

AD717171

THE USE OF CO AND CO₂ LASERS TO
DETECT POLLUTANTS IN THE ATMOSPHERE

by

Robert T. Menzies

California Institute of Technology
Pasadena, California 91109

December 1970

This document has been approved for public release and sale;
its distribution is unlimited.

Grant Number AFOSR-68-1492, Project Number (9768-02)

Research sponsored in part by Air Force Office of Scientific
Research, Office of Aerospace Research, United States Air Force

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

RECEIVED
JAN 21 1971
B

Qualified requestors may obtain additional copies from the Defense Documentation Center; all others should apply to the Clearinghouse for Federal Scientific and Technical Information.

Section 1		
DTI	UNITE SECTION	☒
C	DEF SECTION	☐
UNANNOUNCED		☐
IDENTIFICATION		
DISTRIBUTION/AVAILABILITY CODES		
DIST.	AVAIL. and/or SPECIAL	
1		

Reproduction, translation, publication, use, and disposal in whole or in part by or for the United States Government is permitted.

THE USE OF CO AND CO₂ LASERS TO DETECT
POLLUTANTS IN THE ATMOSPHERE

by

Robert T. Menzies

California Institute of Technology
Pasadena, California

Abstract

Several spectral coincidences between CO laser emission lines and infrared absorption lines of oxides of nitrogen have recently been observed. Using existing infrared spectroscopy data, we predict additional spectral coincidences; the Q-switched CO laser emits certain lines which overlap SO₂ absorption lines, and certain frequency doubled CO₂ laser lines overlap NO and CO absorption lines. Other spectral overlaps involving the CO₂ laser have been reported elsewhere. Based on such coincidences remote sensing of these atmospheric constituents can be accomplished by observing resonant absorption, thermal emission, or fluorescence. We discuss sensitivities for each of these methods, using data on line strengths and pressure broadened line widths. Wide band heterodyne receivers offer high sensitivity when they can be used; our discussion includes the use of this type of receiver system.

Introduction

There are two basic laser systems which have the capability of sensing certain molecular constituents in the atmosphere. One system involves visible or, preferably, ultraviolet radiation and interacts with electronic transitions; the other system uses infrared radiation, which interacts with the nuclear vibration-rotation resonances.

Lidar systems which have been developed to date have predominantly used visible or ultraviolet radiation. (References [1] and [2] review applications and present developments of the lidar technique). The use of these sources of radiation for sensing molecular constituents is usually confined to the observation of Raman scattering, a relatively weak interaction effect, although resonant Raman scattering, absorption, or fluorescence could be observed if strong sources of ultraviolet radiation were developed which emitted frequencies matching the strong electronic excitation frequencies of the molecules. At present this has not been accomplished for many of the major pollutant molecules.

Infrared lasers cover a broad region of the spectrum, and many of the laser emissions overlap absorption lines of various molecules [3,4]. Numerous molecules exhibit absorption bands in the 2 - 15 micron region of the infrared [5]; hence lasers in this spectral range can be used to detect several molecular constituents by observing selective absorption of certain laser lines passing through a path of interest in a double-ended system, or, in the case of monitoring smoke stack effluents, by observing certain thermal emission lines with a remote heterodyne radiometer. For other applications a single-ended system which

could record fluorescence from a pulsed infrared laser transmitter would be valuable for remote monitoring. (Fluorescence cross sections are several orders of magnitude larger than Raman scattering cross sections. After taking fluorescence quenching into account, the process is in most cases still more efficient in providing a return signal than Raman scattering.) These three configurations are sketched in Figures 1 and 2.

High power lasers are needed to obtain suitable sensitivities with the fluorescence type of system. At present the CO_2 and CO lasers offer high enough power output in the infrared to be useful for remote laser fluorescence detection. These two lasers are capable of emitting hundreds of different lines in the region of the infrared where numerous molecular absorption bands occur, including those of NO, NO_2 , O_3 , SO_2 , and CO. Hence their applicability to remote sensing should not be overlooked.

Several important spectral coincidences which were not listed in reference [3] are reported in the following section. Line strengths and pressure broadened line widths for various infrared absorption lines are then discussed, along with sensitivities of instruments which measure direct absorption of select laser lines. The next sections involve sensitivity calculations for thermal emission heterodyne radiometer receivers and for fluorescence receivers, both of which are single-ended, with the latter system using a pulsed laser transmitter. Quenching of fluorescence is discussed; quenching data for the NO fundamental band fluorescence is available in the literature, and similar quenching data for other molecules is estimated for purposes of sensitivity calculations.

Spectral Coincidences

Table I lists several spectral overlaps involving the CO and CO₂ lasers. The available wave number data is not listed here; for further information regarding the absorber line identifications see reference [4] and the others listed in the table. It is quite probable that many more pollutants absorb certain lines of these two lasers; P. Hanst [3] has noted that the CO₂ laser can be made to emit certain lines which are selectively absorbed by O₃ (ozone) and SO₂, although the latter interaction is a weak one.

In order to predict spectral coincidences, it is of course necessary to have accurate spectroscopic data available. Because the pressure broadened half-widths of the typical pollutant absorption lines are of the order of $.05 \text{ cm}^{-1}$ when they are in the atmosphere, data which is accurate to a few hundredths of a wavenumber is necessary. The wavelengths of the multitude of lines which the liquid-nitrogen cooled, Q-switched CO laser emits are known to within a few hundredths of a wavenumber [7,10]. However the CO laser emits many other lines when it is running at higher temperatures [13]; careful measurements of these wavelengths would be helpful.

Recently very accurate spectroscopic data for several simple molecules has become available as a result of work done by K. N. Rao and others at the Ohio State University. Carbon monoxide and nitrogen dioxide are two examples. As a result, we are able to predict coincidences involving these molecules with a high degree of certainty. For example the frequency-doubled P(20) line of the $00^{\circ}1 \rightarrow 02^{\circ}0$ band from the CO₂ laser is found to lie within $.01 \text{ cm}^{-1}$ of the P(5) line in the CO fundamental band.

Our original predictions of coincidences between CO laser lines and NO absorption lines was based on the work of Shaw [6]. However as a result of laboratory measurements [4], we have found his wavenumber data to be a few hundredths of a wavenumber too high. More accurate studies of this band are presently under way at the Ohio State University. The SO₂ data which we used is that of Shelton and Nielsen [9]; further investigation of these predicted coincidences should be undertaken.

Absorption Strengths

The absorption lines of molecules in the atmosphere take the form:

$$k(\nu) = \frac{S}{\pi} \frac{\Delta\nu}{(\nu - \nu_0)^2 + \Delta\nu^2} \quad (1)$$

near their line centers, where S is the line strength, ν_0 is the center frequency, and $\Delta\nu$ is the pressure broadened line width.

The line strength of a particular transition in a vibration-rotation band is dependent on the number of molecules in the initial energy level and on the quantum numbers describing the level. The transition matrix elements for the lines in the CO fundamental band are of the form [14]

$$|R^{0J,1J\pm1}|^2 = K_{01} S_J \quad (2)$$

where K_{01} is dependent on the band strength, and S_J depends on the total angular momentum of the initial level. $S_J = J$ for the P-branch and $S_J = J + 1$ for the R branch, where J is the total angular momentum of the lower, or initial level. The number of molecules in a given level can be calculated quickly from the formulae:

$$N_J = (N/Q_r)(2J + 1) \exp[-F(J)hc/kT], \quad (3)$$

$$\text{where} \quad F(J) \approx BJ(J + 1) \quad (4)$$

$$\text{and} \quad Q_r = \sum_J (2J + 1) \exp[-F(J)hc/kT] \quad (5)$$

$$\approx kT/hcB$$

and where $N = \sum_J N_J$, Q_r = rotational partition function, $F(J)$ =

energy of J th rotational level. The line strength, line width, and partition function data for NO are slightly more complicated due to the fact that the electronic ground state is a $^2\Pi$ doublet. References [15,16] contain detailed calculations and some experimental results for NO. A typical value for an NO line strength in this band is $1 \text{ cm}^{-1}/\text{atm cm}$. The line strengths for the nonlinear triatomic molecules SO_2 and NO_2 are much more difficult to calculate. One can estimate line strengths in these cases by obtaining band intensity data, which is available in the literature, followed by a study of the relative line strengths in a high resolution band absorption spectrum.

The last column of Table I gives the concentrations in parts per million necessary to produce a 1% decrease in signal strength as the cited laser line passes through a 100 meter path. For example the absorption coefficient $k(\nu)$ of the NO $R(18\frac{1}{2}), \Omega = 3/2$ line, at $\nu = 1935.48 \text{ cm}^{-1}$, the frequency of the 7-6 band, P(13) CO laser line, is about $2 \text{ atm}^{-1} \text{ cm}^{-1}$.

Water vapor absorption can cause considerable interference in the

5- μ to 8- μ region. However several laser lines in this region which are suitably displaced from water vapor lines should be able to pass through kilometer path lengths of the atmosphere with only a few per cent absorption due to water vapor. References [17] through [21] contain data on the water vapor ν_2 band line strengths and their locations; using these works one can predict which laser lines should be influenced least by water vapor absorption. Eventually field data for various humidity levels would be necessary as a matter of calibration.

The Heterodyne Radiometer Receiver

Since molecules thermally radiate at the same wavelengths which they absorb, a heterodyne radiometer using an overlapping laser line as a local oscillator signal would be able to selectively sense a particular pollutant in smoke stack emissions from a remote location. Heterodyne receivers with 1 GHz IF bandwidth capability have been constructed. Since the molecular emission line widths are about $.1 \text{ cm}^{-1}$ or 3 GHz (full width at half maximum intensity), a heterodyne receiver which responds to radiation within ± 1 GHz of the laser line would cover virtually the entire linewidth.

The heterodyne receiver should have the capability of operating with two closely spaced laser l.o. lines, one of which overlaps the pollutant's emission line. Then if neither laser line overlapped some other molecular emission line, the receiver would selectively sense thermal emission from the pollutant of interest, in addition to a broad-band background radiation. In the 4- μ to 8- μ region most of the clear sky background radiation comes from thermal emission of water

vapor molecules [22]. By carefully picking wavelength regions which do not overlap water vapor lines, one should be able to operate in a region in which sky background radiation is one-tenth that of a 300° K blackbody or less. For example the region near the 7-6 band, P(13) CO laser line previously mentioned is not near any water vapor emission lines and could be used to sense NO.

The noise equivalent power (N.E.P.) for a Dicke type heterodyne infrared radiometer is [23-25]

$$\text{N.E.P.} = \frac{h\nu}{\eta} \cdot \frac{1}{\sqrt{B_{\text{IF}} \cdot \tau}}, \quad (6)$$

where ν is the frequency at which the radiometer is sensitive, η is the quantum efficiency of the mixer, B_{IF} is the IF bandwidth, and τ is the post-detection integration time.

The infrared heterodyne radiometer is, in effect, both a receiver and an antenna [26]. It has an effective aperture $A_e(\Omega)$ for plane waves in the right wavelength region which are incident from any direction Ω . In reference [26] it is shown that for any heterodyne configuration the integrated effective aperture is

$$\iint A_e(\Omega) d\Omega \approx \lambda^2 \quad (7)$$

where λ is the wavelength to which the receiver is sensitive. For a configuration such as that shown in Figure 3, the solid angular field of view is

$$\Omega_R \approx \frac{\lambda^2}{D^2} \quad (8)$$

When the heterodyne receiver is pointing at a portion of the sky, the received power per unit bandwidth will be

$$w = \frac{1}{2} \int \int B(\theta, \phi) A_e(\theta, \phi) d\Omega, \quad (9)$$

where $B(\theta, \phi)$ is the sky brightness in watts $m^{-2} Hz^{-1} rad^{-2}$, and the direction $\theta = 0, \phi = 0$ corresponds to the optic axis of the configuration shown in Figure 3. The factor of $1/2$ takes care of the fact that the local oscillator is linearly polarized. If the sky could be characterized as a blackbody at $300^\circ K$ in the spectral region at which the receiver is sensitive ($\lambda = 5.25\text{-}\mu$, for example), then

$$B = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1} \quad (10)$$

$$= 5 \times 10^{-17} \text{ watts/cm}^2 \text{ Hz rad}^2,$$

and

$$w \approx \frac{1}{2} B \lambda^2 = 6 \times 10^{-24} \text{ watts/Hz}$$

The N.E.P. for a heterodyne receiver operating at $\lambda = 5.25\text{-}\mu$, using equation (6) and assuming $\eta = \frac{1}{2}$, $B_{IF} = 10^9 \text{ Hz}$, $\tau = 10 \text{ sec.}$, would be

$$(h\nu/\eta) \cdot \frac{1}{\sqrt{B_{IF} \cdot \tau}} = 6 \times 10^{-25} \text{ watts/Hz}$$

Thus the signal to noise ratio in this case would be 10 if a reflecting chopper were used which directed the receiver to a cold reference body ($T_R \lesssim 220^\circ K$).

Let us calculate the sensitivity of a heterodyne receiver to NO coming out of a stack, assuming the receiver is using the 7-6 band, P(13) CO laser line, previously mentioned, as a local oscillator signal. Using the fact that the absorption coefficient of NO at this wavelength is $\alpha(\lambda) = 2 \times 10^{-6} \text{ p.p.m.}^{-1} \text{ cm}^{-1}$ (p.p.m. stands for parts per million), and using Kirchhoff's law to obtain the emissivity $\epsilon(\lambda)$ of the NO sample:

$$I(\lambda)/I_0(\lambda) = 1 - \epsilon(\lambda) \quad , \quad (11)$$

where $I(\lambda)$ and $I_0(\lambda)$ are the transmitted and incident intensities of radiation at wavelength λ passing through the sample, we arrive at the value

$$\epsilon(\lambda) = 2 \times 10^{-6} \text{ p.p.m.}^{-1} \text{ cm}^{-1}$$

for NO at the wavelength of the 7-6 band, P(13) CO laser line. If we use the heterodyne radiometer discussed in the previous paragraph to detect NO emitted from a stack whose effluent temperature is 350°K, then a concentration-depth of 10^4 p.p.m. cm would give a unity signal to noise ratio. This would correspond to 100 p.p.m. in a path depth of 1 meter. If the temperature of the effluent gases were 440°K, a concentration of 20 p.p.m. in a path depth of 1 meter would give a unity signal to noise ratio. Figure 4 plots the concentration-depth of NO at 390°K necessary to give a unity signal to noise ratio using a receiver with various values of $B_{IF} \cdot \tau$. These figures assume the NO sample is filling the field of view of the receiver.

If the pollutant is confined to a region which does not fill the field-of-view of the receiver, then the sensitivity of the receiver is

smaller. Using equation (9), and considering the case where

$$B(\theta, \phi) = B_1 \quad \text{for } 0 < \theta, \phi < \Omega_p$$

and

$$B(\theta, \phi) = B_0 \quad \text{for } \Omega_p < \theta, \phi \leq \Omega_A,$$

where Ω_p is the solid angle subtended by the pollutant plume or cloud, and Ω_A is the solid angular field of view of the receiver, the apparent brightness when the receiver is pointing toward the plume is

$$B_A = \frac{\int \int B(\theta, \phi) A_e(\theta, \phi) d\Omega}{\int \int A_e(\theta, \phi) d\Omega} \quad (12)$$

$$\approx \frac{(B_1 \Omega_p + B_0 \Omega_A) A}{\lambda^2}$$

where A is the area of the collecting lens in Figure 3. The received power per unit bandwidth will be

$$w \approx \lambda^2 B_A \approx (B_1 \Omega_p + B_0 \Omega_A) A \quad (13)$$

In practice the solid angular field-of-view of an infrared heterodyne radiometer can easily be as small as desired in order to detect samples of pollutants emanating from stacks at distances of kilometers without loss of efficiency due to this matter.

Turbulence in the atmosphere will degrade the phase fronts of nearly plane waves traveling from the radiation source to the distant heterodyne receiver. Phase front degradation will reduce efficiency of the receiver.

However Fried [27] has shown that for receivers operating at 5- μ wavelength receiving apertures can be made as large as a meter in diameter with very little loss in heterodyne efficiency over a range of several kilometers. A receiving mirror of 1 meter diameter would give the receiver a solid angular field of view of $\sim 2.5 \times 10^{-11} \text{ rad}^2$, which means a sample of 1 cm^2 cross section would fill the receiver field of view at a range of 2 kilometers.

The presence of a large background concentration of a particular pollutant can hamper the effectiveness of this type of receiver when it is used to remotely monitor emissions of that pollutant from a stack. The loss in sensitivity occurs largely because of the absorption of the thermal radiation along the path from the stack to the receiver. Following a development similar to that found in Chapter 3 of reference [25], we can compute the signal received from a pollutant arising from a stack when in a background concentration of the same constituent. First we write an expression for the brightness of the radiating volume of the stack plume which is in the receiver field-of-view, assuming no background concentration:

$$B = \frac{1}{4\pi} \int_{r_1}^{r_2} j\rho_1 \, dr = \frac{1}{4\pi} j\rho_1(r_2 - r_1) \quad , \quad (14)$$

where j_1 = emission coefficient, watts/kg - Hz, ρ_1 = density of constituent in the volume kg/m^3 , and r_1, r_2 are the radial distances of the plume boundaries from the receiver. Expression (14) assumes resonant absorption of the thermally emitted radiation as it passes through the plume is negligible. To take this into account, consider the effective

brightness of a layer between r and $r + dr$, where $r_1 \leq r \leq r_2$,

$$dB = \frac{1}{4\pi} j_1 \rho_1 \exp\left[-\int_{r_1}^r K \rho_1(r') dr'\right] dr \quad (15)$$

Here $K\rho_1$ = absorption coefficient m^{-1} . Now if we have a background concentration ρ_0 with an emission coefficient j_0 , the expression for the brightness which the receiver sees is

$$B = \frac{1}{4\pi} \int_0^{r_p} j(r) \rho(r) \exp\left[-\int_0^r K \rho(r') dr'\right] dr, \quad (16)$$

$$\begin{aligned} &= \frac{j_0}{4\pi K} [1 - \exp(-K\rho_0 r_1)] + \frac{j_1}{4\pi K} [\exp(-K\rho_0 r_1)][1 - \exp(-K\rho_1(r_2 - r_1))] \\ &+ \frac{j_0}{4\pi K} [\exp(-K\rho_0 r_1)][\exp(-K\rho_1(r_2 - r_1))][1 - \exp(-K\rho_0(r_p - r_2))], \end{aligned} \quad (17)$$

where

$$j(r) = j_0 \quad \text{for } 0 < r < r_1, \quad r_2 < r < r_p$$

$$= j_1 \quad \text{for } r_1 < r < r_2$$

$$\rho(r) = \rho_0 \quad \text{for } 0 < r < r_1, \quad r_2 < r < r_p$$

$$= \rho_1 \quad \text{for } r_1 < r < r_2$$

and where r_p is the range for which the background concentration exists.

The quantity $j/4\pi K$ is called the intrinsic brightness of the medium.

Now when the receiver is pointed toward an adjacent portion of the sky

which does not contain the stack plume, the expression (17) with $\rho_1 j_1$ replaced by $\rho_0 j_0$ everywhere will give the brightness. If $j_1 \gg j_0$, the major cause of sensitivity loss is the factor $\exp(-K\rho_0 r_1)$, which causes the second and third terms to diminish relative to the first term.

Let's apply expression (17) to the NO receiver previously characterized. On a smoggy day in the Los Angeles basin the background NO concentration is around 0.1 p.p.m. Assume a stack is 1 kilometer from the receiver, and the concentration, temperature, and path depth of the NO emissions are 100 p.p.m., 390°K, and 1 meter. If $r_p = 10$ kilometers, then

$$B = .02(B_{290}) + .02(B_{390}) + 0.2(B_{290})$$

where B_T is the brightness of a T °K blackbody. $B_{390} \approx 10 B_{290}$, so the signal when the receiver is pointed at the stack is approximately twice that of the signal received when the receiver is looking at an adjacent portion of the sky, and the change in signal is about twice the size of the noise level. In this case the factor $\exp(-K\rho_0 r_1)$ is very small, and the presence of the background concentration has negligible effect on the receiver sensitivity. We have not included other sources of attenuation or atmospheric turbulence effects here. These effects would further attenuate or degrade a signal received from large distances, and they would depend on weather conditions such as humidity. However, these sources of interference should not be bothersome for distances up to a few kilometers.

The heterodyne radiometer receiver might also be used to sense background concentration levels of various pollutants. This type of

remote detection system requires a low power laser, producing a cw output of a few milliwatts, and it offers relative simplicity when compared with other remote laser sensor systems.

The Remote Fluorescence Detector

Using a high power pulsed laser transmitter and a receiver with range gating circuitry, one can lock at the fluorescence or Raman scattering return signal from a localized region of the atmosphere and determine concentrations of various molecular constituents in those regions. The return signal power is given by the equation:

$$P_r(R) = P_t \exp\left(-\int_0^R \sigma_e(r, \lambda_t) dr\right) \beta(R) L A_e R^{-2} \exp\left(-\int_0^R \sigma_e(r, \lambda_r) dr\right) \quad (18)$$

- where P_t = transmitter pulse power,
- $\sigma_e(r, \lambda)$ = extinction coefficient at range r for wavelength λ ,
- R = range,
- A_e = effective receiver aperture,
- $\beta(R)$ = $\sigma \cdot \rho(R)$ = volume scattering or fluorescence coefficient
- σ = scattering or fluorescence cross section,
- $\rho(R)$ = density of constituent,
- L = the range increment from which signals are simultaneously received at a given time. For scattering systems this equals $c\tau/2$, where τ is the laser pulse duration. For fluorescence systems τ is the larger of the pulse duration and the effective fluorescent lifetime.
- λ_t & λ_r = wavelengths of the transmitted and received signals, respectively.

The values of σ for Raman scattering are highest when ultraviolet laser sources are used, due to the ν^4 dependence on the exciting frequency. There is also a possibility of resonant Raman scattering if the laser exciting frequency falls near a resonant frequency in an electronic absorption band of a molecule. Two popular high power pulsed laser sources in this spectral region are the N_2 laser emitting at $\lambda = 3371 \text{ \AA}$, and the frequency doubled ruby laser emitting at $\lambda = 3472 \text{ \AA}$.

Only if the Raman scattering process is resonant or near resonant will the cross sections be large enough to compare with fluorescence cross sections, even when quenching of fluorescence by atmospheric constituents is taken into account. Consider Raman scattering cross sections for the CO molecule. The long wavelength edge of the CO electronic absorption bands lies around $2000 \text{ \AA}$; with existing high power laser systems this precludes the possibility of a resonant Raman effect. The Raman scattering cross section for CO when the doubled ruby laser is used is about $3 \times 10^{-29} \text{ cm}^2$ [28]. The Raman cross section for NO, whose strong electronic absorption bands lie at wavelengths less than $2300 \text{ \AA}$, is probably of the same order of magnitude around $3400 \text{ \AA}$ as that of CO. The molecule SO_2 has a very weak electronic band between $2600 \text{ \AA}$ and $3400 \text{ \AA}$. Thus the possibility of a resonant enhancement of Raman scattering exists below $3400 \text{ \AA}$. Raman scattering has not been observed with NO_2 because it absorbs and fluoresces throughout most of the visible and ultraviolet region [29].

The fluorescence cross sections for molecules which are resonantly excited by infrared radiation are of the order of 10^{-19} cm^2 , if the infrared absorption is strong, as is the case for those molecules listed

in Table I. The fluorescence radiation consists of a number of lines covering a spectral region at least as wide as that of the absorption band. Quenching of this fluorescence due to collisional relaxation can reduce the cross section by several orders of magnitude. Water vapor is a most effective quencher if the molecule's absorption band lies near any of its infrared bands. The probability of vibrational relaxation of the NO $v = 1$ state for a collision with a ground state H_2O molecule has been measured to be 7×10^{-3} [30], which is quite high; this would mean a relaxation time of about 10^{-6} seconds for NO existing in a 50% relative humidity atmosphere. The quenching by H_2O is far faster than that of N_2 or other atmospheric constituents in this case. The radiative lifetime of the NO $v = 1$ state can be calculated from the expression [31]

$$S = \int k_\nu d\nu = \frac{\lambda_0 g_2}{8\pi g_1} \frac{N_a}{\tau}, \quad (19)$$

where S = the absorption line strength,

λ_0 = the radiative wavelength,

g_1, g_2 = the upper and lower level degeneracies,

N_a = the number of atoms in the lower (absorbing) level,

τ = radiative lifetime.

The radiative lifetime for a level in the $v = 1$ state of NO is a few tenths of a second. Thus the quenching of NO fluorescence in this case reduces the fluorescence cross section to about 10^{-24} cm^2 . The quenching of CO fluorescence in the infrared is probably not as great as it is for NO because the CO vibration band lies further away from a

water vapor band. The quenching of NO_2 infrared fluorescence by H_2O could be quite high, however.

NO_2 fluorescence in the visible has been studied by a number of people [29,32]. (Reference [32] contains fluorescence quenching data for several molecules which are excited in the visible and ultraviolet). The NO_2 broadband visible fluorescence cross section is about 10^{-19} cm^2 [29], and quenching of the fluorescence when NO_2 is in an atmosphere of dry air reduces the cross section by a factor of about 30,000 [33].

Quenching of fluorescence is both a bane and a boon to pulsed laser remote detection systems. It reduces the cross section by several orders of magnitude, but it also reduces the fluorescence lifetime, making range gating techniques possible. The fluorescence lifetimes without quenching are of the order of several milliseconds at the least; these are much too long for a system which should be capable of spatial resolution. However the quenching process usually reduces the lifetime to 10^{-6} second or less, meaning a resolution of at least 300 meters is possible.

The use of a high power pulsed infrared laser, such as the CO or CO_2 lasers, in conjunction with a heterodyne receiver should be capable of quite high sensitivities as a remote detector of pollutants. The N.E.P. of a heterodyne receiver using a boxcar integrator to detect the pulses is given by (6) if we consider the effective cw power of the return signal instead of the pulse power. Using (6) and (18) we calculate that a system with $B_{\text{IF}} = 10^9 \text{ Hz}$, $\tau = 30 \text{ sec.}$, $P_t = 2 \text{ kilowatts}$, pulse duration of 500 nsec., pulse repetition rate of 400 sec^{-1} , and $A_e = 1 \text{ m}^2$ can detect a concentration of 0.1 p.p.m. NO in a 300 meter path length

at an average range of 1 km, if the relative humidity is 50%. The heterodyne receiver can only detect the fluorescence radiation occurring at one line because of its narrow spectral bandwidth. Since fluorescence from molecules such as CO and NO is mainly distributed among about 50 lines, the cross sections used in equation (18) should be reduced by this factor. For the wavelengths at which the heterodyne receiver is sensitive, it is fundamentally limited in sensitivity by photon noise. This is true also for a photon counting type of receiver in the visible or ultraviolet, although background radiation can also decrease the sensitivity of a photon counting system. Since the photon noise is about a factor of 10 larger in the visible or ultraviolet region than it is in the infrared, the ir heterodyne receiver is inherently more sensitive over its narrow spectral range.

Conclusions

The CO and CO₂ infrared lasers promise to be useful in remote pollution detection systems which respond to direct absorption, thermal emission, or fluorescence. The pollutants which can be selectively detected in this manner include NO, NO₂, CO, SO₂ and O₃. It is also quite possible to use these or other infrared lasers to detect certain hydrocarbons in the atmosphere [3]. Sensitivities using these systems compare favorably with Raman scattering lidar systems while simultaneously requiring less laser power. The thermal emission heterodyne radiometer would appear to be useful in monitoring smoke stack effluents remotely, while a lidar system based on fluorescence would be capable of making certain ambient atmospheric concentration measurements.

Acknowledgments

The author wishes to thank Nicholas George at Caltech and Michael S. Shumate at the Jet Propulsion Labs for their stimulating discussions and encouragement.

TABLE I

Overlaps Between Laser Lines and Molecular Absorption Lines

Pollutant	Center of IR Absorption Band (μ)	Reference	Laser Line	Reference	Concentration necessary for 1% absorption in a 100 meter path
NO	5.3	[6]	CO: 7-6, P(13)	[7]	0.5 p.p.m.
			7-6, P(15)	[7]	0.3 p.p.m.
			9-8, P(9)	[7]	
			9-8, P(13)	[7]	
			9-8, P(23)	[4]	1.0 p.p.m.
			10-9, P(17)	[4]	1.0 p.p.m.
NO			CO ₂ (doubled):		
			00°1 → 10°0,		
			P(8)	[11]	0.5 p.p.m.
			P(24)	[11]	0.5 p.p.m.
			R(8)	[11]	
NO ₂	6.2	[8]	CO: 18-17, P(13)	[7]	
			19-18, P(8)	[7]	
			20-19, P(6)	[7]	0.5 p.p.m.
			20-19, P(10)	[7]	0.5 p.p.m.
			22-21, P(10)	[7]	
			23-22, P(8)	[7]	
			23-22, P(11)	[7]	
SO ₂	7.4	[9]	CO: 30-29, P(9)	[10]	
			30-29, P(10)	[10]	
			31-30, P(9)	[10]	≈ 1 p.p.m.
			31-30, P(11)	[10]	
			32-31, P(5)	[10]	≈ 1 p.p.m.
			32-31, P(6)	[10]	≈ 1 p.p.m.
			32-31, P(8)	[10]	
			32-31, P(10)	[10]	
CO	4.7	[7]	CO ₂ (doubled):		
			00°1 → 02°0, P(20)	[11]	0.05 p.p.m.

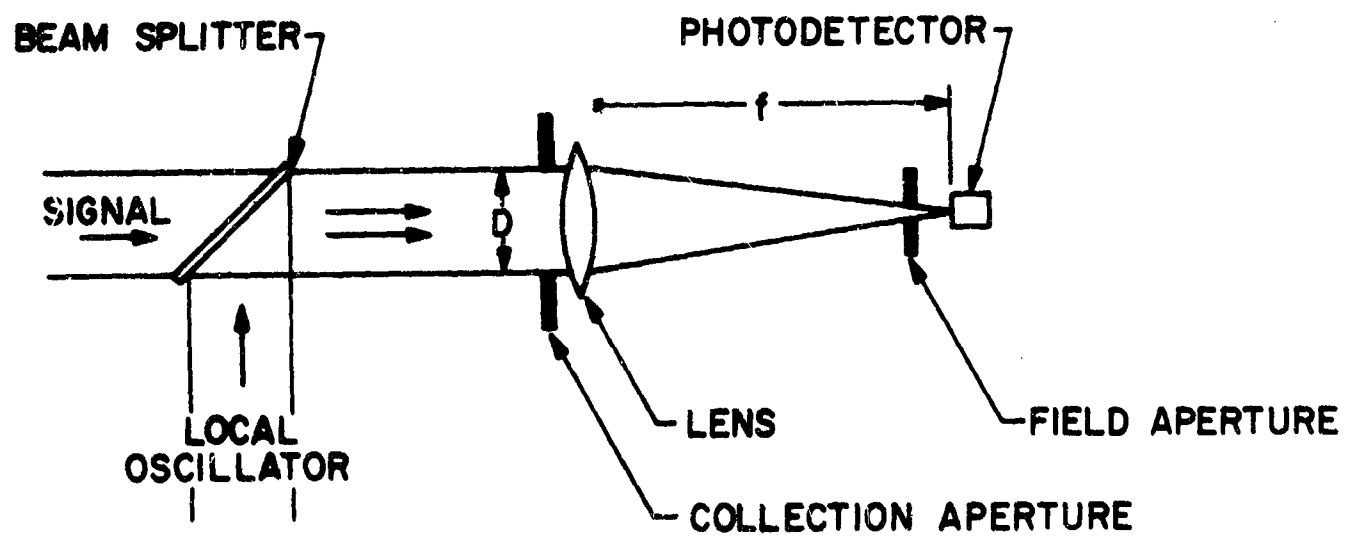
Figure Captions

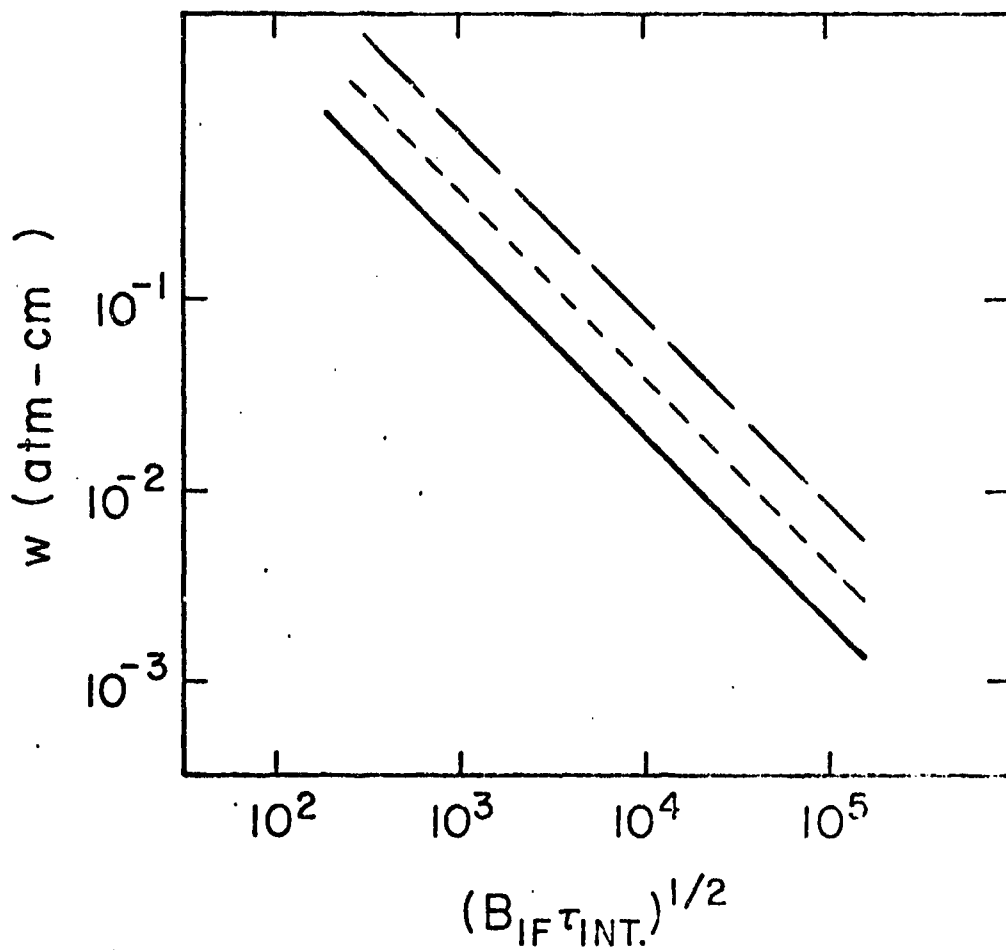
- Figure 1: Diagrams of direct absorption and thermal emission radiometer techniques of detecting air pollutants.
- Figure 2: Diagram of a system which is sensitive to fluorescence induced by the laser transmitter.
- Figure 3: A heterodyne receiver system. For larger collection apertures, a reflecting mirror system would replace this lens system.
- Figure 4: Sensitivity limits of a heterodyne radiometer to nitric oxide, assuming the mixer quantum efficiency $\eta = \frac{1}{2}$. The ordinate is concentration-path depth product, given in atmosphere-centimeters. The abscissa is the bandwidth-integration time product. The solid line denotes an NO temperature of 440 °K, the short dashed line denotes 390 °K, and the long dashed line denotes 350 °K.

References

1. R. T. H. Collis, Applied Optics 9, 1782 (1970).
2. V. E. Derr and C. G. Little, Applied Optics 9, 1976 (1970).
3. P. L. Hanst, Applied Spectroscopy 24, 161 (1970).
4. R. T. Menzies, N. George, and M. K. Bhaumik, IEEE J. Quantum Electronics, QE-6, December, 1970.
5. R. H. Pierson, A. N. Fletcher, and E. S. C. Gantz, Analyt. Chem. 28, 1218 (1956).
6. J. H. Shaw, J. Chem. Phys. 24, 399 (1956).
7. A. W. Mantz, E. R. Nicholas, B. D. Alpert, and K. N. Rao, J. Mol. Spectroscopy 35, 325 (1970).
8. S. C. Hurlock, Ph.D. Dissertation, Ohio State University, 1970.
9. R. D. Shelton and A. H. Nielsen, J. Chem. Phys. 21, 2178 (1953).
10. J. T. Yardley, J. Mol. Spectroscopy 35, 314 (1970).
11. T. K. McCubbin, Jr., Air Force Cambridge Research Laboratories Report AFCRL 67-0437 (1967).
12. K. M. Evenson, J. S. Wells, and L. M. Matarrese, Appl. Phys. Letters 16, 251 (1970).
13. Personal communication with M. Bhaumik, M. Mann, and W. Lacina at Northrop Corp. Labs., Hawthorne, Calif.
14. G. Herzberg, Molecular Spectra and Molecular Structure, Vol. I, Spectra of Diatomic Molecules, D. Van Nostrand Co., Inc., Princeton, New Jersey, 1950, Chapter 3.
15. R. O. B. Carpenter and M. A. Franzosa, J. Quant. Spectroscopy and Rad. Transfer 5, 465 (1965).
16. T. C. James, J. Chem. Phys. 40, 762 (1964).
17. H. H. Nielsen, Phys. Rev. 59, 565 (1941).
18. W. S. Benedict, H. H. Claassen, and J. H. Shaw, J. Res. N.B.S. 49, 91 (1952).
19. F. W. Dalby and H. H. Nielsen, J. Chem. Phys. 25, 934 (1956).

20. K. N. Rao, L. R. Ryan, and H. H. Nielsen, J. Opt. Soc. Am. 49, 216 (1959).
21. J. G. Williamson, Ph.D. Dissertation, Ohio State University, 1969.
22. E. Bell, L. Eisner, J. Young, and R. Oetjen, J. Opt. Soc. Am. 50, 1313 (1960).
23. M. J. Teich, Proc. IEEE 56, 37 (1968).
24. F. R. Arams, E. W. Sard, B. J. Peyton, and F. P. Pace, IEEE J. Quantum Electronics QE-3, 484 (1967).
25. J. D. Kraus, Radio Astronomy (with the chapter on Receivers written by M. E. Tiuri), McGraw-Hill, 1966.
26. A. E. Siegman, Proc. IEEE 54, 1350 (1966).
27. D. L. Fried, Proc. IEEE 55, 57 (1967).
28. Several Raman scattering data were kindly furnished to the author by T. Hirschfeld, Block Engineering, Inc.
29. K. Sakurai and H. P. Broida, J. Chem. Phys. 50, 2404 (1969).
30. A. B. Callear, Disc. Far. Soc. 33, 28 (1962).
31. A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge, University Press, 1961, Chapter 3.
32. H. D. Mettee, J. Phys. Chem. 73, 1071 (1969).
33. Personal communication with M. Birnbaum and J. Gelbwachs at the Aerospace, Corp., El Segundo, Calif.

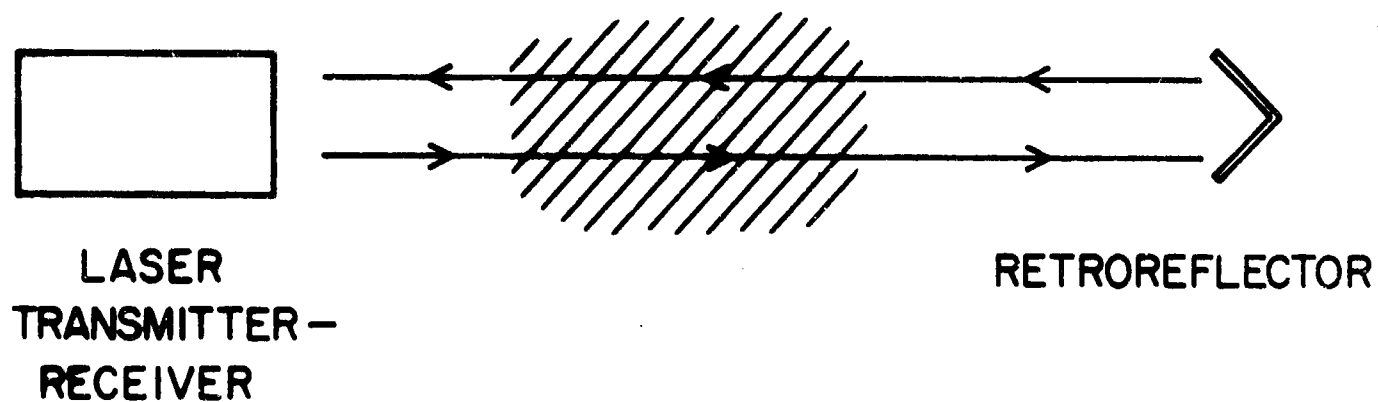




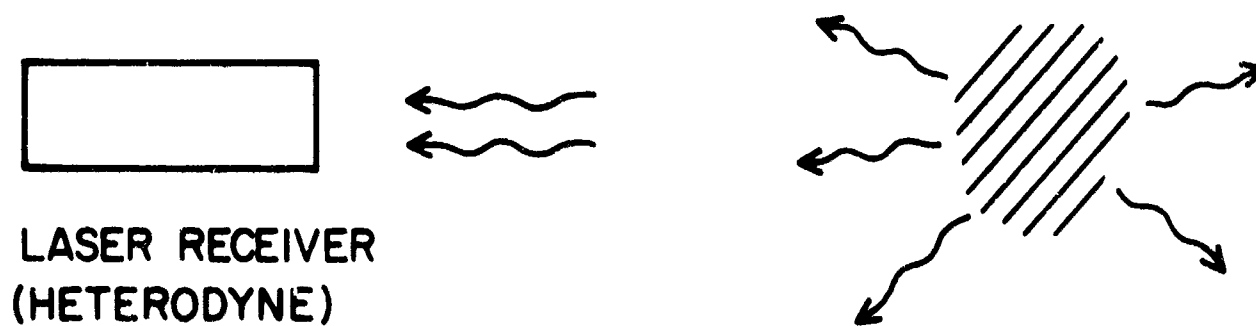
RADIOMETER SENSITIVITY TO NITRIC OXIDE

(Assuming NO cloud subtends full
field of view of receiver)

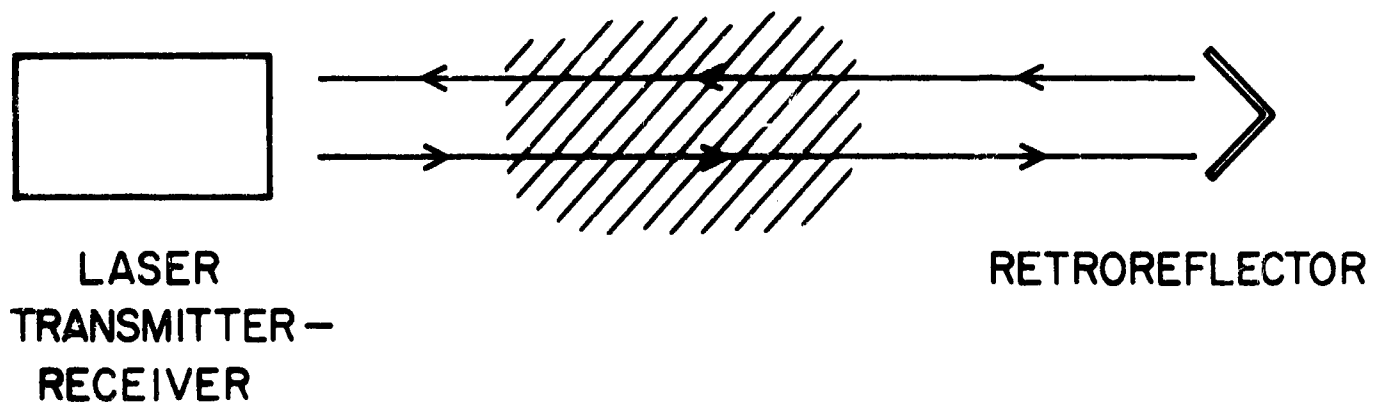
I. ABSORPTION:



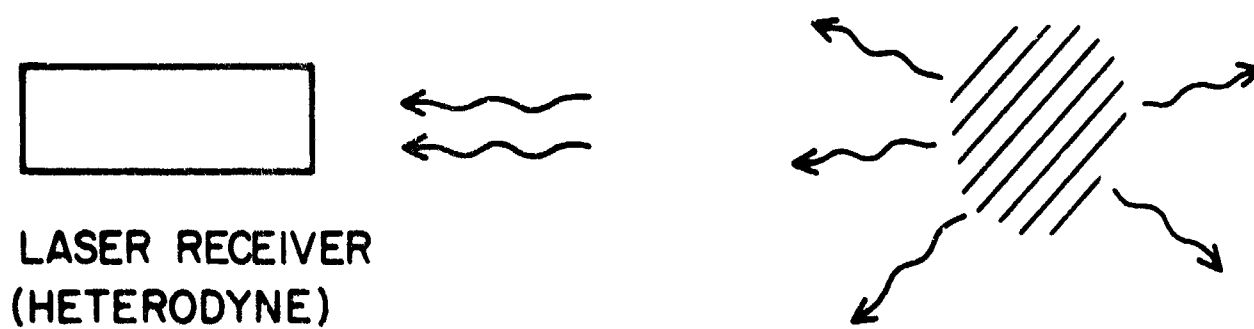
II. THERMAL EMISSION:



I. ABSORPTION :



II. THERMAL EMISSION :



UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Engineering and Applied Science Division California Institute of Technology Pasadena, California 91109		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE THE USE OF CO AND CO ₂ LASERS TO DETECT POLLUTANTS IN THE ATMOSPHERE			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Scientific Interim			
5. AUTHOR(S) (First name, middle initial, last name) Robert T Menzies			
6. REPORT DATE December, 1970		7a. TOTAL NO. OF PAGES 23	7b. NO. OF REFS 33
8a. CONTRACT OR GRANT NO. AFOSR-68-1492		8b. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO. 9768-02			
c. 614301F 61102F		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFOSR 68-1492 TR	
d. 681305			
10. DISTRIBUTION STATEMENT 1. This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES TECH, OTHER		12. SPONSORING MILITARY ACTIVITY AF Office of Scientific Research (SRR) ^{NE} 1400 Wilson Boulevard Arlington, Virginia	
13. ABSTRACT Several spectral coincidences between CO laser emission lines and infrared absorption lines of oxides of nitrogen have recently been observed. Using existing infrared spectroscopy data, we predict additional spectral coincidences; the Q-switched CO laser emits certain lines which overlap SO ₂ absorption lines, and certain frequency doubled CO ₂ laser lines overlap NO and CO absorption lines. Other spectral overlaps involving the CO ₂ laser have been reported elsewhere. Based on such coincidences remote sensing of these atmospheric constituents can be accomplished by observing resonant absorption, thermal emission, or fluorescence. We discuss sensitivities for each of these methods, using data on line strengths and pressure broadened line widths. Wide band heterodyne receivers offer high sensitivity when they can be used; our discussion included the use of this type of receiver system.			

DD FORM 1 NOV 68, 1473

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Spectral Coincidences CO Laser CO ₂ Laser Atmospheric Monitoring SO ₂ Absorption NO ₂ Absorption NO ₂ Absorption CO ₂ Absorption Laser heterodyne receivers						