\mu\text{g}/\text{m}^3$	
			Best previously reported value	LIMF
Vitamin A acetate	337.1	500	100 000	1000
Vitamin B ₂ (riboflavin)	375.0	540	38	0.5
Flavin adenine dinucleotide	267.0	525	—	39
Vitamin B ₆ (pyridoxine)	337.1	410	1 500	50
Tryptophan	270.0	358	3 000	50
Arginine/Fluorim	390.0	500	5 000	10

coherent anti-Stokes Raman scattering, and Raman-induced Kerr-effect scattering.

Figure 1 schematically represents the experimental apparatus we assembled. Analog detection—such as that which measures the fluorescent light emitted in a short period following a laser pulse irradiation—was found to be more desirable than photon counting (digital) techniques. Besides being more than ten times more sensitive under similar experimental conditions, analog signal processing permits a more rapid sample turnaround time.

MOLECULAR FLUORESCENCE

We have examined a number of biologically and environmentally important molecules that represent several significant chemical classes of compounds and span a wide range of fluorescence properties. In addition to their intrinsic interest and significance to applied and basic research problems, these molecules provided a test for our efforts to improve analytical sensitivity and selectivity through laser-induced molecular fluorescence.

Riboflavin (vitamin B₂) was one of the first molecules chosen for study because of its nearly ideal fluorescence properties² and because, as an essential vitamin, it is the subject of much research that could benefit from a detection system that is more sensitive by several orders of magnitude.

Riboflavin is converted *in vivo* to one of two coenzymes: flavin mononucleotide (FMN) or flavin adenine dinucleotide (FAD). The absorption and

emission spectra of FAD and FMN are identical to those of riboflavin in visible and near-ultraviolet light, but the adenine in FAD serves as an acceptor for efficient internal energy transfer, resulting in nonradiative decay. This makes the quantum yield for fluorescence of FAD almost ten times less than that of riboflavin, and correspondingly increases the observed limit of detection. Any local decrease in the pH will make the molecule uncoil, moving the adenine farther from the riboflavin chromophore and hence increasing the fluorescence quantum yield.

The limit of detection we achieved with riboflavin was $0.5 \mu\text{g}/\text{m}^3$, nearly a hundred times better than any previous method. Much of the improvement could be traced to our use of a monochromator for wavelength discrimination, a use made possible by the high intensity of the light pulses from our nitrogen-pumped dye laser. Table 1 summarizes the detection limits we achieved for vitamins and other biochemicals in water and contrasts them with the best values reported in the literature.³

Table 1 also includes the results for tryptophan, by far the most fluorescent of the amino acids, and for arginine, which is totally nonfluorescent. We can study such nonfluorescent compounds by covalently attaching another compound that, ideally, becomes fluorescent in the combination. Such fluorescent labels are of wide use in chemical analysis.

In the case of arginine, a popular and widely used fluorescent labeling procedure, the ninhydrin reac-

tion, permitted detection at a level of $300\,000\ \mu\text{g m}^{-3}$. A more efficient tag, Fluram, extended the limits of detection using conventional excitation sources to $5000\ \mu\text{g m}^{-3}$. Laser-induced molecular fluorescence further extended this detection limit to $10\ \mu\text{g m}^{-3}$.

We also investigated some of the polycyclic aromatic hydrocarbons (PAH), an increasingly significant class of organic compounds containing many potent carcinogens. These hydrocarbons, from fossil fuels and combustion, underlie much of modern organic chemistry and are an intrinsically interesting class of compounds.

Table 2 presents the limits of detection for PAH achieved using laser-induced molecular fluorescence.⁴ The results for benzene and aniline illustrate the advantages of using a fluorescent label when studying a compound of low intrinsic fluorescence. Without the Fluram label, aniline

would have about the same fluorescence and limits of detection as benzene, but Fluram improves the limit of detection by more than a factor of 5000.

Two of the compounds studied (pyrene and fluoranthene) had radiative lifetimes significantly longer than the laser pulse. This property permitted temporal resolution to further lower the limit of detection. Figure 2 illustrates how delaying the window for observing the fluorescence until after the scatter and impurity fluorescence has decayed away lowers the background and improves the signal-to-noise ratio.

To extend our capabilities in temporal resolution, we are currently developing a synchronously pumped dye laser as an excitation source. This tunable laser has ultrashort pulses (about 20 ps), a high repetition rate (in the megahertz range), and intermediate peak power (hundreds of watts). We are also developing the instrumentation necessary

Table 2. Limits of detection of polycyclic aromatic hydrocarbons in water.

Compound	Excitation wavelength, nm	Fluorescence wavelength, nm	Limits of detection, $\mu\text{g m}^{-3}$	
			Best previously reported value	LIMF
Benzene	259.95	273	—	19 000
Aniline/Fluram	390.0	500	>40 000	3.5
Naphthalene	273.0	340	30	1.3
Anthracene	254.0	404	30	4.4
Fluoranthene	287.0	450	170	1
Pyrene	273.0	395	150	0.5

Table 3. Fluorescence data for the study of benzo[a]pyrene (BaP) and its carcinogenic metabolite, diol-epoxide BaP.

Compound	Excitation wavelength, nm	Fluorescence wavelength, nm	Solvent	Lifetime, ns	
				In air	In argon
Pyrene	273	395	Hexane	16	483
			H ₂ O	160	190
			p-dioxane	61	278
BaP	295	405	Hexane	17	73
			H ₂ O	32	30
			p-dioxane	34	50
Diol-epoxide BaP	316	400	p-dioxane	50	98

Fig. 2. Time-resolved laser-fluorescence signal of a polycyclic aromatic hydrocarbon (PAH), fluoranthene. The narrow blue peak represents the laser pulse, observed as the Rayleigh scattered light at the excitation wavelength of 287 nm. The broad red peak represents the fluorescent emission of fluoranthene at 450 nm. The shift in wavelength and the longer lifetime of the fluorescent signal make it easy for the detection system to discriminate against the background of excitation radiation. In the instrumental configuration illustrated in Fig. 1, for example, one can set a temporal window for detection of a delay of 1 ns to 50 ns and a width of 30 ps to 50 μ s, corresponding to that period when there is little noise from the incident pulse but when the fluorescence has not yet decayed.

for detection, data acquisition, and data reduction of subnanosecond pulses at megahertz repetition rates.⁵

Laser-induced molecular fluorescence extended the limits of detection by more than a hundredfold for many of these important PAH compounds. The analytical working curves obtained were linear over a range of one to a million. These advances in detection sensitivity have made it feasible, for example, to consider monitoring for PAH in local water supplies.

APPLICATIONS

Among the various problems to which we have applied our improved analytical capabilities is an investigation into the action of benzo[a]pyrene (BaP) on DNA. BaP is metabolized by a cellular enzyme, aryl hydrocarbon hydroxylase (AHH) to a diol-epoxide of BaP. This diol-epoxide BaP binds to and sometimes cleaves molecules of DNA.

One of our goals is to use fluorescence to monitor the binding of diol-epoxide BaP to DNA *in vivo*. Cells would be initially treated with BaP; the diol-epoxide BaP would be synthesized *in vivo* outside the cell nucleus and would then finally bind to DNA in the nucleus. Enough differences exist between the fluorescence (and absorption) spectra of the two compounds that we can distinguish between the precursor, BaP, and its carcinogenic metabolite, diol-epoxide BaP.

Table 3 summarizes the data obtained *in vitro*. Working in collaboration with researchers at the University of California's Laboratory of Biodynamics, we examined BaP, diol-epoxide BaP, and pyrene (a compound very similar to diol-epoxide BaP in its spectroscopic properties) in various solvents to investigate any potential changes in fluorescence properties between the aqueous cytoplasm and the more hydrophobic cell nucleus. We found that only the fluorescence lifetime is a sensitive function of the molecular environment.

Figure 3 illustrates the fluorescence signal obtained in preliminary experiments from BaP-labeled and unlabeled cells. The fluorescence of unlabeled cells comes largely from tryptophan residues in cellular proteins and has a lifetime of less than

Fig. 3. Time-resolved laser fluorescence signals of unlabeled cells and cells treated with BaP (and hence with diol-epoxide BaP bound to DNA). Although both kinds of cells fluoresce at about 400 nm, the much longer fluorescence lifetime of the labeled cells makes it possible to detect them unambiguously.

10 ns. The fluorescence from the labeled cells has a lifetime of 130 ns, indicating that the molecular environment in these cells (at least where the diol-epoxide BaP is bound to the DNA) is even more hydrophobic than p-dioxane (see Table 3 for trends).

We have also begun preliminary experimental studies of the photobleaching of AHH and the kinetics of its subsequent recovery. AHH is a component of the cell wall, and its response to polarized laser light depends on its alignment at the instant of irradiation. An analysis of this response indicates how freely the AHH molecule can rotate and hence the relative rigidity or fluidity of the cell membrane. The fluidity of the cell membrane, in turn, is an indication of how well the cell is functioning and may be a valuable diagnostic aid in a variety of diseases.

Furthermore, we are using our new picosecond laser source⁶ to excite dyes that bind to DNA. Ethidium bromide, for example, has a fluorescence lifetime of 22 ns when bound to DNA and less than 1 ns when free. We expect lifetime studies of bound dyes to provide an additional marker for flow cytometry⁷ and to be useful for investigating the mechanism of dye binding to and intercalating into DNA.

We have also applied laser-induced fluorescence to such varied projects as trace detection of uranium,⁸ studies of stress and materials aging,⁹ particle-attachment phenomena related to rainout, materials problems related to lasers, and pressure-monitoring in a diamond-anvil high-pressure cell used in equation-of-state studies of actinides.

FUTURE DIRECTIONS

The high sensitivity of laser-induced molecular fluorescence naturally suggests its use for analyzing transients in chemical systems. We are currently collaborating with researchers at Purdue University to examine chemical transients resulting from irradiation of electrodes in aqueous solutions.¹⁰ Electrons ejected from the surface by a laser pulse are scavenged by the solution, and the resulting anionic species is spectroscopically probed by the same or a subsequent laser pulse. These studies directly relate to understanding the mechanism of

photovoltaic processes. Consequently, laser-induced photoelectrochemistry relates to both solar energy conversion and prevention of material damage by radiation.

Our work with subnanosecond laser pulses has also led to the development of a detector with a 30-ps risetime. Such a detector has many potential applications besides measuring subnanosecond fluorescence-decay times.

The inherent sensitivity, chemical selectivity, and spatial sampling characteristics of laser-induced fluorescence make this a valuable addition to the instrumental techniques for chemical analysis, ideally suited as a detector for liquid chromatographic separations. Lasers are even being made sufficiently small and rugged for use in the field. Although no single technique will solve all the problems of chemical analysis, the many advantages of the laser fluorescence technique will undoubtedly place it among the first to be considered in future analytic applications.

Key Words: carcinogens, chemical analysis—instrumentation, fluorescence analysis, lasers—applications, time-resolved spectroscopy, vitamins

NOTES AND REFERENCES

1. J. H. Richardson and S. M. George, *A Comparison of Different Experimental Configurations in Pulsed Laser-Induced Molecular Fluorescence*, Lawrence Livermore Laboratory, Rept. UCRL-80251 (1977); also *Anal. Chem.* **50** (1978) (in press).
2. J. H. Richardson, B. W. Wallin, D. C. Johnson, and L. W. Hrubesh, "Sub-part-per-trillion Detection of Riboflavin by Laser-Induced Fluorescence," *Anal. Chim. Acta* **86**, 263 (1976).
3. J. H. Richardson, "Sensitive Assay of Biochemicals by Laser-Induced Molecular Fluorescence," *Anal. Biochem.* **83**, 754 (1977).
4. J. H. Richardson and M. E. Ando, "Sub-part-per-trillion Detection of Polycyclic Aromatic Hydrocarbons by Laser-Induced Molecular Fluorescence," *Anal. Chem.* **49**, 955 (1977).
5. G. R. Haugen, L. L. Steinmetz, J. D. Breshears, B. W. Wallin, and F. E. Lytle, Lawrence Livermore Laboratory, personal communication, 1977.
6. L. L. Steinmetz, J. H. Richardson, and B. W. Wallin,

Applications of the Mode-Locked Near-UV Output from a Krypton-Ion Laser in Chemical Analysis, Lawrence Livermore Laboratory, Rept UCRL-80736 (1978)

- 7 Flow cytometry is described in the July 1977 *Energy and Technology Review* (UCRL-52000-77-7), p. 20
- 8 I. B. Stephens, G. R. Haugen, and J. H. Richardson, *Trace Uranium—Its Measurement via Time-Resolved Fluorescence*, Lawrence Livermore Laboratory, Rept UCRL-17549 (1977)
- 9 J. H. Richardson, G. R. Haugen, I. S. Penn, J. H. Leiken, and R. J. Sherry, *The Effect of Stress on the Fluorescence of Aqueous Urea*, Lawrence Livermore Laboratory, Rept UCRL-17333 (1976)
- 10 J. H. Richardson, S. M. George, J. I. Harrat, and S. P. Petrone, *Laser-Induced Photochemistry: Dependence of Photoemission-Related Currents on Laser Characteristics*, Lawrence Livermore Laboratory, Rept UCRL-80402 (1977), also *J. Phys. Chem.* **82** (1978) (in press)

The Ozone Layer: Assessing Man-Made Perturbations

Since 1972, LLL has been using numerical models to assess the potential chemical impacts on the ozone layer of engine effluents from high-altitude supersonic and subsonic aircraft and their subsequent climatic results. Since 1974, we have been assessing how nitrogen oxides from atmospheric nuclear explosions affect this layer. In addition, we are studying the potential environmental effects of chlorofluoromethanes, which are used as aerosol spray propellants, refrigerants, and foaming agents. The rapid evolution of our understanding of atmospheric chemistry and other physical processes has led to major changes in these environmental assessments.

Ozone is produced in the stratosphere through a series of photochemical reactions known as the Chapman cycle. Molecular oxygen is photolyzed by light at wavelengths less than 242 nm to yield oxygen atoms, which then combine rapidly with molecular oxygen to form ozone.

About one-fifth of the photochemical removal of ozone occurs by reaction with atomic oxygen to regenerate molecular oxygen and by photolysis of ozone at high altitude. In the middle and lower stratosphere, ozone removal occurs mainly by catalytic cycles in which a species (X) abstracts an oxygen atom from ozone and is then regenerated in a reaction with atomic oxygen:

Contact Frederick M. Luther (422-1825) for further information on this article.

Such cycles have been recognized for X = H, HO, NO, Cl, and Br.

Current research in stratospheric modeling deals with the complex chemical interactions involving these catalytic cycles and the impact of various man-made perturbations on their natural balances. For example, engine effluents from high-altitude aircraft are a source of additional nitrogen oxides (NO_x) and hydrogen oxides (HO_x). Atmospheric nuclear explosions produce NO in the fireball; for high-yield weapons, this NO is then injected into the stratosphere. Chlorofluoromethanes (CFMs), which are released at the ground, are slowly transported upward into the middle stratosphere where they are photolyzed, releasing chlorine. Rocket exhaust from the space shuttle will release chlorine directly into the stratosphere.

The nature and importance of the stratospheric ozone layer are discussed in the box on p. 22.

STRATOSPHERIC MODELING

The modeling effort at LLL covers five major areas of research: photochemical kinetics, coupled kinetics and transport, radiative transfer, climate modeling, and meteorological analysis. The modeling of photochemical kinetics must span gas-phase and gas-particle reaction processes, constant and varying photochemical reaction rates, a wide range of ambient temperatures and pressures, neutral and ionized species, and processes with both accurately and poorly known reaction rates.

We use numerical models that couple chemical kinetics and transport to study the structure of the atmosphere and to assess the potential stratospheric response to injections of trace species. The models currently available to us for the stratosphere are

either one-dimensional (vertical) or two-dimensional (vertical and latitude).

One-dimensional models include as complete a set of the important chemical reactions as is feasible, along with detailed photochemistry. However, they use a highly parameterized (that is, approximate) representation of vertical transport. Some models are capable of diurnal calculations, but most include some form of averaging over the day-night cycle. Our models are designed for time-dependent perturbation and sensitivity studies.

Two-dimensional models provide for variation of the transport, radiation fields, and species concentrations with latitude, altitude, and season. They also follow hemispheric differences in both atmospheric composition and response to perturbations.

In radiative transfer research, we apply detailed models to assess how changes in stratospheric composition affect both the ultraviolet radiation received at the ground and the fluxes of solar and longwave (infrared) radiation in the atmosphere. The latter effect is important because of the coupling between temperature and atmospheric composition. Changes in the concentration of radiatively active species affect atmospheric temperature; temperature changes affect chemical reaction rates; and changes in reaction rates affect species concentrations, including that of ozone.

To assess the effects of changes in atmospheric composition on the global climate, we use a two-dimensional (vertical and latitude) climate model. This model is unique in the large number of physical processes and feedback mechanisms included. Among the former are solar and longwave radiation, cloud cover, convective precipitation, proportional surface type, surface energy and hydrologic balances, and annual variability in land ice, snow, and sea ice.

Meteorological analysis provides guidance and support during modeling, enabling us to make in-depth studies of atmospheric processes and phenomena. A primary responsibility in this research is to develop test situations for validating various aspects of the numerical models.

HIGH-ALTITUDE AIRCRAFT EMISSIONS

Early concern about aircraft emissions focused on the effects of supersonic transport fleets (SSTs), expected to fly in the stratosphere. Although subsonic aircraft emit the same effluents, they fly mostly in the troposphere where these effluents are transported and removed more rapidly. As our air corridors become more crowded, however, and new subsonic aircraft are designed to fly at higher altitudes, they too will have to be considered in future assessments.

The engine emissions of concern are nitrogen oxides, water vapor, and SO_2 . Nitrogen oxides (NO and NO_2) and water vapor are the only species of chemical significance related to ozone. SO_2 contributes to the formation of sulfuric acid aerosols in the stratosphere which affect the solar and longwave radiative fluxes, but its climatic effect is small.¹ A fleet of 100 British/French Concorde would inject approximately 6×10^7 kg NO_x/yr and 4×10^9 kg $\text{H}_2\text{O}/\text{yr}$ at cruise altitude (about 17 km), assuming each flies an average of 4.4 hr/day at this altitude.

We have conducted studies of stratospheric pollution under funding from the Department of Transportation. The one-dimensional transport-kinetics model we use for stratospheric assessments includes 28 chemical species and 83 chemical and photochemical reactions. Species concentrations are computed at 44 levels extending from the ground to an altitude of 55 km. The model accounts for multiple scattering in computing photodissociation rates and can include temperature coupling between changes in composition and reaction-rate coefficients. Vertical transport is parameterized with a one-dimensional diffusion formulation, which describes hemispheric (or global) average net vertical transport by an altitude-dependent diffusion coefficient. The profile for this coefficient is empirically determined by a fit to actual concentration data of tracerlike species.

Ozone chemistry is more complex than implied by the simple catalytic cycles described above. Instead of being independent, these cycles are coupled such that changes in one may enhance or retard ozone destruction by another. We have shown that

the relative importance of the various cycles (and thus model sensitivity to stratospheric perturbations) depends upon certain key chemical rate coefficients, several of which have large uncertainties.²

In 1974 several numerical modeling groups, including LLL, funded under the Climatic Impact Assessment Program (CIAP) of the Department of Transportation, assessed the potential impact on total ozone of a large fleet of SSTs. The results of these studies—and of more recent LLL calculations—are shown in Fig. 1. For the sake of comparison, an injection rate of 1.23×10^9 kg NO_x/yr into a hemisphere was assumed, that is, approximately equivalent to 2000 Concorde. Our 1974 results are typical of those from the various one-dimensional models available at that time. The final CIAP curve was based on an average of our results and those from a model used by the National Academy of Sciences.

Since 1974 there have been many changes to these

numerical models.³ New species (mostly containing chlorine) and reactions have been added. Poorly known reaction rates have been remeasured more accurately, and the photodissociation rate calculation has been improved. Temperature coupling and feedback on reaction rates have been added. Diurnal averaging has been accounted for more precisely. Most of these changes have led to a reduction in the computed effect of NO_x on ozone (see Fig. 1).

Most of the difference between our 1976 and 1977 results is due to a change in one key reaction rate, that of $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$, that has been measured to be many times faster than previously thought. The calculations now show a slight increase in ozone from NO_x emissions from aircraft in the lower stratosphere. Other models not at LLL also show an ozone increase for a 17-km injection altitude; for a 20-km injection altitude, however, results range from a slight ozone decrease to a slight increase. The models predict an ozone decrease for injection altitudes above 20 km. Until stratospheric chemistry is better understood and reaction rates are known more accurately, there will continue to be uncertainties associated with these results. A large uncertainty also stems from the variety of vertical transport parameterizations currently in use.

Figure 2 shows the change in local ozone concentration for NO_x injections at 20 km. The net effect of a NO_x injection on total ozone depends on the relative magnitudes of the increase in ozone concentration below 23 km and the decrease above 23 km. The increase occurs because the additional NO_x interferes with the HO_x catalytic cycle, which is the principal destruction process in this region. Although the change in total ozone is small, there are significant increases or decreases in the local ozone concentration, which relates to the stratosphere's temperature structure and stability. How these changes might affect vertical transport is yet to be assessed.

Increased concentrations of ozone and NO_2 near the level of the tropopause (around 15 km in altitude) would tend to increase the local heating due to absorption of solar and longwave radiation. It has been hypothesized that if there is an increase

Fig. 1. Ozone column change results computed by various models. The assumed injection rate is 1.23×10^9 kg NO_x (as NO_2) per year into a hemisphere. This is an arbitrary rate selected simply as a standard for purposes of comparing different models; it is not related to a particular number of aircraft. Data points represent our calculations for injections at 17 and 20 km, cruise altitudes for today's and future advanced SSTs, respectively. The curves are based on one-dimensional model results. As our 1976 and 1977 data points indicate, changes in these models have led to lower predictions of the effect of NO_x injections on ozone. Our latest results actually show a slight increase in ozone.

Fig. 2. Change in local ozone concentration at steady state from various NO_x injections at 20 km. The net effect of an NO_x injection on total ozone depends on the relative magnitudes of the increase in ozone concentration below 23 km and the decrease above 23 km. These localized ozone concentration changes influence how temperature varies with altitude and can thus modify the stratosphere's stability. An injection rate of $6.2 \times 10^8 \text{ kg NO}_x/\text{yr}$ represents SST fleets of about 1000 aircraft.

in the temperature of the tropical tropopause, then more water vapor would be transported upward, resulting in an increase in the stratospheric water vapor concentration.

We have estimated the change in ozone concentration from this increase in water vapor concentration with calculations that consider both chemical and heat-balance effects. The chemical effect is a decrease in total ozone, but temperature feedback compensates for the chemical effect of increased water vapor, resulting in very little net change (less than 1%) in total ozone.

CHLOROFUOROMETHANES AND THE SPACE SHUTTLE

The two chlorofluoromethanes most widely used and eliciting the greatest concern are CFCl_3 (F-11) and CF_2Cl_2 (F-12). CFMs were originally developed as refrigerants, but their major current use is as aerosol propellants. From 1965 to 1974, F-11 production grew 9%/yr in the United States and 20%/yr abroad. The corresponding growth rates for F-12 production are 7%/yr in the United States and 13%/yr abroad. Production rates have been nearly

Fig. 3. Reduction in total ozone from a constant production of chlorofluoromethanes at the 1973 rate and at one-half of that rate. The long-term effect of CFMs on ozone depends upon the production rate chosen; the 1973 rate is customarily assumed for assessment purposes. The shaded region for both rate curves represents the effect of using different diffusion coefficient profiles in the calculations. For the 1973 production rate, ozone reduction at steady state is about 15%.

Fig. 4. Change in local ozone concentration from a constant production of CFMs at the 1973 rate. In these calculations, we assumed either fixed temperature or a self-consistent temperature feedback. The results here contrast markedly with those shown in Fig. 2 for NO_x injections. In particular, CFM injections produce little or no increase in local ozone concentration in the lower stratosphere.

constant since the potential effect of CFMs on ozone was pointed out in 1974. A complete ban on the use of CFMs as aerosol propellants in the United States alone would only reduce world production by about 25%.

About 90% of the total production of F-11 and F-12 is released to the atmosphere. Once they are released, relatively rapid tropospheric mixing occurs. Because they have no significant tropospheric loss mechanisms, CFMs gradually accumulate in the troposphere and rise slowly into the stratosphere, where the sun's ultraviolet radiation decomposes them at altitudes above 25 km. The chlorine atoms and chlorine oxide produced directly or indirectly by this decomposition then catalytically react to remove ozone.

Figure 3 shows our calculations of the decrease in total ozone for two CFM production rates. Ozone is depleted gradually over many decades, taking 40 to 50 years to reach half of the total reduction that would eventually occur at steady state. The shaded area shows the range of our projections as a function of time depending on the choice of a diffusion coefficient profile. The model currently predicts about a 15% ozone reduction at steady state from

the 1973 CFM production rate.

If CFM production were stopped completely, ozone would continue to be depleted for 7 to 14 years, after which there would be a very slow recovery. This delay in reaching a maximum ozone reduction occurs because the troposphere acts as a reservoir of F-11 and F-12, which are only slowly transported upward into the stratosphere.

The vertical distributions of the ozone change resulting from CFM and NO_x perturbations vary greatly. The change in local ozone concentration from CFM injections is shown in Fig. 4. The largest ozone reduction occurs near 40 km; only relatively small changes in ozone concentration occur below 30 km. In the case of the NO_x injection due to engine effluents (Fig. 2), the local ozone concentration decreases above about 23 km but increases below this altitude.

Through cooperation with NASA, we have also studied the potential impact of the space shuttle on stratospheric chemistry. One of the major components of space-shuttle engine exhaust is HCl. Assuming 60 space shuttle flights per year, we have calculated a 0.27% ozone reduction due to the additional stratospheric chlorine. Other shuttle engine

exhaust by-products, such as NO and water, have also been studied and found to be insignificant.

ATMOSPHERIC NUCLEAR DETONATIONS

Atmospheric nuclear detonations inject NO_x into

the stratosphere. The major NO production mechanism is the high-temperature chemical equilibrium among molecular and atomic oxygen, nitrogen, and NO_x. In the fireball, N₂ is dissociated and oxidized to form NO. The relatively fast cooling of the hot cloud leads to thermal quenching of

STRATOSPHERIC OZONE: HOW IT AFFECTS US

The atmosphere is usually represented as being divided into layers whose boundaries correspond to temperature minima or maxima. The lowest layer is the troposphere, which extends from the ground to an altitude of about 16 km near the equator and 8 km near the poles. Here mean temperature decreases with height. Its upper boundary, the tropopause, is defined by the altitude at which temperature holds constant or begins to increase with height. The tropopause is an artificial boundary separating the troposphere and stratosphere. In the stratosphere, temperature increases to a maximum near 50 km, a level known as the stratopause. Because of this structure, the stratosphere is stable with respect to convective overturning, and this leads to very limited vertical motions. A tracer will remain in the stratosphere from one to several years; in the much less stable troposphere, it would mix rapidly and be subject to several removal mechanisms.

Almost all ozone is in the stratosphere. Although it is customary to speak of an ozone layer, the concentration of ozone in fact never exceeds a few parts per million. The total amount of ozone in a vertical column corresponds to only about 3 mm of pure ozone at standard temperature and pressure. Vertical profiles of ozone concentration typically show a maximum concentration near 23 km in middle latitudes.

Ozone is an effective absorber of ultraviolet radiation, essentially preventing radiation at wavelengths shorter than 290 nm from reaching the ground. It also absorbs some solar radiation in the visible region and longwave (infrared) radiation. Solar absorption by ozone is the primary warming mechanism for the stratosphere. Changes in ozone abundance are important because they affect the transport of solar and longwave radiation, which has climatic consequences, and because they affect the amount of ultraviolet radiation reaching the ground, which has biological consequences.

Perhaps the most widely discussed effect of increased ultraviolet radiation is the projected increase of skin cancer among humans. In the United States there are about 300 000 new skin cancer cases each year, of which about 2500 are fatal. The incidence rate increases toward the south: in middle latitudes (30 to 45° N), it doubles for each 10° decrease in latitude. Most of the contribution to skin cancer is believed to come from radiation in the 280- to 320-nm wavelength region. Because of the strong attenuation of solar radiation by ozone in this wavelength region, a small ozone reduction causes a much larger increase in the ultraviolet flux. For example, a 10% ozone reduction at middle latitudes leads to about a 20% increase in ultraviolet flux. In terms of the increased risk of skin cancer, this is equivalent to moving about 400 km south. Such a reduction would lead to some 60 000 new cases of skin cancer per year in the United States.

A reduction and redistribution of ozone might also lead to significant climatic effects. Based on simplified, one-dimensional, climate model calculations, the change in global mean surface temperature from supersonic aircraft and chlorofluoromethanes would be less than ±0.2 K, but there could be much larger changes regionally, especially at high latitudes. Calculations with two- and three-dimensional models suggest that an increase in surface temperature would increase the intensity of the hydrologic cycle, thus increasing global mean precipitation. Uncertainties regarding cloud feedback processes and how climate changes will affect cloudiness, however, make it difficult at this time to quantify such climatic changes.

The accompanying article reports on LLL studies into how engine effluents from high-altitude aircraft, chlorofluoromethanes, and atmospheric nuclear explosions may affect the stratospheric ozone layer.

the equilibrium state. The rates of NO production and destruction become negligibly slow when the cloud cools below 2000 K, which occurs about a minute after detonation.

The NO produced is injected into the atmosphere at the cloud stabilization height, which depends on the amount of thermal heating and the amount of ambient air that is mixed with the fireball as it rises through the atmosphere. The stabilization height also depends on the atmospheric temperature structure, which varies with latitude. Variations in the height of burst within 0 to 3 km of the earth's surface do not significantly affect the cloud stabilization height. The device yield must be greater than 4.2 PJ (1 Mt) for the cloud to penetrate into the stratosphere.

Estimates of the total amount of NO produced per 4.2-PJ yield in a nuclear explosion vary, but we use the value of 6.7×10^{31} molecules/4.2 PJ.⁴ For ozone perturbations up to several percent, the response of our model varies approximately linearly with the total NO injection; thus, if NO production per 4.2 PJ should be readjusted in the future, our computed ozone perturbations would scale linearly.

There have been several analyses of global ozone measurements during the atmospheric nuclear test series of the 1950's and early 1960's. These have concluded that any ozone reductions caused by the nuclear tests must have been less than about 3%, which is the claimed noise level of the data. A gradual ozone reduction of 3 to 4% might not be inconsistent with the ozone record.

Under funding from the Division of Military Applications, we have computed the effect of the nuclear test series on total ozone in the Northern Hemisphere.⁵ Figure 5 shows our results with both our current model chemistry (1977) and that of a year ago. The 1977 model is preferred, but both sets of calculations are presented to show the significance of the changes in model chemistry during the past year and to give a feeling for the magnitude of the chemical uncertainties. We also use two parameterization schemes to prescribe the cloud stabilization altitude as a function of yield. Since one scheme overestimates and the other underestimates this altitude, we expect to bracket the

true values by using both.

Our calculation with 1976 chemistry predicted a maximum ozone reduction that was large compared with the 3% reduction estimated to be compatible with observations. With our 1977 chemistry and the low stabilization height estimates, we compute ozone increases from the 1950's tests and ozone reductions throughout the testing period of less than 2%.

The peak ozone reduction follows a number of high-yield detonations in late 1962. Since our one-dimensional model assumes uniform horizontal mixing, this would be a poor representation for the first several months after detonation while the debris is undergoing horizontal mixing and transport. Consequently, the model would tend to overestimate the peak ozone reduction. Our current results, therefore, may be comparable to the upper limit permitted by the ozone record.

We have also assessed the potential effect on ozone of a large number of nuclear detonations such as might occur during a large-scale nuclear exchange with individual yields of 1 to 21 PJ (250 kt to 5 Mt). Detonations within the range of 1 to 2 PJ have stabilization heights very close to the tropopause, so predictions of their effect on ozone are sensitive to the method used to estimate these heights. A variation in height of ± 1 km can significantly affect the amount of NO that is injected into the stratosphere.

Figure 6a shows the potential effect of 1-PJ (250-kt) devices on ozone in the Northern Hemisphere, computed with 1977 chemistry. According to these calculations, total ozone may increase or decrease depending upon the total yield.

Small NO_x injections due to nuclear explosions cause an increase in the ozone concentration near 16 km similar to that shown in Fig. 2. For small NO_x injections, the increase in ozone below about 20 km is greater than the reduction in ozone at higher altitudes, resulting in a net increase in total ozone. Very large NO_x injections cause the NO_x catalytic cycle to become dominant, resulting in a decrease in ozone concentration near 15 km.

Our calculations for the potential effects of 4.2- and 21-PJ (1- and 5-Mt) devices on total ozone in

the Northern Hemisphere are shown in Figs. 6b and 6c. These results are also based on our 1977 model chemistry. Because of their higher stabilization altitude (which is close to the altitude of peak ozone concentration), 21-PJ (5-Mt) devices reduce the ozone more than 4.2-PJ (1-Mt) devices for the same total yield. The peak ozone reduction occurs within the first year after detonation, followed by a period of recovery to near-normal ozone levels lasting 2 to 4 years.

In addition to changing total ozone, variations in weapon yield also affect the amount of radioactive fallout. Because of the lower stabilization height, the radioactive debris from low-yield weapons does not remain in the atmosphere so long. With less time for the debris to decay before it reaches the

ground, radiation levels are higher.

SUMMARY

We are continuing to study the potential chemical and climatic effects of several man-made perturbations to the stratosphere. In addition to our one-dimensional transport-kinetics model that has been used extensively for assessment studies, we are developing a two-dimensional version. This model will help us simulate and interpret the effects of high-yield nuclear detonations at high northern latitudes, as occurred during the 1960's. It will also be used to predict the latitude variation of ozone changes due to aircraft flight corridors at middle latitudes. We are continuing efforts to improve chemistry modeling, an area of major changes over

Fig. 5. Computed effect on total ozone in the Northern Hemisphere of atmospheric nuclear tests during 1956-1962. We assume that the total yield from high-yield detonations over this period was 1.8 EJ (429 Mt) with 1.4 EJ (335 Mt) occurring in 1961-1962. Results are shown for calculations with both our 1976 and 1977 model chemistry. The range for both sets of calculations stems from the use of two estimates of cloud stabilization heights; the upper boundaries correspond to the lower stabilization altitude estimate, the lower boundaries to the higher estimate. Our 1977 results are comparable to the upper limit permitted by ozone measurements made during the test period.

Fig. 6. Change in total ozone for the Northern Hemisphere from atmospheric nuclear explosions such as might occur during a large-scale nuclear exchange. Yields on the curves are for total yields during an exchange. All calculations were made with our 1977 model chemistry. Because of their higher cloud stabilization altitude, 21-PJ (5-Mt) devices have the greatest impact on total ozone.

the past few years. We anticipate further changes as more work is devoted to model validation and the reduction of uncertainties.

Current model calculations predict only small changes in total ozone from large fleets of high-altitude aircraft, but there may be significant changes in the local ozone concentration. CFMs are estimated to cause about a 15% reduction in total ozone at steady state, assuming a constant release rate at 1973 levels. The atmospheric detonation of a large number of nuclear devices with yields greater than 4.2 PJ (1 Mt) may cause ozone reductions much greater than 15%, returning to near-normal ozone levels after a few years.

Key Words: atmospheric nuclear explosions; chloro-fluoromethanes; ozone; ozone—chemical reactions; ozone—depletion; ozone—distribution; supersonic transport—environmental studies.

NOTES AND REFERENCES

1. A. Grobecker, S. Coroniti, and R. Caanon, Jr., *CJAP Report of Findings, The Effects of Stratospheric Pollution by Aircraft*, U.S. Department of Transportation, Washington, D.C., Rept. DOT-TST-75-50 (1974).
2. W. Duewer, D. Wuebbles, H. Ellsaesser, and J. Chang, "Catalytic Ozone Destruction: Sensitivity to Rate Coefficients," *J. Geophys. Res.* **82**, 935 (1977).
3. Our post-1974 modeling studies have been funded by the Federal Aviation Administration's High Altitude Pollution Program. The effect of recent changes in the model are summarized in the *Annual Report of Lawrence Livermore Laboratory to the High Altitude Pollution Program—1977*, Lawrence Livermore Laboratory, Rept. UCRL-50042-77 (1977).
4. This figure is from *The Report of the Committee on Meteorological Effects of Stratospheric Aircraft (1972-1975)*, United Kingdom Meteorological Office, Bracknell, 1975.
5. J. Chang, W. Duewer, and D. Wuebbles, *The Atmospheric Nuclear Tests of the 50's and 60's: A Significant Test of Ozone Depletion Theories*, Lawrence Livermore Laboratory, Rept. UCRL-80246 (1977).

PAST TITLES

Articles in the *Energy and Technology Review* have been organized into subject areas approximately corresponding to the Assistant Secretaries' areas of responsibility in the Department of Energy. These subject areas are listed below with references to some recent articles in each category. (A semiannual index appears in the June and December issues.)

CONSERVATION AND SOLAR APPLICATIONS

Car for Tomorrow: A Quasi-Electric-Drive Vehicle (*June 1977*)
Transportation's Role in the Energy Problem (*March 1977*)

DEFENSE PROGRAMS

A Dissector-Restorer Framing Tube for Recording Very Fast Experiments (*October 1977*)
Glasses for High-Power Fusion Lasers (*September 1977*)
Laser Fusion Program Overview (*August 1977*)
Probing Nuclei with LLL's Electron Linear Accelerator (*July 1977*)

ENERGY RESEARCH

Hydrogen Production by Thermochemical Decomposition: The Zinc Selenide Cycle
(*November/December 1977*)

ENERGY TECHNOLOGY

Magnetic Fusion Energy

Mirror Fusion Test Facility (*October 1977*)
Neutral Beams for Magnetic Fusion (*September 1977*)
TMX: A New Fusion Plasma Experiment (*July 1977*)

Solar, Geothermal, and Electric Energy

Solar Power for Industrial Process Heat (*November/December 1977*)
Taming Geothermal Brines for Electrical Power (*July 1977*)
Wind-Energy Assessment (*June 1977*)

ENVIRONMENT

Safeguards Research: Assessing Material Control and Accounting Systems (*November/December 1977*)
Developing Criteria for the Management of Nuclear Wastes (*October 1977*)
Microwave Gas Analyzer Development at LLL (*September 1977*)
Flow Cytometry in Cervical Cancer Diagnosis (*July 1977*)

RESOURCE APPLICATIONS

Western States Uranium Resource Survey (*May 1977*)

LABORATORY TRENDS

Continuing Education at LLL (*May 1977*)