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Detection of Air Pollutants with Tunable Diode Lasers

Sensitive, specific detection of pollutant gases can be obtained with tunable semiconductor lasers.

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In this article we describe the use of tunable $Pb_{1-x}Sn_xTe$ semiconductor diode lasers in remote or long-range sensing and point sampling of molecular pollutant gases. Remote sensing can be accomplished by means of measurements of the infrared absorption or emission lines characteristic of a particular pollutant at atmospheric pressure. Point sampling permits gas pressures to be reduced until the Doppler-broadened infrared absorption structure is revealed, thereby making possible very high specificity. Since one measurement technique is used for all the pollutant gases, the operational requirements are simplified. Moreover, the essentially instantaneous response is advantageous for a number of applications.

Several optical techniques for the detection of pollutant gases are now being explored in various laboratories. They range from classical methods in which selective filters, spectrographs, interferometers, and optical-correlation instruments are used (*1*) to the use of lasers for direct absorption (*2*) and Raman scattering measurements (*3*). One advantage of optical sensing (*4*) over conventional wet chemical methods is that one can perform the measurements in situ by measuring emission spectra, by detecting scattered laser radiation, or by making transmission measurements over relatively long atmospheric paths. Infrared spectroscopy is considered an important technique since each of the major molecular pollutants contains at least one strong band in the region from 3 to 15 micrometers. Dispersive infrared instruments now being used in the field usually have resolutions that are much poorer than the linewidths of typical gases at atmospheric pressure, and thus potentially useful information is lost. Even when high-quality spectrometers are used, the resolving power must usually be reduced in order to maintain a reasonable signal-to-noise ratio with the relatively low power per unit spectral range available from incoherent sources. The use of gas lasers as nondispersive instruments, on the other hand, is severely restricted by the fact that these lasers cannot be tuned appreciably from their nominal wavelengths, and the match to pollutant gas absorption lines is seldom ideal (*2*).

Semiconductor lasers of $Pb_{1-x}Sn_xTe$ can be "tailored" chemically, by an adjustment of the composition factor x, to emit anywhere in the wavelength range from 6.5 to 32 micrometers (*5*), thereby permitting an ideal match to the strong infrared absorption lines of most of the molecular pollutant gases. Individual lead-salt lasers can be tuned by applying pressure (*6*), by applying an external magnetic field (*7*), or by varying the laser temperature (*8*). In a simple manifestation of temperature-tuning, a $Pb_{1-x}Sn_xTe$ diode laser can be tuned over a range of 40 reciprocal centimeters quasi-continuously (from one continuously tunable longitudinal mode to another) by changing the diode curent. This tuning range is sufficient to permit identification of the spectral signature of a given pollutant even in the presence of other molecular species, and to permit a quantitative determination of its concentration. These features overcome the major limitations of conventional gas lasers in monitoring applications.

Other tunable laser sources may also be useful for air pollution monitoring. These include the spin-flip Raman lasers (*9*), organic dye lasers, and systems involving parametric oscillators or difference frequency generators. At the present time these devices are much more complex than the tunable semiconductor diode lasers; nevertheless, their wide tuning ranges should soon find many applications in spectroscopy.

Tunable Diode Lasers

The diode lasers are fabricated from vapor-grown single crystals of Pb_{1-x}-Sn_xTe semiconducting material (*10*) by cleaving the crystals into rectangular parallelepipeds (each containing a *p-n* junction) of approximate overall dimensions 0.12 by 0.05 by 0.03 centimeter. Low-resistance ohmic contacts are formed, and the laser is then mounted onto the cold-finger of a cryogenic Dewar. Liquid helium temperatures are presently required for continuous laser operation, with pulsed operation possible at liquid nitrogen temperature (77°K). 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

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frequency can be fine-tuned by a small change in the diode current (*11*), which alters the refractive index of this mixed-crystal semiconductor (which has low thermal conductivity) through heating. A single diode laser can be "tuned" in this manner over 40 reciprocal centimeters in continuous bands up to 2 reciprocal centimeters wide; but because of a change in laser operation from one cavity mode to another, emission occurs at only about one-half of the frequencies in this tuning range. Although continuous tuning is essential for fundamental high-resolution spectroscopic studies (*12*), the broader, quasi-continuous tuning is quite adequate for application to the detection of pollutant gases. That the diode laser provides effectively infinite resolution for these applications was demonstrated by a heterodyne experiment involving a carbon dioxide laser (*13*), in which we showed that the linewidth of a 0.24-milliwatt $Pb_{0.88}Sn_{0.12}Te$ diode laser at 10.6 micrometers was 54 kilohertz (1.8×10^{-6} reciprocal centimeter). By comparison, the narrowest Doppler-broadened linewidths of even the heaviest molecular pollutants are tens of megahertz at room temperature.

Application to Pollutant Detection

In a typical monitoring application, several $Pb_{1-x}Sn_xTe$ diode lasers would be used, each tailored to emit in a strongly absorbing infrared region of one of the pollutant gases. This arrangement is necessary because of the limited current-tuning range of these lasers, and desirable because it provides for increased specificity. The small size of these lasers makes it possible for several to be mounted into the same cryogenic Dewar. Specific applications to pollutant detection can be divided into three categories: point sampling, long-path atmospheric transmission, and remote emission sensing.

Point sampling. Use of this technique permits the absorption spectra to be measured at reduced pressure where possible overlap with neighboring spectral lines of the gas (or with other gases in the atmospheric sample) is minimized. Several experiments have been performed with $Pb_{0.88}Sn_{0.12}Te$ diode lasers in the 10.6-micrometer region to illustrate their usefulness in such an application. Figure 1 shows absorption profiles of the strong $sP(1,0)$ line of ammonia at several pressures. At low pressure the full linewidth at half peak absorption is seen to approximate the Doppler-limited value of 85 megahertz. As the ammonia pressure is increased to 0.5 torr, the cell (10 centimeters long) becomes essentially opaque to radiation near the line center. The improvement in sensitivity of this nondispersive technique can be appreciated if a comparison is made between this spectrum and one obtained with a grating spectrometer having a resolution of 0.1 to 0.2 reciprocal centimeter (*14*). With such a grating spectrometer an ammonia pressure of 5 torr in a cell 200 centimeters long produced the same maximum absorption as that shown here for the curve at a pressure of 50×10^{-3} torr where the amount of ammonia in the optical path is 2000 times smaller.

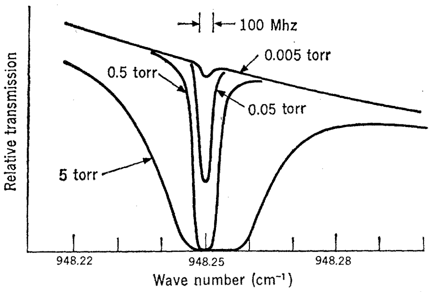

Fig. 1. Absorption spectra of the $sP(1,0)$ line of ammonia taken at various gas pressures with a tunable $Pb_{0.88}Sn_{0.12}Te$ diode laser. Cell length, 10 centimeters; temperature, 300°K. Resolution (diode laser linewidth) is better than 0.1 megahertz (3.3×10^{-6} reciprocal centimeter).

Figure 2 shows the ν_3 vibration-rotation band of sulfur hexafluoride obtained with a high-resolution grating spectrometer (*15*), as well as a segment of this band taken with a tunable $Pb_{0.88}Sn_{0.12}Te$ diode laser. Since sulfur hexafluoride is not usually present in the atmosphere, except near leakage sources such as high-voltage transformers, it can be used as a trace gas in certain monitoring applications (*16*). Sulfur hexafluoride has an exceedingly complex spectrum in the infrared region, which, as shown in Fig. 2, cannot be resolved in the 950-reciprocal centimeter region even with a high-quality grating spectrometer, but which is resolved by the diode laser scan. The widths of these lines correspond to the 29-megahertz value predicted for the Doppler-broadening of sulfur hexafluoride at room temperature, as compared with 85 megahertz for ammonia. Since a determination of mass can be made from the Doppler width, we can use tunable lasers to distinguish between gaseous species on the basis of their molecular weights, and thereby confirm pollutant identification by point sampling at reduced pressure. The abscissa of Fig. 2 was precisely calibrated relative to the $P(16)$ carbon dioxide laser line by viewing on a spectrum analyzer the wide-band heterodyned signal between this line and that from a tunable diode laser, with an absorption cell in the path of the diode laser beam (*12*).

Ethylene is one of the many hydrocarbons present in automobile exhaust. It is not usually monitored separately, but is lumped with the other hydrocarbons in a single measurement of total hydrocarbons. Figure 3A shows the absorption spectrum of ethylene near the Q branch of the ν_7 vibration-rotation band. The 25 percent drop in laser intensity near 949.24 reciprocal centimeters is produced by a shift of laser power from this longitudinal mode (*17*). By modulating the diode current with a small (0.1 percent) superimposed sinusoidal current at a frequency of a few hundred hertz, the laser emission frequency is modulated, thus allowing synchronous detection to be obtained without mechanical chopping, and, in addition, yielding the derivative of the absorption spectrum. This is shown in Fig. 3B where the top trace is a calibration spectrum of ethylene [1000 parts per million (ppm) in nitrogen]. A total gas pressure of 5 torr produces a maximum derivative signal for ethylene, representing a balance between pressure-broadening (upper limit) and a reduced total number of absorbing molecules (lower limit). The three lower traces represent spectra obtained from automobile exhaust specimens, also taken at a pressure of 5 torr, but with increased amplifier gain. By measuring the signal amplitudes and comparing them with the calibration curve, ethylene concentrations of from 22 to 74 ppm are deduced. It is unmistakably clear that each automobile exhaust sample contains ethylene, and that there is no interference from water vapor or any other molecular constituents present. Moreover, the poin at which the diode laser power changed abruptly is easily identifiable, and this power change affects neither the qualitative nor the quantitative comparisons.

There is no question that this technique is very specific at low pressure where Doppler-broadening is predomi nant and collision-broadening is negligible. Here each line is about 6×10^7 hertz (2×10^{-3} reciprocal centimeter) wide. The total (compositional) tuning range of the $Pb_{1-x}Sn_xTe$ diode lasers is about 3×10^{13} hertz. If we assume 50 gaseous molecular species in the atmosphere, each with 2000 reasonably strong lines in this range, the separation between individual lines should average about five times the linewidth.

The maximum absorption constant per unit pressure of the strongest lines of ammonia, sulfur hexafluoride, and ethylene approximate 2 reciprocal centimeters per torr. A detection limit of 0.3 ppm is expected for such lines in a cell 1 meter long on the basis of these initial experiments; but this limit should improve to the low parts-per-billion (ppb) range with the use of longer path-length multireflection cells and improved electronics. Moreover, noting that the strengths of strong absorption lines of these three quite different gases are nearly equal, we expect those for a number of pollutant gases to have the same general values, thus yielding ultimate detection limits that are also in the low parts-per-billion range.

Long-path atmospheric transmission. Even at atmospheric pressure the collision-broadened widths of spectral lines for typical gases are well below the resolution limit of infrared spectrometers now available for field use. If a tunable diode laser is used, the resolution limit is imposed by the pressure-broadened linewidth of the gas itself, to yield all the available optical information within the tuning range. Monitoring of pollutant gases in the atmosphere by long-path transmission has the advantage over point sampling in that it produces an *average* value for the pollutant gas concentration over the path, which may be of greater overall significance in ambient air analysis.

If we assume that the pressure-broadened linewidth of the pollutant gas equals the Doppler width at about 5 torr, and if we use a Doppler-broadened absorption constant per unit pressure of 2 reciprocal centimeters per torr, the absorption constant α (in reciprocal centimeters) at the center of a strong line at atmospheric pressure is

$$\alpha \approx 10^{-5} c \qquad (1)$$

where c is the concentration in parts per million. Over a 1-kilometer path, a pollutant gas with an average concentration of 1 ppb will produce a 0.1 percent change in transmission as we tune through this absorption line.

We shall now consider the collection efficiency. The emitting area of the diode laser (which operates in a low-order transverse mode) is 500 by 40 micrometers. If a $\times 20$ beam expander is used, a laser beam near a wavelength of 10 micrometers diverges to an area of about 10^5 square centimeters 1 kilometer from the source. For a collection area of 100 square centimeters and a 1-watt (peak) pulsed diode laser (tuned by varying either the pulse width or the repetition rate), the collected power in the absence of attenuation is 1 milliwatt. For an average pollutant concentration of 1 ppb over this path, a signal change of 1 microwatt is produced, and this change can be measured easily by the use of synchronous detection techniques. A corner reflector (of the order of 100 square centimeters or greater area to avoid diffraction losses in the return beam) situated remotely would eliminate the requirement of having instrumentation at two locations. By positioning a number of corner reflectors at various points around the source, many radial measurements could be made from the same monitoring station. It should also be pointed out that heterodyne detection of absorption lines, with an offset local oscillator, should yield an improved signal-to-noise ratio because of the narrow emission linewidth of the laser.

Transmission experiments should be performed with these diode lasers, operating both pulsed and continuous, to

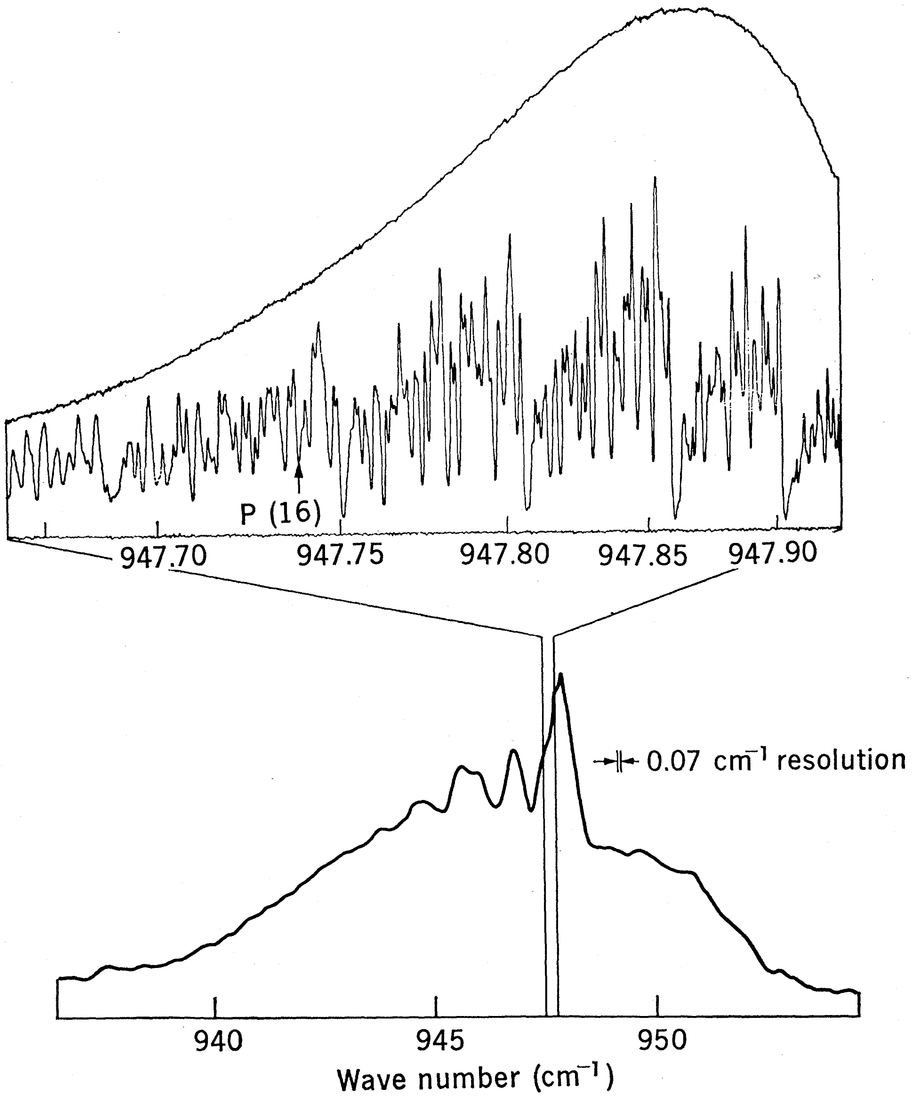

Fig. 2. (Bottom) Grating spectrometer absorption curve of the ν_3 band of sulfur hexafluoride at room temperature [adapted from the curve of Brunet and Perez (*15*)]; sulfur hexafluoride pressure, 0.1 torr; cell length, 25 centimeters. (Top) Diode laser transmission scan of a segment of this band near the $P(16)$ carbon dioxide laser line; sulfur hexafluoride pressure, 0.1 torr; cell length, 10 centimeters; resolution, 3×10^{-6} reciprocal centimeter.

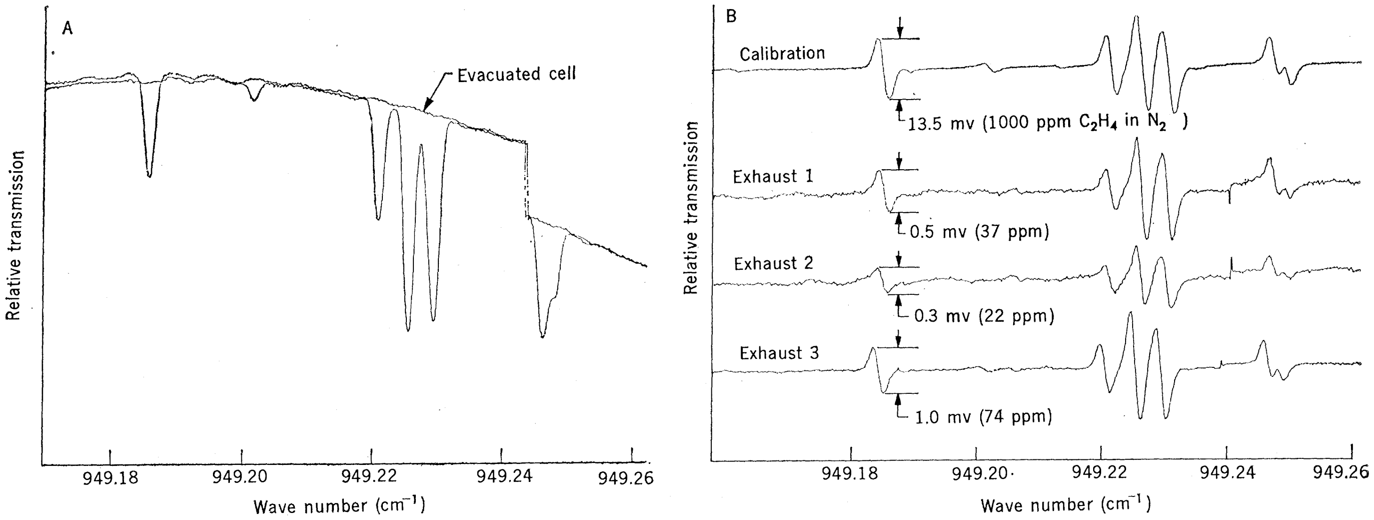

Fig. 3. (A) Absorption spectrum near the *Q* branch of ethylene at a pressure of 25×10^{-3} torr; cell length, 30 centimeters. See (*17*) for experimental procedure. (B) Derivative spectra of a calibration sample of ethylene (1000 ppm in nitrogen), and three automobile exhaust samples at different amplifier gain settings. Total pressure, 5 torr; cell length, 30 centimeters.

test the feasibility of long-path monitoring, and to show whether or not specificity in identifying a particular gaseous pollutant can be retained in the presence of absorption lines from other molecular constituents. As is well known, the high abundances of water vapor and carbon dioxide in the atmosphere can cause serious interference with infrared spectroscopy. We therefore restrict ourselves to considering the atmospheric "window" between 8 and 13 micrometers, which is approximately 500 reciprocal centimeters wide. For example, lasers tailored to emit in the 8.6-micrometer region are better suited to sulfur dioxide detection than those tailored to the (somewhat stronger) 7.5-micrometer absorption band. Even in the "window" region, absorption in the wings (many linewidths away from the line center) of water vapor and carbon dioxide lines may be greater than that corresponding to pollutants in small concentrations; however, this effect is somewhat compensated by the fact that the slopes of these wings are relatively flat in relation to the slope of a pollutant absorption line near its peak. Derivative spectroscopy, similar to that shown in Fig. 3B, will improve detection of these small peaks relative to the slowly varying Lorentzian wings of the dominant atmospheric absorption lines.

We shall now consider the interference between pollutant molecules at atmospheric pressure and start with the assumption that there are 25 molecular species present that absorb in the "window" between 8 and 13 micrometers. At atmospheric pressure the lines are broadened to about 6×10^9 hertz, and most of the structure within individual *J* values of the *P* and *R* branches disappears; the *Q* branch, if present, also loses most of its structure since closely spaced strong lines overlap and weak lines become lost in the tails of strong lines. We estimate, therefore, that at atmospheric pressure there are only 100 resolvable lines per molecule; this estimation implies that, on the average, the peaks of the lines are separated by one linewidth. On the assumption that each line is resolvable if a frequency interval three linewidths wide ($\sim 18 \times 10^9$ hertz) is not occupied by an absorption line from another molecule, and that there is a uniform probability distribution, there should be an average of five resolvable lines per molecular species.

Remote emission detection. One of the more difficult problems in air pollution monitoring is gaining access to industrial smokestacks. Optical remote-sensing techniques can be extremely useful for such applications.

If the $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$ diode laser is used as a tunable local oscillator, infrared heterodyne detection techniques (*18*) may be used to detect spectral emission lines from pollutants present in smokestack effluent (*19*). (The technique is similar to that used by radio astronomers to detect weak emissions from distant sources.) For heterodyne detection with an ideal photon counter (unit quantum efficiency and zero excess noise), the signal divided by the local oscillator-generated noise is given by

$$\frac{S}{N} = \frac{1}{h\nu}\left(\frac{\partial P_s}{\partial \nu}\right)(B\tau)^{1/2} \qquad (2)$$

where $\partial P_s/\partial \nu$ is the received signal power per unit frequency range in a single spatial mode, $h\nu$ is the infrared photon energy, *B* is the intermediate-frequency (IF) bandwidth of the detection system, and τ is the postdetection integration time. For the case where the solid angle subtended by the source at the detector is larger than the diffraction-limited solid angular resolution of the collection optics—a situation usually valid for smokestack plumes at ranges up to 1 kilometer and with optics as small as 1 square centimeter—the signal-to-noise ratio becomes

$$\frac{S}{N} = (1 - e^{-\alpha L})\,(B\tau)^{1/2} \times \left[\frac{1}{\exp\dfrac{h\nu}{kT_s} - 1} - \frac{\epsilon_b}{\exp\dfrac{h\nu}{kT_b} - 1}\right] \qquad (3)$$

where *L* is the thickness of the plume and T_s is its temperature, ϵ_b is the emissivity of the background at temperature T_b, and *k* is Boltzmann's constant. We have assumed: (i) that the IF bandwidth is less than the emission linewidth; (ii) that the emission and absorption due to the pollutant in the ambient atmosphere is not important because of the low concentration of the pollutant in the atmosphere relative to that in the plume; (iii) that the background attenuation from the wings of other molecular absorption lines is negligible; and (iv) that the local oscillator has sufficient power to overcome the other sources of noise (this requirement is readily satisfied with a 1-milliwatt diode laser). Since ϵ_b is often much smaller than unity (about 0.1 in the 10-micrometer region of the infrared when there are no clouds in the background), the source does not have to be hotter than the background; in fact, it could be colder. If we choose the following representative values for the parameters: $B = 10^8$ hertz, $\tau = 1$ second, $\alpha = 10^{-5}\, c$ reciprocal centimeters (where c is the concentration in parts per million), $L = 1$ meter, $h\nu = 0.125$ electron volt, $T_s = 400°\text{K}$, $T_b = 300°\text{K}$, and $\varepsilon_b = 1$, we find that

$$\frac{S}{N} \approx 0.2\, c$$

It should be possible, therefore, to carry out remote detection of pollutant molecules such as sulfur dioxide in smokestack plumes in concentrations greater than 10 ppm. In order to make absolute measurements of concentration, αL must be less than unity and the gas temperature must be known. If αL exceeds unity, so that the plume is optically dense, then a weaker emission line can be selected. Gas temperature can be measured in several ways: (i) by heterodyne detection of one of the stack gases at two wavelengths; (ii) by multicolor broadband radiometric measurements; or (iii) by direct measurement at the top of the stack.

Atmospheric turbulence may cause fluctuations in the received signal. This fluctuation can be overcome by alternately tuning the local oscillator between the peak emission wavelength of the pollutant gas and a wavelength of negligible emission in a time short enough so that turbulent effects are negligible (~ 1 millisecond), and then summing the excess pollutant signal for a large number of measurement intervals. Two local oscillators could also be used simultaneously, one operating at the emission peak and the other offset from it.

General Considerations

The absorption bands of a few of the major molecular pollutant gases (such as carbon monoxide and nitric oxide) are beyond the compositional tuning range of $Pb_{1-x}Sn_xTe$ diode lasers (*20*). Development of other semiconducting materials, for example, $PbS_{1-x}Se_x$, which has lased with an electron beam as pump source (*21*), may yield tunable diode lasers useful for detecting these gases as well. Semiconductor lasers that operate in the region from 3 to 6.5 micrometers should have the added advantage of a higher ultimate operating temperature.

Although temperatures below 20°K are presently required for continuous operation, pulsed laser emission can be obtained at liquid nitrogen temperature (77°K). With the availability of relatively inexpensive cryogenic coolers, it appears possible to achieve fast on-line monitoring of gases present in automobile exhausts or in chemical processing plants by direct absorption techniques with the use of diode lasers, each of which is tailored to a strong absorption line of one of the gases to be monitored. It is expected that further improvements in materials fabrication will eventually permit continuous operation at this temperature as well.

Summary

Preliminary experiments indicate that tunable $Pb_{1-x}Sn_xTe$ diode lasers will be useful in the identification and sensitive detection of most of the atmospheric pollutant gases. For point-sampling applications, concentrations in the parts-per-billion range should be measurable with very high specificity. For long-range atmospheric transmission techniques, the improved resolution capability and tunability of these diode lasers make them attractive replacements for spectrometers and fixed-frequency laser sources where operation at cryogenic temperatures is not a serious impediment. By using these lasers as tunable local oscillators in the infrared heterodyne configuration, remote passive detection of gases present in smokestack effluent appears possible. Finally, pulsed operation at temperatures available with simple cryogenic coolers permits immediate application to the fast detection of gases present in automobile exhaust and in chemical processing plants.

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