case is the computed total average annual spread between maximum and minimum gravity rather than the average of either.

There are strong correlations between frequency of eruption and variation in earth tidal force. During times of high tidal force, around 1930, 1955, and 1970, Grand Geyser erupted two to three times daily, only to become almost dormant during the years 1943 and 1960, when the tidal force was lowest. Grand's behavior is similar to although more striking than that observed in Old Faithful of California (*1*). On the other hand, the major activity of Steamboat is just the opposite, the tremendous eruptions occurring during periods of low tidal force. The correlation coefficient between frequency of eruption and variation in tidal force is 0.5 for Grand and -0.4 for Steamboat. However, a 1-year phase shift increases the correlation of Steamboat to -0.9, which suggests that there may be a short time delay in the response of the geyser to the tidal force. A similar shift in the case of Grand causes a slight decrease in correlation.

Geyser activity is controlled largely by the rate of heat flow to the geyser reservoir, the heat input being in the form of intermittent injections of superheated water flowing through the porous fractured mass of the geothermal area in which the geyser is located (*5*), so that it is not surprising that forced compression and expansion of the mass would influence the rate of flow. It is somewhat unexpected that an increase in the tidal force may in one instance increase and in the other instance decrease the rate of flow. However, Grand and Steamboat lie in distinctly different types of geothermal areas, which could well react differently. In this connection, it is probably noteworthy that Norris Basin began acting up during the summer and fall of 1971 (*6*), a time of relatively high tidal force. The pools and mud pots became exceedingly active while geyser activity lessened, which suggests that the high tidal forces changed the pattern of circulation, sapping energy from the geysers to feed the pools. No such shift was observed in the Upper Geyser Basin.

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Air Pollution: Sensitive Detection of Ten Pollutant Gases by Carbon Monoxide and Carbon Dioxide Lasers

Abstract. *Detection sensitivities of a few parts per billion for ten gaseous pollutants have been evaluated by measuring the strength of the absorption of infrared radiation from carbon monoxide and carbon dioxide lasers. Ethylene concentrations as small as 5 parts per billion have been detected in air. The measured absorption strengths indicate that in mixtures of pollutants, such as nitrogen dioxide and water vapor, the sensitivity is reduced by overlapping absorption bands. However, calculations indicate that it should be possible to detect nitrogen dioxide concentrations of 0.01 part per million in the presence of water vapor concentrations of* 10^5 *parts per million.*

The absorption of infrared radiation at various emission wavelengths of the CO and CO_2 molecular gas lasers has been measured for ten different gaseous pollutants. It was found to be large enough to allow detection of pollutants in concentrations as small as a few parts per billion, and specific enough to allow identification of a gas in the presence of (10^4 times) larger concentrations of other absorbing gases. The ten gases were selected because of their importance in air pollution studies. They include some of the more photochemically reactive hydrocarbons in automobile exhaust and also NO and NO_2. These gases are important contributors to photochemical smog. In this report we show that the detection technique for gaseous pollutants is simplified if molecular gas lasers (*1*) are used together with the optoacoustic detection scheme (*2*) rather than the more complex spin flip Raman laser (*3*). Also, we find that the detection sensitivity is greater by more than one order of magnitude over previous reports.

The experimental apparatus is represented in Fig. 1A. Infrared absorption in the gas sample is measured by means of the optoacoustic effect (*2*). An amplitude-modulated beam of infrared radiation is directed through the gas sample, which is enclosed in a container. The energy absorbed by the gas causes its temperature and pressure to rise. This pressure rise, which is periodic because of the amplitude modulation of the infrared beam, is detected by a microphone placed inside the sample container. The electrical signal from the microphone is proportional to the infrared beam power and the gas absorption strength. Absorption strengths as small as 4×10^{-9} cm^{-1} per watt of beam power have been detected. In order to detect small absorptions due to low concentrations of air pollutants, high beam power is required. Specificity, the ability to prevent other gases from interfering with the measurement, requires that the spectral width of the radiation be narrow. In conventional infrared spectroscopy, blackbody sources and grating or prism monochromators have been used to provide beams of narrow spectral width. These sources cannot provide sufficient power over a narrow enough spectral range to give adequate sensitivity and specificity. They have been useful for detecting gases in high concentrations when no other sample constituent absorbs in the wavelength range of interest. Hydrocarbons and CO in automobile exhaust can be detected by this means, but the nitrogen oxides cannot because of interfering absorption by water vapor, which is a normal constituent of automobile exhaust and ambient air.

These difficulties can be largely overcome by using a laser infrared source. Nitric oxide has been detected (*3*) by using a spin flip Raman laser, which has continuous wavelength tuning. Molecular gas lasers are not continuously tunable but can be made to emit in a number of discrete wavelengths corresponding to transitions between various inverted energy levels in the laser gas. An emitted wavelength is selected by rotating a diffraction grating, which forms one end of the laser optical reson-

Table 1. Noise-limited sensitivities for detecting pollutant gases.

Gas	Sensitivity (ppb)	Laser	Infrared source transition	Wavelength (μm)
Ammonia	0.4	CO	P_{19-18} (15)	6.1493
Benzene	3	CO_2	00°1–02°0 P(30)	9.6392
1,3-Butadiene	1	CO	P_{20-19} (13)	6.2153
1,3-Butadiene	2	CO_2	00°1–10°0 P(30)	10.6964
1-Butene	2	CO	P_{19-18} (9)	6.0685
1-Butene	2	CO_2	00°1–10°0 P(38)	10.7874
Ethylene	0.2	CO_2	00°1–10°0 P(14)	10.5321
Methanol	0.3	CO_2	00°1–02°0 P(34)	9.6760
Nitric oxide	0.4	CO	P_{8-7} (11)	5.2148
Nitrogen dioxide	0.1	CO	P_{20-19} (14)	6.2293
Propylene	3	CO	P_{19-18} (9)	6.0685
Trichloroethylene	0.7	CO_2	00°1–10°0 P(24)	10.6321
Water	14	CO	P_{17-16} (13)	5.9417

ator. Absorption measurements made with the spin flip Raman laser will be more useful for analyzing complex gas mixtures because of its continuous tunability. However, our results indicate that in many cases of practical interest the simpler molecular gas laser may give sufficient analytical information. The detection sensitivity is approximately the same for both systems since their total beam power is about the same.

Our results were obtained with CO (*4*) and CO_2 lasers (*5*). Together, these lasers could emit in more than 100 different wavelengths distributed more or less uniformly over the ranges 5.2 to 6.3 μm and 9.2 to 10.7 μm. The output power was about 1 watt. Since the lasers were old-fashioned, the gas mixture had to be flowed through the laser tube, and the CO laser was cooled with liquid nitrogen. Both of these complications can be avoided in future systems; lasers with sealed tubes have been demonstrated in operation at room temperature (*6*).

The absorption strengths of ten gases were measured at 19 laser emission wavelengths. The gas samples were prepared by diluting pure gases, or saturated vapors obtained above liquids, to a standard concentration of 1000 ppm. The pollutants were diluted with N_2 from which water vapor had been removed by a liquid nitrogen cold trap. Water vapor absorption was measured at higher concentrations. All measurements were made at a total sample pressure of 500 torr. The laser power passing through the gas cell was measured by a homemade Golay detector with a noise equivalent power of 1 μw. Signals from the microphone in the sample cell and the Golay cell were detected by using standard lock-in amplifier techniques. The ratio of the microphone signal to the Golay cell signal, which is proportional to the gas absorption strength, was measured by a digital voltmeter. The calibration was made by using a gas sample with known absorption strength.

The measured gas absorption strengths have been used to estimate the noise-limited sensitivities for detecting small gas concentrations. These gas concentrations (Table 1) produce a signal equal to the noise level of the microphone and associated electronics when the signal averaging time is 1 second. Since the noise level corresponds to an absorption strength of 4×10^{-9} cm^{-1} per watt of incident power, the concentrations in Table 1 have this absorption strength at the listed laser emission wavelengths. A background signal of 5×10^{-7} cm^{-1}, which is independent of wavelength, is observed in all gas samples. This is due to absorption in the cell windows and scattered radiation from the window surface, some of which is absorbed by the cell walls. In order to achieve the noise-limited sensitivities in Table 1 it is necessary to subtract this background signal from the measured signals. Since the background is 125 times the noise level, measurements must be made with an absolute accuracy of a little better than one part in a hundred.

In order to verify that small pollutant concentrations could be detected, we measured a low concentration of ethylene in air. A small amount of ethylene

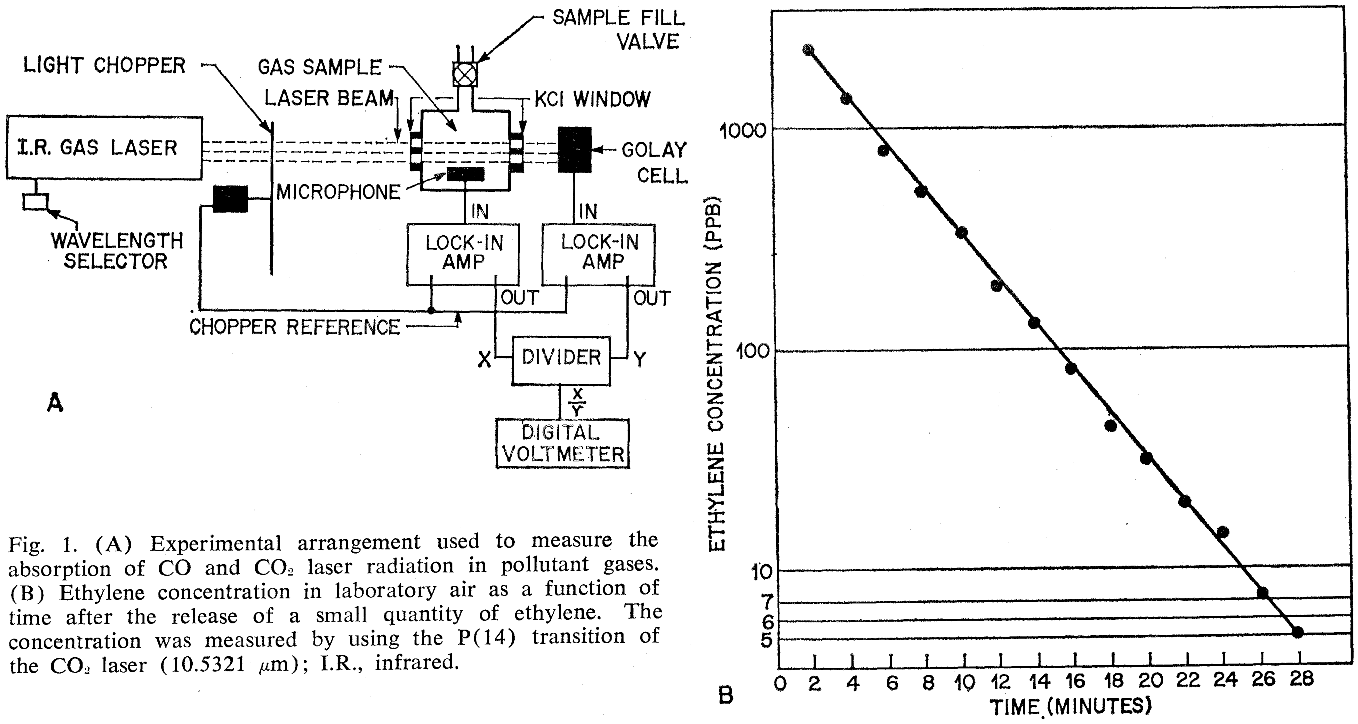

Fig. 1. (A) Experimental arrangement used to measure the absorption of CO and CO_2 laser radiation in pollutant gases. (B) Ethylene concentration in laboratory air as a function of time after the release of a small quantity of ethylene. The concentration was measured by using the P(14) transition of the CO_2 laser (10.5321 μm); I.R., infrared.

was released into the laboratory air at the start of the experiment. For the next ½ hour fresh samples of room air were introduced into the apparatus at 2-minute intervals, and absorption at the P(14) line (10.5321 μm) of the CO_2 laser was measured. The background signal was subtracted from the measured signals, which were then converted into equivalent gas concentrations. The gas concentration decreased rapidly because of the forced ventilation of the laboratory. The ethylene concentration, which was initially 2000 ppb, fell to 5 ppb in approximately ½ hour. A plot of the logarithm of the concentration as a function of time (Fig. 1B) yields a straight line, with a scatter of less than 1 ppb in the data points at low concentrations. Thus, the detection sensitivity for ethylene calculated from calibration measurements at high concentrations could be realized at low concentrations.

In most air pollution measurements the sample contains more than one gas that absorbs in the infrared. It is not usually possible to find a wavelength that is absorbed by the component of interest and not by any other component. Thus, the problem of interference will be present and must be overcome. The concept of a rejection ratio is useful for evaluating interferences. Suppose that it is desired to detect a gas A and that this measurement is interfered with by a gas B. Then there will be some concentration C(B) of gas B that just prevents the unambiguous detection of a concentration C(A) of gas A. The rejection ratio is defined as C(B)/C(A). Its size depends on the relative absorption strengths of the two gases and on the precision with which their concentrations may be measured. With our present apparatus we can measure concentrations with an accuracy of 0.1 percent. This gives a rejection ratio equal to 10^3 times the absorption strength of gas A divided by the absorption strength of gas B, measured at the wavelength used to detect gas A. It is assumed that there is another wavelength where the concentration of gas B may be measured. Care must be taken to control the sample temperature since different gases have different temperature dependences for absorption.

Rejection ratios for the gases listed in Table 1 have been calculated from measured absorption strengths by using the experimentally achieved measurement accuracy of 0.1 percent. The most severe problem occurs between NO and water vapor. Since NO is a diatomic molecule it has only one strong infrared absorption band, which is centered at about 5.3 μm and is overlapped by strong H_2O absorption bands. In practice, it is often necessary to detect small concentrations of NO in the presence of large water vapor concentrations. Automobile exhaust may contain as much as 10 percent water vapor, and measurements of ambient air are required up to 120°F and 100 percent relative humidity. If NO is measured at the CO laser emission wavelengths of 5.2640 and 5.3080 μm and water vapor is detected at 5.8292 and 5.9417 μm, the rejection ratio is 10^6. That is, for sources with 10 percent (10^5 ppm) water vapor the detection limit for NO is 0.1 ppm, and for ambient air at 120°F and 100 percent relative humidity the limit is 0.01 ppm. Nitrogen dioxide detection is also interfered with by water vapor. If CO laser transitions at 6.2272 and 6.2552 μm are used, the rejection ratio is 10^7. Thus, NO_2 concentrations of 0.01 ppm should be detectable in automobile exhaust, and concentrations of 1 ppb should be detectable in ambient air. Typical uncontrolled automobile exhaust contains NO and NO_2 in concentrations of 100 to 1000 ppm (*7*), and ambient urban air in most cities has NO and NO_2 in concentrations of 0.01 ppm or more 99 percent of the time (*8*). Thus, the above sensitivities should be adequate for this type of measurement.

The rejection ratios between all pairs of gases in Table 1 exceed 10^4. This rejection ratio, combined with the sensitivities listed in Table 1, provides a measure of the practical utility of this technique. Not all gaseous air pollutants absorb in the emission range of the lasers used in this experiment. However, many different laser transitions have been demonstrated in the infrared (*9*). It should be possible to find appropriate transitions for most pollutants and to achieve rejection ratios large enough so that samples of mixed gases can be analyzed.

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Second-Order Scattering from the Sea:

Ten-Meter Radar Observations of the Doppler Continuum

Abstract. Ten-meter radar observations of the sea have been used to study second-order interactions between waves in electromagnetic scattering from the sea. Techniques of coherent, pulsed radar provide echo frequency spectra from several range intervals. The echo spectra are resolved with an analysis window of a few millihertz. These spectra show a clear second-order echo continuum which appears as sidebands about the first-order Bragg scattering lines. Up to one-half of the total echo power has been observed in these sidebands. The principal characteristics of these sidebands vary with time, apparently in response to the sea state. The form of the echo spectra is consistent with the results of perturbation theory computations based on Rice's method.

Bragg scattering is generally accepted as the principal scattering mechanism responsible for medium-frequency and high-frequency radar returns from the sea. As first suggested by Crombie (*1*), electromagnetic waves of length λ_e are backscattered from ocean waves of one-half that length, $\lambda_e/2$. According to this hypothesis, the radar echo frequency is shifted because of the movement of the ocean waves. Furthermore, the magnitude of the Doppler shift as a function of wavelength is given by the dispersion relation for gravity wave propagation. Many additional observations of radar echoes from the sea, primarily in the high-frequency (3 to 30 Mhz) portion of the radio-frequency spectrum, have supported this hypothesis. Generally reported features of