# Laser Light in the Extreme Ultraviolet

## *Rare gas-halogen excimer lasers, supersonic gas jets, and nonlinear optics add up to laser-like coherent radiation at 35.5 nanometers*

Despite all the ballyhoo about x-ray laser antimissile defense systems, there are no reliable (and certainly no published) accounts demonstrating the existence of such a short-wavelength laser. The current world's record for the shortest wavelength spatially and temporally coherent (that is, laser-like) light is 35.5 nanometers (nm). Recently set by researchers at Bell Laboratories, this is a slim 2.5 nm shorter than the previous mark set 6 years ago by scientists at the Naval Research Laboratory. Two innovations used to get the newer result suggest, however, that even shorter wavelengths on the border of the soft x-ray region at 10 nm are possible.

Laser aficionados make a careful distinction between lasers and coherent sources. Lasers are devices that convert energy (chemical, thermal, electrical, optical, and so on) into coherent radiation. Coherent sources convert laser light of one wavelength into radiation of another wavelength; that is, contrary to their name, they are not the original producers of coherent light. Jeffrey Bokor, Philip Bucksbaum, and Richard Freeman of Bell Laboratories generated their 35.5-nm radiation by means of a coherent source that used the 248-nm light from a krypton fluoride laser as its input. The spectral region between about 100 and 10 nm is nowadays called the extreme ultraviolet or XUV, in part because there are no optically transmitting solid materials in this range of wavelengths. Bucksbaum described the 35.5-nm coherent source at the Conference on Lasers and Electro-Optics (CLEO) in Baltimore last month.*

Nonlinear optics is the name of the class of processes by which longer-wavelength light is converted to shorter-wavelength light. The simplest of these is wavelength division by a factor of 2 or frequency-doubling. Light incident on a suitable crystalline material induces a polarization in the material of the same frequency. If the light is intense enough, a polarization wave whose frequency is double that of the incident light (second harmonic) is also generated. The polarization wave reradiates light at the new frequency. Alternatively, one can think of two photons from the incoming light being converted into one photon with twice the frequency. The same thing holds for higher harmonics. Gases and liquids can be used to generate odd but not even harmonics.

A very similar process is wavelength or frequency mixing. Two light waves of different frequencies can be converted into light whose frequency is either the sum or the difference of the initial frequencies. Frequency-doubling is just the special case when the two incoming light waves have the same frequency.

Although it all sounds straightforward, putting the idea into practice runs into complications at the short wavelengths of the XUV. For example, the conversion is never perfectly efficient, so some light is lost each time the frequency is multiplied. By the time the light from an infrared laser reaches the XUV, there may not be enough photons left to make a useful light source. The XUV is particularly a problem because the most efficient nonlinear materials are crystals such as potassium and ammonium dihydrogen phosphate (KDP and ADP), which do not work for wavelengths shorter than 200 nm. The alternative is an atomic or molecular gas (metal vapors or rare gases), but the frequency conversion is considerably less efficient.

**Even shorter wavelengths bordering the soft x-ray region at 10 nm are possible.**

An early short-wavelength record was set in 1973 by Andrew Kung, James Young, and Stephen Harris at Stanford University by the use of argon as the nonlinear medium. The investigators achieved 88.7 nm in two steps. First, the 1.06-micrometer light from a solid-state (Nd:YAG) laser was frequency-doubled twice in KDP and ADP to produce 266-nm light. Then, this radiation was frequency-tripled in argon.

This approach was pushed to the limit in 1977 by John Reintjes, Chiao-Yao She, Robert Eckardt, and their co-workers at the Naval Research Laboratory. The group was able to generate the seventh harmonic of 266-nm light in helium gas, thereby producing coherent radiation at 38 nm. The highest intensity created was at a helium pressure of 150 torr (20,000 pascals), where the conversion efficiency was about $10^{-5}$ percent. The two stages of frequency-doubling of the Nd:YAG laser light to reach 266 nm were each 70 percent efficient.

All XUV experiments required a differential pumping scheme in which the light generated in a gas cell immediately exits through a slit into an evacuated chamber because there are no window materials that can transmit XUV radiation. Moreover, even the best gas, helium, is opaque at 50 nm and below.

All of these experiments also started with Nd:YAG because this type of laser can be operated in a particular way (mode locked) that produces very short (30-picosecond) pulses. Hence, the effective power density of a focused beam is enormous and makes the generation of such high harmonics feasible. However, even Nd:YAG runs out of steam, argued Bucksbaum, and there have been no reports of wavelengths shorter than 38 nm until the recent Bell Laboratories work.

What is new is the use of excimer lasers and supersonic pulsed gas jets. Excimers are molecules that exist only in an excited quantum state. On relaxing to the lowest energy, ground state, the molecule dissociates. One of the first excimer lasers was molecular xenon ($Xe_2^*$), which emits 172-nm radiation as the excited molecule decays into two xenon atoms. Commercially available excimer lasers include argon fluoride (193 nm), krypton chloride (222 nm), krypton fluoride (248 nm), xenon chloride (308 nm), and xenon fluoride (351 nm).

In principle, excimer lasers could be primary, high-power sources of ultraviolet laser light that could be then converted into the XUV by nonlinear optics techniques. The difficulty is that the quality of the radiation is not up to usual laser standards. In 1976, Henry Hutchinson, Timothy Ling, and Daniel Bradley of Imperial College (London) managed

*Conference on Lasers and Electro-Optics, Baltimore, Maryland, 17 to 20 May 1983.

to frequency-triple the radiation from a molecular xenon excimer laser to produce 57-nm light, which was a short-wavelength record at the time. And 2 years ago, Reintjes, Lawrence Tankersley, and R. Christensen of the Navy laboratory were able to generate the fifth harmonic of light from a xenon chloride laser to obtain 61.6-nm light. However, because of the difficulty of achieving high spectral purity and spatial coherence with excimer lasers, researchers have also pursued alternatives.

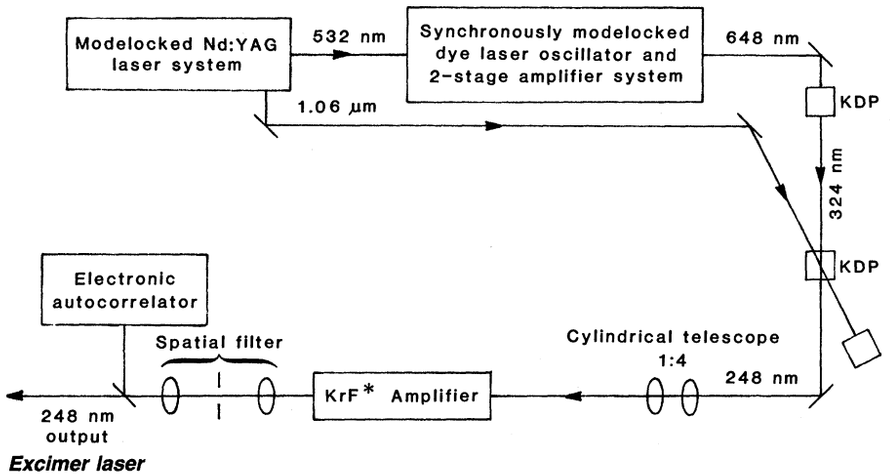
A different way to use excimers has been pioneered by a group headed by Hans Egger, Herbert Pummer, and Charles Rhodes at the University of Illinois at Chicago Circle. Their idea was to use excimer lasers as amplifiers of laser light generated by another source that had good optical properties. A series of experiments culminated last year in an argon fluoride laser that was tunable over a range of wavelengths and had a peak pulse power of 4 gigawatts (40 millijoules in a pulse 10 picoseconds long). The laser was tunable because the original light source was a dye laser that emits over a wide band in the visible and because excimer lasers themselves are intrinsically tunable over a limited range. The power of the visible light was boosted by a string of three dye lasers operated as amplifiers. The visible light was converted to ultraviolet by frequency-tripling in strontium vapor. Two argon fluoride excimer lasers then amplified the ultraviolet light.

In experiments with this system plus the addition of a third argon fluoride amplifier, the Chicago Circle group frequency-tripled and -quintupled this radiation to produce light with wavelengths near 64 nm and 38.4 nm respectively. The XUV power at the longer wavelength was 20 kilowatts in a 10-picosecond pulse, which is about $10^{11}$ photons per pulse, and 200 watts or $10^9$ photons per pulse at the shorter wavelength.

Another Chicago innovation was the design of a special differential pumping assembly that prevents the nonlinear gas (molecular hydrogen) from flowing through the pinhole exit slit through which the laser radiation passes and thereby from reabsorbing some of the generated XUV. However, a newer idea is the use of pulsed supersonic gas jets.

Pulsed jets began to be used in molecular beam studies of the kinetics of chemical reactions about 5 years ago. Among their virtues is that expansion of the high-temperature gas through a nozzle to produce a supersonic stream "cools" the molecules so that only the lowest energy rotational and vibrational quantum states are occupied. This well-defined initial state, in conjunction with laser excitation and laser-induced fluorescence, for example, permits detailed studies of a reaction in terms of the particular quantum states involved.

As applied to the nonlinear optics problem of the generation of XUV light, the cooling can play a role in that the gas pulse flows perpendicular to the laser beam. Since there is little gas particle motion in the direction of the laser, there is little broadening due to the Doppler effect of any optical absorption lines. This is important in nonlinear optics when so-called resonant enhancement effects come into play. Resonant enhancement is the increased efficiency of frequency conversion that occurs when the energy of one or multiple photons matches the energy of an optical transition in the nonlinear medium.




*Block diagram of the Bell Laboratories system shows how infrared light from a Nd:YAG laser is converted by nonlinear optics to 248-nm UV radiation that is amplified by a krypton fluoride excimer laser.* [*Figure adapted from* Optics Letters]

In fact, resonant enhancement is widely used in frequency mixing. At the CLEO meeting, for example, Keith Bonin, Mark Morris, and Thomas McIlrath of the University of Maryland reported on the production of coherent radiation near 94 nm by a process called four-wave fixing. Two photons from a laser beam of wavelength 216 nm add together to match an optical transition in krypton gas. A third photon from a tunable dye laser is mixed in to create the tunable XUV radiation, which is the fourth wave. The investigators reported a conversion efficiency of about $10^{-3}$ percent at 94.2 nm.

The use of pulsed gas jets in nonlinear optics has been pursued independently by Kung, who is now at the San Francisco Laser Center of the University of California at Berkeley, and by the Bell Laboratories group. The main virtue of the gas jets, which are timed to occur in synchronism with the pulsed laser light that is to be converted to a shorter wavelength, is that the gas is only in the focal region of the laser beam and thereby does not interfere with XUV after it is generated. Kung argued at CLEO that the well-defined beam geometry also permitted a wider variety of nonlinear gases to be used and that the vacuum pumping requirements were much simplified.

Kung described a tunable (97.3 to 102.3 nm) XUV coherent source that he and Ernesto Marinero, Charles Rettner, and Richard Zare of Stanford have constructed entirely of commercially available components. The system starts with a tunable dye laser. The light from the dye laser is frequency-doubled to the ultraviolet with a nonlinear crystal. Finally, the ultraviolet is frequency-tripled in a pulsed argon gas jet to create nanosecond-long pulses of XUV. The possibility of resonant enhancement of the frequency-tripling was also demonstrated by replacing the argon with carbon monoxide. In this case, two of the three photons needed for frequency-tripling add together to match an optical transition in the carbon monoxide. Kung said that the efficiency of the conversion was enhanced by a factor of 100 by this means.

At Bell Laboratories, Bokor, Bucksbaum, and Freeman combined the use of excimer laser amplifiers and pulsed jets of helium gas to generate the 35.5 nm coherent radiation. Their system started with a Nd:YAG laser and ended with a krypton fluoride excimer laser amplifier (see figure). What they saw after passing this light through the helium were three harmonics of the 248-nm radiation from

the krypton fluoride: the third at 82.8 nm, the fifth at 49.7 nm, and the seventh at 35.5 nm. Each successive harmonic was weaker than the preceding one, with about $10^{11}$ photons per pulse in the third harmonic, $10^8$ per pulse in the fifth, and $10^5$ per pulse in the seventh. The efficiency of the seventh harmonic conversion was estimated to be $3 \times 10^{-9}$ percent at a helium pressure of about 7 torr. The system operated at 10 pulses per second, as have most of those described previously.

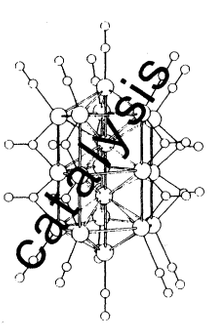
To improve the light output, Bucksbaum speculated, there are several possibilities. One is to increase the density of gas atoms in the jet by a factor of up to 100, which could add a factor of 1000 to the photon flux produced. A nonlinear optical technique called phase matching, if a suitable gas mixture could be found, might increase the flux by another factor of 100. Phase matching means that the incoming light wave and the frequency-converted light wave "stay in step" over a certain distance so that there is time for the short-wavelength wave to build up at the expense of the longer-wavelength light. Shorter pulses would help, as well, because the output of the *n*th harmonic increases with the *n*th power of the intensity of the incoming light. Pulses from krypton fluoride as short as 0.2 picosecond may be possible. Finally, a more efficient collector of the XUV than the diffraction grating used in the experiment is being developed at Bell Laboratories that may gather ten times as many photons, thereby using those that are produced more effectively.

What is all this good for? Many researchers are eyeing a less expensive alternative to synchrotron radiation, which has been the most intense source of tunable XUV light going. Kung says that the 100-nm source there would cost from $75,000 to $100,000 to replicate. Excimer lasers up the ante by $50,000 or more apiece. Bokor says the Bell Laboratories XUV system with one krypton fluoride laser would require $150,000 to construct. And Egger, Pummer, and Rhodes have estimated a cost of about $500,000 for the argon fluoride–based XUV source with three excimer lasers. It is difficult to compare these figures with the price of synchrotron radiation facilities, because these produce light over an extremely wide wavelength range and can serve dozens of researchers simultaneously. A conservative guess is that the two types of light sources will be complementary.

Finally, what are the prospects for even shorter wavelength coherent sources? Bucksbaum predicted that the next likely candidates are the ninth harmonic of krypton fluoride and the seventh of argon fluoride, both of which are close to 27.6 nm. Development of subpicosecond excimer lasers would mean there would be enough intensity to carry harmonic generation of excimer laser light to as short as 10 nm, according to Bokor. Ultimately, the construction of XUV lasers with outputs of the order of 20 nm together with nonlinear optics to shorten their wavelengths could lead to honest to goodness coherent x-ray sources (in marked contrast to what one reads about now).—**ARTHUR L. ROBINSON**

# Activating Unreactive C–H Bonds

## *It is now possible to "get a handle" on hydrocarbons for further reaction by inserting a metal atom in a homogeneous reaction*




"One of the most intriguing—and yet elusive—goals of organometallic chemistry has been the use of transition-metal complexes to 'activate' carbon-hydrogen bonds in completely saturated organic compounds," says Robert G. Bergman of the University of California, Berkeley. "Saturated hydrocarbons are among the most ubiquitous, and chemically stable, of all organic materials," he adds. They appear in petroleum, in coal, in synthetic fuels produced by liquefaction of coal and other fossil fuels, and in synthetic fuels produced by Fischer-Tropsch chemistry from syngas.

These hydrocarbons can be burned for their fuel value, but many investigators are now much more interested in their potential as feedstocks for the chemical industry. That use, however, requires that the hydrocarbons be functionalized, given a double bond or some other functional group that serves as a "handle" for further chemical reactions. Those investigators would like to use homogeneous systems to perform that functionalization because they hold the greatest promise of selectivity,* but their research has been, in Bergman's words, "tantalizing and frustrating."

The saturated hydrocarbons are, of course, not completely unreactive. They can be oxidized by heat, free-radical reactions, ozone, hydrogen peroxide, and superacids; but these reactions, says Bergman, "often require large amounts of energy and are usually very unselective." A homogeneous process might well require less energy.

There have been "tantalizing" glimpses that suggest that a homogeneous process is attainable. In the late 1960's, it was shown that acid solutions of certain platinum salts could catalyze the exchange of hydrogen and deuterium in alkanes, a process that requires scission of the carbon-hydrogen bond. This reaction is still controversial, however, because some investigators believe it is heterogeneous. Several investigators have also shown that metal atoms can mediate the oxidation of hydrocarbons through free-radical reactions.

More recently, investigators such as John T. Groves of the University of Michigan and Craig L. Hill of the University of California, Berkeley, have shown that metal-porphyrin complexes can catalyze the oxidation and functionalization of hydrocarbons. These homogeneous complexes are similar to biological cofactors, such as cytochrome P-450, that participate in biological oxidations, and they also operate through free radicals. In contrast, what Bergman and others have been seeking is a so-called oxidative addition in which a metal atom is inserted into a carbon-hydrogen bond in the same manner that has been observed for gases such as hydrogen or chlorine, as well as mercaptans, disulfides, and carboxylic acids.

The prototype for insertion of a metal atom into an alkane carbon-hydrogen bond is the well-known insertion of the

*Selectivity is discussed in earlier articles of this series: 4 February, p. 474; 25 February, p. 944; 25 March, p. 1413; 6 May, p. 592; and 3 June, p. 1032.