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FEASIBILITY OF THE REMOTE DETECTION OF POLLUTANTS USING RESONANCE RAMAN SCATTERING *

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We present calculations of the Resonance Raman cross-section for several diatomic molecules. We use these results along with recent measurements of large resonance enhancements in NO_2 and SO_2 to estimate the sensitivity of a Lidar system based on the Resonance Raman effect.

In this paper, we wish to assess the implications of recent measurements of large resonance Raman cross-sections in NO_2(1) and SO_2(2) for remote detection of these pollutants in the atmosphere by means of a Lidar system. We shall also present calculations for the resonance Raman cross-sections of various diatomic molecules and use these calculations to expand our estimates of the sensitivity of a resonance Raman Lidar system.

Raman Lidar systems have been used for some time to study major atmospheric constituents.(3) However, the fact that Raman cross-sections are quite small ($\sim 10^{-30}$ cm^2/sr) has made this technique difficult to use to detect minor atmospheric constituents such as pollutants. In spite of this difficulty, S. Nakahara et al.(4) and Melfi et al.(5) have reported detection of SO_2 in power plant stack plumes at a range of 200 m at night, and Hirschfeld et al.(6) using a powerful doubled ruby laser have been able to measure SO_2 concentrations of 30 ppm at 200 m in full daylight with a good signal to noise ratio.

It is well known that Raman cross-sections are enhanced if the laser source is tuned close to an absorption line in a gas. Such enhancements could dramatically increase the sensitivity of a Raman Lidar system. Most measurements of the resonance Raman effect (7) have been made in I_2 vapor, where large enhancements have been observed. (10) Recently, we have measured a resonance Raman cross-section of 1.7×10^{-24} cm^2/sr(9) in I_2 with an excitation wavelength of 5466.36 Å and Penney et al.(2) have reported a cross-section of 10^{-25} cm^2/sr for SO_2 with a laser excitation near

3002 Å. These cross-sections are, respectively, 4 x 10^6 and 2.6 x 10^4 times the Raman cross-section for N_2 at equivalent excitation wavelengths. Resonant inelastic scattering cross-sections (11) of the order of 10^{-20} - 10^{-21} cm^2/sr have also been observed for OH(12,13), and Wang and Davis (13) were able to measure atmospheric concentrations of OH at a level of 2 parts in 10^{13}.

We have just completed an extensive search for large enhancements of scattering into the ν_2 Raman mode of NO_2 using a nitrogen-laser-pumped dye laser. The investigation was carried out by tuning the laser through most of the visible absorption spectrum of NO_2 between 4200 Å and 6100 Å with a laser bandwidth of .1 Å. We will present the details of these experiments elsewhere,(1) but wish to report that we have seen large resonance enhancements, and have measured a cross-section of 5.6 x 10^{-27} cm^2/sr for narrow band (∿1Å) re-emission into the ν_2 Raman mode at the peak of one of the resonances for 1mm of NO_2 plus 1 atm of N_2 buffer gas. All of these measurements, along with the results of the following calculation, allow one to make reasonable estimates of the sensitivity of a resonance Raman Lidar system operating under various conditions.

One can easily estimate the resonance Raman cross-section for diatomic molecules which have known oscillator strengths and Franck-Condon factors. For an infinitely narrow exciting laser near an isolated absorption line, the cross-section can be written, approximately, as:(14)

$$\frac{d\sigma}{d\Omega} \simeq \frac{e^4\ \omega_\ell\ \omega_s{}^3\ |\langle I|r|M\rangle|^2\ |\langle M|r|F\rangle|^2\ \rho_I}{\hbar^2\ c^4\ [(\omega_\ell-\omega_o)^2 + \gamma_T{}^2]} \qquad (1)$$

where $<I|r|M>$ is the matrix element from the initial to intermediate vibrational-rotational state, while $<M|r|F>$ is the matrix element between the intermediate and final state. ω_ℓ is the laser frequency, ω_s the scattered frequency, ω_o the central frequency of the resonance and ρ_I is the relative thermal population of the initial vibrational-rotational state. γ_T is the pressure broadened linewidth. This expression is valid if γ_T is dominated by inelastic collisions and is larger than the linewidth due to the combination of natural, doppler, and hyperfine broadening. For most molecules at atmospheric pressure, the linewidth is, in fact, primarily due to pressure broadening. Even though the assumption that γ_T is dominated by the contribution of inelastic collisions may be invalid, a calculation based on that assumption will provide a lower limit for the cross-section.

We can rewrite Eq. 1 in terms of the oscillator strength, f, and the Franck-Condon factors S_{ij} by making the substitution:

$$|<I|r|M>|^2 = \frac{\hbar}{2m\omega_o} \frac{f\,S_{IM}}{3}$$

$$|<M|r|F>|^2 = \frac{\hbar}{2m\omega_o} f\,S_{MF}$$

The factor of 3 in the first matrix element occurs because we assume that the oscillator strength is equally divided between the P, Q, and R branches of the absorption line. For $\omega_\ell = \omega_o \approx \omega_s$ we get:

$$\frac{d\sigma}{d\Omega} \cong \frac{r_o^2\,\omega_s^2\,S_{IM}\,S_{MF}\,f^2\,\rho_I}{12\gamma_T^2} \qquad (2)$$

where r_o is the classical radius of the electron. For molecules where the oscillator strengths and Franck-Condon factors are known,(15-25) we can use Eq. 2 to make an estimate of the resonance Raman cross-sections. We assume that the molecules are initially in their ground vibrational state and choose the intermediate and final vibrational states to maximize $S_{IM}S_{MF}$. We also choose the initial rotational state with the maximal thermal population and use standard methods to calculate ρ_I.(26) We choose γ_T on the basis of our previous work(9) with I_2 where we found $\gamma_T = 2 \times 10^{10}$ radians/sec for 1 mm of I_2 in one atm of N_2. The results of these calculations as well as experimentally determined cross-sections are presented in Table 1.

We would now like to consider the practical implications of resonantly enhanced Raman cross-sections for pollutant detection by means of a Lidar system. For such a system, the number of signal photons detected is:

$$S = 2.69 \times 10^5 \, \eta N \frac{E}{\hbar\omega_o} \frac{AL}{R^2} \rho \frac{d\sigma}{d\Omega} \quad e^{-[\alpha_s+\alpha_o]R}$$

with

η - total detection efficiency (optical and quantum efficiency)

N - number of laser pulses

E - laser pulse energy (joules)

ω_o - laser frequency (radians/sec)

A - collector area (cm^2)

L - range increment (m)

R - range (km)

ρ - concentration of pollutant (ppm)

$\frac{d\sigma}{d\Omega}$ - Raman scattering cross-section (cm^2/sr)

α_o - atmospheric absorption coefficient at laser frequency

α_s - atmospheric absorption coefficeint at scattered frequency

The number of counts collected during the same number of pulses from skylight is:

$$B = \eta\, N \frac{W(\omega_s)\Delta\lambda}{\hbar\omega_s} A\, \phi \frac{2L}{c}$$

with

$W(\omega_s)$ - background irradiance at the scattered wavelength (watts/cm^2sr Å)

$\Delta\lambda$ - detector bandwidth (Å)

ϕ - detector field of view (sr)

ω_s - Raman shifted frequency

$\frac{2L}{c}$ - gate time for range increment (sec)

A useful measure of the sensitivity of a Lidar system can be obtained by considering the signal to noise ratio (SNR). When detecting scattered light with wavelength >3000 Å, we will assume that the noise is dominated by the fluctuations in the background irradiance, so that SNR = $S/\sqrt{B}$. For detection at wavelengths <3000 Å, where the stratospheric ozone layer effectively absorbs sunlight, and for night-time detection, we will assume that the noise is caused by fluctuations in the signal, so that SNR = $\sqrt{S}$. We will ignore, in this paper, the possible problems associated with additional background due to the fluorescence of aerosols.(27) This background may cause trouble for a Lidar system which depends on ordinary

Raman scattering. However, since the useful resonance cross-sections are at least 3 orders of magnitude larger than ordinary Raman cross-sections, we feel justified in ignoring this problem for the purposes of our illustrative calculations.

Suppose we now choose reasonable receiver parameters (i.e. $\eta = .1$, $A = 10^4 cm^2$, $\phi = 10^{-5}$ sr, $\Delta\lambda = 1$ Å) and a laser transmitter which emits a beam of $10^3 cm^2$ cross-sectional area. In order to comply with the laser safety standard for direct viewing,(28) we will limit the laser energy to .05 mJ/pulse for a repetition rate of 100 Hz. This limitation applies for lasers with wavelengths >4000 Å. For shorter wavelengths, the limits appear to be less stringent, but since there are no standards for very short pulses, we will assume the same standard as for wavelengths >4000 Å. We use the data of Baum and Dunkelman(29) to evaluate α_o, α_s and that of Knestrick and Curcio(30) for $W(\omega_s)$. We further assume a range resolution of 10 m and calculate the concentration of pollutant which yields SNR = 10 with an integration time of 100 sec. In Figure 1, we present the results of that calculation for NO_2, SO_2, and NO using the cross-sections in Table 1.

Figure 1 shows that, with the marginal exception of daylight detection of NO_2, a Lidar system making use of resonance Raman scattering can easily detect the pollutant concentrations typical of smoke plumes (>10 ppm) at a range of a few hundred meters using lasers with only very modest energies. A useful comparison can only be made with the recent report (6) of detection of SO_2

using ordinary Raman scattering. In that case, the laser used had an average power of .4 watts and an energy/pulse of .2 joules, and was able to detect 30 ppm at 200 m with SNR ∿ 10. Our calculation shows that using a laser of 5 mW average power and .05 mJ/pulse, one could achieve a sensitivity of a factor of 10 better by making use of the resonance Raman effect. In addition, if there is an enhanced cross-section in SO_2 for $\lambda_o < 2800$ Å, comparable to that for $\lambda_o = 3002$ Å, then the resonance Raman Lidar sensitivity for daylight detection of SO_2 will be the same as for night-time detection, since sky background interference with the detected radiation will no longer be a problem. The fact that the SO_2 absorption spectrum shows features at $\lambda < 2800$ Å similar to that at $\lambda \sim 3000$ Å leads one to expect that comparable enhancements will be found for such wavelengths.

Using presently available technology, one could construct a nitrogen laser-pumped dye laser which has the required pulse energy and repetition rate (31) and by using non-linear doubling crystals could extend its tuning capability to ∿2300 Å.(32) In order to detect NO, however, one needs a laser at 2260 Å. At present, the non-linear crystals available for frequency doubling to this wavelength are not very efficient.(33) However, at least one efficient technique for up-conversion of light with $\lambda > 2500$ Å to span the wavelength region 2000-2350 Å has been reported.(34) It should be noted that even if the efficiency of conversion of visible light to light at 2260 Å were only ∿.01%, there would still be enough sensitivity to monitor smokestacks at ∿200 m.

Figure 1 also shows that monitoring of ambient concentrations (∿.1 ppm) at distances of order 1 Km is certainly out of the question, given the safety constraint we have imposed on the calculation. If one could be sure that there will be no eye exposure to the light from the Lidar transmitter, then one might be able to use high-energy tunable lasers to gain the required sensitivity.

In conclusion, it seems to us that the advantages in sensitivity and safety associated with the use of resonance enhancements in a Raman Lidar system outweigh the additional problems associated with the use of a tunable laser as a Lidar transmitter. The fact that an instrument for use in populated areas will probably have to comply with stringent eye safety standards implies that the use of resonance enhancements will be the only avenue to a workable Raman Lidar system for remote smokestack monitoring.

FOOTNOTE AND REFERENCES

*Research supported by National Science Foundation from RANN Division and U. S. Atomic Energy Commission.

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FIGURE AND TABLE CAPTIONS

FIG. 1 Lidar sensitivity vs. range for E = .05 mJ and N = 10^4 pulses assuming a signal to noise ratio of 10 and a visibility of 10 km.

TABLE I Resonance Raman cross-sections for various small molecules determined either experimentally or from Eq. (2).

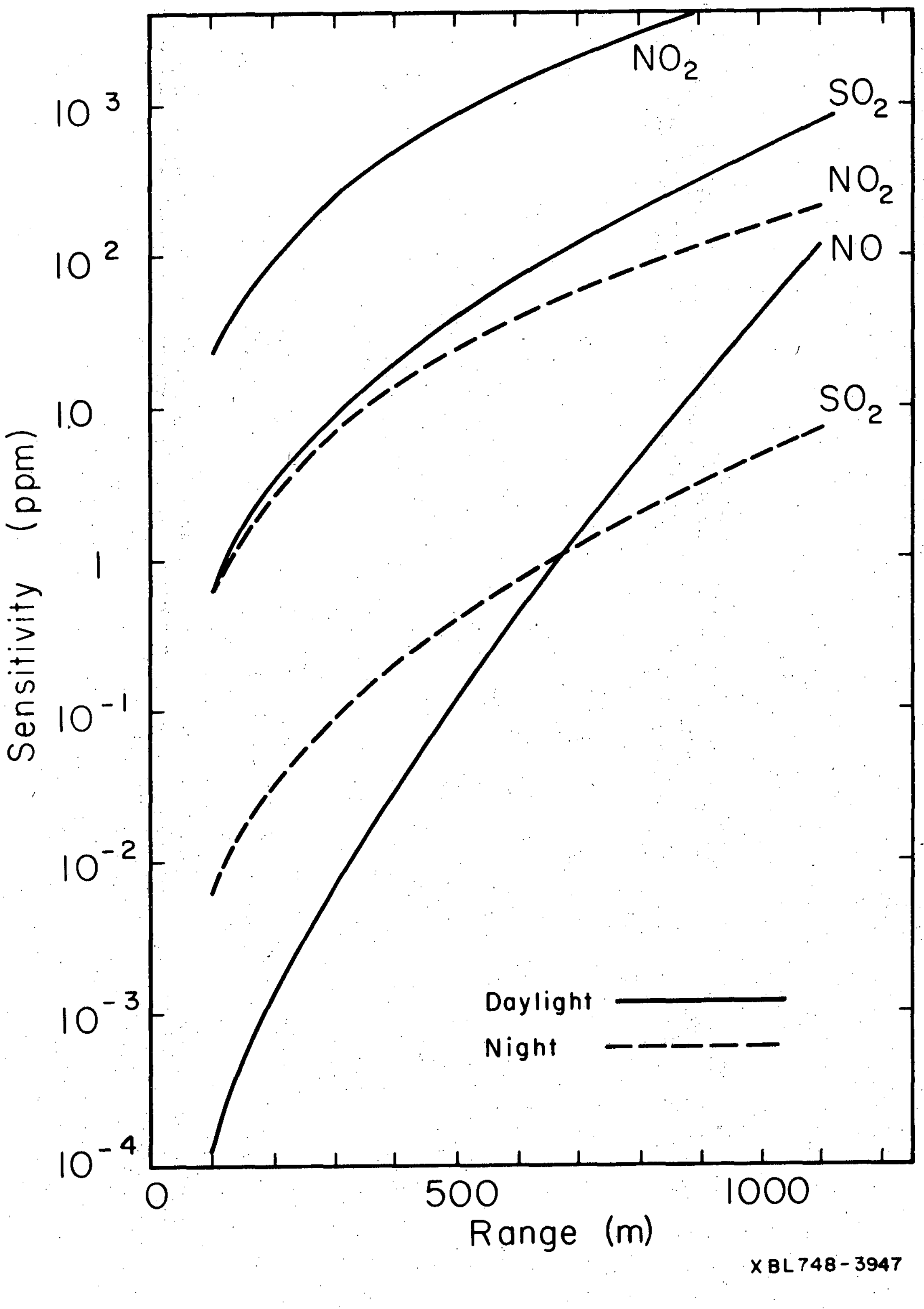

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Fig. 1.

Molecule	Electronic Transition	Vibrational Transition	λ_L(Å)	$\frac{d\sigma}{d\Omega}$(cm^2/ster)$_{CALC.}$	$\frac{d\sigma}{d\Omega}$ (cm^2/ster)$_{EXP.}$	REFERENCES
CO^+	$A\ {}^2\Pi_i - X\ {}^2\Sigma^+$	0-1, 1-1	4913	2.5×10^{-20}		15
SO	$A\ {}^3\Pi_0 - X\ {}^3\Sigma^-$	0-2, 2-0	2579	1.3×10^{-20}		16
OH	$A\ {}^2\Sigma^+ - X\ {}^3\Pi_i$	0-0, 0-1	3064	2.4×10^{-22}	$\sim 10^{-20} - 10^{-21}$ (11)	17,18
NO	$A\ {}^2\Sigma^+ - X\ {}^2\Pi$	0-0, 0-3	2262	1.3×10^{-23}		19,20
I_2	$B\ {}^3\Pi^+_{0u} - X\ {}^1\Sigma^+_g$	0-25, 25-1	5466.36	1.2×10^{-24}	1.7×10^{-24}	21,22
SO_2	$\tilde{A}\ ({}^1B_1) - \tilde{X}\ {}^1A_1$		3002		1×10^{-25}	
$^{79}Br^{81}Br$	$B\ {}^3\Pi^+_{0u} - X\ {}^1\Sigma^+_g$	0-28, 28-1	5264.0	7.8×10^{-27}		23,24
NO_2	$\tilde{A}\ ({}^2B_1) - \tilde{X}\ {}^2A_1$ (?)		4547.4		5.6×10^{-27}	
CO	$a\ {}^3\Pi - X\ {}^1\Sigma^+$	0-0, 0-1	2063	4.5×10^{-30}		15
Cl_2	$A\ {}^3\Pi^+_{0u} - X\ {}^1\Sigma^+_g$	0-15, 15-3	4933	7×10^{-31}		23,25

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