

Using tunable lasers

These variable-frequency sources, which are based on dye or semiconductor lasers, or on devices with nonlinear interactions, are moving from the experimental to the applications stage.

Howard R. Schlossberg and Paul L. Kelley

Lasers whose output can be varied over a wide range of frequencies offer the opportunity for a new kind of spectroscopy. These tunable sources are welcome in industry, in environmental monitoring and in medicine as well as in basic research. In absorption spectroscopy, for example, tunable coherent sources are bringing about developments, both evolutionary and revolutionary in character, that recall the way powerful fixed-frequency lasers revitalized the rather moribund field of Raman spectroscopy a few years ago. And an interesting analogy exists between the klystron and microwave spectroscopy on the one hand and tunable lasers and optical spectroscopy on the other.

Here we review the operating principles and properties of several tunable laser sources: the dye laser, semiconductor laser and devices with nonlinear interactions, such as the spin-flip Raman laser, optical parametric oscillators and optical mixers. We shall describe current and potential applications and give a sampling of the available experimental results.

Types of tunable lasers

Dye lasers operate by optical pumping from the ground state to an excited singlet electronic state of high rotational and vibrational energy.^{1,2} Sub-

sequently the vibration-rotation energy is thermalized by very rapid nonradiative relaxation, so that a population inversion exists, and stimulated emission occurs, between low vibration-rotation energy levels of the first excited singlet electronic state and higher vibration-rotation levels of the ground electronic state (according to the Franck-Condon principle). These high lying vibration-rotation levels then rapidly decay nonradiatively. Electronic singlet-triplet energy transfer, followed by triplet absorption of laser radiation, complicates the situation. Because of the high density of vibration-rotation levels of the large dye molecules and the large widths of these levels in solution, very broad, continuous bands of radiation are emitted, typically several hundred angstroms wide. To narrow the laser linewidth, making it tunable within the broad emission band, highly frequency-selective optical resonators are used. An example is seen in figure 1. With these resonators most of the laser energy can be retained because of the rapid nonradiative processes ("cross relaxation").

Lasers have been made from dyes of the oxazole, xanthene, anthracene, coumarin, acridine, azine, phthalocyanine and polymethine families.² Both flash lamps and lasers have served as pumps. Among the achievements of these lasers are

- ▶ output from 1.2 to 0.34 microns, in the pulsed mode
- ▶ linewidths as narrow as 35 MHz¹ (7 MHz, with an external Fabry-Perot interferometer³)

- ▶ peak powers of 10⁸ watts
- ▶ average powers of about 300 milliwatts¹ in pulsed operation
- ▶ conversion efficiencies (pump to dye laser) of 50%
- ▶ single TEM₀₀ mode continuous-wave operation from 0.525 to 0.708 microns, with an argon laser pump
- ▶ short-term stability—35 MHz, cw⁴
- ▶ long-term stability—180 MHz or better, cw⁴
- ▶ power outputs—milliwatts to watts, cw

The lasers we have been discussing are in the form of organic or aqueous solutions; extensive research is now being done on vapor-phase dye lasers.

Recombination-radiation semiconductor lasers operate⁵ by stimulating emission across a band gap. Population inversion is achieved by electron injection across a band gap either with a current (diode), or by optical pumping or electron-beam excitation. A typical semiconductor diode laser geometry is seen in figure 2. Infrared semiconductor laser materials in the 1-30 micron region include binary compounds such as InAs, InSb, GaSb, PbSe, PbS, PbTe and pseudobinary alloys such as Pb_{1-x}Sn_xTe, PbS_{1-x}Se_x, Hg_{1-x}Cd_xTe, In_xGa_{1-x}As and GaAs_xSb_{1-x}. Materials such as GaAs, InP, Ga_xAl_{1-x}As, GaAs_xP_{1-x} and GaAs_xSb_{1-x} can be used as tunable lasers in the visible and near infrared. We shall discuss only the lead-salt diode lasers,⁶ because most tunable diode laser experience has been with these devices.

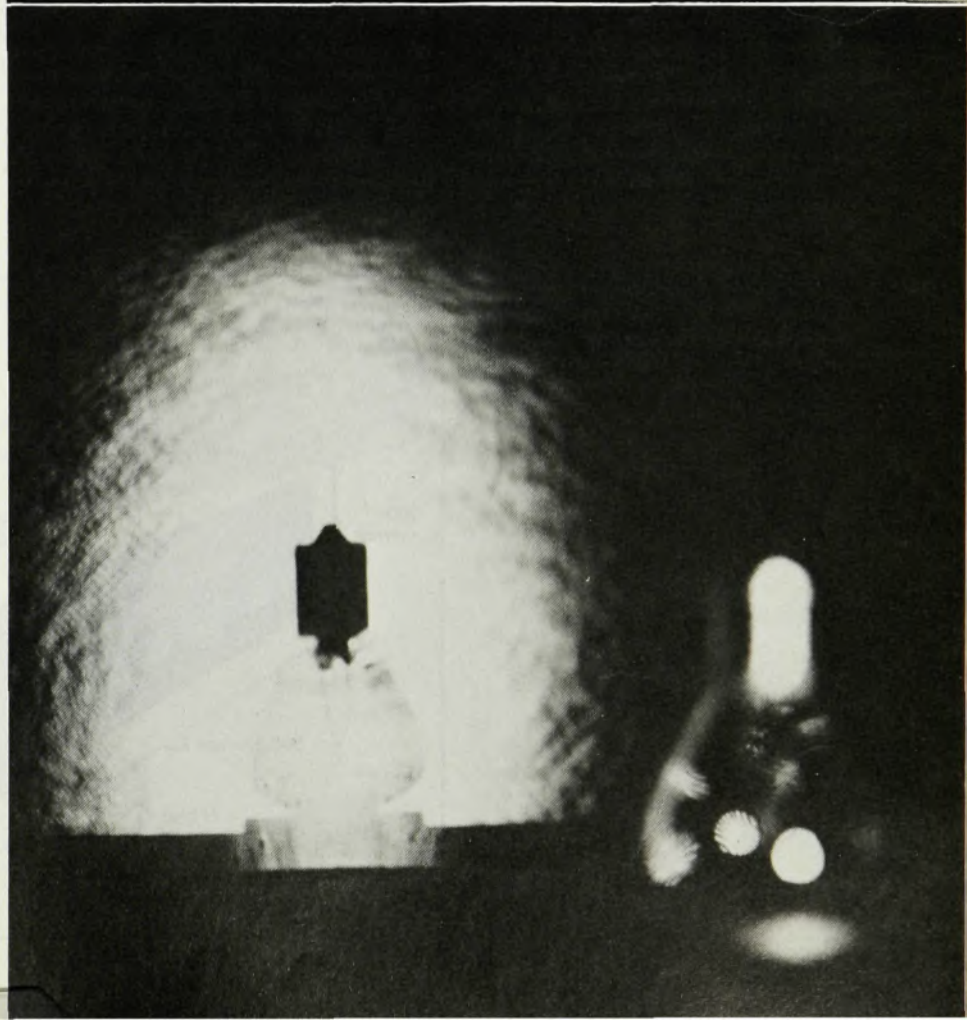
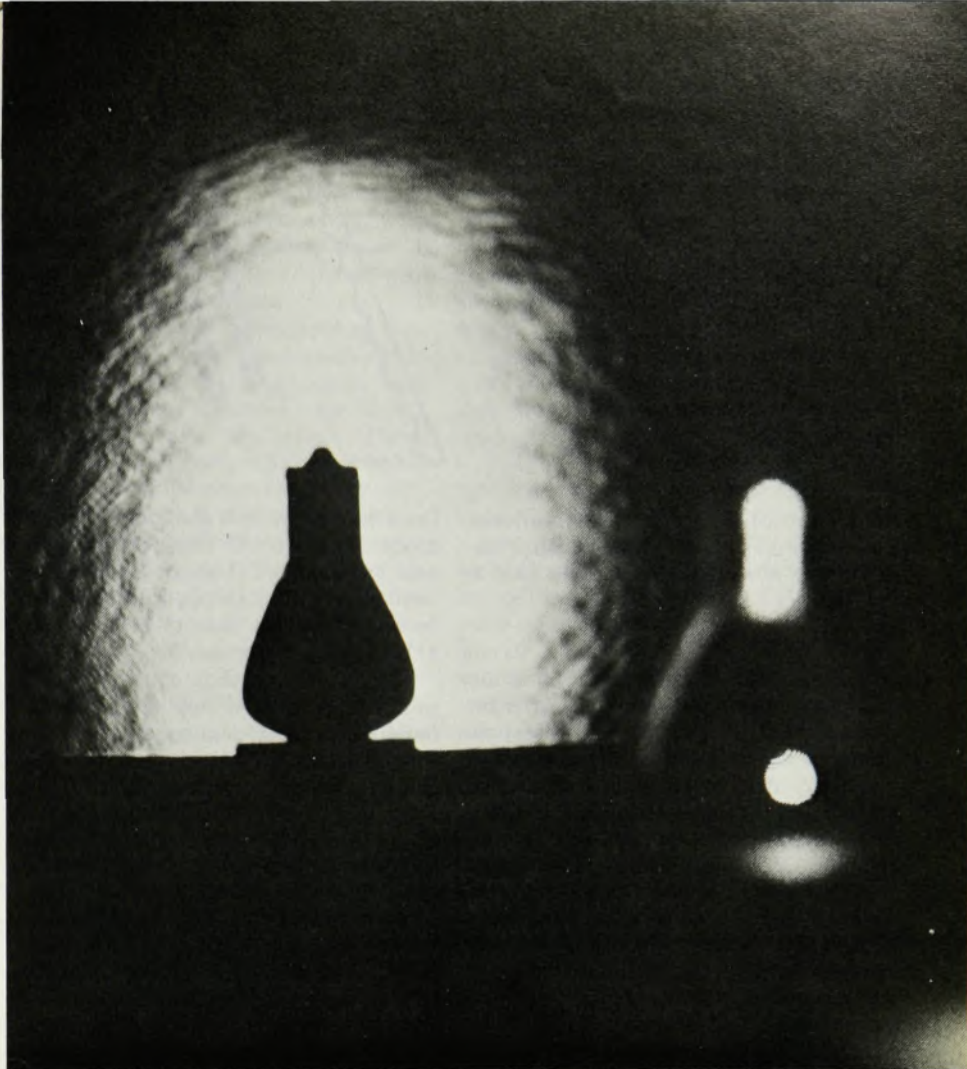
Lead-chalcogenide diode lasers can

Howard Schlossberg is with the Optical Physics Laboratory at the Air Force Cambridge Research Laboratory, and Paul Kelley is with the Lincoln Laboratory of the Massachusetts Institute of Technology.

Resonance absorption in sodium vapor demonstrates the spectroscopic uses of tunable narrow-linewidth lasers. In both photos, the expanding dye-laser beam travels from lower right toward the sodium-vapor filled cell, which is at 200 deg C. If the dye laser is tuned to the NaD_2 line at 5889.95 Å, resonance absorption occurs, the cell is opaque to the laser beam, and a shadow is cast. If the dye laser is tuned to 5889.85 Å, a wavelength change of 0.10 Å, the sodium cell does not strongly absorb the radiation, and no shadow results. Photos from Alan Pike and Michael Hercher.

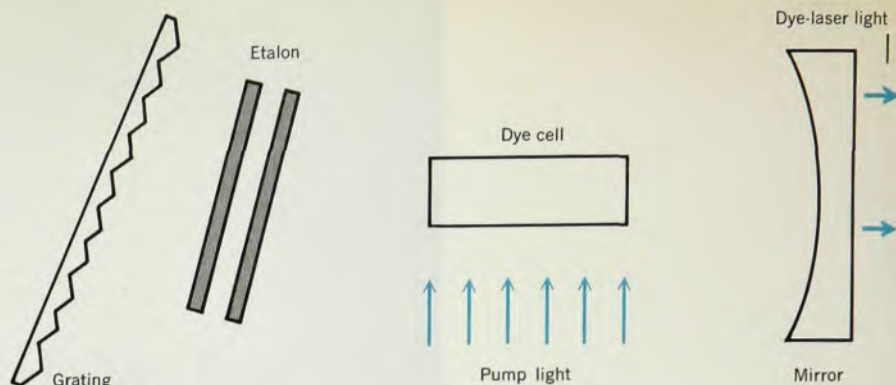
produce about 1 mW continuous, tunable, narrow-line radiation at liquid-helium temperature and 10 watts pulsed at 77 K. The infrared frequency of these lasers has been coarse-tuned by adjusting the chemical composition ($\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ and $\text{PbS}_{1-x}\text{Se}_x$ lasers), which changes the energy gap of the semiconductor, and, while operating as lasers, by changing pressure, temperature or magnetic field. PbSe diodes, for example, have been pressure-tuned from 8 to 22 microns. The magnetic-field tuning rate of these materials is about 0.5 cm^{-1} per kG. Fine tuning can also be obtained by pressure, temperature, and magnetic-field variations of the index of refraction and thus, the cavity-mode frequency.

The infrared emission frequency of the laser is, within the spontaneous-emission bandwidth, determined by the refractive index of the semiconductor and the physical length of the cavity. This frequency can be fine-tuned most easily by a small change in the diode current,⁷ which alters the refractive index of the mixed-crystal semiconductor (which has low thermal conductivity) through heating. A single diode laser can be "tuned" in this manner over 40 cm^{-1} in continuous bands up to 2 cm^{-1} wide, but, because of a change in laser operation from one cavity mode to another ("mode hopping"), emission occurs at only about one half of the frequencies in this tuning range. That the diode laser is a high-resolution source has been demonstrated by a heterodyne experiment with a carbon-dioxide laser, in which



A typical narrow-band dye-laser arrangement. The grating, etalon, mirror combination forms an optical resonator only over a very narrow wavelength region. The dye emission line, although broad, is homogeneous, so that all of the excited molecules can be made to emit within the resonator linewidth.

Figure 1



the linewidth of a 0.24-milliwatt $\text{Pb}_{0.88}\text{Sn}_{0.12}\text{Te}$ diode laser at 10.6 microns was shown to be 54 kHz ($1.8 \times 10^{-6} \text{ cm}^{-1}$).⁸

Nonlinear optical devices

The spin-flip Raman laser⁹ is a device that uses a fixed-frequency laser (at present, a CO or CO_2 gas laser) to pump a semiconductor crystal in a magnetic field (see figure 3). The pump-laser photons lose energy when they collide with an electron in the crystal and flip its spin. The downshifted Raman photon is separated in energy from the pump photon by the change in electron spin energy $g\beta H$, where g is the gyromagnetic ratio of the conduction electron, β is the Bohr magneton and H is the magnetic field strength. Consequently, the Raman photon frequency depends on magnetic field. At sufficiently high pump power, stimulated emission of Raman photons can exceed losses, and exponential gain and oscillation occurs.

In the most widely studied spin-flip Raman laser, n-type indium antimonide is the semiconductor crystal. This

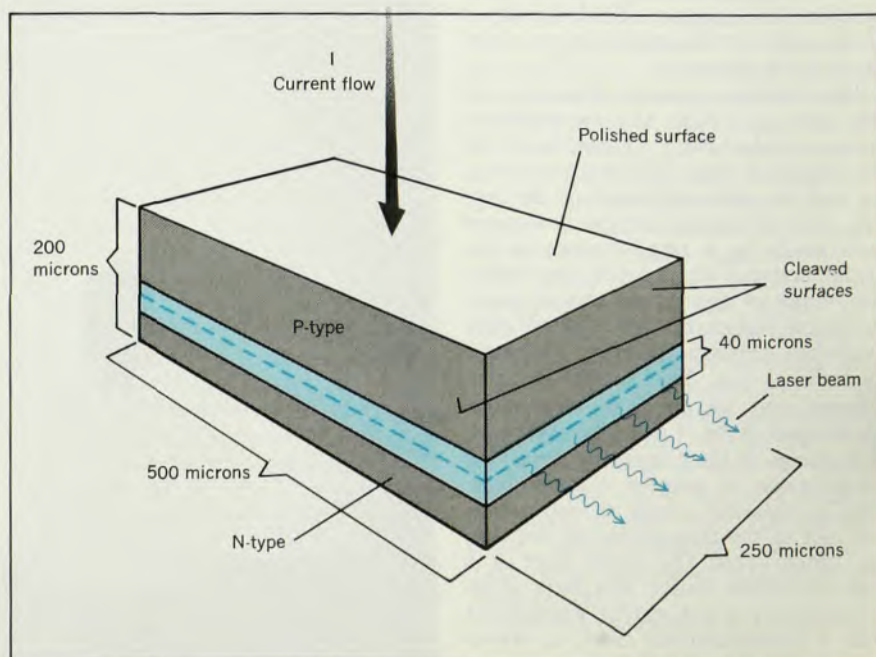
laser has been operated in the pulsed mode (CO_2 or CO laser as pump^{9,10}) and cw mode (CO pump). Under cw conditions, short-term stability relative to the CO pump laser of better than 1 kHz has been observed.¹¹

The resonance that exists when the pump laser is at a frequency near the band gap of the semiconductor allows cw operation with low pump threshold powers at these frequencies.¹⁰ Less than 50 mW of TEM_{00} pump-laser power in an estimated 50- to 100-micron focal diameter in the crystal has been found sufficient for the case in which incident pump and Raman beams were colinear, with maximum output powers in excess of one watt cw. In this case, over 75% of the pump energy is converted to the first downshifted Raman mode. At high conversion efficiencies, the beam divergence of the Raman laser is less than 40 mrad, consistent with a TEM_{00} mode divergence from a 250-micron-diameter laser cavity. Operation in single axial and single transverse modes has been observed, as well as mode hopping during magnetic-field tuning. About 40%

of the overall tuning range is covered, with continuous tuning in each mode of about one-third of a wavenumber. Mode pulling by the emission peak causes the fine tuning, in contrast to the diode laser case, in which a change in refractive index tunes the cavity.

The other important nonlinear optical device concepts that have been developed, optical mixing and optical parametric oscillation, rely on the properties of a nonlinear crystal. In this noncentrosymmetric crystal a significantly large dielectric polarization, quadratic in the strength of an applied laser field, can be induced. The nonlinear polarization can radiate, permitting harmonic generation or sum- and difference-frequency generation when fields at two frequencies are applied. For a substantial buildup of radiation at these new frequencies one must satisfy the "phase matching" condition: The wave vectors of the applied fields and the generated field must have the same relationship as their frequencies, so that, for sum-frequency generation where $\omega_1 + \omega_2 = \omega_3$ then $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3$. The usual way to satisfy this condition

Geometry of a lead-salt semiconductor diode laser. The radiating area here is 40 microns by 250 microns; dashed line shows the position of the p-n junction. Figure 2



is to select the propagation direction and crystal temperature so that crystal birefringence offsets the effects of dispersion.

If we have a tunable laser in one region of the spectrum we can get tunable outputs at shorter or longer wavelengths with sum-frequency and difference-frequency generation. Dye lasers are often the original tunable source. Pulsed difference-frequency generation from the output of a ruby laser plus a dye laser has achieved 6 kilowatts¹² of infrared power tunable between 3.1 and 4.5 microns, with a bandwidth of about 10 cm^{-1} . The lower limit here can easily be extended to 1.7 microns with a different dye and the bandwidth reduced to better than 1 cm^{-1} . With the most recently developed dye lasers,¹ peak infrared powers of several hundred watts could be generated at repetition rates up to 30 pulses per second, with long-term stability better than 0.05 cm^{-1} . Longer wavelengths can be generated with other crystals; proustite (AgAs_2S_3) and HgS are usable to about 12 microns. If the two input frequencies are very close, far-infrared frequencies can be generated, for example in LiIO_3 . With the spin-flip laser as the input, far-infrared radiation could be generated in GaAs and Te , among other materials.

Sum-frequency generation has also been accomplished by mixing ruby-laser and dye-laser output.¹³ Between 100 and 200 kW were generated in a 7-nanosec pulse with a 15 cm^{-1} bandwidth. This technique, with ammonium dihydrogen phosphate (ADP) as the nonlinear material, can provide an output tuned down to about $2350\text{\AA}$. Recently, second-harmonic generation, where $\omega_1 = \omega_2 = \omega_3/2$, of a dye

laser in ADP has given¹⁴ megawatt pulses with about 20 millijoules of energy tunable from 2800 to $2900\text{\AA}$ with a 30 cm^{-1} bandwidth. With the most advanced dye lasers, this technique could give kilowatts of peak power with a reasonable repetition rate (about 30 pulses per sec) and long-term bandwidths of less than 0.15 cm^{-1} .

Currently under development as nonlinear materials in the infrared are I-III-VI₂ and II-IV-V₂ compounds with the chalcopyrite structure, for example, AgGaS_2 and ZnGeP_2 . These phase-matchable materials can be used for sum- and difference-frequency generation as well as in parametric oscillators. Further developments in materials technology could yield materials with improved optical quality that can be widely employed in infrared nonlinear optical devices.

Optical parametric oscillator

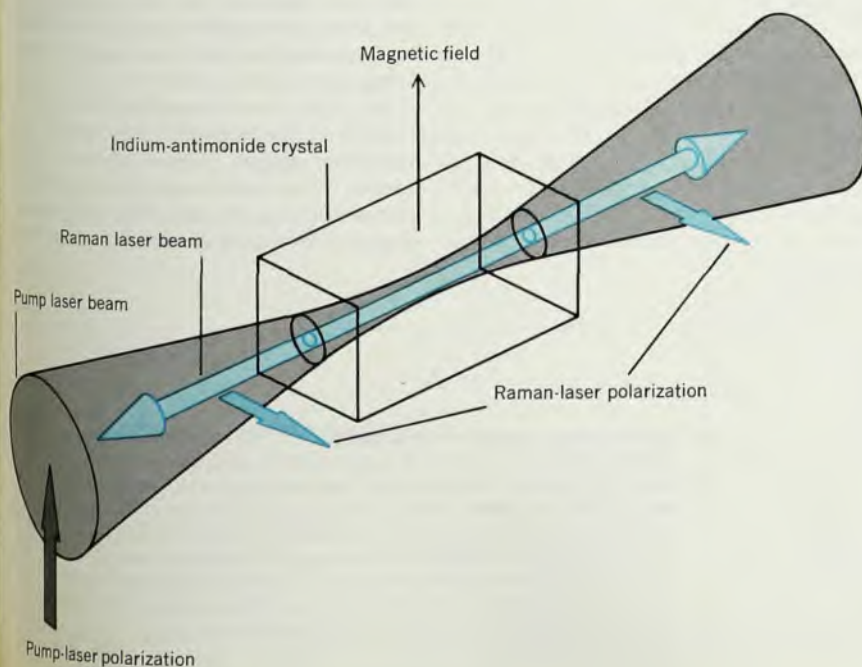
The optical parametric oscillator closely resembles microwave parametric oscillators and amplifiers, and its operation is also closely related to difference-frequency generation.¹⁵ The basic device is a nonlinear crystal placed between two wavelength-selective mirrors to form an optical cavity. A laser field at a frequency ω_p (the pump frequency) is applied to the crystal, usually through one of the end mirrors. Initially the pump radiation mixes with photon noise in the crystal, leading to a buildup of radiation at two frequencies ω_s (the signal frequency) and $\omega_i = \omega_p - \omega_s$, which are mutually phase matched for difference-frequency generation with the pump. If losses in the cavity are less than the gain of the buildup process, oscillation occurs. To change the phase-matched wave-

lengths, thereby tuning the oscillator, the indices of refraction of the crystal are varied with temperature, crystal rotation or electric field.

Optical cavities can be resonant for both ω_s and ω_i ("doubly resonant") or for only one ("singly resonant"). Although singly resonant cavities have advantages in terms of frequency stability, and mirror coatings for them are easier to make, they need greater pump power to reach oscillation threshold. Internal parametric oscillators, in which the nonlinear crystal is within the cavity of the pump laser, have advantages under some conditions.¹⁶

Parametric oscillators operate cw, as well as pulsed, and cw thresholds can be as low as 2.8 mW.¹⁵ Continuous-wave devices, however, are difficult to operate, need careful geometric design and tend to be unstable.

A singly resonant LiNbO_3 oscillator, pumped with a ruby laser, has yielded peak power up to 340 kW and has had up to 45% conversion efficiency. The average power is as high as 350 mW near 2.1 microns, with average power-conversion efficiency of 70%, when an internal oscillator with a LiNbO_3 crystal in a repetitively Q-switched Nd:YAG laser cavity is used.¹⁶ In the 9–12 micron region, R. L. Herbst and Robert Byer achieve parametric oscillation by using the 1.8-micron line of Q-switched Nd:YAG as pump and CdSe as the nonlinear material.¹⁷ No single optical parametric oscillator has been tuned over a very wide region because of difficulties with mirror coatings and materials. A commercial device is available, however, that, with changes of mirrors on both the oscillator and pump laser, operates anywhere be-



Continuous-wave spin-flip Raman laser geometry. Pump-laser photons lose energy when they collide with an electron in the crystal and flip its spin; this dependence results in a Raman-photon frequency that is magnetic-field dependent. Figure 3

tween 0.55 and 3.5 microns, with peak powers of 80 watts to several hundred kilowatts and average powers between 1 and 40 mW, depending on wavelength. Long-term bandwidths of less than 0.05 cm^{-1} have been achieved. Although interference techniques have allowed single-mode operation in several systems, long-term stability has not been carefully measured. One recently proposed and demonstrated scheme for long-term stability is to lock a parametric oscillator wavelength to a gas absorption line.¹⁵ Recently, linewidths of less than 0.001 cm^{-1} , within the molecular Doppler limit, have been achieved in a parametric oscillator op-

erating at 2.5 microns.¹⁸ Chromatix Corp, Mountain View, Calif., has developed an optical parametric oscillator system with a similar linewidth.

A very promising new technique for generating tunable ultraviolet radiation is that of Stephen E. Harris and coworkers.¹⁹ They have shown that alkali-metal vapors can generate reasonably large fields at the third harmonic of an input field. By mixing-in proper proportions of an inert gas, phase matching can be achieved; the result could be megawatt pulses tunable down to $1000\text{\AA}$.

Numerous molecular gas lasers have been operated in the infrared. These

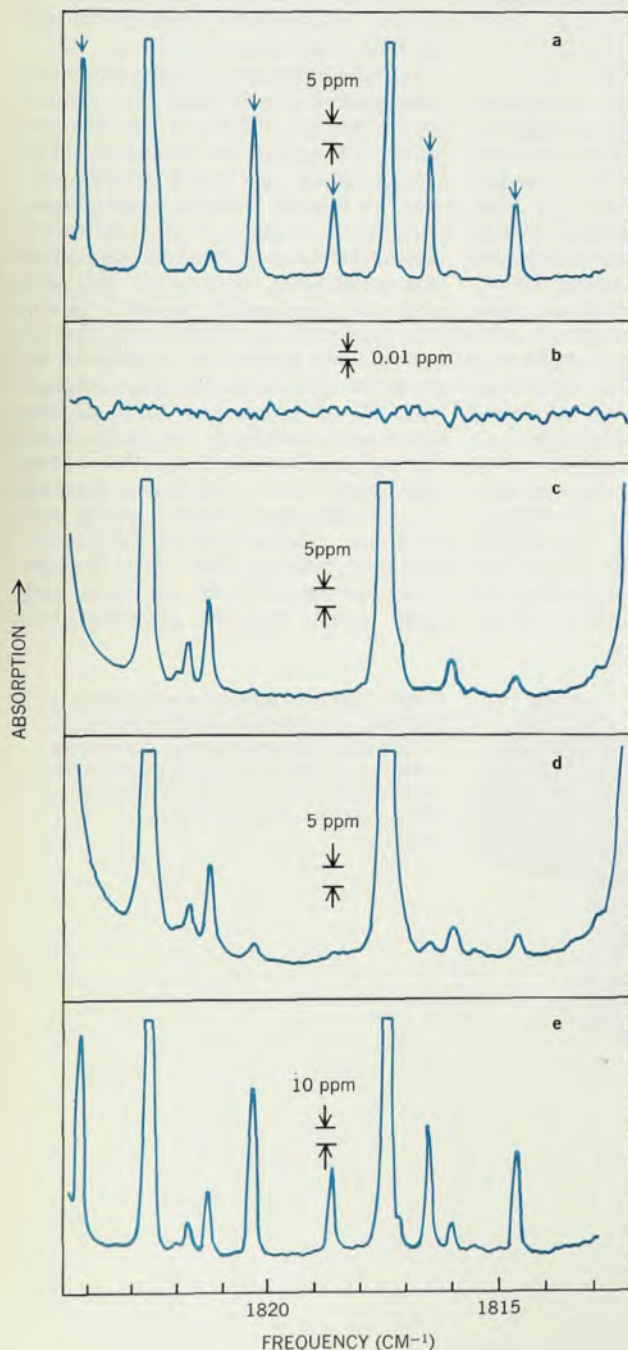
lasers oscillate on many discrete, closely spaced vibration-rotation lines. Recently a number of techniques have been developed for high-pressure operation, both pulsed and cw. At roughly five atmospheres, substantial overlap of the vibration-rotation lines occurs, leading to a very broad gain profile. Continuous tuning could then be obtained as in dye lasers, with very high power. Even at lower pressures one can introduce sidebands on the laser frequencies by conventional modulation techniques to produce tunable radiation in between the discrete lines.²⁰

Tunable-laser properties

For most applications, the lasers must have certain features in addition to tunability, as we shall now summarize. Extremely narrow linewidths have been achieved for all the tunable lasers. Each has been made to operate in a single mode of its optical resonator: in the semiconductor and spin-flip Raman laser by taking advantage of the small size and consequent wide spacing of their resonator frequencies, and in the dye lasers and parametric oscillators by the use of wavelength-selective elements such as diffraction gratings and interferometers.

A linewidth as narrow as 54 kHz has been measured for a semiconductor diode laser.⁸ Less than 1 kHz has been reached with a spin-flip Raman laser.¹¹ For a pulsed dye laser, a linewidth of 35 MHz, corresponding closely to the pulse duration of 10 nanosec, has been reported,¹ and the same linewidth has been obtained from a cw dye laser.⁴ A pulsed parametric oscillator has yielded a linewidth of 30 MHz.¹⁸ An area closely related to linewidth is frequency stability, both long and short term; we have seen that solving this problem depends on how successfully the optical resonator can be stabilized against thermal and mechanical variations, stray fields, and so on.

As with most lasers, an important feature is the spatial coherence of the tunable output. Spatial coherence means that, compared with conventional sources, beams with very small angular divergence can be generated



Optoacoustic spectra of nitric oxide (NO), taken with a spin-flip Raman laser, illustrate the possibilities for tunable lasers in pollution monitoring. Lines marked with arrows are NO lines, others are attributed to water vapor. Spectrum a is of 20 ppm NO in N_2 at 300 torr total pressure. In b we see the noise level with no gas in the cell; this spectrum indicates that concentrations of NO as low as 0.01 ppm can be detected. The three lower spectra are samples, at 300 torr, of (c) laboratory air, (d) air near a moderately busy highway and (e) exhaust from a decelerating car. From reference 22. Figure 4

with proper optics or, if focussing optics are used, much smaller spot sizes and consequently higher intensities can be achieved. Beam divergence or spot size at a focal point can often be made diffraction limited. Small angular divergence is particularly significant in applications of tunable lasers involving long paths, and high intensity is important where nonlinear effects are to be observed. Small spot size is obviously desirable whenever small areas are involved, for example in certain wavelength-sensitive medical applications.

In most applications, the absolute power is less important than the power per unit spectral interval. For example, even the relatively modest power of a cw diode laser yields at least 10^{-9} watts per Hz, which corresponds to that emitted by a 2000-K blackbody having a diameter of the order of meters. The high power per unit spectral interval combines with the coherence in space to give high spectral brightness. Again, using the example of a cw semiconductor laser, the spectral brightness is at least 10^{-5} W/cm²StrHz, orders of magnitude greater than the sun.

Absorption spectroscopy

In addition to the obvious applications in basic research, other important uses for rapid high-resolution laser absorption spectroscopy include ambient air-pollution monitoring, automobile-exhaust analyses and monitoring of industrial processes and pipeline flow.²¹ Preliminary studies of tunable-laser auto-exhaust analyses and ambient air-pollution monitoring have, in fact, already been carried out (see figure 4 and references 21 and 22).

Absorption spectroscopy of gases can be performed with great rapidity at atmospheric pressure when only moderate resolution (relative to the tunable-laser limits), of the order of 0.2 cm^{-1} (6 GHz) is useful. A portion of the first overtone spectrum ($0 \rightarrow 2$) of HBr in the 2-micron region is seen in figure 5. The spectrum of these very weak transitions was taken with a parametric oscillator that had a linewidth of

about 0.3 cm^{-1} . Spectra of NO in the 5.5-micron region have been taken at 300-torr pressure with the spin-flip Raman laser (figure 4).²² In this case an optoacoustic detector was used to give detection limits of one part in 10^8 of NO in the gas sample.

When greater resolution is desired, the gas pressure can be reduced until the Doppler limit is reached. At ten microns wavelength this occurs at ten torr or less, leading to resolutions of a fraction of the $0.001\text{--}0.003\text{ cm}^{-1}$ (30–90 MHz) Doppler widths. Note that the absorption constants do not change until the Doppler limit is reached. A Doppler-limited spectrum of SF₆ obtained with a tunable PbSnTe diode laser²¹ is seen in figure 6. The abscissa of this figure was calibrated relative to the P(16) line of the CO₂ laser by observing the heterodyne signal between the CO₂ laser and a diode laser passed through a SF₆ cell and tuned through the CO₂ laser line. High-resolution studies of other molecules such as CO, NO, SO₂, H₂O, NH₃ and C₂H₄ have also been carried out in the Doppler-limited region with tunable diode lasers. Doppler-limited spectra of HF have recently been obtained by J. Pinard, J. F. Young and Stephen E. Harris, with the parametric-oscillator system described in reference 18. Recently, Doppler-limited spectra of H₂O have been obtained with the spin-flip laser.¹¹ We shall see that saturated absorption techniques can provide even narrower linewidths.

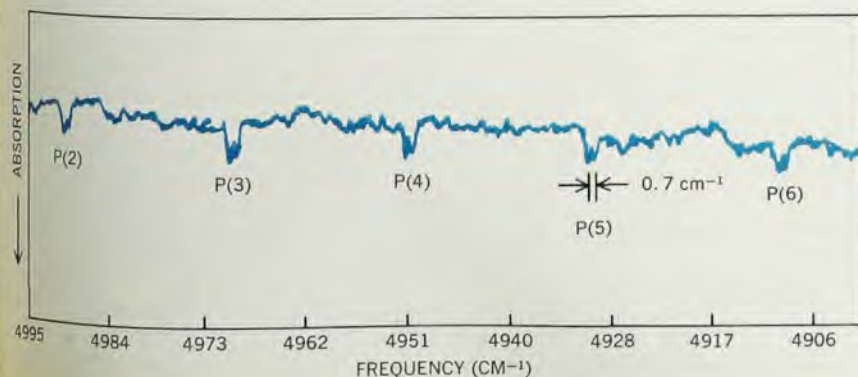
Remote monitoring

The wavelength dependence of atmospheric transmission can be studied at effectively infinite resolution with tunable coherent sources. At atmospheric pressure, linewidths are in the 3–10 GHz range, which, in the infrared region, is much better than the resolution limit of any blackbody-spectrometer systems in field use. Tunable lasers can determine the precise absorption structure of clean air as well as the concentration of atmospheric pollutants down to a few parts in 10^9 . Averages of pollutant concentrations over kilometer paths will be of great

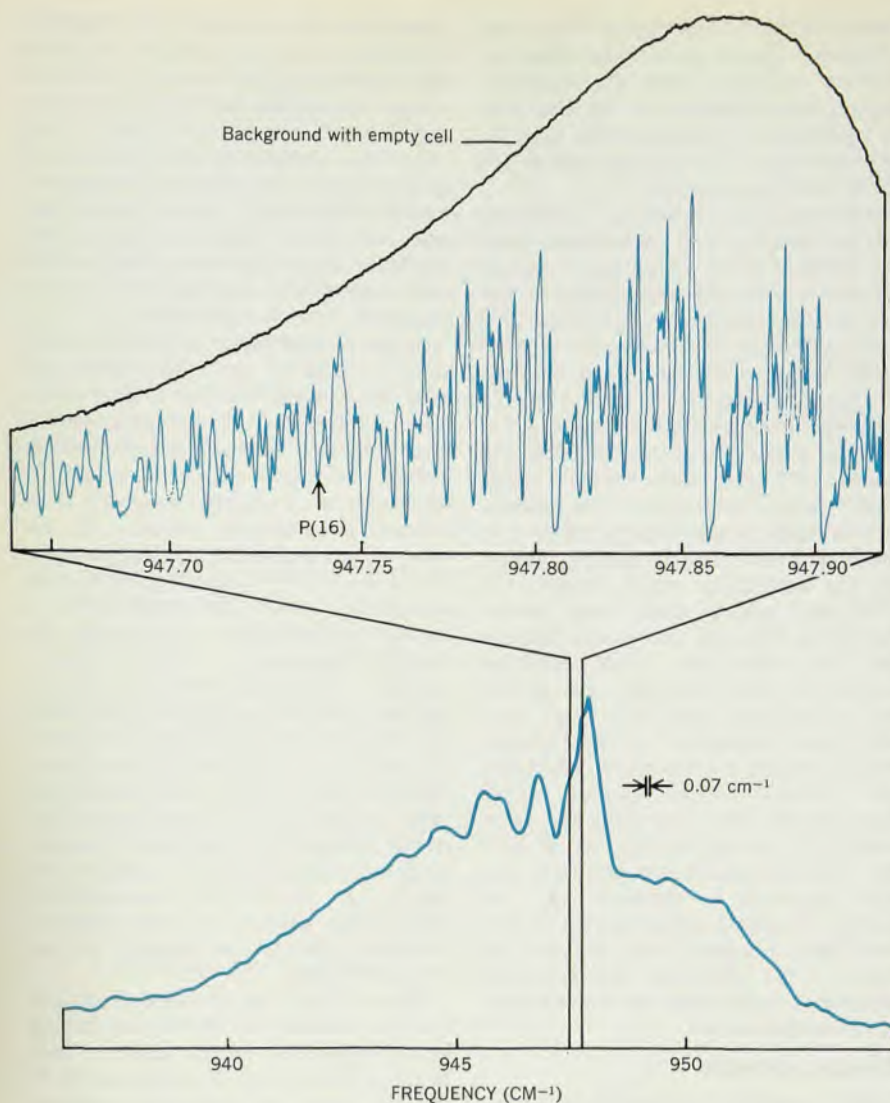
significance in ambient air analyses. In the infrared, this method is generally limited to spectral regions free of strong absorption bands of abundant atmospheric constituents (H₂O and CO₂); the spectral interval from 8–13 microns is an example of a relatively transparent region. In the visible and near ultraviolet, electronic absorption bands in atoms and molecules can be used down to 0.25 microns, the onset of absorption by molecular oxygen.

Infrared heterodyne detection of remote emission²¹ can be carried out with the tunable laser as a local oscillator. Examples of molecular emissions that are detectable in this fashion include pollutant gases in industrial smokestacks, jet-engine exhausts and infrared astronomical sources. In the case of a smokestack of temperature 400 K in a 300-K background of unit emissivity, a 500-MHz bandwidth, a ten-second integration time and an absorption constant $\alpha = 10^{-5}\text{ cm}^{-1}$ (where c is concentration in parts per million), we find a signal-to-noise ratio for ideal photodetection at 10 microns of about $1.4\sqrt{\ell}$, where ℓ is the plume thickness in meters. Thus concentrations in excess of 10 ppm should be readily detectable. The size of the telescope must be sufficient to resolve the plume; at 10 microns, assuming a meter-thick plume, a 2-cm diameter telescope aperture is required at one kilometer range.

Remote detection of molecules might also be carried out by looking at the Raman-scattered return from a laser beam projected into the atmosphere.²³ In this case, the radiation scattered from a given molecular species differs in frequency from the exciting radiation by an amount dependent on the characteristic vibrational and rotational energy changes of the molecule. Return signal strengths decrease at least as the inverse square of distance from the projector to the sample volume; range information can be obtained with a pulsed laser. For fixed-frequency lasers (such as ruby or Nd) this method appears limited to a range of ten to a hundred meters for pollutants in smokestack exhaust gases and to very



Absorption spectrum of the first overtone of hydrogen bromide at one atmosphere pressure, taken with an optical parametric oscillator. Frequency sweep, about 11 cm^{-1} per minute, was accomplished by changing the temperature of the nonlinear crystal. The observed doublet structure is the isotope splitting between HBr⁷⁹ and HBr⁸¹. This spectrum from Richard W. Wallace, Chromatix Corp. Figure 5



Spectra of sulfur hexafluoride. Grating-spectrometer scan of the ν_2 band (bottom), taken in a 25-cm cell at a pressure of 0.1 torr SF_6 has 0.07-cm^{-1} resolution. Diode-laser scan (top, SF_6 pressure 0.1 torr, cell length 10 cm) is of band segment near the P(16) CO_2 laser line. The diode laser is capable of resolving frequencies to $3 \times 10^{-6}\text{-cm}^{-1}$. Grating-spectrometer scan from H. Brunet, M. Perez, *J. Mol. Spec.* **29**, 472 (1969). Figure 6

intermediate molecular excited states, free atoms or radicals, which must be produced at a rate comparable to their relaxation or recombination rate for the reaction to proceed. Photochemistry involves the use of radiation to produce these intermediate species and thus initiate or control the chemical reaction.

Tunable lasers provide a remarkably powerful tool to the photochemist. Extremely fast reactions and short-lived species can be studied with a Q-switched or mode-locked tunable laser as a flash-photolysis source. The high spatial coherence of tunable lasers means large densities of intermediate species can be formed, and very narrow linewidths allow extremely sensitive selection of excited states. In turn this could allow the control of branching ratios and yields in chemical processes.

A number of experiments have illustrated the possibilities for tunable-laser applications to chemistry. Nikolai Basov and coworkers²⁵ have shown how vibrational excitation of molecules can lead to unique products in a reaction, and Vladilen Letokhov and his coworkers²⁶ have demonstrated a technique that selectively dissociates molecules in a mixture of gases.

Separation of isotopes is an important potential application of these ideas. A narrow-band tunable ultraviolet source might be used directly to dissociate only those molecules containing the desired isotope. However, in general it might be hard to find appropriate energy levels with no overlap between isotopic species. Alternatively, molecules containing the desired isotope could be selectively excited to high vibrational states and simultaneously irradiated with ultraviolet light as in Letokhov's experiment. The ultraviolet photons, having insufficient energy to dissociate ground-state molecules, would dissociate only the vibrationally excited ones, thereby creating a high density of atoms of the desired isotope. If a subsequent reaction of these atoms could be arranged, products containing only the desired isotope could be separated chemically. Isotope separation with a high-power infrared laser has also been reported.²⁷

A great variety of relaxation phenomena has already been studied by

short distances for pollutant sampling in ambient air. On the other hand, Raman scattering from N_2 (which forms about 80% of the air) can be observed at tens of kilometers range while H_2O scattering (a few tenths of a percent) has been observed at ranges up to 2.5 kilometers. Tunable lasers and the resultant resonant Raman scattering may allow range increases of about a factor of 30. Difficulties come from background sources such as sunlight, as well as broadband fluorescence, interference from other Raman scatterers and nonzero rejection of laser light in the spectrometer.

Absorption of tunable laser light and subsequent reradiation can be used²³ for remote detection. The return from this process also decreases at least as the inverse-square power of the distance between the laser and the sample volume. In the visible and ultraviolet, collisionally quenched resonance-fluorescence cross sections for molecules are about equivalent to resonance Raman cross sections. Given a range resolution of a few meters, a few kilom-

eters range might be achieved for concentrations typical of smokestacks, but tens of meters is about the maximum range for ambient air. In the infrared, ranges of 10–100 meters are possible for typical smokestack concentrations (10–100 ppm). For atoms, resonance-fluorescence cross sections are larger than for molecules because of stronger absorption, shorter radiative lifetimes and less quenching. It is possible to detect atomic pollutants to better than a part in 10^{11} to ranges of a few kilometers, if we assume the absorption bands do not occur beyond atmospheric cutoff. Atomic sodium has been detected²⁴ by resonance scattering at altitudes of about 90 km in concentration of about 10^4 atoms per cc, with a dye laser tuned to the D lines. The cross section on the line center is about $10^{-12}\text{ cm}^2/\text{Str}$; collisional quenching is negligible at these altitudes.

Photochemistry

The mechanisms by which most chemical reactions proceed involve in-

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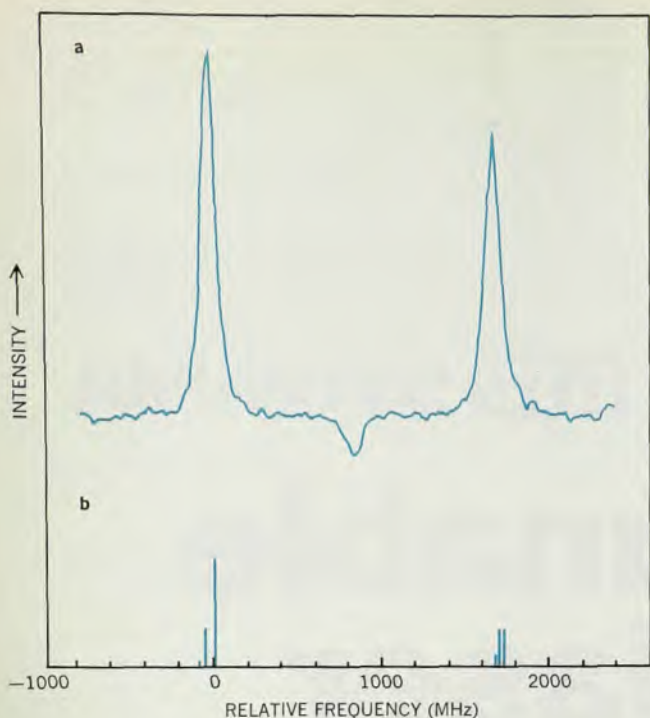
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Saturation spectrum of the sodium D₂ line (a). Probe radiation pulse travelled in a sodium cell in a direction nearly 180 deg relative to a saturating pulse of the same frequency. The two positive peaks correspond to hyperfine components (see b); the dip appears when the radiation frequency is halfway between the two sets of hyperfine components. From reference 3.

Figure 7

means of a fixed-frequency laser. A pulsed laser source excites a sample in one mode, and the population of the ground or some excited state is monitored to determine the rate of energy transfer. Monitoring techniques have included fluorescence, absorption and Raman emission, as well as buildup of translational temperature in a gas. The applicability of this technique to general systems is obviously vastly increased with the availability of tunable pulsed lasers as the exciting source.

The resolution of very closely spaced absorption lines is often obscured in normal spectroscopy by inhomogeneous broadening. In gases the distribution of molecular velocities causes Doppler broadening, whereas in solids, strains or inhomogeneous fields are usually responsible. The limitations of inhomogeneous broadening can be overcome with techniques developed by Ali Javan and his coworkers if the source used has spectral density high enough to cause a saturated absorption. This saturated absorption is associated with energy-level population changes caused by a strong field, and a probe field can detect these changes. With fixed-frequency lasers, fine structure, hyperfine structure, isotope shifts and natural and collision linewidths of transitions have been measured. The availability of tunable lasers will make these non-linear spectroscopic techniques generally applicable to ultraprecision spectroscopy. Figure 7 shows this technique applied³ to the Na D₂ line. An N₂-pumped dye laser was used as the tunable source. The Doppler width of the Na line is about 1.35 GHz.

Saturation resonances of absorptive transitions with tunable lasers, and

frequency mixing of visible, infrared and microwave radiation can be used to develop secondary wavelength standards with accuracies of at least one in 10⁸ through the visible and infrared.

Recently, a tunable GaAs diode laser has been used²⁸ to pump Cs¹³³ vapor, creating a population inversion in the hyperfine levels of the ground state. This achievement should allow development of a Cs¹³³ maser, with possibilities for compact, durable, primary frequency standards.

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