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THE APPLICATION OF STIMULATED RAMAN GAIN AND INVERSE RAMAN SPECTROSCOPY TO THE REMOTE DETECTION OF CHEMICAL AGENTS

by Steven D. Christesen
RESEARCH DIRECTORATE

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Christesen, Steven D.

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The use of inverse Raman spectroscopy/stimulated Raman gain for the remote detection of chemical agents is analyzed. The sensitivity of this technique is calculated for ranges 1 and 10 kilometers and target cloud widths of 10 and 50 m. The sensitivity is also shown to decrease tremendously as the agent or target cloud moves away from the focal point of the laser.

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PREFACE

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TABLE OF CONTENTS

Page

LIST OF FIGURES

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THE APPLICATION OF STIMULATED RAMAN GAIN AND INVERSE RAMAN SPECTROSCOPY TO THE REMOTE DETECTION OF CHEMICAL AGENTS

1. INTRODUCTION

The use of normal Raman spectroscopy for chemical agent remote detection has been the topic of considerable investigation in the past.[1,2] However, research in this area was discontinued when it became evident that the Raman scattering process was too weak to be applicable to the remote sensing of chemical agents. Renewed interest in Raman scattering for remote sensing has surfaced because of the relatively recent discovery and application of coherent Raman spectroscopy,[3,4] specifically, stimulated Raman gain (SRG) and inverse Raman spectroscopy (IRS). In both cases, the overlap of two laser beams in a Raman active medium results in a decrease in irradiance (loss) of one beam and an increase in irradiance (gain) of the other when their frequency difference corresponds to a Raman transition. The advantages of SRG and IRS over normal Raman spectroscopy include increased sensitivity, higher resolution, and rejection of luminescence.

The purpose of this report is to analyze the use of stimulated Raman gain (or inverse Raman) for remote sensing. The sensitivity of the technique will be determined based on reasonable assumptions of laser characteristics and Raman spectroscopic data of chemical agents.

2. BACKGROUND

Simplified energy level diagrams of the spontaneous Raman (SR), stimulated Raman gain, and inverse Raman processes are shown in Figure 1. In the case of spontaneous Raman, a photon at the laser frequency ν_P is annihilated and one at $\nu_S = \nu_P - \nu_R$ is created where $h\nu_R$ is the energy of an allowed Raman transition. SRG and IRS involve the use of two laser beams: one at ν_P and the other at ν_S. Where their frequency difference $(\nu_P - \nu_S)$ corresponds to an allowed transition, a photon of energy $h\nu_P$ is lost and one of energy $h\nu_S$ is gained. SRG involved monitoring the gain in irradiance of the beam at ν_S and IRS the loss in irradiance at ν_P.

An expression for the gain in irradiance at ν_S is given by

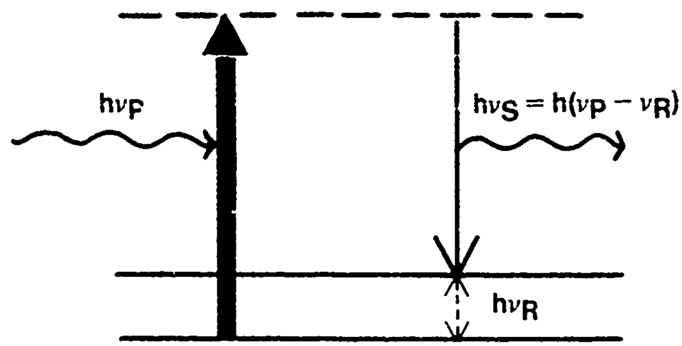
$$I_S(R) = I_S(-R)e^G \qquad (1)$$

where $I_S(-R)$ is the Stokes or probe laser irradiance before the sample, $I_S(R)$ is the Stokes laser irridiance after the sample, and G is the gain coefficient. The loss (L) at ν_P is related to the gain by the equation $L = (\nu_P/\nu_S)G$. The gain coefficient can be written as

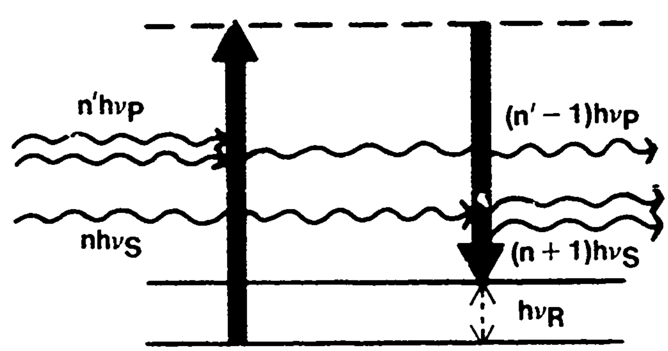
$$G = (\lambda^3_S N)/(hc\Pi\, \Delta\nu_R \times (d\sigma/d\Omega) \times \int_{-R}^{R} I_P(z)dz \qquad (2)$$

where

λ_S = the Stokes wavelength (cm),
N = the number density (molecules/cc),
$\Delta\nu_R$ = the Raman linewidth (sec^{-1}),
$(d\sigma/d\Omega)$ = the Raman cross section (cm^2/molecule), and
I_p = the pump laser irradiance (W/cm^2)



A. Spontaneous Raman.



B. Stimulated Raman Gain (SRG) and Inverse Raman Spectroscopy (IRS).

Figure 1. Spontaneous Raman, Stimulated Raman Gain, and Inverse Raman Spectroscopy Energy Level Diagrams

For a collimated beam, the integral over the sample length from -R to R in Equation 2 is simply I_p times the distance 2R. When the beams are focused, however, the irradiance depends on the spot size which changes with distance along the beam path. The radius as a function of the distance z from the beam focus is

$$r(z) = r_0 [1+(\lambda z)^2/(\Pi r_0^2)^2]^{1/2}. \quad (3)$$

The irradiance as a function of z is $I(z) = P_p/\Pi r^2(z)$ where r_0 is the beam radius at focus (z = 0), and P_p is the pump beam power in watts. The integral in Equation 2 then becomes

$$Q(R) = \int_{-R}^{R} P_p/\Pi r^2(z)dz = (2P_p/\lambda_p) \tan^{-1}(\lambda_p R/\Pi r_0^2) \text{ and} \quad (4)$$

$$G(R) = (\lambda^3{}_S N/(hc\Pi\lambda\nu_R)) \times (d\sigma/d\Omega) \times (2P_p/\lambda_p) \tan^{-1}(\lambda_p R/\Pi r_0^2). \quad (5)$$

If the gain medium can be considered to be of infinite extent, Q(R) reduces to $Q(\infty) = \Pi P_p/\lambda_p$ and G(R) becomes

$$G(\infty) = (\lambda^3{}_S N)/(hc\Delta\nu_R) \times (d\sigma/d\Omega) \times P_p/\lambda_p. \quad (6)$$

The distance from the focus at which the beam area doubles is called the Rayleigh range (Z_R) and is equal to $\Pi r_0^2/\lambda$. This is an important distance as it can be shown that $Q(Z_R) = Q(\infty)/2$ and therefore, that $G(Z_R) = G(\infty)/2$. Consequently, half of the gain comes from a region whose length is just twice the Rayleigh range (from $-Z_R$ to $+Z_R$). For a 350-nm laser beam focused at 1 km with 1-m diameter focussing optics, r_0 equals 2.2×10^{-2} cm, and Z_R equals 44 cm. Typically, the gain medium or sample is much larger than $2Z_R$, and Q(R) and the gain can be approximated by $Q(\infty)$ and $G(\infty)$, respectively.

3. REMOTE SENSING

3.1 Introduction.

Assuming that the backscattered signal is detectable, the limiting factor in the sensitivity of SRG (IRS), as well as differential absorption lidar (DIAL), is the minimum fractional change in backscattered return ($\Delta I/I_0$) that can be accurately measured.[5] This factor is governed by the actual lidar equipment regardless of the species to be detected. In the application of SRG (IRS) to remote sensing, ΔI is the difference in probe backscattered irradiance measured with the pump laser on and off. Menyuk, Killinger, and DeFeo[5] have stated that the minimum detectable $\Delta I/I_0$ for their IR DIAL system is approximately 1% at ranges of up to 1-km. SRI has also claimed that a stimulated Raman gain remote sensor could detect a fractional change of 1%.[6] A value of 0.01 for $\Delta I/I_0$ translates into a detectable gain of approximately 0.01. In the following sensitivity calculations, it will be assumed that the minimum detectable gain is 0.01.

3.2 Sensitivity Calculations.

Setting G to 0.01, Equation 5 can be used to calculate a sensitivity (N) in molecules/cc. The following laser specifications and Raman cross section and linewidth data will also be used in the calculations:

$\lambda p = 3.5000 \times 10^{-5}$ cm,
$\lambda s = 3.5892 \times 10^{-5}$ cm,
$\Delta \nu_R = 8.994 \times 10^{9}$ cm (0.3 cm^{-1}),
$d\sigma/d\Omega = 1.0 \times 10^{-28}$ cm^2/molecule, and
$Pp = 10^9$ W.

In addition, it must be assumed that the lasers are diffraction limited and have linewidths less than the Raman linewidth. The required linewidth is achievable in an excimer laser with an output power of 10^9 watts using pulse compression and injection-locking techniques.[7]

A cross section of 10^{-28} cm^2/molecule-sr at 350 nm is assumed for the sensitivity analysis. A value of 31.1×10^{-30} was measured for liquid GB with 363.8-nm excitation.[8] This corresponds to a vapor phase cross section of 10.8×10^{-30}. The vapor cross section for DMMP is approximately 16×10^{-30}.[9,10] The cross section used in the calculation, therefore, is almost 10 times larger than that measured for GB and DMMP. The vapor phase linewidth for GB has not been measured, but a value of 11.9 cm^{-1} was determined for DMMP at 32 torr.* A linewidth of 0.3 cm^{-1} is used for the calculations and represents an absolute lower limit.

The atmospheric attenuation for mid-latitude summer was used to calculate the irradiance of the pump beam at a point just before the target cloud.[11] At 1 km, $P = 0.79 \times P_o = 0.79 \times 10^9$ watts if a laser power (P_o) of 10^9 watts is used. The power at 10 km is 10^8 watts. Using the values for laser power, laser linewidth, Raman cross section, and Raman linewidth given previously and assuming that the sample extends from at least $-Z_R$ to greater than $+Z_R$ so that $Q(R_C)$ can be approximated by $Q(\infty)$, the sensitivity is calculated from Equation 5 to be roughly 1.7×10^{13} molecules/cc at 1 km and 13.5×10^{13} molecules/cc at 10 km. For GB, which has a molecular weight of 140, this corresponds to a sensitivity of approximately 0.73 ppm at 1 km and 5.8 ppm at 10 km.

The assumptions made in the sensitivity analysis have been very generous and values of 0.73 and 5.8 ppm are probably 10 to 100 times better than one could expect for GB or DMMP. All of these calculations have also assumed a sample or target cloud centered at the laser focus. This assumption of an exact overlap of the target with the focus is unfounded because the focal length of the system is fixed, while the target range is variable. The following analysis will determine the dependence of the sensitivity on the distance of the target cloud from the focal point of the transmitting optics.

A schematic of SRG (IRS) as applied to remote sensing is shown in Figure 2. Two laser beams are focused at some distance from the transmitter. Light backscattered from the probe pulse (ν_s in the case of SRG and ν_p

*Bischel, W. K. Unpublished data.

for IRS) is collected by the telescope, and its irradiance measured. The probe beam is then transmitted alone. The SRG (IRS) signal is the difference in the backscattered probe beam irradiance with and without the pump beam being transmitted. A spectrum is obtained by scanning the pump beam frequency while keeping the probe frequency fixed.

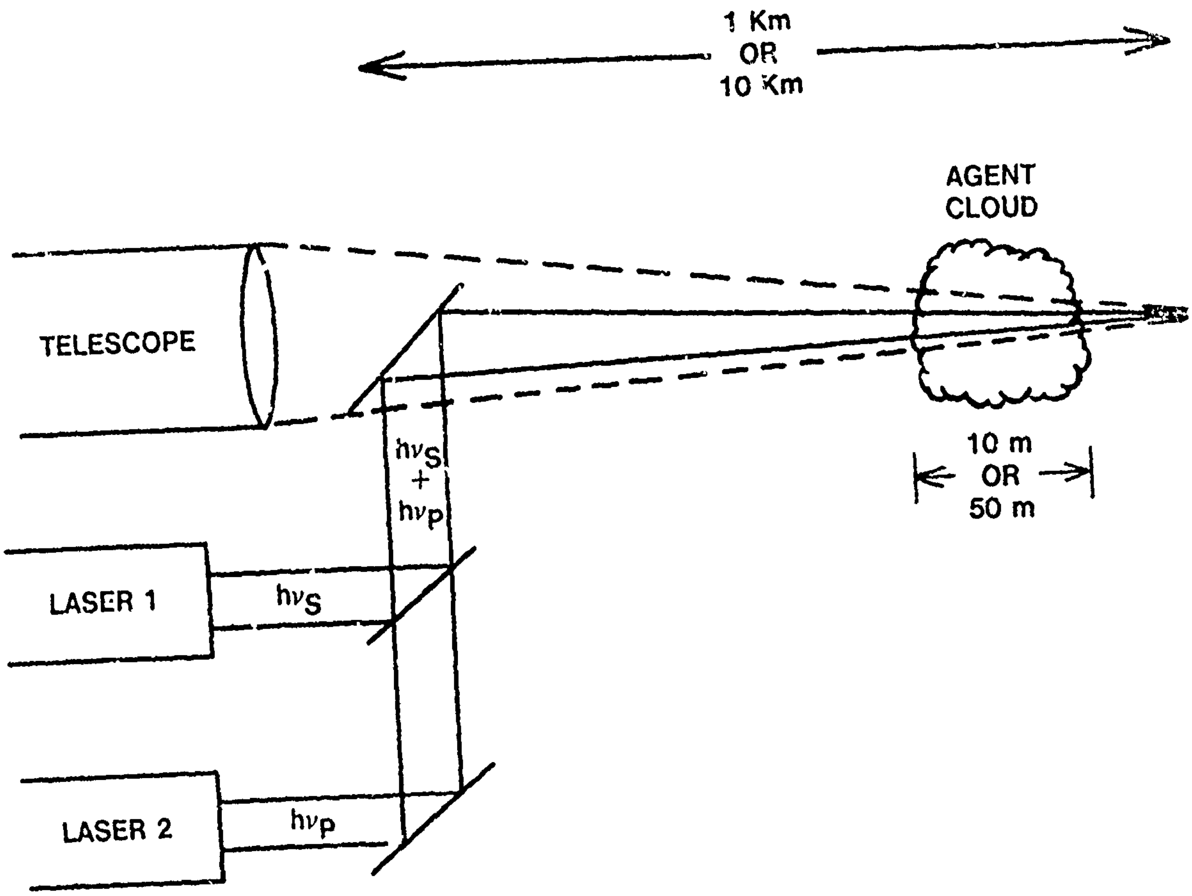


Figure 2. SRG/IRS Remote Sensing Schematic

Figures 3 and 4 show plots of the gain evaluated for clouds centered at a distance R from the focus of the lasers [G(R)] divided by the gain calculated for a cloud of infinite extent [G(∞)]. In this case, R no longer represents the cloud width but instead stands for the distance from the laser focus. Because the cloud is not necessarily centered at z = 0, the limits of integration in Equation 4 become R-C/2 and R+C/2 where C is the cloud width. The gain peaks when the cloud is centered at the focus (z = 0) and drops off very quickly as |R| increases. The peak of the ratio G(R)/G(∞) is very much less than 1 in Figure 4; because, at 10 km, the cloud width (10- or 50-m) is less than twice the Rayleigh range (92-m). Focusing at 1 km, the Rayleigh range is only 44 cm, and G(∞) is a very good estimate of the gain for both the 10 and 50 m wide clouds.

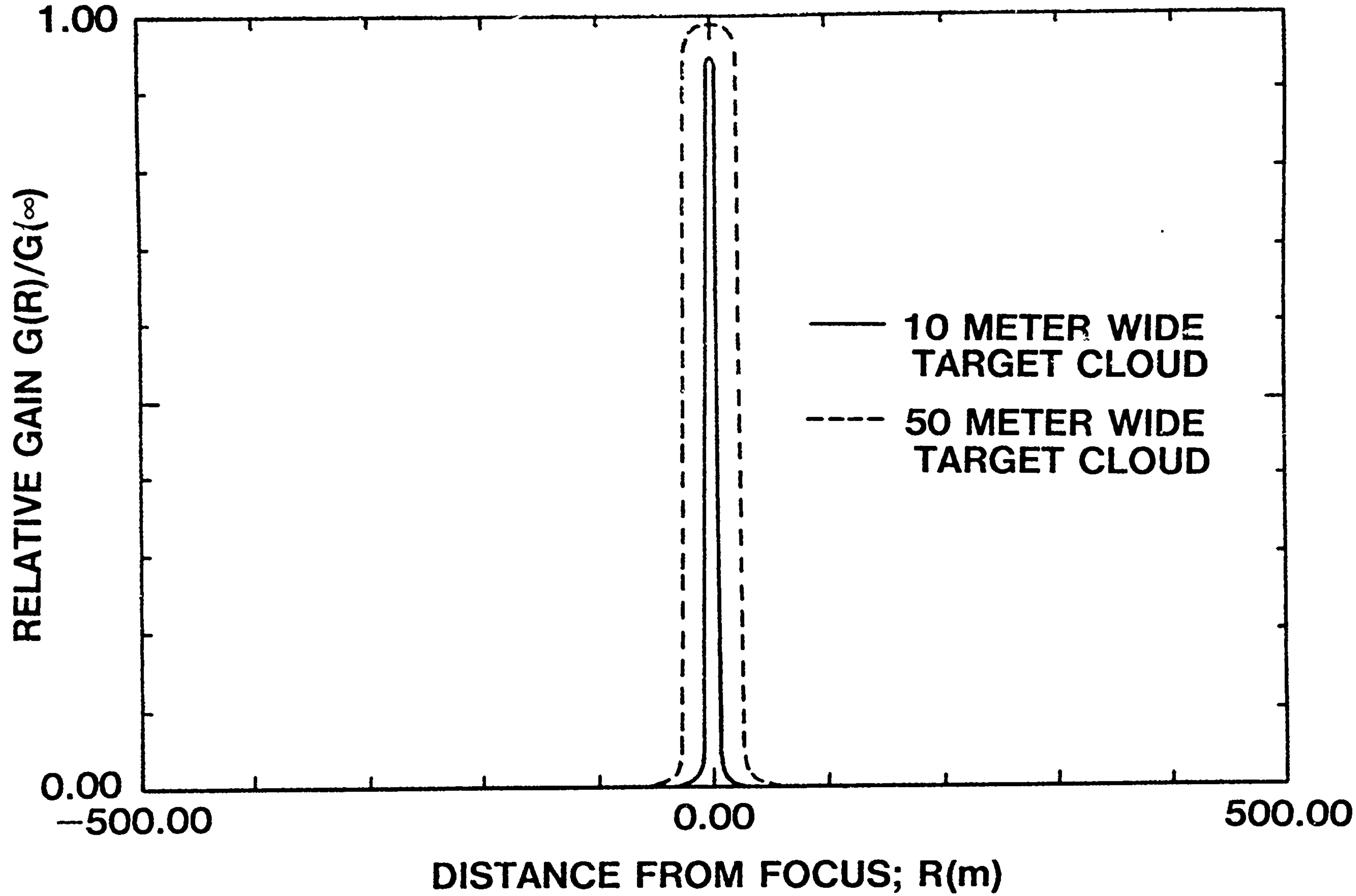


Figure 3. $G(R)/G(\infty)$ as a Function of Distance From the Focus (R): Focus at 1 km.

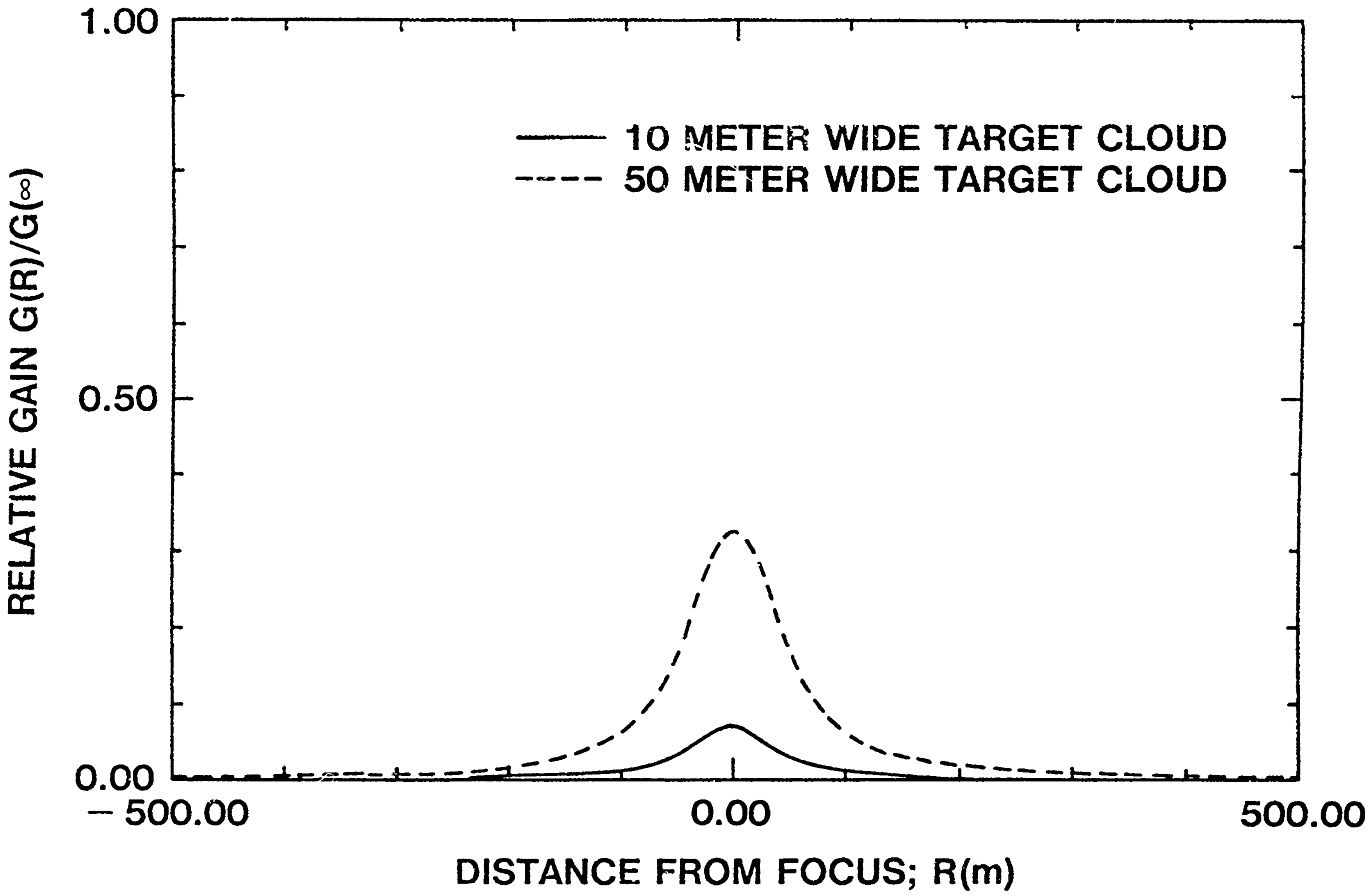


Figure 4. $G(R)/G(\infty)$ as a Function of Distance From the Focus (R): Focus at 10 km.

Figures 5 and 6 are semi-log plots of the sensitivity in ppm vs the distance R from the focus. The minimum detectable concentration increases to 1000-ppm when the target cloud range and the focal length of the transmitting optics differ by as little as 5%. The result is that the cloud will not be detected unless the target overlaps the focal point.

4. CONCLUSIONS

Coherent Raman spectroscopy has been shown to be very sensitive in laboratory applications.[4,12] As a remote detection concept, however, SRG and IRS suffer from the severe drawback that, because of the dependence of the gain on the pump irradiance, the lasers must be focused in the sample. Figures 5 and 6 show the tremendous reduction in sensitivity that results when the laser focus and target cloud do not overlap. For any practical application where the target distance is unknown, the optical focus must be scanned along with the transmitter or receiver direction. This aspect of the SRG/IRS stand-off detector had not been fully analyzed before.

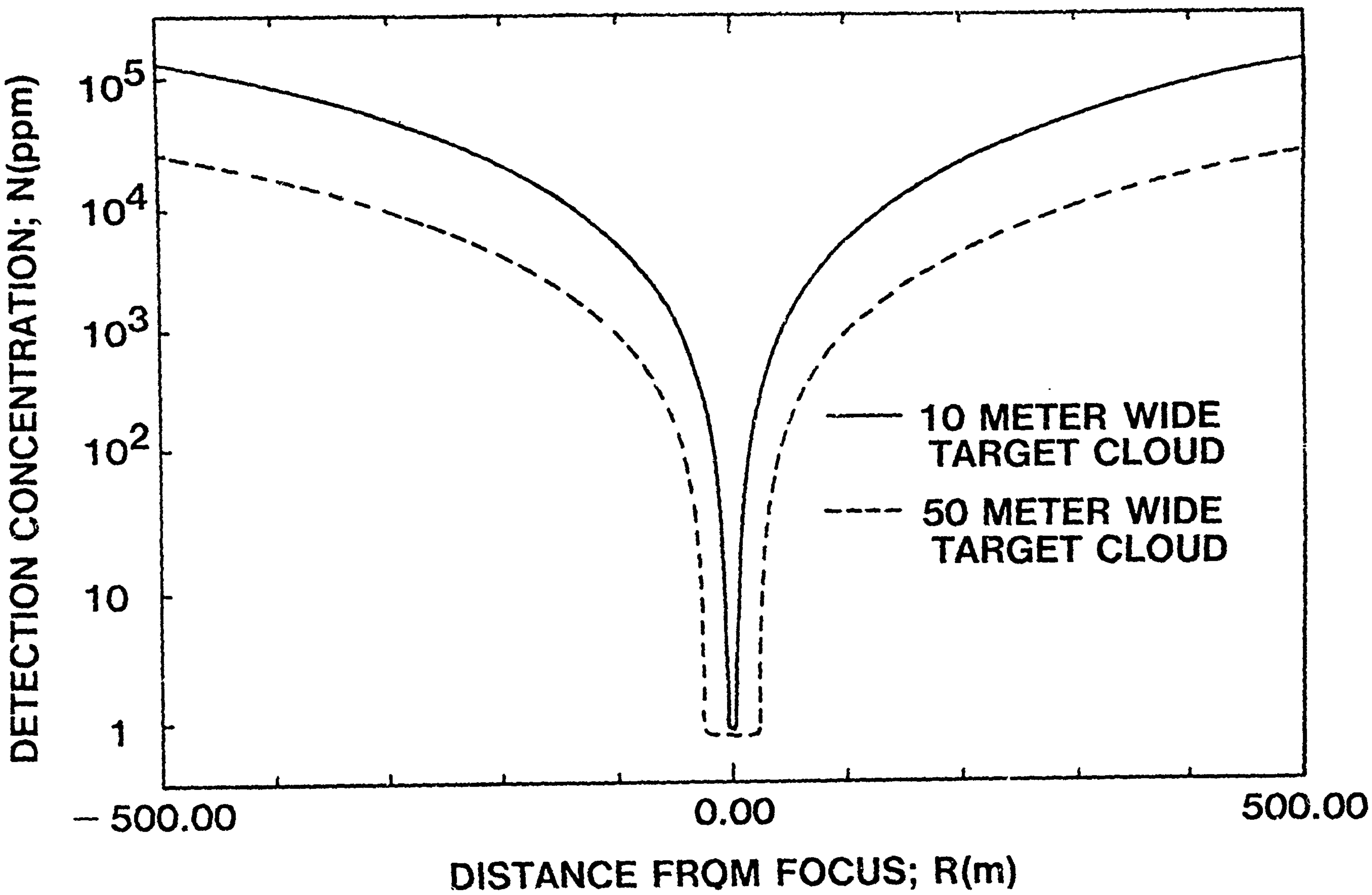


Figure 5. Sensitivity as a Function of Distance From the Focus (R): Focus at 1 km.

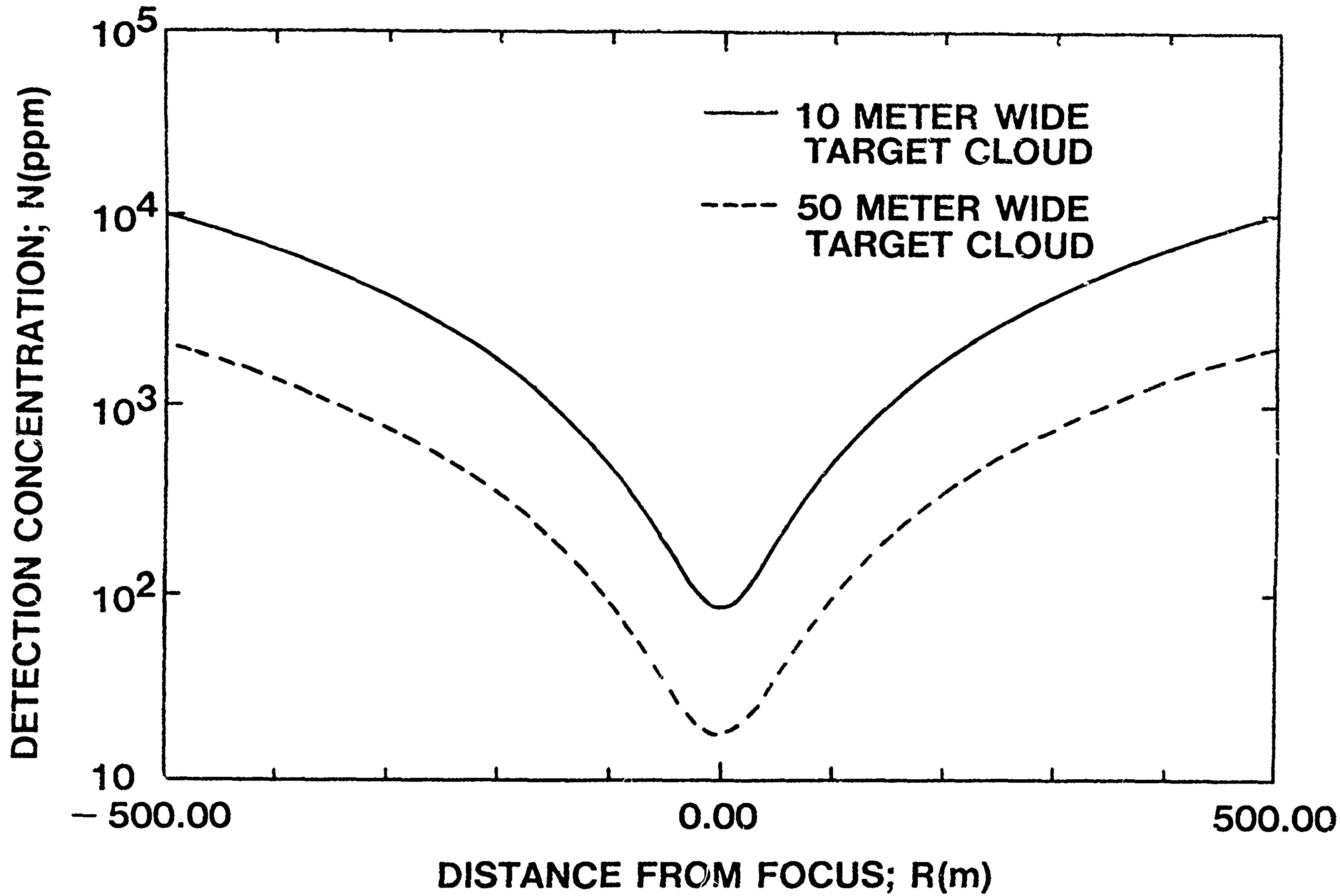


Figure 6. Sensitivity as a Function of Distance From the Focus (R): Focus at 10 km.

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