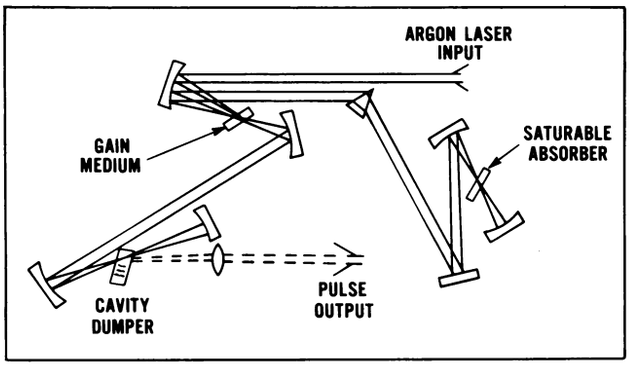
CHEMISTRY BY LASER LIGHT

Light 'bullets' from the fastest lasers in the west target new kinds of chemistry

BY DIETRICK E. THOMSEN



Bell Labs

Schematic of the fastest laser in the world. Subpicosecond pulses permit study of reactions so fast there is no other way to follow them.

The invention of the laser made possible many things in physical science and technology that had been textbook curiosities as well as some things that no one had thought of. Many processes—holography is an example—had been described in textbooks and theoretical treatises with the notation that they could be done in practice if only a source of coherent light were available. Suddenly there was one, and scientists began to do things of which their teachers had only dreamed.

Chemistry is a branch of science where the use of lasers has spread very fast. The coherence and monochromaticity of laser light make possible the use of it to induce chemical reactions that have a precision and specificity impossible before. With a laser, the chemist can excite a particular reaction that is wanted without the necessity of taking along unwanted side effects. Particular isotopes of atoms or molecules can be excited and studied, as well as the rates of reactions and the step-by-step processes of energy exchange. A comprehensive review of the subject would fill one or more sizable volumes. As one of the early workers in the field once told SCIENCE NEWS, the new procedures are available to any chemistry professor who has access to a laser, and that is a large population. However, a number of examples representative of the sorts of things now being done in the various countries were reported at the recent Conference on Laser Engineering and Applications in Washington.

In the study of reactions, chemists have usually been in the position of knowing what has happened and how much. They could tell what had combined with what, and what had come loose from what and in what proportions. But they often didn't know how it had happened, what was the sequence of steps from beginning to result. Now the monochromaticity of laser light and the time resolution possible with fast pulsed lasers permits chemists to follow many reactions step by step.

An example, cited by Robert J. Gordon of the University of Illinois at Chicago, is his work with Ezra Ben-Ziv and Jerry Moy on a reaction of vital importance to all life, the combination of nitric oxide and ozone to make nitrogen dioxide and molecular oxygen, or as it is written in symbols: $NO + O_3 \rightarrow NO_2 + O_2$. One place where this reaction operates is in the production of photochemical smog from automobile exhausts. The nitrogen dioxide produced is highly poisonous and responsible for many of the deleterious effects of urban smog. Another location is in the stratosphere where nitric oxide exhaust is accused of depleting the ozone layer on which life below depends for shielding against toxic amounts of solar ultraviolet radiation. Much of the argument over the damage done by fluorocarbon-powered sprays, for example, depends on comparing the rates of reactions like this one that deplete the ozone to the rates of those that replenish it.

The light of a given laser has a sharply defined wavelength. It will excite only the particular atomic or molecular process with which it resonates. The traditional method of making chemical reactions go, heating, excites a lot of things at once. The laser may excite a particular orbital state of an electron or particular vibrational or rotational mode of a molecule. In this particular case, as Gordon relates it, a carbon dioxide laser excites a particular vibrational mode of the ozone molecule, and the experimental question is: How efficiently is this vibrational energy used in the reaction?

The reaction is done at various temperatures to provide a basis for comparing the necessary amounts of heat energy and vibrational energy. The reaction produces an excited form of nitrogen dioxide that emits red light. So the brightness of this light can be used to determine the use of the vibrational energy. The answer is that about 50 percent of the vibrational energy is used in the reaction; the rest is dissipated in other ways.

(When excited by a laser, the red light of the nitrogen dioxide can be used to determine the nitrogen dioxide concentration in a sample of air where the chemist already knows it is, say along the margin of a highway. The use of lasers to measure concentrations of chemical species in this way is a whole other application of lasers to chemistry.)

Lasers can induce reactions using nonreactants as sensitizers. The sensitizer picks up energy and transfers it to the reactants. For example, sulfur hexafluoride can be used as a sensitizer in the ozone reaction cited earlier. The sequence by which it absorbs laser energy and transfers it to the ozone can be followed. Sulfur hexafluoride is a very efficient absorber of laser light, says Gordon, so efficient that it will absorb many photons and then dissociate. That is one of the reasons it has been extensively used in early laser-chemical experiments. In an experiment done by S. H. Bauer of Cornell University and collaborators, excited sulfur hexafluoride mixed with silicon hydride gives an explosive reaction that yields excited sulfur dimers plus silane (SiF_4) and hydrofluoric acid. The sulfur dimers give off light. This has been suggested as the basis of a visible laser.

Another general use of lasers mentioned by Gordon is to enable reactions that usually require high temperatures to happen at room temperature. An example is the reaction of trimethyl boron, $B(CH_3)_3$, with hydrogen bromide, work done by H. R. Bachman, H. Nöth and R. Rinck of the University of Munich and K. L. Kompa of the Max Planck Institute. This produces three different brominated compounds, depending on whether it is done at 150°C, 250°C or 450°C. Lasers can make all three of these reactions go at room temperature, and they can make them go separately. With heating, a chemist who wants to study the 450° reaction has to take the other two along with the one he wants. With a laser, he can induce only the one he wants and study it in isolation.

In biology, many of the important reactions happen millions or billions of times as fast as the eye can blink. This is necessarily so in the reactions associated with vision. As example cited by Erich P. Ippen of Bell Telephone Laboratories is the use of what he calls "a laser system that produces the shortest pulses ever, 0.3 picosecond," to study the exci-

tation of rhodopsin. A picosecond is a trillionth of a second. Rhodopsin is a red dye found in bacteria that live in salt marshes and in the retina of the eye, where it plays a role in color vision.

When light strikes the retina, the process that excites rhodopsin happens on the picosecond timescale. The action of rhodopsin has not yet been fully unraveled, says Ippen, but the first step has to be something simple like the transfer of a single atom one step over in the molecule. The step happens too fast to be something more complicated like isomerization. Another fast biochemical reaction of basic interest being studied with this system is the association and dissociation of hemoglobin with oxygen and carbon dioxide.

The uses of the picosecond laser pulses, which even at the speed of light produce "bullets" one-fiftieth of an inch long, extend farther than biochemistry. A large class of uses is in solid-state chemistry. The chemical changes in solids, especially the ways and rates in which atoms in solids pass electrons among themselves, are important to the uses of solids as components in modern electronic systems. Since the picosecond laser system is faster than present or future electronics, not to mention bunsen burners, it provides the only method for studying some of these processes.

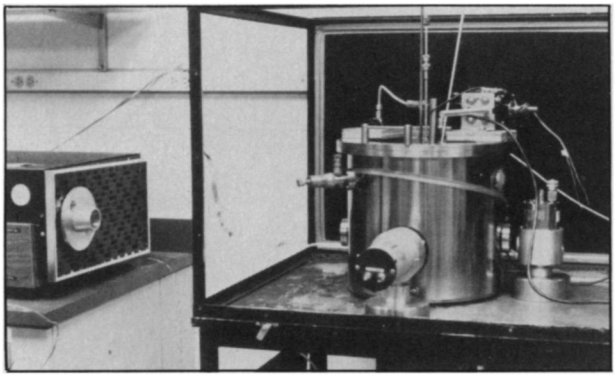
Another feature unique to laser chemistry is the ability to separate one isotope of an element from another, something ordinary chemistry cannot do efficiently. The resonant frequencies of one isotope of a given element generally differ from those of another, so a given laser may be able to excite one isotope and make it chemically or physically reactive while leaving the others alone. Then appropriate physical or chemical reactions can be used to separate the excited isotope from the others. One of the highlights of the Conference on Laser Engineering and Applications was the presence of two scientists from the Kurchatov Institute in Moscow, Nicholas Karlov and V. S. Letokhov, who reported some of the directions isotope separation research is taking in the Soviet Union.

Mention of isotope separation always brings up the question of separating fissile from nonfissile isotopes of uranium for use as reactor fuel or bomb charges. Much work has been done on uranium separation in various parts of the world. In spite of the fears expressed by many people about laser separation of uranium, Karlov says he does not think laser separation will compete with the older methods, gaseous diffusion and centrifuging. (However, people who worry about laser separation of uranium are seldom concerned about the United States, the Soviet Union or China. They see it as a method that would permit proliferation of weapons among countries or groups of people that do not have the capital or the technological organization necessary to set up the other methods. Indeed, the remark about the technique being available to any chemistry professor, was made in the context of a discussion of laser separation of isotopes.)

One of the major directions of isotope separation work in the Soviet Union, says Karlov, involves the rare earths. The rare earths make up a large part of the periodic table of elements. They are found in small amounts in various natural minerals, and a knowledge of their behavior can have important applications in mineral refining and in the manufacture of materials designed to have particular properties—electronic circuits, for example. The rare earths present particular problems for the technique of isotope separation, because most of them are highly refractory, and the separation work must be done in the gaseous state. Some of them can be vaporized by heating in molybdenum crucibles, but a few can be vaporized only by high-energy beams of electrons (which happens to be another specialty of Soviet scientists).

Questioned about what he thought the first practical application of laser separation of isotopes was likely to be, Karlov suggested the production of identifiable, but nonradioactive, isotopes for use as tracers in biological processes. For example, he cites studies of the efficiency with which plants use the nitrogen from fertilizer in the production of proteins. Agriculture involves much semiskilled and unskilled labor, and it would be more economical and safer to use nonradioactive isotopes as tracers than to teach the laborers how to handle radioactive ones.

Asked about possible cooperation between Soviet and American scientists in isotope separation, Karlov said that as human beings the Soviet scientists would be delighted, but Letokhov said the U.S. government seems to have a negative attitude. There is exchange of ideas, but not cooperation, he says. □



Apparatus used to study laser-induced reaction of nitric oxide and ozone (left). Data from NO + O_3 reaction (lower right) show nearly exponential fall-off in red light intensity as reaction saturates. When reaction is sensitized with SF_6, (lower left) intensity rises as energy is transferred to ozone, then declines.