A COMPARATIVE STUDY OF LASER METHODS
OF AIR POLLUTION MAPPING

Prepared for the
Canada Centre for Remote Sensing

THE DEPARTMENT OF ENERGY, MINES AND RESOURCES
OTTAWA 4, ONTARIO

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Dr. R. M. Measures
Associate Professor

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ABSTRACT

A comparative study has been made of three laser methods of remotely mapping gaseous pollutants of our atmosphere. It has been found that, in the case of NO$_2$ and SO$_2$, Differential Absorption and Scattering has superior performance potential with regard to range and sensitivity than either Laser-Induced Fluorescence or Raman Back-scattering. However, because of the sophistication of this system and the difficulty of interpretation, it is strongly recommended that from the long term point of view the fluorescence approach be pursued further as it has a range and sensitivity far superior to Raman back-scattering for a given laser power. An analysis of the fluorescence return expected from a local source of NO$_2$ indicates that a plume of about 10 ppm could be detected at a range of several kilometers. However, due to absorption effects, care must be used in the interpretation of signals emanating from local concentrations in excess of about 10 ppm.
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1. INTRODUCTION

The development of the Q-switched ruby laser gave rise to the optical analogue of Radar - which is designated Lidar*. This technique has been employed to evaluate the spatial distribution of the aerosol and particulate components of the atmosphere (Refs. 1, 2). Mie scattering of the laser radiation is the pertinent process involved in this approach. The use of high power ruby lasers generating intense bursts of radiation at 3472 Å through second harmonic conversion has given rise to the possibility of extending the Lidar concept to measure the spatial distribution of many of the gaseous constituents in our atmosphere by Raman Scattering (Refs. 3, 4). In this process the laser radiation suffers a change of frequency on being scattered by a molecule. The shift in the frequency is a characteristic of the molecule and so by observing the radiation at the appropriate frequency emanating from a given region of the laser beam, the concentration of the molecule of interest can be ascertained.

The recent development of the 100 pulse per second nitrogen laser operating at 3371 Å with an output of 100 kilowatts may enable the extension of this laser-radar technique to mapping the gaseous pollutants emitted by chimney stacks. The advent of the high power tunable dye laser suggests two additional concepts that might enable the spatial distribution of specific gaseous pollutants to be measured over an urban area. The first technique uses fluorescence where the laser radiation has been chosen to be at a frequency such that a molecule is raised into an allowed excited state, rather than a virtual state. The cross-section for this process can be very many orders of magnitude greater than that observed in Raman Scattering. However, the increased lifetime of the state results in the possibility of collisional quenching which reduces this advantage to some extent. The second technique has been used by Schotland (Ref. 5) to determine the vertical profile of water vapour in the atmosphere. We shall refer to this as Differential Absorption and Scattering. This concept exploits the difference in the backscattered signal received from a laser beam when the frequency of the probing radiation is tuned to coincide with that of an absorption line in a particular molecule, and then slightly detuned from the line.

In view of the potential of these three laser air pollution mapping techniques it was deemed appropriate to make a comparative study in order to ascertain their relative merits. In particular, we have attempted to evaluate which system will detect the lowest concentration at a given range for the same laser power. It is recognized that in view of the large energy required to electronically excite some molecules, for example CO, only Raman Scattering has universal application. However, a number of air pollutants, SO₂, O₃, NO₂ is becoming one of the most important urban pollutants we have concentrated on NO₂. There are two reasons why NO₂ is becoming increasingly important; first it is not easily eliminated from the combustion process and second its ability to create carcinogenic substances, like PAN, is becoming a considerable concern.

It should be noted that all three of the techniques considered can be used to monitor air pollution by day or night, in a variety of

* Acronym for Light Detection and Ranging
weather conditions, in either the vertical or horizontal plane and can be mounted on a tall building, a truck or an aircraft. One of the most useful applications would be that of monitoring remotely the effluent of a stack or a jet engine under a wide range of conditions. The latter applications may have particular relevance in view of the current interest in STOL airports that are to be placed close to areas of high population densities.

2. LASER INDUCED FLUORESCENCE

2.1 Basic Theory of Fluorescence

The molecular structure and processes of interest in this report can be represented by a relatively simple vibrational electronic model illustrated in Figure 1.

When the molecule is exposed to laser radiation of a suitable frequency a number of molecules that were originally in the ground vibrational state of the ground electronic state (represented by \( v'' \)) are elevated into the \( v' \) vibrational state of the excited electronic state. Some of these excited molecules will undergo collisions that will either transfer them into other vibrational states of the excited electronic state (\( v' \)) or return to some vibrational state (\( v'' \)) of the ground electronic state. The former collisions essentially represent vibrational quenching, while the latter collisions can be regarded as electronic quenching. Alternatively, an excited molecule in the \( v' \) state can decay to the \( v'' \) state by emission of a photon.

A basic assumption that is implied in this model is that the rotational relaxation rate is so fast that the distribution of the population amongst the different rotational levels of each vibrational state are maintained in an equilibrium state determined exclusively by the translational temperature of the gas.

Under these conditions the volume emission coefficient for the \( v'_O, v'' \) band is given by

\[
\epsilon(v'_O, v'') = \frac{1}{4\pi} h\nu(v'_O, v'') N(v'_O) A(v'_O, v'')
\]  

(2.1)

where \( \nu(v'_O, v'') \) is the mean frequency corresponding to the band \( (v'_O, v'') \), \( N(v'_O) \) is the population density of the \( v'_O \) level and \( A(v'_O, v'') \) is the Einstein spontaneous emission coefficient for the \( (v'_O, v'') \) band.

The equation describing the rate of change of the population in the \( v'_O \) level is of the form

\[
\frac{dN}{dt}(v'_O) = N(v''_O) R(v''_O, v'_O) - N(v'_O) \left[ A(v'_O) + M(v'_O) + R(v'_O, v''_O) \right]
\]

(2.2)

where

\[
R(v''_O, v'_O) = B(v''_O, v'_O) \int \frac{I'(v)}{4\pi} G_{v''_O} (v) \, dv
\]

(2.3)

\[
A(v'_O) = \sum_{v''} A(v'_O, v'')
\]

(2.4)

is the total radiative decay rate for level \( v'_O \).
\[ K(v',o') = Q(v',o') + V(v',o') \]

is the total quenching rate coefficient for level \( v' \).

\[ Q(v',o') = \sum_{v''} Q(v',o',v'') \]

is the total electronic quenching rate coefficient for level \( v' \).

\[ V(v',o') = \sum_{v'} V(v',o',v') \]

is the total vibrational relaxation rate coefficient for level \( v' \).

\( M \)

is the number density of the quenchers.

\[ B(v',o') \]

if the appropriate Milne absorption coefficient.

If we consider a step form of excitation, then eventually a balance will be reached such that

\[ \frac{N(v',o')}{N(v',o')} = \frac{R(v',o')}{[A(v',o') + MK(v',o') + R(v',o',v'')] } \]

We have assumed in attaining this result that the levels adjacent to \( v' \), only act as a sink. This is a conservative assumption regarding the fluorescence signal.

2.2 Strong Beam Limit

In the "strong beam limit", \( R(v',o') \gg A(v',o') + MK(v',o') \) and

\[ \frac{N(v',o')}{N(v',o')} = \frac{R(v',o')}{[A(v',o') + MK(v',o')] + R(v',o',v'')] } \]

where \( g(v',o') \) and \( g(v',o'') \) are the respective degeneracies of the upper and lower levels of the laser pumped transition. The time to reach this balance is inversely proportional to the power of the laser radiation; in fact the approximate exponential growth time for the upper level population is given by

\[ \tau_R = \frac{1}{(1+g)B(v',o') \int_{v''}^{v'} g(v',o') G(v',o') \nu \, d\nu} \]

in the strong beam limit, where the lower level population is assumed to be redistributed between \( v' \) and \( v'' \) in a time sufficiently short that little quenching of the upper level population has occurred, viz

\[ N(v',o') + N(v',o'') = N^0(v',o'') \]

\( N^0(v',o') \) being the population in the lower level prior to irradiation.

In the strong beam limit the peak values of the fluorescence emission is obtained from equations (2.3), (2.8) and (2.10):
This can be written in the form

$$\epsilon_{\text{max}}(v) = \frac{1}{4\pi} \frac{h\nu N_0(v''')}{(1+g)} A(v_o', v'') q(v_o', v'')$$

(2.12)

where \( \nu \) is the mean frequency of the \((v_o', v'')\) band

\( N_0 \) is the ground vibrational state population prior to irradiation

\( \tau \) is the radiative lifetime of the upper level and

\( q(v_o', v'') \) is the appropriate Frank-Condon factor.

i.e.

$$A(v_o', v'') = A(v_o') q(v_o', v'') = q(v_o', v'')/\tau$$

(2.13)

If the laser radiation is switched off as soon as the peak emission is attained, i.e., if the duration of the laser pulse is short, then the observed fluorescence signal will decay with a lifetime that is approximately given by

$$\tau_F \approx \frac{1}{A(v_o') + MK(v_o')}$$

(2.14)

A more rigorous transient analysis would have to account for the fact that the levels adjacent to \( v' \) are not infinite sinks for the excited state population. Such an analysis is now in progress but is not likely to make a substantial difference.

### 2.3 Weak Beam Limit

In the "weak beam limit", \( A(v_o') + MK(v_o') \gg R(v', v'') \) and it is assumed that the lower level population is only slightly perturbed from its value prior to excitation. Thus in this situation the peak emission is obtained from equations (2.3) and (2.7), viz:

$$\epsilon_{\text{max}}(v) = \frac{h\nu N_0}{4\pi[1 + \tau MK(v_o')]} \left\{ B(v_o'', v_o') \int \frac{I_0(v)}{4\pi} G(v_o'') dv ight\}$$

(2.15)

If the laser radiation is constant in time then equation (2.15) can be expressed as a Stern-Volmer relation

$$\frac{P_N}{F} = D(1 + a_M P_M)$$

(2.16)

where \( F \) is the fluorescence signal

\( P_N \) is the partial pressure of the gas undergoing the fluorescence (torr)

\( P_M \) is the partial pressure of the quenching gas (torr)

\( a_M \) is a factor that takes into account the quenching rate and the lifetime of the radiating state (torr\(^{-1}\))
D is a factor that accounts for the exciting intensity, the absorption coefficient, and various other geometrical and instrumental effects.

If we assume that the laser intensity is reasonably constant over the \((v', v'')\) band but is zero outside this spectral region, then it is possible to write

\[
\frac{h \nu}{2\pi} N_0 B(v''', v''') \int_{\Delta \nu} I^2(\nu) G(v') \Delta \nu < \kappa_\nu > \Delta \nu = I^2 < \kappa_\nu > \Delta \nu
\]  

(2.17)

where \(< \kappa_\nu >\) is the corresponding mean absorption coefficient (cm\(^{-1}\)) of the gas at the frequency of interest.

\(I^2\) is the intensity of the laser radiation (watts cm\(^{-2}\) Hz\(^{-1}\))

\(\Delta \nu\) is the appropriate bandwidth of the laser Hz, and

\(P^2(= I^2 \Delta \nu)\) is the power density of the laser beam (watts cm\(^{-2}\))

Under these conditions it is possible to reduce equation (2.15) into an effective scattering relation

\[
\epsilon_{max}(v) = N_0 \sigma_F P^2
\]

(2.18)

where \(\sigma_F\) is the "equivalent fluorescence cross-section", to be compared later with the Raman scattering cross-section. From equations (2.18), (2.17) and (2.15) it is clear that

\[
\sigma_F(v', v'') = \frac{< \kappa_\nu > q(v', v'')}{N_0 [1 + \tau MK(v')] \pi} \quad \text{(cm}^2\text{sr}^{-1})
\]

(2.19)

This equivalent fluorescent cross-section, \(\sigma_F(v', v'')\) can be separated into two components, an absorption cross-section \(\sigma_A\), and a quantum yield factor, \(\phi(v', v'')\),

\[
\sigma_F(v', v'') = \sigma_A \phi(v', v'')/4\pi
\]

(2.20)

where

\[
\sigma_A = < \kappa_\nu >/ N_0
\]

(2.21)

is the absorption cross-section per molecule and

\[
\phi(v', v'') = \frac{q(v', v'') A(v'')}{[A(v'') + MK(v'')]}
\]

(2.22)

is the quantum yield factor that can be seen to be equal to the rate of emission into the relevant band divided by the total rate of decay for the excited state population.

Now if the background radiation is not a problem, then the detector for the fluorescence radiation could possibly have a sufficient bandwidth that the signal obtained arises from several of the strongest emission bands assoc-
iated with the upper level. In which case the effective quantum yield

\[ \phi = \frac{1}{1 + \tau \text{MK}(v_0')} \]  

(2.23)

as

\[ \sum_{v''} q(v_0', v'') = 1. \]

Unfortunately, in order to use spectral discrimination against background laser scattered radiation the fluorescence wavelength must be well separated from the exciting laser wavelength.

In order to determine which regime provides a better description of the real situation the ratio

\[ \gamma = \frac{R(v_0', v_0'')}{A(v_0') + \text{MK}(v_0')} \]  

(2.24)

is evaluated. With the same assumption concerning the spectral characteristics of the laser radiation as used above, equation (2.17), we may write

\[ R(v_0', v_0'') \propto \frac{4\pi \langle k \nu \rangle}{h\nu N_0} P^l = \frac{4\pi}{h\nu} \sigma_A P^l \]  

(2.25)

Thus with

\[ \gamma = \frac{4\pi \sigma_A P^l}{[1 + \tau \text{MK}(v_0')] h\nu} \]  

(2.26)

and using weak beam limit \( 0.1 \leq \gamma \leq 10 \) strong beam limit, the constraint on the laser power density, \( P^l \), for each regime is clear.

2.4 Fluorescence Return Signal

The general lidar equation can be expressed for the fluorescence case in the form

\[ F^F(r) = \xi E \rho N(r) A(r) \lambda P^l(r) T^T F^F / r^2 \]  

(2.27)

where

- \( F^F(r) \) is the fluorescence power received from range interval \((r, L)\)
- \( E \) is the total optical efficiency (including the transmittance of the narrow-band filter)
- \( P^l(r) \) is the transmitted power density at \( r \) in the absence of attenuation
- \( L \) is the increment of range over which the fluorescence signal
is integrated*

\[ \sigma_F \] is the equivalent fluorescence cross-section

\[ N(r) \] is the fluorescent constituent density at range \( r \)

\( \zeta \) is a geometrical factor that accounts for the overlap of the transmitted and received beams

\( T^L \) and \( T^F \) are the respective one way transmittances at the laser and fluorescent wavelength.

For a monostatic system,

\[ T^L T^F = \exp \left[ - \int_0^r \left\{ \varepsilon(\lambda^L) + \varepsilon(\lambda^F) \right\} \, dr \right] \tag{2.28} \]

where \( \varepsilon(\lambda) \) is the total extinction coefficient, allowing for both scattering and absorption, at wavelength, \( \lambda \). Moreover, if the scattering losses originate from constituents that are reasonably uniform we may introduce a mean scattering extinction coefficient, \( \varepsilon_S \), that will apply at both wavelengths, their separation being small. This enables equation (2.27) to be written in the form

\[ F^F(r) = \zeta F^L(r) \, \sigma_F N(r) \, \frac{A^L(r)}{r^2} \, L \exp \left[ - r \left\{ 2\varepsilon_S + \varepsilon_A(\lambda^L) + \varepsilon_A(\lambda^F) \right\} \right] \tag{2.29} \]

where \( \varepsilon_A(\lambda) \) is the mean extinction coefficient due to absorption at \( \lambda \).

For a well designed system both \( E \) and \( \zeta \) are close to unity. If \( \zeta \) is close to unity then the spreading laser beam is assumed always to be within the field of view. In which case we may assume \( P^L(r)a(r) = P^L_o \), where \( P^L_o \) is the total transmitted power. Thus we may write

\[ F^F(r) = P^L_o \, \sigma_F N(r) \, \frac{A^L}{r^2} \exp \left[ - r \left\{ 2\varepsilon_S + \varepsilon_A(\lambda^L) + \varepsilon_A(\lambda^F) \right\} \right] \tag{2.30} \]

A schematic diagram of the laser-radar system is shown in Fig. 2.

2.5 \( \text{NO}_2 \)-Fluorescence

The lower electronic structure of \( \text{NO}_2 \) has been studied by Burnell et al (Ref. 7) and Fink (Ref. 8), Douglas and Huber (Ref. 9) have identified the absorption in the visible as arising from \( A^2B_1^+ - X^2A_1^+ \) transitions. The expected radiative lifetime for levels in the \( 2B_1 \) state should be about 0.3 \( \mu \)sec according to the absorption coefficients as measured by Hall and Blacet (Ref. 10). However, several authors (Refs. 11-16) have recently studied the fluorescence of \( \text{NO}_2 \) and have observed radiative lifetimes about two orders of magnitude larger than the value predicted from the integrated absorption coefficient. Although there is a substantial spread in the reported lifetimes, ranging from 44 \( \mu \)sec to 90 \( \mu \)sec, until recently (Ref. 17) there has

* \( L \) will depend upon the duration of the excitation and the effective lifetime of the fluorescence. If it were not for strong quenching, \( L \) would be large and so good spatial resolution not attainable.
been no evidence of the expected short lifetime. Douglas (Ref. 18) has proposed several mechanisms to account for this anomalous lifetime and both Keyser et al (Ref. 15) and Schwartz and Johnston (Ref. 16) have indicated that electronic mixing is probably the most likely mechanism.

Although most of the fluorescence work has indicated that NO₂ emission is extremely complex and almost a continuum, Sakurai and Broida (Ref. 17) have demonstrated that if the bandwidth of the excitation is very narrow, fairly sharp lines can be made to stand above the continuum emission. Schwartz and Johnston (Ref. 16), Keyser et al (Ref. 15), and Sakurai and Broida (Ref. 17) have shown that the electronic quenching rate is much smaller than the vibrational transfer rate and this in part explains the range of quenching cross-sections observed. Keyser et al (Ref. 15) and Schwartz and Johnston (Ref. 16) have clearly shown that the apparent quenching rate decreased with increasing observation bandwidth but also with increasing separation between the excitation and fluorescent monitoring wavelengths. These authors (Refs. 15, 16) discuss a step ladder vibrational relaxational model to account for these observations and deduce an effective vibrational transfer rate, $K(v')$, of about $4 \times 10^{-10}$ cm³ molecule⁻¹ sec⁻¹ for (NO₂,NO₂) collisions. This corresponds to a vibrational quenching cross-section of about 710Å² so that practically every gas kinetic collision is effective in producing vibrational relaxation. Myers et al (Ref. 12) measured the quenching of NO₂ induced by a number of other gases including, N₂ and O₂. These were found to be comparable in their cross-sections and about half as effective as NO₂.

It is evident from these studies that if a broad band could be used in monitoring the laser-induced fluorescence then a much lower quenching rate would be observed and so a larger signal would be detected. Unfortunately, in order to discriminate against the solar background a narrow spectral interval would have to be used in the detection system. Sackett and Yardley (Ref. 17) have recently been the first to excite NO₂ with very narrow band radiation, tuned to selectively excite what is believed to be a set of unperturbed $^2B_1$ levels at about 4550Å. They used a flashlamp-pumped 7-Diethylamino 4-Methylcoumarin dye laser and observed a component of the NO₂ fluorescence with a lifetime of about 0.5 μsec. Unfortunately, they were not able to ascertain the relative strength of these shortlived transitions because they observed the temporal variation of the fluorescence with a Corning 3-69 filter, which accepts all emission with wavelength greater than 5200Å.

We present in Table I a summary of the information that we shall use in evaluating NO₂ laser induced fluorescence.

In Table II we indicate the values of interest concerning the potential of fluorescence as a means of detecting NO₂ in the atmosphere.

It is clear from Table II that the effective lifetime of the excited level undergoing fluorescence is very short. This is somewhat of a mixed blessing for it means that the radiative power obtained will be severely restricted, but it also means that good spatial resolution should be possible. It should be restated that the actual value of this effective lifetime depends upon the bandwidth of observation. The larger the detector bandwidth the greater is the manifold of vibrational-rotational states encompassed within the spectral interval of observation. In the limit of a wide band detection system that would observe the entire fluorescence continuum
the quenching rate would be essentially that of electronic quenching which is about two orders of magnitude smaller than the vibrational-rotational transfer rate. In the context of remote monitoring of \( \text{NO}_2 \), a fairly narrow band detection system is likely to be required in order to discriminate against background emission.

**TABLE I**

RELEVANT PROPERTIES OF \( \text{NO}_2 \) ASSUMING EXCITATION AT ABOUT 4550 Å

<table>
<thead>
<tr>
<th>Radiative Lifetime ( \tau )</th>
<th>Quenching Rate Coefficient for Air ( K(v) )</th>
<th>Mean Absorption Coefficient ( &lt;k_v&gt; )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5x10^{-6} sec</td>
<td>2x10^{-10} cm^3 sec^{-1}</td>
<td>10^{-5} cm^{-1} ppm^{-1}</td>
</tr>
<tr>
<td>Ref. 17</td>
<td>Refs. 12 &amp; 15</td>
<td>Ref. 13</td>
</tr>
</tbody>
</table>

**TABLE II**

VALUES PERTINENT TO AIR POLLUTION MONITORING OF \( \text{NO}_2 \)

<table>
<thead>
<tr>
<th>Effective fluorescence lifetime</th>
<th>( T_{\text{eff}} )</th>
<th>5.4x10^{-9} sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent absorption cross-section</td>
<td>( \sigma_A )</td>
<td>3.7x10^{-19} cm^{-2}</td>
</tr>
<tr>
<td>Quantum yield in ( (v_o',v'') ) band ( ^{(a)} )</td>
<td>( \phi(v_o',v'') )</td>
<td>3.7x10^{-4} q(v_o',v'')</td>
</tr>
<tr>
<td>Equivalent fluorescence cross-section in ( (v_o',v'') ) band</td>
<td>( \sigma_F(v_o',v'') )</td>
<td>1.37x10^{-22} q(v_o',v'') cm^{-2} sr^{-1}</td>
</tr>
<tr>
<td>Stimulated emission rate to quenching rate ( ^{(b)} )</td>
<td>( \gamma )</td>
<td>1.95x10^{-9} ( P^2 )</td>
</tr>
<tr>
<td>Volume emission coefficient in ( (v_o',v'') ) band</td>
<td>( e_F(v_o',v'') )</td>
<td>3.7x10^{-9} q(v_o',v'') ( P^2 ) watts cm^{-3} ppm^{-1} sr^{-1}</td>
</tr>
</tbody>
</table>

(a) \( q(v_o',v'') \) is the "Frank-Condon Factor" for the appropriate band
(b) \( P^2 \) is the power density of the laser radiation (watts cm^{-2})
### TABLE III

RELEVANT PROPERTIES OF SO$_2$ ASSUMING EXCITATION AT ABOUT 3000 Å

<table>
<thead>
<tr>
<th>Radiative lifetime $\tau$</th>
<th>Quenching rate coefficient for air $K(v_o')$</th>
<th>Mean absorption coefficient $&lt;k_v&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2x10$^{-5}$ sec</td>
<td>2x10$^{-10}$ cm$^3$ sec$^{-1}$</td>
<td>1.12x10$^{-5}$ cm$^{-1}$ ppm$^{-1}$</td>
</tr>
<tr>
<td>Ref. 19</td>
<td>Ref. 20</td>
<td>Ref. 21</td>
</tr>
</tbody>
</table>

### TABLE IV

VALUES PERTINENT TO AIR POLLUTION MONITORING OF SO$_2$

<table>
<thead>
<tr>
<th>Effective fluorescence lifetime $\tau_{eff}$</th>
<th>$\tau_{eff}$</th>
<th>5.4x10$^{-9}$ sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent absorption cross-section $\sigma_A$</td>
<td>$\sigma_A$</td>
<td>4.2x10$^{-19}$ cm$^2$</td>
</tr>
<tr>
<td>Quantum yield in $(v_o', v'')$ band(a)</td>
<td>$\phi(v_o', v'')$</td>
<td>4.4x10$^{-6}$ q(v_o', v'')</td>
</tr>
<tr>
<td>Equivalent fluorescence cross-section in $(v_o', v'')$ band</td>
<td>$\sigma_F(v_o', v'')$</td>
<td>1.85x10$^{-24}$ q(v_o', v'') cm$^2$ sr$^{-1}$</td>
</tr>
<tr>
<td>Stimulated emission rate to quenching rate(b)</td>
<td>$\gamma$</td>
<td>1.47x10$^{-9}$ pl</td>
</tr>
<tr>
<td>Volume emission coefficient in the $(v_o', v'')$ band</td>
<td>$\epsilon_F(v_o', v'')$</td>
<td>5x10$^{-11}$ q(v_o', v'') pl watts cm$^{-3}$ ppm$^{-1}$ sr$^{-1}$</td>
</tr>
</tbody>
</table>

(a) (b) See Table II
If we assume that the detection system is set for the strongest $(v', v'')$ band, that is also sufficiently displaced from the exciting wavelength for discrimination against back-scattered laser radiation, then it is not unreasonable to expect a value of 0.1 for the Franck-Condon factor $q(v', v'')$. Under these conditions the "equivalent fluorescence cross-section, $\sigma_F \approx 1.37 \times 10^{-23} \text{ cm}^2\text{sr}^{-1}$, and the "volume emission coefficient", $\varepsilon''(v', v'') = 3.7 \times 10^{-10} \text{ Watts cm}^{-3} \text{ppm}^{-1} \text{sr}^{-1}$ is also evident from Table II that $\varphi_0 < 1$ for any practical laser system to be used for air pollution monitoring and so the weak beam limit is an appropriate model.

2.6 $\text{SO}_2$-FLUORESCENCE

Sulphur dioxide is very similar to nitrogen dioxide in certain respects. In particular measurements (Refs. 18, 19) of the radiative lifetime of the $\text{A}^1\text{B}_1 \rightarrow \text{X}^1\text{A}_1$ transitions also indicate a disagreement of about two orders of magnitude between the observed lifetime and that calculated from the integrated absorption coefficient. Douglas (Ref. 18), Strickler and Howell (Ref. 20) and Mettee (Ref. 21) have discussed this anomaly again in terms of a mixing of the levels of the excited singlet state with those of the ground electronic state. The luminescence spectra of $\text{SO}_2$ has been shown (Refs. 20, 21) to possess a series of well defined bands, in the 4000-4500 Å region, which are attributed to phosphorescence.

The absorption spectra for $\text{SO}_2$ comprises a series of strong absorption bands in the 2800-3100 Å region. To date there has been no narrow band excitation of these bands to see if there are any unperturbed excited states that could be used for remote sensing of $\text{SO}_2$. The results of quenching experiments (Refs. 20, 21) have indicated, as with $\text{NO}_2$, a very high quenching rate: $K(v') = 2 \times 10^{-10} \text{ cm}^3\text{sec}^{-1}$, which amounts to saying that quenching occurs at every gas kinetic collision.

In Table III the relevant basic information required in evaluating $\text{SO}_2$ laser-induced fluorescence is presented. In view of the lack of data to the contrary we have used in this instance the long radiative lifetime observed (Refs. 18, 19) although it should be realized that these results may well be too pessimistic by two orders of magnitude if it turns out that by using narrow band laser radiation it is possible to excite unperturbed stated of the $^1\text{B}_1$ level.

In Table IV we indicate the estimated values of interest concerning the potential of laser-induced fluorescence as a means of detecting $\text{SO}_2$ in the atmosphere.

3. RAMAN BACKSCATTERING RADAR

3.1 Theory of Raman Scattering

If monochromatic radiation is incident upon a molecule, one of several events may occur. If the frequency of the radiation coincides with that of an allowed transition of the molecule then a photon may be absorbed from the radiation field and the molecule elevated to an excited state. Alternatively, if the molecule was, prior to irradiation, in the upper level of the transition...
then the radiation field may induce the molecule to return to the lower level with the emission of a photon. If the frequency of the radiation does not coincide with an allowed transition two other interactions are possible. If the incident photon is elastically scattered, that is to say its direction but not its frequency is changed, then this is termed Rayleigh scattering. If on the other hand the incident photon is inelastically scattered so that both its direction and frequency are modified then this is referred to as Raman scattering.

The Raman scattered radiation comprises photons whose energy, and therefore, frequency has been changed by an amount characteristic of the energy differences between stationary states of the molecule encountered. The shift can result in an increase of frequency (Anti-Stokes Line), or a decrease of frequency (Stokes Line) of the scattered radiation. These processes are illustrated in Fig. 3. This energy shift of the scattered photon is a unique characteristic of the scattering molecule and is independent of the frequency of the scattered radiation. According to quantum mechanics a Raman transition between two atomic or molecular levels A and C is only possible when there exists at least one third level B, such that AB and BC are allowed transitions. In fact it is possible to think of the Raman transition as being a two photon process. A photon of frequency $\nu$ is absorbed and the molecule is elevated into a virtual state from which it immediately* descends to either the initial state (Rayleigh scattering) with emission of a photon of frequency $\nu$, or to some other level with the emission of some photon of frequency $(\nu \pm \nu_0)$, where $h\nu_0$ corresponds to the energy difference between the initial and final states, see Figure 3. It is clear from these remarks that the selection rules for the Raman effect are somewhat different from those applied to dipole transitions. It might also be mentioned at this point that the quantum yield for Raman scattering is unity since this is essentially a two photon process, or put another way there is insufficient time for quenching of the molecule in the virtual state.

The intensity of the Raman components of the scattered radiation can be determined from a perturbation analysis of the quantum interaction of radiation with matter. Placzek (Ref. 22) introduced the concept of a polarizability tensor, $\alpha$, which can lead to a simplified evaluation of the appropriate transition probability.

The intensity of the Stokes component of the scattered radiation at an angle $\theta$ to the exciting beam is given by

$$I_R(\theta) = \frac{(2\pi^2)^5}{135} \left( \frac{(\bar{\nu}-\Delta\nu)^4 N h \nu}{[1-\exp\left\{-\frac{hc\Delta\nu}{kT}\right\}]^2 \pi^2 c^2 \Delta\nu} \right) \left\{ \frac{[45(\bar{\nu}^{'})^2+7(\gamma^{'})^2](\bar{\nu}^{'})^2 \cos^2 \theta}{6(\gamma^{'})^2 \sin^2 \theta} \right\} P_\nu^2 \tag{3.1}$$

where $\bar{\nu}$ is the wavenumber of the exciting beam of power density $P_\nu$.

$\Delta\nu$ is the Raman wavenumber shift

* The word, "immediately", implies in the present context a time short enough for the energy uncertainty of the atom or molecule to comply with the Heisenberg uncertainty principle. The usual value quoted is about $10^{-14}$ sec.
N is the number of scattering molecules per unit volume.

g the degree of degeneracy.

h and k are the Planck and Boltzmann constants.

c is the velocity of light.

T is the temperature of the molecules.

$\bar{\alpha}'$ is the isotropic part of the derivative of the polarizability tensor and

$\gamma'$ is the anisotropic part of the derivative of the polarizability tensor.

The \[ 1 - \exp \left\{ -\frac{\hbar c \Delta v}{kT} \right\} \] factor accounts for those molecules that were in excited states prior to irradiation (Ref. 23). For our purpose it is sufficient to simply write for the backscattered component of the Raman emission:

$$\varepsilon_R = N \sigma_R P^L$$

(3.2)

where it should be noted from (3.1) that the Raman scattering cross-section has a fourth-power dependence on the exciting frequency, provided the frequency does not approach the value corresponding to an allowed transition. This strong increase of scattering with frequency indicates the advantage of working with short wavelength lasers. If the frequency should coincide with that of an allowed transition the cross-section is increased by several orders of magnitude and this process is termed "Resonance Raman Scattering" (Ref. 24). However, the potential of this interaction may be limited to some extent by interference with fluorescence, although in situations where quenching and broadening of the fluorescence is appreciable the narrow lines (Ref. 25) associated with the Resonance Raman scattering may still be resolved.

3.2 Laser-Raman Radar for Pollution Monitoring

Although some of the first applications of Laser-Raman Radar (LRR) were concerned with studying the more basic properties of the atmosphere (Refs. 3, 4, 26), several authors have recently discussed its application to remote air pollution monitoring (Refs. 27, 28, 29). The particular advantages of LRR are its ability to remotely map the air pollution whilst evaluating the relative concentrations of the various pollutant species. It is unaffected by Rayleigh or aerosol scattering and can allow for changes in atmospheric pressure or temperature by using the nitrogen Raman signal as a reference.

Derr and Little (Ref. 30) have estimated the variation in the number of Raman scattered photons observed as a function of range using a nitrogen pulsed laser operating at 3371 Å with 100kW peak power. They indicate the SNR values one might expect from any gas having the same backscattering cross-section as $N_2$. They also show that for daytime operation the system will be sky-background limited since even under twilight operation the RMS fluctuations in the sky background exceed the detector noise by at least an
order of magnitude. The RMS values are the most significant, in the absence of saturation, since temporal discrimination can be used against the mean value of the sky background. It can be seen from their calculations that for most normal concentrations of urban pollutants the range of a Raman lidar system will be extremely limited. Moreover, an increase of collector diameter does not improve matters when the SNR is background limited. On the other hand an increase of the laser output power certainly will help.

A significant increase of the SNR could be obtained by operating at wavelengths below 2900 Å, where the strong solar absorption by stratospheric ozone lowers the background noise to a level below that of the best detectors. Moreover, the strong dependence of the Raman cross-section upon wavelength would also mean an increase in the number of scattered photons. Boudreau (Ref. 31) has indicated that care must be shown in decreasing the wavelength of the radiation used because the Rayleigh scattering cross-section also has a fourth power dependence upon frequency and so attenuation starts to limit the range of application.

Kobayasi and Inaba (Ref. 32) have recently produced a spectral analysis, shown in Figure 4, of the Raman scattered radiation from a tenuous oil plume situated at 20 m from a 30 cm collector. The source of excitation in this case was a Q switched ruby laser operated at its fundamental frequency of 6943 Å. A summary of Raman scattering data presently available in the literature is collected in Table V.

**TABLE V**

**SUMMARY OF RAMAN SCATTERING PARAMETERS FOR LASER-RAMAN RADAR**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Raman Shift (cm⁻¹)</th>
<th>Excitation Wavelength</th>
<th>Raman Backscattering Cross-section (cm²sr⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>1150.5</td>
<td>6493, 3371</td>
<td>3.0 × 10⁻³¹, 4.8 × 10⁻²⁹</td>
<td>31, 29</td>
</tr>
<tr>
<td>CO₂</td>
<td>1388.3</td>
<td>6943, 3371</td>
<td>7.3 × 10⁻³¹, 5.5 × 10⁻²⁹</td>
<td>31, 30</td>
</tr>
<tr>
<td>O₂</td>
<td>1566</td>
<td>6943, 3371</td>
<td>2.0 × 10⁻³¹, 2.4 × 10⁻²⁹</td>
<td>31, 30</td>
</tr>
<tr>
<td>CO</td>
<td>2145</td>
<td>6943</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>N₂</td>
<td>2330.7</td>
<td>6943, 3371</td>
<td>1.9 × 10⁻³¹, 1.9 × 10⁻²⁹</td>
<td>31, 30</td>
</tr>
<tr>
<td>NO</td>
<td>1882</td>
<td>3371</td>
<td>1.0 × 10⁻²⁹, 5.5 × 10⁻²⁹</td>
<td>31, 30</td>
</tr>
</tbody>
</table>
4. DIFFERENTIAL ABSORPTION AND SCATTERING

4.1 The Transfer Function

If a beam of radiation is directed through a medium the ratio of the flux received to the flux transmitted is termed "The Transfer Function," T. The concept referred to as "Differential Absorption and Scattering," DAS, is concerned with that component of the received radiation which has the same wavelength as the transmitted beam. Under these circumstances we may neglect any contribution to the returned radiation arising from fluorescence or Raman scattering. In which case only Rayleigh scattering, Mie scattering and absorption will be considered. In view of the earlier statement absorption is only taken into account as an extinction process as it is assumed that the fraction of fluorescence radiation occurring at the exciting wavelength is completely negligible in comparison to the scattered component.

Schotland, Chermack and Chang (Ref. 33) developed the appropriate transfer equation for a narrow band, beam of radiation to be used to probe the atmosphere. In general we can write,

\[ T(r,\lambda) = \frac{P(r,\lambda)}{P_0(\lambda)} = \frac{E \Delta t}{2\pi} \left[ \beta_1 + \beta_2 + \beta_3 \right] \exp\left[-2r \left( \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_A(\lambda) \right) \right] \] (4.1)

where \( T(r,\lambda) \) is the transfer function for range \( r \), at wavelength \( \lambda \).

\( P(r,\lambda) \) is the flux returned from the interval \((r,\Delta r)\) with \( \Delta r = \frac{\Delta t}{2} \).

\( P_0(\lambda) \) is the flux radiated.

\( E \) is the optical efficiency of the detection system.

\( \Delta t \) is the duration of the pulse of exciting radiation.

\( c \) is the velocity of light.

\( \beta_1 \) is the Rayleigh back-scattering coefficient for molecules at range \( r \).

\( \beta_2 \) is the Rayleigh back-scattering coefficient for aerosols of diameter smaller than the wavelength of the radiation, at range \( r \).

\( \beta_3 \) is the back-scattering coefficient for aerosols of diameter of the order of the wavelength (described by the Mie scattering theory).

\( \varepsilon_1 \) is the mean extinction coefficient due to molecular Rayleigh scattering.

\( \varepsilon_2 \) is the mean extinction coefficient for aerosol Rayleigh scattering.

\( \varepsilon_3 \) is the mean extinction coefficient for Mie scattering aerosols, and

\( \varepsilon_A(\lambda) \) is the mean extinction coefficient due to absorption in the species of interest.
With an appropriate choice of wavelength the spectral dependence of each of the coefficients will be weak in comparison to that of $\varepsilon_{A}(\lambda)$ and so if we take the ratio of the transfer function at two wavelengths with a small separation, then

$$ \frac{T(r,\lambda_1)}{T(r,\lambda_2)} = \exp \left[ \left\{ \varepsilon_{A}(\lambda_2) - \varepsilon_{A}(\lambda_1) \right\} \frac{2r}{2} \right] $$

(4.2)

Furthermore, if the transmitted flux may also be assumed to be effectively independent of wavelength over the small spectral interval of interest, then we can write

$$ \frac{P(r,\lambda_1)}{P(r,\lambda_2)} = \exp \left[ 2 \int_{0}^{r} N(r)dr \left\{ \sigma_{A}(\lambda_2) - \sigma_{A}(\lambda_1) \right\} \right] $$

(4.3)

where $P(r,\lambda_1)/P(r,\lambda_2)$ is the ratio of flux returned from range interval $(r,\Delta r)$ at wavelengths $\lambda_1$ and $\lambda_2$,

$\sigma_{A}(\lambda_1)$ and $\sigma_{A}(\lambda_2)$ are the respective absorption cross-section per molecule at $\lambda_1$ and $\lambda_2$, \[
\left\{ \varepsilon_{A}(\lambda) = \sigma_{A}(\lambda) \int_{0}^{r} N(r)dr \right\}
\]

$N(r)$ is the density distribution of the species of interest.

4.2 Range Considerations

It can be seen that the spatial profile of the species can be calculated from the expression

$$ N(r) = \frac{1}{2\sigma} \frac{d}{dr} \left\{ \log e \xi(r) \right\} $$

(4.4)

where we have introduced $\bar{\sigma} \equiv \sigma_{A}(\lambda_2) - \sigma_{A}(\lambda_1)$, the difference in the absorption coefficients, and $\xi \equiv P(r,\lambda_1)/P(r,\lambda_2)$, the ratio of the signals from $(r,\Delta r)$ at $\lambda_1$ and $\lambda_2$ respectively. It is easy to show from equation (4.4) that the necessity of being able to distinguish between the returned signals at the two wavelengths requires a minimum range of operation. Let $\sigma(\lambda_2) > \sigma(\lambda_1)$, so that $\xi(r) > 1$, and let us introduce $<N>$ as the mean density of the species between the transmitter and the point of observation. Then it follows from equation (4.3) that

$$ \xi(r) = \exp \left\{ 2<\sigma> r \bar{\sigma} \right\} $$

(4.5)

If $\xi_{\text{min}}$ corresponds to the minimum value of the ratio of the signals that can be resolved then from (4.5) it is clear that

$$ r_{\text{min}} = \frac{\log e \xi_{\text{min}}}{2\bar{\sigma}<N>} $$

(4.6)

This gives the minimum range of operation from consideration of the differential signal. It is clear that the minimum range is inversely proportional to the
difference in the absorption coefficient at the two wavelengths. From
the inverse dependence of $r_{\text{min}}$ on the difference in the absorption coefficient
at the two wavelengths it is clear that the best spatial resolution, for a
given $\xi_{\text{min}}$, will be obtained by a careful choice of the two wavelengths. The
ideal arrangement would use one wavelength at the peak of a strong absorption
band whilst the other wavelength would lie in the adjacent minimum of the
absorption spectra. In this way the actual separation of the wavelengths
might only be a few angstroms and the assumption of no change in the other
parameter is reasonable.

In order to evaluate the maximum range of operation we need to
consider the scattering processes in a little more detail. Elterman (Ref.
34) states that in conditions of good visibility* the aerosol content, within
a 3 km region above the earth's surface, accounts for over 70% of the extinction
of radiation at 5500 Å. Consequently, in polluted atmospheres where invariably
the aerosol concentration will be higher we may safely assume aerosol scattering
dominates the molecular Rayleigh losses. Furthermore, the Mie component is
very much larger than the Rayleigh component so that the general laser-radar
equation (4.1) can with good confidence be put into the form

$$P(r,\lambda) = P_0(\lambda) \frac{E_{\text{ext}} \beta}{2r^2} \exp \left[-2r \left(\xi_M + \xi_A(\lambda)\right)\right]$$

(4.7)

where we now use $\beta$ for the back-scattering coefficient, and $\xi_M$ the mean
extinction coefficient for the aerosols described by the Mie-scattering
theory. The more exact equation is described by Schotland et al (Ref. 33)
it will suffice to say that in reality the situation is very complex, but
since we are only trying to estimate the limits on the range of the DAS
concept this conservative approximation will be adequate.

We have estimated above, equation (4.6), the minimum path length
necessary to discriminate between the back scattered signals at $\lambda_1$ and $\lambda_2$.
In order that $\xi_{\text{min}}$ be as small as possible, to get as good resolution as
possible, we require that the weaker back-scattered signal be large enough
that its RMS value is much less than the expected minimum difference in
the signals. This criterion may be expressed in the form

$$\langle N_1^e \rangle - \langle N_2^e \rangle \gg \sqrt{\langle (\Delta N_2^e)^2 \rangle}$$

where $\langle N_1^e \rangle$ and $\langle N_2^e \rangle$ are the mean number of photo electrons created by
the back-scattered radiation from range $r$, at wavelengths $\lambda_1$ and $\lambda_2$
respectively. If we can assume that these bursts of photo electrons are
described by Poisson statistics then $\langle (\Delta N_2^e)^2 \rangle = \langle N_2^e \rangle$ and the criterion
can be put into the form

$$(\xi-1) \gg \langle N_2^e \rangle^{-1/2}$$

(4.8)

where we assume that

$$\xi(r) \equiv \frac{\langle N_1^e \rangle}{\langle N_2^e \rangle}$$

(4.9)

*Good visibility corresponds to a Meteorological range of 23km. Koschmieder
[Beitr.Phys.Atmos. 12, 33, 171 (1924)] defines the meteorological range, $V$, in terms of the total extinction coefficient, $\xi$:

$$V = 3.91/\xi$$

where $\xi$ in km$^{-1}$. 17
It is clear that the greater the range, the larger the right hand side of (4.8) and so the more difficult to satisfy. Let us require

$$(\xi - 1) \geq \frac{10}{\sqrt{<N_2^e>}}$$

for reliable discrimination. That is to say:

$$(\xi_{\text{min}} - 1) \approx \frac{10}{\sqrt{<N_2^e>}} \quad (4.10)$$

and we see from (4.6) that the minimum path length required to resolve the difference in the backscattered signals increases with range. This means that the greater the range the worse the spatial definition. If we assume that $\Delta$ is the smallest range increment of interest, then (4.6) can be combined with (4.10) to yield an expression

$$<N> = \frac{5}{\sigma \Delta \sqrt{<N_2^e>}} \quad (4.11)$$

that relates the minimum detectable mean density of the absorbing species over the range interval $(r, \Delta)$ to the corresponding mean number of photoelectrons created by backscattered radiation emanating from this range increment. The mean number of photoelectrons can be obtained from (4.7).

$$<N_2^e> = n \frac{E\alpha\beta P}{2r^2 \Delta f \nu} \exp \left[ -2r \left( \frac{\varepsilon_M}{\Delta f} + \varepsilon_A(\lambda_2) \right) \right] \quad (4.12)$$

where $n$ is the quantum efficiency of the photomultiplier photocathode,

$\Delta f$ is the frequency bandwidth of the system and

$\nu$ is the energy of a backscattered photon.

We may thus rewrite equation (4.11) in the form

$$<N> = \frac{5r \exp \left[ r \left( \frac{\varepsilon_M}{\Delta f} + \varepsilon_A(\lambda_2) \right) \right]}{\sigma \Delta B \sqrt{P_o}} \quad (4.13)$$

where

$$B = \left\{ \frac{n E\alpha\beta A}{2\Delta f \nu} \right\}^{1/2} \quad (4.14)$$

It is clear from equation (4.13) that the minimum detectable density increases with range but decreases with increasing transmitted power or increasing difference in absorption coefficient at $\lambda_1$ and $\lambda_2$.

In order to draw a comparison with the laser-induced fluorescence and Raman scattering techniques we need to consider the difference in the number of photoelectrons arising from the backscattered radiation at wavelengths $\lambda_1$ and $\lambda_2$, 

18
Thus

$$\Delta N_e = <N_1^e> - <N_2^e>$$

(4.15)

Thus

$$\Delta N_e = \frac{B^2P}{r^2} \exp \left[ -2r \left\{ \varepsilon_M + \varepsilon_A(\lambda_2) \right\} \right] \left\{ \exp(2\sigma <N>/r) - 1 \right\}$$

(4.16)

where

$$\varepsilon_A(\lambda_2) = \sigma_A(\lambda_2) <N>$$

It should be noted that it is $\Delta N_e$, not $<N_1^e>$ or $<N_2^e>$, that has to be compared with the RMS of the sky background to ensure a good signal to noise ratio.

5. **COMPARISON OF LASER TECHNIQUES**

5.1 **Basis For Comparison and System Characteristics**

The first question that has to be answered is, on what basis should the comparison be made; on the cost of the system for a given sensitivity or on the sensitivity for a given output power of the laser. The latter was chosen in this study because it is felt that with the rapid and dramatic changes that are so much a part of the laser technology evolution a comparison based upon sensitivity for a given output power would have more general application. Furthermore, a cost comparison can always be ascertained from these results, once the laser-detector systems are specified.

In this analysis we have assumed that the laser provides only a single, narrow band output pulse of peak power 100 kilowatts. The absolute sensitivity for a given technique calculated on this basis is rather conservative as these assumptions are somewhat modest. In many instances the output power of the laser can be increased and repetitive pulsing is possible to improve the signal to noise ratio. For daytime operation solar background dominates the noise problem. The 100 kilowatts was chosen as being practically achievable today for each technique. However, it should be mentioned that high power ruby lasers, with second harmonic generators, can be used for the Raman work with output powers in excess of $10^6$ watts at 3472Å for a single pulse operation. Nevertheless, improvements in the tunable dye laser field should erode this advantage to a large extent. Moreover, such very high powers are not conducive for urban area monitoring.

The basic operational characteristics assumed for the laser-radar system considered in this analysis are listed in Tables VI and VII respectively. The pertinent NO₂ and SO₂ properties were listed in Tables I, II, III, IV and V, where we have assumed a Frank-Condon factor of 0.1 for both gases.

In the Differential Absorption and Scattering technique there exist two parameters that depend upon the aerosol distribution. These are the scattering extinction coefficient, $\varepsilon_M$, and the backscattering coefficient, $\beta$. Unfortunately the relationship between $\beta$ and $\varepsilon_M$ depends upon several factors including the aerosol size and refractive index. In any given situation substantial averaging will occur and so according to the work of Barrett and Ben-Dov (Ref. 1) and Rensch and Long (Ref. 35) it would not
seem unreasonable to assume $\beta = 4 \times 10^{-2}$, where $\epsilon$ could be taken as the total Rayleigh-Mie extinction coefficient, and that $\epsilon = 0.45$ km$^{-1}$ for a light fog, whilst $\epsilon = 0.1$ km$^{-1}$ for a clear day.

5.2 Results of the Comparison for Nitrogen Dioxide and Sulphur Dioxide

The laser radar equation can be put into a common form which will apply for all three techniques of interest.

TABLE VI

<table>
<thead>
<tr>
<th>LASER TRANSMITTER CHARACTERISTICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technique</td>
</tr>
<tr>
<td>Total Output Power</td>
</tr>
<tr>
<td>Pulse Duration</td>
</tr>
<tr>
<td>Laser Wavelength</td>
</tr>
</tbody>
</table>

*The additional 5 ns in the effective duration of the pulse arises from the quenched lifetime for the fluorescence.

TABLE VII

<table>
<thead>
<tr>
<th>DETECTOR CHARACTERISTICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collector Diameter</td>
</tr>
<tr>
<td>Filter Bandwidth</td>
</tr>
<tr>
<td>Optical Efficiency</td>
</tr>
<tr>
<td>Range Resolution</td>
</tr>
</tbody>
</table>

$$P^\alpha(r) = E \, \sigma \, N_\alpha(r) \frac{AL}{r^2} \, P^\epsilon \xi_\alpha(r) \tag{5.1}$$

where

- $\sigma_\alpha$ is the appropriate mean cross-section
- $N_\alpha(r)$ is the relevant constituent number density and
- $\xi_\alpha(r)$ is the corresponding attenuation factor.
For a photodetection system having an integration time \( T \), and a photocathode quantum efficiency \( \eta \), the number of photoelectrons produced per range increment, \( \Delta N_e \), is given by

\[
\Delta N_e = \eta \frac{E_{\text{TOTAL}} P^L}{hv r^2} \left\{ \sigma_{\alpha} N_{\alpha}(r) \xi_{\alpha}(r) \right\}
\]

(5.2)

Now, for the fluorescence technique

\[
\sigma_{\alpha} N_{\alpha} = \sigma_{T} N_{T}, \quad \text{and} \quad \xi_{\alpha}(r) = \exp \left[ \frac{-2r(\varepsilon + \varepsilon_{A})}{L} \right]
\]

for the Raman backscattering technique

\[
\sigma_{\alpha} N_{\alpha} = \sigma_{R} N_{R}, \quad \text{and} \quad \xi_{\alpha}(r) = \exp \left[ \frac{-2r\varepsilon}{L} \right]
\]

whilst for the DAS technique

\[
\sigma_{\alpha} N_{\alpha} = \beta, \quad \text{and} \quad \xi_{\alpha}(r) = \exp \left[ \frac{-2r\varepsilon}{L} \right] \left\{ \exp \left[ -2r\varepsilon_1 \right] - \exp \left[ -2r\varepsilon_2 \right] \right\}
\]

where

\[
\varepsilon_A = \frac{1}{r} \int_{0}^{R} \sigma^A(\lambda) \xi N(r) \, dr
\]

is the mean extinction coefficient for the fluorescing constituent and

\[
\varepsilon_1 = \frac{1}{r} \int_{0}^{R} \sigma^A(\lambda_1) \xi N(r) \, dr
\]

and

\[
\varepsilon_2 = \frac{1}{r} \int_{0}^{R} \sigma^A(\lambda_2) \xi N(r) \, dr
\]

are the respective mean extinction coefficients for the absorbing constituent at the laser wavelength \( \lambda_1 \) and \( \lambda_2 \).

If we assume that the constituent of interest has a uniform distribution then equation 5.2 can be used to calculate the number of photoelectrons created per range increment for each technique, as a function of range, for a given concentration. The results of these calculations are shown in Figures 5, 6, 7 and 8. In Figure 5, the three techniques are compared for \( \text{SO}_2 \) for concentrations of 10 ppm, 1.0 ppm and 0.1 ppm under conditions of light haze, \( \varepsilon = 0.45 \text{ km}^{-1} \), whilst in Figure 6, the comparison is made again for \( \text{SO}_2 \), but for a clear day, with \( \varepsilon = 0.1 \text{ km}^{-1} \). In the case of \( \text{NO}_2 \), there is no Raman backscattering at 3371°A and so the comparison is essentially between Fluorescence and DAS. However, in order that one may obtain some feel for the relative magnitudes of the signals the \( \text{SO}_2 \) Raman results are included on the \( \text{NO}_2 \) figures.

The solar scattered background will also give a contribution to the number of photoelectrons being created. The magnitude of this contribution
can be calculated using an equation similar to (5.2). In this instance the mean number of background generated photoelectrons is given by

\[
< N^B_e > = \eta \frac{E^* \Omega B(\lambda) \Delta \lambda}{h \nu}
\]

(5.3)

where \( \Omega \) is the acceptance solid angle of the detector and \( B(\lambda) \Delta \lambda \) is the radiative background flux incident on the detector within the spectral interval \( \Delta \lambda \), permitted through the filter. It should be mentioned that the optical efficiency parameter \( E^* \) does not, in this case, include any transmitter losses that might arise in the laser-radar system.

If we assume that these bursts of background photoelectrons are described by Poisson statistics, then the RMS value of the fluctuations

\[
\Delta N^B_e = \left\{ \eta \frac{E^* \Omega B(\lambda) \Delta \lambda}{h \nu} \right\}^{1/2}
\]

(5.4)

We can also write

\[
B(\lambda) \Delta \lambda = \pi a^2 S^B(\lambda) \Delta \lambda
\]

where \( \pi a^2 \) is the effective area, at range \( r \), within the field of view, and \( S^B(\lambda) \) is the solar background radiance of the sky in watts \( \text{cm}^{-2} \text{sr}^{-1} \), \( \lambda \) in the 3500-4500 \( \text{Å} \) range on a clear day. Thus if we take \( \Delta \lambda = 10^\circ \text{A} \), \( \theta = 1 \text{mrad} \), \( E^* = 80\% \), \( \lambda = 4500^\circ \text{A} \) and the other parameters as listed in Table VII, then a fairly conservative value for \( \Delta N^B_e \) is 10 photoelectrons per range increment, which is indicated on the figures.

It is immediately evident from Figures 5, 6, 7 and 8, that the DAS technique offers the greatest sensitivity, whilst Raman backscattering offers the least sensitivity, for a given concentration of either SO2 or NO2. Moreover, reference to the RMS of the sky background, \( \Delta N^B_e \), for a bright day indicates a potential range for the DAS approach of several kilometers, even for single pulse operation. It is also clear from these figures that although the signal increases with concentration for short range operation, the accompanying attenuation suffered by the laser beam prevents the range from being increased for high concentration of species under conditions of uniform distribution.

In general it is to be expected that when only local regions of high concentration occur the range limitation will be considerably improved.
In particular, in Section 6 we shall demonstrate that in the case of the fluorescence technique the maximum range for the detection of local high concentrations of NO₂ is extended by a factor of about 4. This strong attenuation problem is of course part of the price paid for having the laser wavelength selected to coincide with an absorption band and hence does not arise in the Raman scattering technique. In the case of fluorescence the problem is compounded by the very low quantum yield factors, which necessitate the absorption of many laser photons in order that a few are converted into fluorescence photons that may be detected.

6. FLUORESCENCE AND LOCALIZED SOURCES

6.1 Two Limiting Plume Distributions

In this section we wish to consider the effects of localized sources of high concentration on the expected return signals. We shall limit the calculations to the fluorescence technique, and in particular to NO₂ mapping. Nevertheless, it is felt that from the results obtained, a better understanding will emerge which can then be generalized. We shall consider two limiting plume concentration profiles in this analysis. We shall take a Gaussian distribution as representative of a highly localized source, while a Lorentzian distribution will be taken as representative of a rather diffuse source. In general we can write the number density of the constituent of interest

\[ N(r) = 2.7 \times 10^{13} \left[ \left( p_{\text{max}} - p_o \right) G(r) + p_o \right] \]  

(6.1)

where

\[ G(r) = \exp \left[ - \left( \frac{r-r_o}{W} \right)^2 \right] \]

for the Gaussian plume and

\[ G(r) = \frac{W^2}{(r-r_o)^2 + W^2} \]

for the Lorentzian plume. \( W \) being the e⁻¹ half width for the Gaussian distribution and the half width at half maximum for the Lorentzian distribution, \( r_o \) is the distance of the centre of the distribution from the laser-radar system in each case. \( p_{\text{max}} \) and \( p_o \) are the respective peak and average values of the concentration of the constituent in ppm. We can then write the number of photoelectrons created per range increment, due to laser induced fluorescence

\[ \Delta N_e^F(r) = \eta \frac{\text{ETALP}^F \sigma_F}{h \nu} \frac{N(r)}{r^2} \exp \left\{ -2 \pi \epsilon \int_0^r \sigma_A(\lambda_f^F)N(r)dr - \int_0^r \sigma_A(\lambda_f^F)N(r)dr \right\} \]

This can be expressed in the form
\[ \Delta N^F_e = B^F \exp\left\{ -2 \left[ \frac{N(r)}{r^2} \right] \right\} \]

if we make the reasonably conservative assumption

\[ \sigma_{\lambda^F} = \sigma_{\lambda^L} = \sigma_A \]

and we introduce

\[ B^F = \eta \frac{ETAL \sigma_F}{h\nu} \]

6.2 Results for Localized Sources

\[ \Delta N^F \] for NO\(_2\) has been evaluated as a function of range for a number of \(P_{\text{max}}\), \(r_0\), and \(\nu\) cases using equations (6.1) and (6.2). Two sets of results are shown as Figures 9 and 10. Figure 9 shows a sequence of pulses that would be observed from a Gaussian plume, of \(e^{-1}\) half width 20m, located at a range of \(10^2\), \(2 \times 10^2\), \(5 \times 10^2\), \(7.5 \times 10^2\), \(10^3\) or \(1.5 \times 10^3\)m. Figure 10, on the other hand, shows the corresponding sequence of pulses that might be obtained from a Lorentzian plume, of HWHM = 20m, and located at a range of \(10^2\), \(2 \times 10^2\), \(5 \times 10^2\), \(7.5 \times 10^2\), \(10^3\) or \(1.5 \times 10^3\)m. \(P_{\text{max}}\) was taken as 10 ppm in both cases and \(r_0\) is assumed equal to 0.1 ppm throughout this work. It should be mentioned at this point that time and distance are interchangeable for the abscissa scale in these figures due to the radar mode of operation.

A study of the corresponding sequence of pulses arising from higher peak concentrations clearly indicates that absorption within the plume causes severe distortion of the observed plume profile. This distortion results in a considerably reduced peak amplitude and an apparent shift towards the observer of the peak concentration. These effects are illustrated in Figures 11 and 12 for both types of plume distribution. As might be expected the Lorentzian distribution yields the strongest distortion due to its extensive nature, and the larger the width of a plume, for a given peak concentration, the more severe the distortion. With regard to interpretation of an observed plume return, it is clear that the severe distortion is accompanied by a step in the background signal. Under certain conditions this jump in the background could contain sufficient information to allow a correction to be made to the plume signal. In fact, there is no ambiguity, for even if two returns have the same amplitude, the size of the step in the background preceding the pulse will distinguish the high from the low concentration regions.

Figure 13 illustrates the saturation in the peak amplitude of the return signal which is observed with increasing concentration. It is also clear from this figure that the magnitude of the fluorescent return associated with the centre of the plume actually reaches a maximum and then declines with further increases in peak concentration. It is evident from Figure 13, that for a plume full width of about 40 m, the fluorescent return signal is reliable for either type of plume profile provided \(P_{\text{max}}\) is less than about 10 ppm. This is again indicated in Figure 14 where it is seen that for \(P_{\text{max}} = 10\) ppm, the fluorescence signal is practically
independent of the plume shape. Figure 14 also shows the improved range of this fluorescence technique over that estimated from the mean concentration curves, such as seen in Figure 7. Since the absorption characteristics of SO₂ are quite similar to that of NO₂ it is felt that similar results would be obtained with SO₂.

7. CONCLUSIONS AND RECOMMENDATIONS

The comparative study of laser methods of air pollution mapping discussed in this report has been completed. The major results of the analysis and the conclusions to be drawn from these results will be summarized as they concern NO₂ and SO₂ monitoring.

(1) It is evident from our work that with regard to range and sensitivity, Differential Absorption and Scattering has the potential of somewhat superior performance compared to the Fluorescence method of monitoring gaseous pollutants in the atmosphere, and both should have considerably better performance than could be achieved with the Raman Backscattering Technique.

(2) The fairly strong absorption bands used in either the DAS or the Fluorescence technique leads to appreciable attenuation of the return signals at high concentrations of the constituent of interest. This attenuation is in fact more than sufficient to compensate for the increase in signal arising from the higher concentration. Consequently, both of these techniques have a built-in disadvantage when it comes to observing high concentrations over long range.

(3) We have shown that when localized sources of pollutant are of interest the range of detection can be considerably extended and in particular we have indicated that for NO₂ it should be possible even in daylight conditions, to attain reasonably reliable measurements of localized concentrations (less than 10 ppm) to a distance of several hundred meters using the Fluorescence method with a single 100 kw laser pulse. This range could be extended to several kilometers if the laser power is increased by a factor of ten or a repetition rate of 100 pps is used.

(4) For localized concentrations of NO₂ in excess of 10 ppm considerable distortion of the return signal has been predicted. This distortion takes three forms; an appreciable attenuation of the signal amplitude, an apparent shift of the location of the peak concentration towards the observer and lastly a substantial fall in the background signal subsequent to the region of high concentration. It is believed that a similar distortion would occur for other constituents which have a small quantum yield, such as SO₂.

Although it is clear that the Differential Absorption and Scattering technique might offer the greatest sensitivity for a given laser power, the additional sophisticated equipment required in both the laser and processor is not available at present and is likely to be expensive. Moreover, the interpretation of the return signal associated with this technique is difficult because it relies on Mie backscattered laser radiation which in turn depends upon the size and type of aerosol distribution along the path of the laser beam. In view of these problems we recommend that the
that the Fluorescence approach be pursued as it offers a relatively inexpensive system which has the potential to detect and map a number of the more harmful constituents of our urban atmosphere. It is strongly suggested that a further study be undertaken to extend this analysis to other gases of concern, such as ozone. In situations where extensive regions of high concentration of pollutant are of interest the Raman approach would appear to have application for there is virtually no saturation effect associated with this technique, due to its effective quantum yield of unity.

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FIG. 5
FIG. 6

FLUORESCENCE, RAMAN AND DAS SIGNALS vs RANGE
FLUORESCENCE, RAMAN AND DAS SIGNALS vs RANGE

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FIG. 12
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FIG. 14 NO₂—FLUORESCENCE SIGNAL VS RANGE FOR LOCALIZED SOURCES
A comparative study has been made of three laser methods of remotely mapping gaseous pollutants of our atmosphere. It has been found that, in the case of NO and SO₂, differential absorption and scattering has superior performance potential with regard to range and sensitivity than either laser-induced fluorescence or Raman back-scattering. However, because of the sophistication of this system and the difficulty of interpretation, it is strongly recommended that from the long term point of view the fluorescence approach be pursued further as it has a range and sensitivity far superior to Raman back-scattering for a given laser power. An analysis of the fluorescence return expected from a local source of NO indicates that a plume of about 10 ppm could be detected at a range of several kilometers. However, due to absorption effects, care must be used in the interpretation of signals emanating from local concentrations in excess of about 10 ppm.

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