The Remote Measurement of Nitric Oxide from an Airplane or Space Platform

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Nitric oxide is a very common atmospheric pollutant, being produced in virtually all atmospheric combustion processes as well as through natural decomposition of organic matter. There is also serious concern over the effects of NO emission by SST's upon stratospheric ozone concentrations. Determination of sources, sinks, and transport processes as well as study of detailed atmospheric chemistry effects requires a versatile remote sensing system. This paper describes a system which can be carried in either an airplane or a space vehicle and is useful in measuring and mapping nitric oxide concentrations in the atmosphere. The system is based on measuring fluoresced light from NO excited by a CO laser emission. Depending on the mission, the system can be configured as monostatic, bistatic and pulsed, or CW.

I. Introduction

Why Measure NO?

NITRIC oxide is a very common atmospheric pollutant, being produced in virtually all atmospheric combustion processes as well as through natural decomposition of organic matter. There is not yet evidence of significant adverse effects by atmospheric NO directly on humans, but damage to vegetation has been observed.[1] Furthermore, severe effects upon laboratory animals have been produced.

There is serious concern over the effects of nitrogen oxide emission by SST's upon stratospheric ozone concentrations. Johnston[2] has calculated that, based on SST traffic projections by FAA, a reduction in stratospheric ozone by a factor of two could occur by 1985. This would be, according to Johnston, a result of the reaction producing NO_2 and O_2 from NO and O_3. The NO_2 so produced would be, in the presence of sunlight, photo-dissociated back to NO and O. The atomic oxygen produced could then react with more NO_2, yielding NO and O_2. In this fashion it is concluded that the catalytic action of NO in reducing O_3 concentration could result finally in a greatly increased ultraviolet exposure at the surface of Earth. Just how long the nitrogen oxides exist at stratospheric levels in view of the vast multitude of atmospheric reactions which can occur is central to the issue. This question can be answered only through a program of field observations.

At the Earth's surface there must be strong scavenging processes for, although the natural production of NO is very great, the global concentrations remain quite low.[1] These processes are not yet understood but could involve soil and microbial action as seems to be the case for many other pollutants.[3]

Nitrogen oxides play a very strong role in the photochemical production of smog and may, in fact, be mainly associated with many of the adverse effects produced by other pollutants.

Measurements of NO on a local scale at the Earth's surface can be accomplished by direct sampling techniques. However, determination of global circulation patterns, identification of large scale sources and sinks, and investigation of stratospheric chemical effects requires a remote sensing technique. This paper presents such a technique and considers its use in airborne and spaceborne applications.

The Fluorescence Technique

Several reradiation processes may be distinguished. First, the incident light may suffer no change (to first order) in its wavelength and we speak of resonance fluorescence. Next, the absorption may raise the molecule to an excited state from which it radiatively proceeds to a final state other than the initial state in the absorption process. This results in a changed wavelength. Or the absorption may raise the molecule to a particular excited state from which the molecule may proceed nonradiatively to another excited state with a radiative transition from that second excited state. This also results in a change of wavelength. Finally, the molecule excited through absorption may transfer its energy by collision to another molecule which can then radiate according to its own spectral properties. Generally, when energy is transferred to a different molecule (quenched), subsequent reradiation is not useful as a means of identifying the absorbing molecule. However, in certain cases for example, where the quenching occurs in an accurately predictable fashion with easily measured quenchant concentrations, the subsequent reradiation could be useful.

Processes in which reradiation occurs directly from the excited molecule but at a shifted frequency can be used advantageously, for through such a fluorescence process the backscatter from aerosols and particulates is eliminated.

In order to devise a practicable system based on the fluorescence process it is necessary to have a source of light at a wavelength corresponding to an absorption line in the spectrum of the species sought to be measured. It is also necessary to have significant reradiation in a line or lines which can be effectively detected and distinguished from nearby lines of other atmospheric constituents.

A search was made of available laser sources.[4] Their emission lines were compared with the absorption spectrum of NO to determine the existence of coincident features. It was determined that the carbon monoxide lasing spectrum contained several features "coincident" with nitric oxide absorption features. Table 1 lists five wavelengths for which an NO fundamental absorption feature and a CO laser line nearly coincide.[5]

The infrared rotation-vibration fundamental band of NO is in general much more complex than that of the usually singlet sigma diatomic molecule—for example, CO. Since the NO ground state is known to be a $^2\pi$ state, it is split by spin orbit interactions into $^2\pi_{1/2}$ and $^2\pi_{3/2}$ components. The energy separation between these two components is approximately 120 cm^{-1} and the rotation-vibration spectrum consists of two sub-bands corresponding to the spectrum of the $^2\pi_{1/2}$ component and spectrum of the $^2\pi_{3/2}$ component. Since the effective rotational and vibrational constants are nearly the same for these two sub-bands, the sub-bands nearly coincide, which causes the spectrum to appear as a series of double lines. In addition to this spin

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Table 1 Expected lambda splitting and relative intensities of the NO lines

CO laser line (cm^{-1})	NO absorption line (cm^{-1})	λ Splitting (cm^{-1})	Re-emitted line & relative intensity		
			R	P	Q
1935.48	$R(18-1/2)$, $\Omega = 3/2$, 1935.53	0·068 1935.56 1935.49	1935.53(.51)[a]	1798.54(.49)	...
1927.28	$R(15-1/2)$, $\Omega = 3/2$, 1927.31	0.040 1927.33 1927.29	1927.31(.51)	1810.70(.48)[b]	...
1884.37	$R(3/2)$, $\Omega = 3/2, 1/2$, 1884.35	..., 0.024 1884.35 $\Omega = 3/2$ 1884.362 1884.338 $\Omega = 1/2$	1884.35(.48) 1884.35(.57)	$\Omega = 3/2$ 1863.69(.27) $\Omega = 1/2$ 1864.22(.40)	~1876(.25) ~1876(.03)
1842.82	$P(9-1/2)$, $\Omega = 1/2$, 1842.98	0.12 1843.04 1842.92	1903.13(.52)	1842.98(.47)	~1876(.01)
1784.33	$P(24-1/2)$, $\Omega = 1/2$, 1784.40	0.30 1784.55 1784.25	1944.73(.51)	1784.40(.49)	...

[a] ( ) Relative intensity.
[b] Obscured by water.

splitting, the $^2\pi$ state will exhibit a further splitting due to its finite orbital angular momentum (λ doubling) and therefore each component in this spectrum will be further split into pairs. This splitting is quite small and is different for the $^2\pi_{1/2}$ and the $^2\pi_{3/2}$ components. The rotation-vibration spectrum for NO will therefore consist of two sub-bands, each component of which consists of two very close unresolved lines.

It will be important to consider the actual NO line shape in the calculation of the laser absorption and fluorescence expected for given amounts of NO. Even if the components of the line appear to be unresolved, it is necessary to know the actual, possibly overlapped, line shape due to the four components in calculating the effective absorption coefficient.

A further consequence of the nonsigma ground state of NO is that in addition to the usual R and P rotational structures, a Q-branch will also be present. Therefore, although the laser absorption results in the population of a particular rotational level, J, for $V = 1$, the re-emitted light, as a result of branching, will appear as R, Q, and P lines.

Based on the above considerations, estimates have been made of the expected λ-splitting and relative intensities of the re-emitted branches for the various CO laser lines having coincidences with NO. These estimates were made using the data given by James[6] and Shaw.[7] The results are presented in Table 1.

In principal, then, the remote detection of NO consists in measuring the fluoresced light from a volume through which the exciting laser light has been propagated. The exciting laser line is chosen, first, on the basis of there being a relatively strong absorption by NO; second, on the convenience and utility of the expected fluorescence spectrum; and finally, with regard to the possibility of interfering species.

Light which is absorbed by molecules other than NO can constitute an interference if it results in reradiated light which reaches the detector. However, by considered selection, a spectral region relatively clear of major interferences but in which an NO absorption and CO laser emission coincide can be selected. There is always the possibility that absorption will occur by a molecule other than NO which has a very strong absorption line whose peak is relatively far removed from the NO line. Radiation absorbed in the wing of such a line would be almost entirely reradiated at the peak of the line and this would be strongly absorbed by the rest of the atmosphere and thus never reach the detector, hence interference does not occur in such a process.

The remote measurement of NO can be performed in two modes—pulsed monostatic and CW bistatic; these will be discussed later. The CW bistatic mode is the basis for an airborne system while the pulsed monostatic mode is used for the spaceborne system.

Data Interpretation

If N_0 photons are launched into the atmosphere in a certain time interval, the number reaching the volume of interest will be $N_0 \exp[-\int \alpha ds]$ where α is the absorption coefficient at the exciting wavelength and the integration is performed over the propagation path. Within the volume of interest each absorption produces an excited molecule which then loses its energy of excitation either by radiation or through a collision with another molecule (quenching). Quenching is dependent upon molecular properties of the colliding partners as well as upon temperature and pressure. At high pressures, quenching of molecular excitations is quite important, whereas at pressures corresponding to high altitudes, quenching may be ignored. Quenching rates of NO by N_2 have been estimated.[8] On that basis, the combined radiative and quenching lifetime (for an e-fold decrease in excited NO) is

$$\tau \approx 1/[A + k(N_2)]$$

where A is the Einstein coefficient for spontaneous radiation ($\sim 12.6\ sec^{-1}$ for NO fundamental) and k is the estimated rate constant ($\sim 1.4 \times 10^{-15}\ cm^3/sec$). At sea level $\tau \approx 3 \times 10^{-5}$ sec and at high altitude $\rightarrow 8 \times 10^{-2}$ sec (the radiative lifetime). Below about 60 km altitude quenching by N_2 is important. The fraction of molecules excited through the absorption process which de-excite radiatively is given by $\tau_Q/(\tau_R + \tau_Q)$. For a volume deep within the atmosphere this fraction is of the order of 4×10^{-4}. Thus, the number of photons reradiated from the volume will be

$$N_{rr} = N_0(1 - e^{-\alpha\Delta})[\tau_Q/(\tau_R + \tau_Q)] \exp\left[-\int \alpha ds\right]$$

where Δ is the thickness of the volume.

Reradiation will occur isotropically; thus, the number of photons reaching the collecting optics from the volume will be

$$N_R = N_0 \exp\left[-\int 2\alpha ds\right](1 - e^{-\alpha\Delta})[\tau_Q/(\tau_R + \tau_Q)]A_0/4\pi d^2$$

where d is the distance from the volume to the sensor and A_0 is the area of the collecting optics. The number of photons transmitted into the detector is smaller by the efficiency of the optical system, ε_0. Hence, the number of signal photons is

$$N_S = N_R \varepsilon_0$$

For present purposes we assumed that the dominant noise source is thermal background. The noise associated with the background arises from a) statistical fluctuations in the arrival rate of photons and b) nonuniformities in the background properties as the field of view changes. The present calculation considers only the statistical noise. The number of background photons arriving at the detector in a passband $\delta\lambda$ in the time δt is

$$N_B = (W/\pi)\, A_0 \varepsilon_0 \pi (\beta\alpha)^2 \delta\lambda \delta t / 4\pi a^2 hf \cdot$$

where W is the blackbody emission in w/cm^3 μm, hf is the photon energy in joules per photon, $\delta\lambda$ is the wavelength passband in μm, and δt is the sensor integration time in sec. The number of "noise photons" is

$$N_N = {N_B}^{1/2}$$

From this the signal-to-noise ratio can be calculated to be

$$\frac{S}{N} = \frac{N_0 \exp[-\int 2\alpha ds](1 - e^{-\alpha\Delta})\tau_Q A_0}{(W/\pi)^{1/2}(A_0\varepsilon_0/4hf)^{1/2}(\delta\lambda\delta t)^{1/2}\beta(\tau_R + \tau_Q)4\pi d^2}$$

For the monostatic case, d can be determined from the time delay between launching of the pulse and detection, whereas for the bistatic case d is determined from the geometry of viewing and illumination. The radiative and quenching lifetimes are to be predetermined for NO in a realistic atmosphere by a series of laboratory measurements. All other parameters can be readily determined. The details of data interpretation will be discussed under the individual systems below.

II. The Airborne System

Technical Factors

The purpose of an airborne system is to provide data on NO concentration in a particular locale over a period of time. This purpose can not be served by the spaceborne system because of limitations of observation time and spatial resolution. Ground-based systems fail to provide the needed mobility and furthermore must observe through the dirtiest part of atmosphere. The airborne system is particularly well suited for measuring the effects due to SST's traversing the stratosphere.

To take maximum advantage of the flexibility and mobility of the airborne system, it is desirable to approach the sample volume quite closely. However, the pulsed monostatic system, which we shall discuss in detail under the heading of spaceborne system, is not suited for such an application. Two factors militate against the use of the pulsed monostatic system in this application. First, with a reasonable value for laser pulse length and time resolution of the system, the sample volume is quite large. Second, since the radiative lifetime of the excited NO is so great, the signal received in the pulsed mode would be predominantly due to the atmosphere quite close to the sensor. Thus we use a bistatic system in which the laser and the detector are separated by a few feet as in Fig. 1.

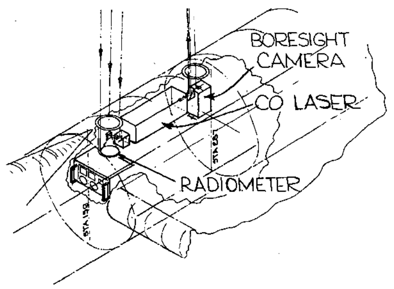

Fig. 1 Bistatic airplane-mounted system.

The viewing geometry for the bistatic case is shown in Fig. 2 with reasonable values for the parameters. The detector field of view will include not only the sample volume shown but also other regions previously excited. The greater such previously excited regions are, the more difficult becomes the interpretation of the data.

This problem can be avoided or minimized in one of two ways. If the source and detector are not both in a plane containing the flight direction, then most of the previously excited volume will lie outside of the detector field of view. Alternatively, the source can be pulsed or gated so that by the time the pulse of interest occurs the NO excited by the previous pulse will be almost entirely de-excited.

Capabilities

We assume that for the airborne case the dominant source of noise is the optics. We take the optics temperature to be 250°K and $\varepsilon = 0.2$. The field of view for this system is assumed to be roughly 1 mrad by 10 mrad, giving a solid angle of the order of 10^{-5} sterad. This gives a noise value of about 10^{-14} w at the detector for a 0.1 μm band at 5.2 μm, an optics area of 5×10^2 cm^2 and receiver efficiency of 80%.

To compute the fluoresced signal we must first know the absorption coefficient for the incident light. Menzies[5] has performed laboratory measurements of the absorption of CO laser lines by NO under several conditions of pressure. We have calculated the NO spectral feature expected at 1927.31 cm^{-1} for those conditions. Figure 3 shows these results on which is

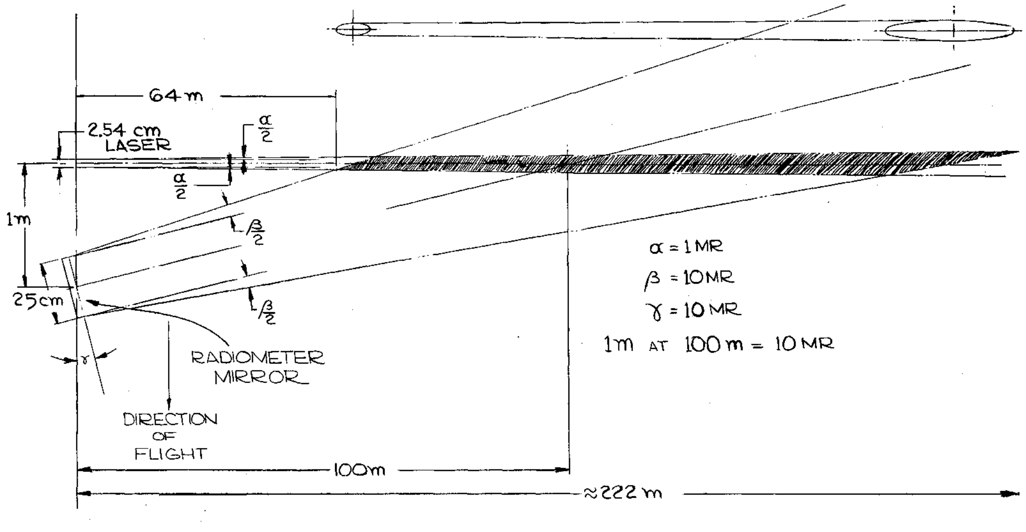

Fig. 2 Viewing geometry for bistatic system.

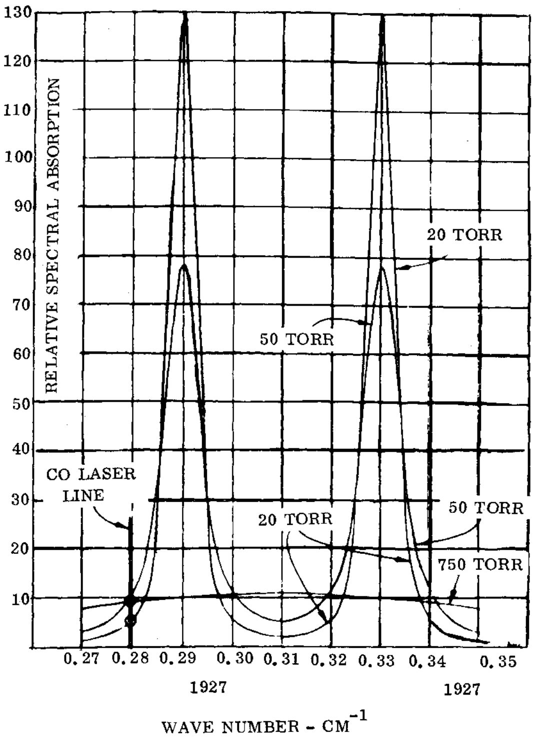

Fig. 3 Spectral absorption at 1927.31 cm^{-1}.

superimposed the CO laser line. From this calculation and Menzies' data the spectral absorption at any wavelength in that feature and at any pressure can be computed. The same can be done for each feature of interest.

Taking for the present calculation the CO line at 1935.48 cm^{-1} and the NO feature at 1935.53 cm^{-1} we have an absorption cross section of 4×10^{-20} cm^2. Assuming that the quenching lifetime is about 10^{-3} sec, the fraction of excited NO molecules which radiatively de-excite is about 10^{-2}.

Let the NO concentration be N molecules/cm^3. Then a sample of volume dV located a distance z from the detector gives rise to a signal at the detector of

$$ds = P_0 N\sigma dz e e_0 A_0/4\pi z^2$$

where P_0 = incident laser power (assumed CW); σ = absorption cross section; e = fraction of radiatively de-excited molecules; e_0 = efficiency of the optical system (assumed above to be 80%); and A_0 = area of the optics. Integrating over the path from z_0 to z_1

$$S = (P_0 N\sigma e e_0 A_0/4\pi)(z_1 - z_0)/z_0 z_1$$

The signal-to-noise ratio is then, for the numerical situation postulated,

$$S/N = P_0 N \times 1.7 \times 10^{-10}$$

If we consider the CO laser to put out a total of 25 w, of which 40% goes into the desired line, and if we assume an 80% optics efficiency, we have a total useful power output of 8 w. Hence for a threshold concentration of NO equal to 10^{10}/cm^3 this system would see a signal-to-noise ratio of about 14.

Mission Profiles

The mission profile desired can be synthesized from compatible choices of a complete set of parameters. For present purposes it is sufficient merely to note the major parameters available for selection in order to point out the flexibility of the system.

The platform parameters include altitude, flight duration, and detailed flight path. Choice of aircraft can be made dependent, on required maneuverability as well. For certain missions accurate repeats of the particular flight path could be a factor.

Viewing/illumination geometry can be fixed or can be scanned. A fixed geometry relies on aircraft maneuverability to provide the required coverage while a scanned field of view can provide the coverage while minimizing the demands made upon the platform. The scanned field situation, however, complicates the data analysis and places more stringent demands upon system calibration and alignment procedures.

A variety of source/sensor parameters is available for selection. These include laser power output, duty cycle (modulation factor), and operating temperature. In addition, detector type and D^*, as well as effective integration time, are selectable. Finally, the data may be analyzed in real time or recorded and processed in detail at a later time.

III. The Satellite Borne System

Technical Factors

The particular advantages of a spaceborne system are, first, that it provides global coverage; second, that it provides synoptic coverage; and, third, that it allows tuning of the laser output lines sufficient to change significantly the relative position of exciting and absorbing spectral features. Tuning is accomplished through the doppler effect.

In Fig. 4 we illustrate the mission geometry. The doppler shift is given by

$$\Delta\nu/\nu = (v_s/c)\sin\alpha$$

where v_s is the satellite speed, c the speed of light, and α the angle between viewing direction and vertical at the satellite. Using typical values for these parameters the excitation source can be tuned over a range of values given by the equation.

In Fig. 5 we have plotted the calculated split NO absorption feature centered at 1927.31 cm^{-1} for several altitudes. Superimposed is the CO laser line at 1927.28 cm^{-1}. It is seen that maximum absorption in this feature is accomplished with a shift of 0.010 cm^{-1} to shorter wavelength. This can be accomplished by illuminating at an angle of 11.2° to the vertical. Also from Fig. 5 we see that scanning the view direction through about 16° has the effect of the scanning through the peak absorption.

The advantages of this tuning capability include the ability to thereby increase the effective absorption coefficient by up to several orders of magnitude for high altitude levels (about 1 order of magnitude at 20 km) and the capability of emphasizing different altitude levels through the choice of illumination direction. It is also conceivable that altitude probing could be accomplished by direction scanning rather than pulse ranging.

Capabilities

In the system under consideration we are concerned with the radiation received at satellite altitude as a function of time after the passage of an exciting pulse of light down through the atmosphere. The light pulse gives rise to a radiation source function of the form $\varepsilon_\nu(h, t)$ where there is a dependency upon frequency (ν), altitude (h), and time (t). The frequency dependence is ascertained from knowledge of the properties of the absorption and emission spectra of the species involved. The time dependence arises mainly from the effective radiation lifetime of the excited species, and that is a determinable function

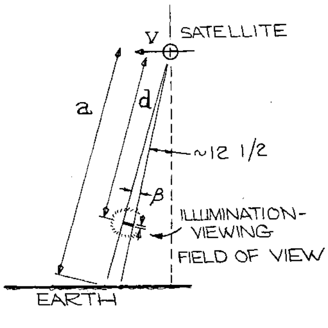

Fig. 4 Geometry for spaceborne system.

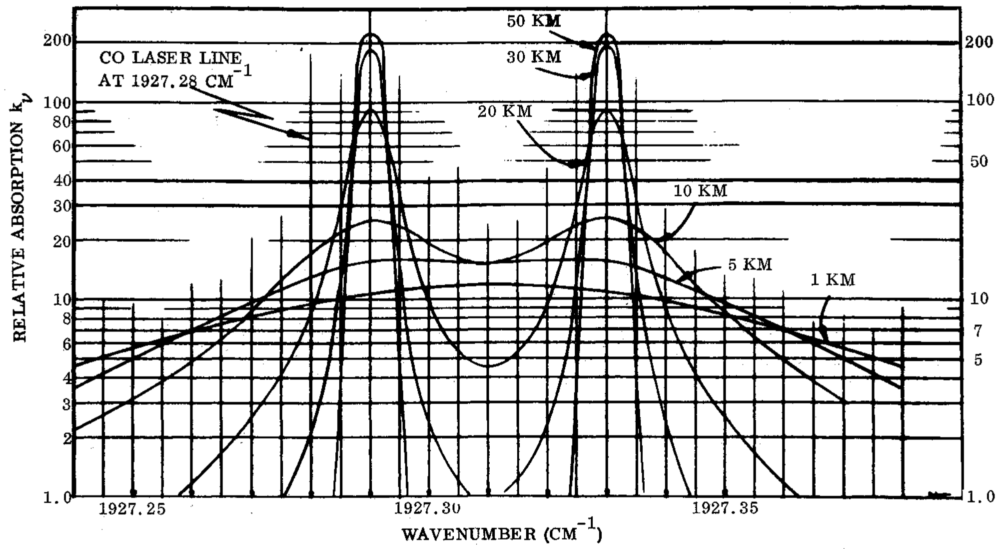

Fig. 5 Calculated Voigt profiles for various altitudes.

of altitude since it depends only upon the undisturbed lifetime and the quenching probability. The altitude-dependent part of ε_ν is a function of pollutant concentration and is the object of experimental measurement.

The radiation received at the satellite (altitude H) from the excited atmosphere is given by

$$I_{\nu s}(H, t) = \int_0^H \frac{\varepsilon_\nu\left[h', t - \left(\frac{H - h'}{c}\right)\right]}{4\pi(H - h')^2} \exp\left[-\int_{h'}^H \alpha_\nu dh''\right] dh'$$

where

$$\varepsilon_\nu\left(h', t - \frac{H - h'}{c}\right) = E_\nu(h') \exp\left[-\left(t - \frac{2(H - h')}{c}\right)/\tau(h')\right]$$

$E_\nu(h')$ is the excitation function to be discussed below and $\tau(h')$ is the effective radiative lifetime taking into account all quenching processes.

In addition to the signal intensity there will occur a background which is given by

$$I_{\nu B}(H) = \frac{I_{\nu_0}}{4\pi H^2} \exp\left[-\int_0^H \alpha_\nu dh'\right] + \int_0^H \frac{\varepsilon_\nu(h') \exp[-\int_{h'}^H \alpha_\nu dh'']}{4\pi(H - h')^2} dh'$$

where $I_{\nu 0}$ is the thermal emission from the Earth's surface, $E_\nu(h)$ is the thermal emission from the atmosphere as a function of altitude.

The measuring instrument will effectively integrate the spectral intensities over some spectral band. Here the actual line profiles are of great importance. At high altitudes, where pressure broadening effects are minimal, the lines are essentially pure doppler shapes, i.e.,

$$\exp[-\ln 2(\nu - \nu_0)/\alpha_D]$$

where α_D, the doppler half-power half-width is

$$\alpha_D = (\nu_0/c)(2R(\ln 2)T/M)^{1/2}\text{cm}^{-1}$$

where T is the temperature (K) and M is the molecular weight. At low altitudes the line is pressure broadened and takes the Lorentz form

$$(1/\pi)\, \alpha_L/[(\nu - \nu_0)^2 + \alpha_L{}^2]$$

where α_L is the half-power half-width of the pressure broadened line. α_L is a function of molecular parameters as well as collision frequency and temperature.

Because in general the spectral line profile is neither pure doppler nor pure Lorentz, several models for general line profile have been developed; among the most useful is the Voigt profile, given by

$$\Phi(x,y) = (1/\alpha_D)(\ln 2/\pi)^{1/2} K(x,y)$$

where

$$x = [(\nu - \nu_0)/\alpha_D](\ln 2)^{1/2}, \quad y = (\alpha_L/\alpha_D)(\ln 2)^{1/2}$$

and

$$K(x,y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{y^2 + (x - t)^2} dt$$

Figure 5, for example, shows the calculated Voigt profiles for the given spectral features and several conditions of pressure.

The amount of light resonantly scattered back into the receiving optics is a function of species concentration, scattering cross section, quenching time, radiative lifetime, and the amount of light launched into the atmosphere. As a demonstration of feasibility of the experiment we shall consider the amount of light expected at the satellite from a thin slab deep within the atmosphere. The configuration assumed for this computation is illustrated in Fig. 4. The view angle is taken to be that corresponding to a doppler shift of approximately 0.01 cm^{-1}. Also the illuminated and viewed volumes are taken to be identical, whereas in the actual case they would be functions of time and in general not boresighted.

For purposes of this calculation we assume that the dominant noise source is the thermal background of the Earth. Actually, over the receiving passband of the system, $\delta\lambda$, there will be significant absorption of the Earth's radiation and reemission at lower characteristic temperature. Thus, the actual background will be less than what we now calculate. The noise associated with the background arises from a) statistical fluctuations in the arrival rate of photons and b) nonuniformities in the background properties as the field of view moves over the surface of the Earth. The present calculation considers only the statistical noise.

The number of background photons arriving at the detector in passband $\delta\lambda$ in time δt was given before as

$$N_B = (W/\pi)[A_0\varepsilon_0\pi(\beta a)^2/4\pi a^2 hf](\delta\lambda\delta t)$$

where W is the blackbody emission of the Earth in w/cm^2 μm, hf is photon energy in joules/photon, $\delta\lambda$ is wavelength in μm, and δt is the sensor integration time in sec. The number of noise counts is again

$$N_N = (N_B)^{1/2}$$

The absorption of CO laser emissions by NO has been measured for certain specific cases by Menzies.[5] The measured values for the absorption of the emission at 1927.28 cm^{-1} by the absorption line at 1927.31 cm^{-1} goes from about $\alpha = 7 \times 10^{-20} \times [\text{NO}]\,\text{cm}^{-1}$ at 20 torr to about $\alpha = 1.1 \times 10^{-19} \times [\text{NO}]\,\text{cm}^{-1}$ at 750 torr.

The signal-to-noise ratio is given by

$$\frac{S}{N} = N_0 \exp\left[-\int_a^{a-d} 2\alpha dh\right](1 - e^{-\alpha\Delta}) \cdot \frac{\tau_Q}{\tau_Q + \tau_R} \frac{A_0 \varepsilon_0}{4\pi d^2}\left[\frac{W}{\pi} \frac{A_0 \varepsilon_0}{4\pi^2} \frac{\beta^2 a^2}{hf} \delta\lambda \delta t\right]^{-1/2}$$

To evaluate this expression we assume the following values for the parameters:

a = satellite range = 1100 km (600 naut miles)
$a - d$ = altitude of slab = 20 km
Δ = slab thickness = 1.2 km
β = field-of-view = 4×10^{-2} mrad (8″ arc)§
A_0 = area of collecting optics = 1/2 m^2
ε_0 = optics efficiency = 50%
$\delta\lambda$ = optical passband = 0.1 *μm*
δt = sensor time resolution element = 8×10^{-6} sec
α = absorption coefficient at line center = $1.1 \times 10^{-18} \times$ [NO] cm^{-1}
τ_R = radiative lifetime = 8×10^{-2} sec
τ_Q = quenching lifetime = 7×10^{-4} sec (20 km alt.)
hf = photon energy = 4×10^{-20} joules/photon

Earth surface temperature = 280°K. This results in

$N_0 = (S/N)\, 0.3 \times 10^{29}/[\text{NO}]$ photons/pulse or

$E_0 = (S/N)\, 1.2 \times 10^{9}/[\text{NO}]$ joules/pulse

If the concentration to be detected at 20 km altitude is $10^{10}/\text{cm}^3$, a light pulse of about $\frac{1}{2}$ joule is required for a S/N of unity. This system will have the capability of measuring an NO concentration of 2×10^{11} cm^{-3} at sea level with S/N equal to one and an output pulse of about 5 joules. The capability for low altitude slabs is nearly independent of viewing direction; i.e., little is gained by doppler shifting as can be seen in the figures.

The signal energy received at time t_0 after the pulse of light is launched originates over a rather large range of altitudes within the illuminated cone. The element at depth d gives rise to a signal which is proportional to $\exp - [(t - 2d/c)/\tau(h)]$ for $t > 2d/c$ and 0 before that. Thus, at any time t, the signal is really the sum of contributions from all altitudes at which excitation has occurred.

$$N_{s|_t} \sim \int_0^d \frac{\alpha\tau_Q f(d) \exp\left[-\left(t - \frac{2d}{c}\right)k[N_2]\right]}{d^2(\tau_R + \tau_Q)}\, d(d)$$

where α, τ_Q, and $[N_2]$ are all assumed to be known functions of d, and f is a function to be discussed below. The concentration of NO appears with $\alpha(d)$ and the object of the data analysis will be to deconvolve the data according to such a relationship to produce [NO] as a function of d for given τ_Q and $[N_2]$ functions.

In addition to the factors in the equation above which have been previously introduced, there is the function $f(d)$ which contains d-dependent factors due to the geometry of the illuminated and viewed fields and related to such mission parameters as pointing direction. The deconvolution of the signal to yield NO concentration profiiles may be done on an analog–digital hybrid system where the large amounts of data expected can be handled with reasonable accuracy without extraordinarily large amounts of computer running time.

Mission Profiles

The sampling density for the spaceborne system can be selected from the great range of values. A particular locale can be sampled in detail on a particular pass or can be studied synoptically. At ground speed of about 8×10^3 m/sec the spacing between samples for a particular sampling frequency (r) is

$$D = 8/r \text{ km}$$

With a field of view of 4×10^{-2} mrad the spot on the Earth's surface illuminated from an altitude of 600 naut miles is roughly 44 m in diam. Making use of the ability to scan the viewing angle, a particular volume can be sampled over a long period at different relative wavelengths. Considering the variation of absorption coefficient with viewing angle, the repetitive sampling at different positions in the absorption feature could in principal allow an improvement in the resolution of the system. For example, for a satellite at 600 naut miles sampling at a rate of one per sec, there could be thirty samples taken in the range of view angles from 12° to 0°. That is, thirty samples in the range of $\Delta\nu = 0$ to $\Delta\nu = 0.011$ cm^{-1}, which is a significant spectral range to scan.

Detailed missions can be formulated in terms of combinations of parameters, among which are: orbital altitude, sampling rate (variable), and look direction.

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§ This is several times larger than the diffraction limit.