

Tunable Far IR Molecular Lasers Developed

Stimulated Raman scattering associated with a series of closely spaced rotational states is the key to wavelength tunability

As spectral regions go, the far infrared or submillimeter wave region is relatively undeveloped. In particular, researchers have lacked the bright, wavelength-tunable sources such as the dye lasers that serve so well in the visible. Extending the range of tunability to both shorter and longer wavelengths is a high priority item with laser scientists, however, and recently two groups have been operating methyl fluoride molecular gas lasers that are continuously tunable over broad portions of the far infrared.

According to theory, these light sources are unlikely ever to have as high a power output as that promised by free electron lasers (*Science*, 14 December 1984, p. 1300, and 12 October 1984, p. 153), which are also being developed as sources of long-wavelength radiation. But they are more than adequate for such applications as molecular spectroscopy says Jerald Izatt of the University of Alabama, who leads one of the groups. And they have the advantage of being inexpensive and small enough for individual researchers to operate them in their own laboratories, adds Richard Temkin of the Massachusetts Institute of Technology (MIT), who heads the other.

Raman scattering is the key to tunability in the far infrared, which is normally emitted at fixed wavelengths when a molecule in a higher energy rotational quantum state relaxes to a lower energy rotational state. Raman scattered light is that which exits from a material with either a longer (Stokes Raman) or shorter (anti-Stokes Raman) wavelength than the light that entered. One can, for example, picture Stokes Raman scattering as occurring when a photon from the incoming light excites a molecule from a particular quantum state to an imaginary or "virtual" quantum state, whereupon the molecule relaxes with no time delay to a vacant real state lying at a higher energy than the initial state. The photon radiated during the relaxation is the Stokes Raman scattered light.

Raman scattering is usually a weak process compared to transmission with no wavelength change or—when the wavelength of the incident light matches a transition between molecular quantum states—to absorption followed by fluorescence. However, there is, in analogy with the stimulated emission process that drives lasers, a stimulated Raman

scattering, which can not only dominate others, if the incident light is intense enough, but generate laser-like light.

The tie-in to tunability is that the energy of the virtual state is fixed only by the wavelength of the incoming light and is not restricted to the energies of the real molecular quantum states. This means that the wavelength of the Raman scattered light can continuously change as the wavelength of the incident light is scanned. However, the details of molecular physics dictate the intensities of the scattered light, and achieving tunability is not a trivial matter.

For example, achieving intense stimulated Raman scattering in the far infrared involving virtual states with energies that are far from those of real states only came in the late 1970's. For far infrared emission, the wavelength of the incoming light source or "pump" is chosen to

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excite a molecule from a particular rotational level in the ground (lowest energy) vibrational quantum state to a virtual rotational level in a higher lying vibrational state. Such excitation requires a near infrared laser that is powerful and itself tunable.

Part of the reason for the power requirement is that the stimulated Raman effect, like ordinary lasing, has a threshold. If the pump power is lower than the threshold, which is the point at which light amplification or gain exceeds losses, the process does not begin. Several factors make for a high threshold power for far infrared stimulated Raman emission.

One is that the Raman gain coefficient is inversely proportional to the wavelength of the scattered light and hence is small at long wavelengths. Since the intensity of the scattered light varies with the exponential of the product of the gain coefficient, the pump intensity, and the length of the gas laser, the main way to compensate for the small gain is to begin with a large pump. Another

factor is that—in contrast to most Raman scattering processes, where the wavelength of the pump and scattered photons are not much different—in the far infrared case, the scattered photon wavelength is much longer than that of the pump. This condition also decreases the efficiency.

The threshold is greatly reduced when the energy of the virtual state is very close to that of a real molecular quantum state because a so-called resonant enhancement dramatically raises the efficiency of the stimulated Raman process. However, relying on resonant enhancement limits the tunability.

One of the first successful attempts at achieving tunability in the far infrared was reported in 1977 by Robert Frey, François Pradère, and Jacques Ducuing of the Quantum Optics Laboratory of the Ecole Polytechnique in Palaiseau near Paris. Their rather involved setup typifies the lengths to which researchers will go to obtain laser light in new wavelength regions. Starting with a ruby laser, which emits visible red light, they obtained high-power (up to 10 joules per pulse) tunable visible light by using the ruby laser to pump a chain of dye cells (oscillator and three amplifiers).

The next step was to get tunable near infrared radiation by means of Raman scattering the visible light in gaseous hydrogen. To get the infrared wavelengths they wanted, the French researchers had to scatter twice; that is, the scattered light beam was itself scattered. The resulting beam consisted of pulses of energy 40 millijoules and duration 2.5 nanoseconds.

This infrared light then entered a long cell containing gaseous hydrogen chloride. A glass pipe within the cell served as a wave guide to confine the far infrared radiation that was generated. The output pulses in the wavelength range 60 to 160 micrometers were of maximum energy 0.02 millijoule. And the tuning range was rather limited—about 2 micrometers around the wavelengths of various transitions between rotational quantum states, which are about 10 micrometers apart.

The same group, with Antonello de Martino replacing Ducuing, did better in the following 2 years by using gaseous hydrogen fluoride in place of hydrogen chloride, obtaining pulse energies as high

as 0.75 millijoule (1). The range of tunability was also enlarged, covering about 50 percent of the region between 40 and 250 micrometers.

In the meantime, the group at MIT (David Biron, Bruce Danly, Temkin, and Benjamin Lax) developed an extensive theory for and began experiments on far infrared generation with a less involved optical system that used a carbon dioxide gas laser to directly pump gaseous methyl fluoride. The first experiment in 1979 did not demonstrate tunability but did show that the power of the carbon dioxide laser was sufficient to produce stimulated Raman scattering involving virtual quantum states with energies about halfway between those of rotational levels in the methyl fluoride. The demonstration of stimulated Raman emission this far from, in the jargon, resonance reduced the question of tunability to building an appropriately tunable pump.

Carbon dioxide lasers emit on any of a multitude of closely spaced wavelengths between about 9 and 11 micrometers. With a diffraction grating at one end of the laser optical cavity, one can select the line of interest, but the infrared output is not continuously tunable. At the time, the MIT group proposed the use of a carbon dioxide gas laser in which the gas pressure was 10 to 12 atmospheres, in contrast to the 1 atmosphere of conventional carbon dioxide TEA lasers. The high pressure broadens the ordinarily narrow emission lines so that they overlap. Addition of a grating then makes the laser tunable.

However, a second group at the University of Laval in Québec comprising Pierre Mathieu (now at the Defence Research Establishment, Courcelette, Québec) and Izatt had already been working with high-pressure carbon dioxide lasers with the general aim of making a tunable pump. Mathieu and Izatt were, therefore, in a position to test the proposal immediately and thereby demonstrated the first continuously tunable methyl fluoride far infrared source. Their 1981 report covered the wavelength range from 220 to 400 micrometers and showed that the far infrared output characteristics closely tracked the predictions of the MIT group's theory (2).

In particular, Mathieu and Izatt obtained far infrared pulses of energy up to 0.2 millijoule over about 85 percent of the wavelength range studied. What keeps the coverage from being 100 percent is one of the details of molecular physics mentioned previously. Because the power threshold is the lowest, most of the pumping of methyl fluoride in-

volves so-called R-branch transitions in which the molecule is excited from a rotational level with quantum number J in the ground vibrational state to a virtual level near a rotational level with quantum number $J + 1$ in the first excited vibrational state. The far infrared radiation is emitted when the molecule relaxes to the rotational level immediately below; that is, the level J in the first excited vibrational state. The energy spacing between the rotational levels increases with J , so that the wavelength of the radiation decreases as rotational levels with higher J values are involved.

Consider the situation when the pump wavelength is such that the virtual level is just below the rotational level $J + 1$. As the wavelength of the pumping radiation decreases (and, consequently, the photon energy increases), the virtual level moves about the rotational level $J + 1$ toward the level $J + 2$. Transitions involving rotational levels two quantum numbers apart would no longer be in the R-branch manifold. At some point,

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therefore, the pumping transition switches to the next higher energy transition in the R-branch—that is, the one involving rotation levels with quantum numbers $J + 1$ in the ground vibrational state to $J + 2$ in the first excited vibrational state. As the pumping (and hence output) wavelength nears this transition, the output power falls drastically. Hence, the far infrared laser is better described as quasi-tunable because there are some wavelengths that are inaccessible.

Last August, Danly, Stephen Evangelides, Temkin, and Lax reported their version of a tunable methyl fluoride far infrared laser (3). They constructed a tabletop-sized, high-pressure carbon dioxide laser that emitted pulses having an energy of 100 millijoules and duration 100 nanoseconds. Using this laser to pump methyl fluoride gas, they obtained 0.1 to 1 millijoule output pulses over the wavelength range 250 to 300 micrometers. The instantaneous power was from 1 to 10 kilowatts, which is more than adequate for such studies as nonlinear effects in semiconductors.

Extension to still more intense outputs is possible, but how much more intense is problematical. Using a more powerful (and hence more expensive) carbon di-

oxide pump laser is a brute force way to increase the energy per pulse. Peak power could be improved by shortening the pulse duration. The MIT group measured the bandwidth (spread in frequency or wavelength) of the far infrared emission to be 1 gigahertz. Since the bandwidth and minimum pulse duration are inversely related, pulses as short as 1 nanosecond are theoretically possible by a technique called mode locking. Finally, the MIT group's theory offers further hope from a process called multiphoton emission, in which each scattering event would generate several photons rather than just one.

If the prospects for more power are uncertain, those for a wider range of tunability are quite good. For starters, the gaps in the range of wavelengths accessible by pumping in the R branch can be covered, though less efficiently, by pumping in other branches, such as the P and Q branches, which involve transitions between other pairs of J -valued rotational levels. Both groups have obtained, for example, stimulated Raman emission with P-branch pumping.

Another easily implemented stratagem is to replace the normal methyl fluoride gas, which contains the carbon-12 isotope, with one containing carbon-13. The different isotope causes shifts in the energies of the rotational and vibrational states and hence in the wavelengths of transitions involving them. At Alabama, Izatt and Bimal Deka have just obtained far infrared in the wavelength region from 142 to 174 micrometers by this means with R-branch pumping at transitions that involve very high rotational quantum numbers J (4). They are now attempting to go the other direction to longer wavelengths with R-branch pumping of transitions involving lower rotational quantum numbers J in methyl fluoride containing only carbon-13.

Whether higher powers come along or not, with a wider tunability range, the existing source is interesting for laboratory-scale research. Both Izatt and Temkin agree that their sources could be reproduced with commercially available components for about \$100,000—and considerably less if built from scratch. All in all, it seems that the outlook for the far infrared is brightening up.

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References

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