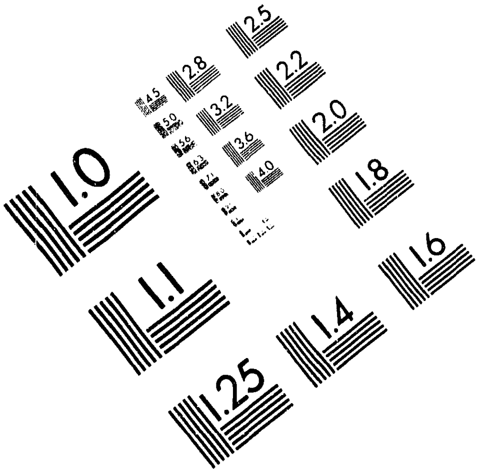

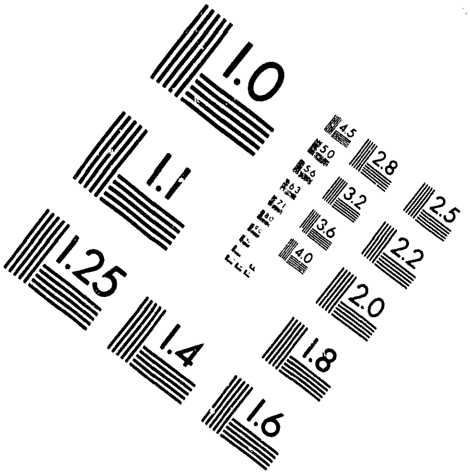

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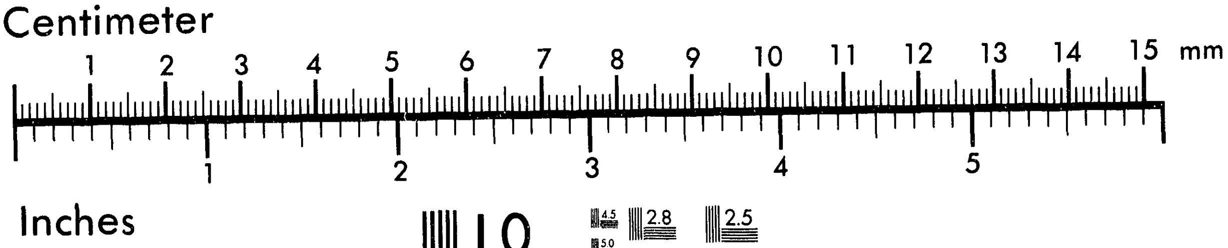

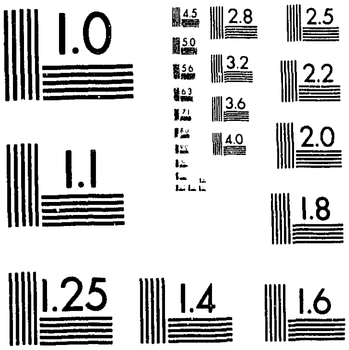

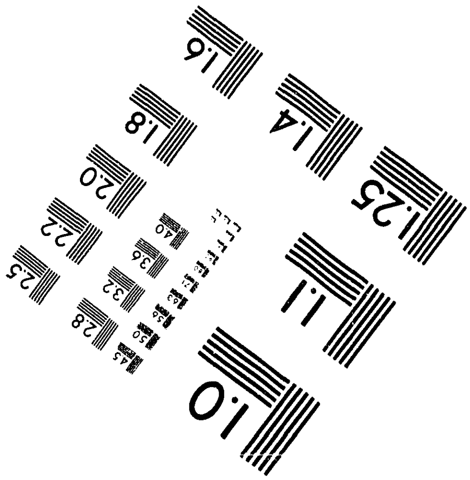

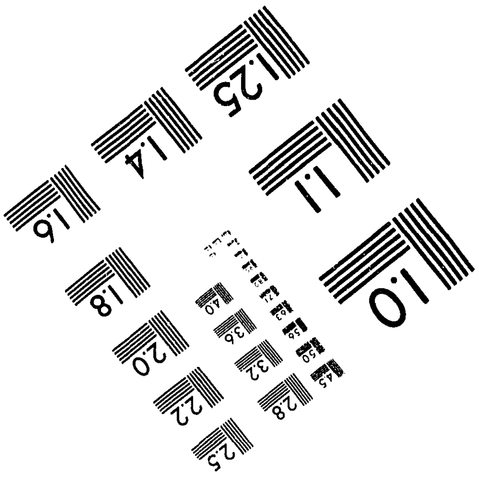

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Informal Report

An Assessment of the Use of CARS for Remote Sensing

R. E. Barletta

April, 1993

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TABLE OF CONTENTS

Page No.

LIST OF FIGURES

LIST OF TABLES

Page No.

An Assessment of the Use of CARS for Remote Sensing*

1. INTRODUCTION

With the increased interest controlling the manufacture of chemical weapons (CW) agents globally as well as the interest in controlling the development and spread of nuclear weapons has come a concomitant need for the development instrumentation which will allow for either remote or clandestine surveillance of potential production and transportation facilities. The ability to monitor the effluent of a suspected weapon's production plant from distances on the order of kilometers would provide the basis for treaty verification or for intelligence gathering.

A number of potential techniques for accomplishing these ends are currently under development. In particular a technique based upon identification of the constituents of a mixture based upon the vibrational spectrum obtained using Raman spectroscopy is under development. Because this approach has range limitation due to the frequency of light being used for interrogation other methods which can accomplish the same ends even more remotely are of interest. To this end, a review of the appropriate literature has been conducted and the results of this review with respect to the application of coherent anti-Stokes Raman spectroscopy (CARS) to the remote detection of chemicals of interest has been conducted. This study is more limited in scope than a detailed developmental program which is currently being under taken by DESE Research, Inc. and is limited to the question as to whether CARS possesses adequate sensitivity to be used as a remote sensing technique.

Since current interest in remote sensing centers around detection of CW production in conjunction with the recently signed international convention in this area. The detection of CW agents and simulants is given prominence in this discussion. It should be understood that the results of this assessment have broader applicability to more general problems of remote sensing in the area of nuclear nonproliferation, drug enforcement, explosive detection, etc. In addition, the use of CARS for microscopic detection of such controlled materials, while not explicitly considered in this report, is a further application of the technology.

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* Research carried out under the auspices of the U. S. Department of Energy, Contract No. DE-AC02-76CH00016

2. CANDIDATE TECHNOLOGIES

The details as to what would constitute an acceptable remote sensing technology under the chemical weapons convention(CWC) are at present uncertain. If the inspecting agent is not allowed access to a facility, or if the ability to collect air soil or water samples is restricted, candidate technologies may be limited to those relying on optical methods to perform chemical analysis. Several criteria appear to be important for a successful technology:

1. It must be capable of remote application, i.e., no sample processing should be required.

2. It must be unobtrusive in its application. This implies a short analysis time on the order of seconds or less.

3. It should be sensitive, i.e., capable of detecting low concentrations of chemicals. It must also be able to discriminate individual components in a multi-component mixture.

2.1 Survey of Technologies

Upon a survey of the available literature, it was concluded that optical techniques which measured the details of the vibrational structure of molecules would have the most chance of success for development as a remote sensing technology. Thus, techniques such as electronic fluorescence were eliminated. Some techniques identified (infrared absorption and Raman spectroscopy) are currently under consideration as remote sensing technologies for the CWC. The relationship of these to the selected technology is discussed below. To understand the reasons for candidate technology selection, however, an overview of the basis for molecular spectroscopy is necessary.

All molecules possess vibrational modes which can be activated due to the absorption of light. The number and frequencies at which these occur are characteristic of the particular structure of the molecule and hence can be used to identify the absorbing species. In general, a nonlinear molecule of n atoms has 3n-6 fundamental vibrational modes. A subset of the possible vibrations of a molecule can be accessed via infrared radiation. These vibrations involve a change in the dipole moment of the molecule. Not all vibrations (e.g., the symmetric stretch of a homonuclear diatomic molecule) result in such a change in the dipole moment. These modes are said to be infrared inactive and although their energy corresponds to the frequency of infrared radiation, light of that frequency will not be absorbed by the molecule. These modes, however, result in a change in the polarizability of the molecule and can be accessed via the inelastic scattering of electromagnetic radiation, the so-called Raman effect. When a molecule is irradiated with light (usually in the visible or ultraviolet frequency regime), the radiation can be inelastically scattered resulting in either higher frequency (anti-Stokes) or lower frequency (Stokes) photons. Some vibrations are both Raman active and infrared active since they involve both a change in the dipole moment and a change in polarizability.

Infrared absorption spectroscopy is a common tool for compound identification and is the basis for Department of Energy (DOE) funded work in the area of remote sensing being conducted at Lawrence Livermore National Laboratory. The Raman effect is weak. Most radiation is elastically scattered and provides no information relevant to the identity of scattering species. Using incident light in the visible region, the cross sections are not large enough to be used as a remote sensing technique even with laser sources As the frequency of the incident light increases, however, the Raman scattering cross section increases in proportion to the fourth power of the frequency. As the frequency of light nears an electronic resonance of the molecule, large increases in the cross section beyond the v^4 dependence occur and enhancement in excess of 10^6 are common. These frequency effects are the basis of the DOE-funded, CWC remote sensing work at Brookhaven National Laboratory (BNL) discussed below.

In an assessment report on the applicability of Raman spectroscopy to the detection of chemical weapons agents, Barletta [1] concluded the technique had applicability for remote sensing, liquid analysis and microscopy. For remote sensing applications, the report concluded that excitation using UV laser sources was necessary to high sensitivity due to the frequency dependence of the cross-section for the Raman effect. It was further noted in the report that using laser frequencies near-resonance with electronic states are also in the UV. Despite the sensitivity of the technique in the UV, it was concluded in this study that the practical range of a UV-based Raman system would be on the order of a kilometer due to atmospheric attenuation of the UV radiation. Such a system is capable of rapid development, however. The conclusions of the BNL study became the basis for the DOE-sponsored work at BNL.

Both infrared reabsorption and Raman spectroscopy are linear optical techniques. That is, in both techniques, the strength of the signal is proportional to the first power of the incident light intensity. In our literature review, non-linear techniques were also considered. In non-linear optical process, the output signal power of the input light intensity. Both types of optical processes can provide information on the identity of molecular species by their vibrational state absorptions or emissions.

Infrared fluorescence is a technique in which upper level vibrational levels are excited in either a single or multi-photon process. The former would be a linear optical process, the latter non-linear. Once excited, inter- and intra-molecular energy transfer processes occur and energy is lost through radiative and non-radiative processes. By measuring the emission from such an excited system, it was hypothesized that the composition of the system could be inferred. A review of the literature did not yield any information which would imply that such a process could be rapidly developed into a viable remote sensing scheme. Researchers contacted about this approach were skeptical of its practicality as well. In light of this, the technology is outside the scope of the current study and has been dropped from further consideration. Much fundamental work in this area is necessary before an assessment concerning the ultimate practicality of this approach can be evaluated.

2.2 CARS

Like Raman scattering, CARS provides information concerning Raman-active vibrational-rotational modes of molecules [2]. Hence, it can be used for species identification in a manner similar to Raman. There are significant differences in the two techniques which will be discussed in detail in Section 2.5. CARS appears to have the potential for relatively rapid development as a remote sensing technology. The effect requires multiphoton absorption of incident light at a pump frequency along with a phase-matched probe beam to produce the output signal. The frequency of the probe laser is Stokes shifted (i.e., shifted to the red of the pump beam) by an amount equal to the frequency of the Raman active vibration. The CARS output signal, like the input signal is a coherent signal at a frequency equal to twice the pump frequency minus the Stokes probe frequency. It is blue shifted from the pump frequency. The process is a three color process, two coherent laser signals irradiate the sample and a third laser-like beam is emitted from the interaction region. A schematic energy diagram for CARS is shown in Figure 2.1.

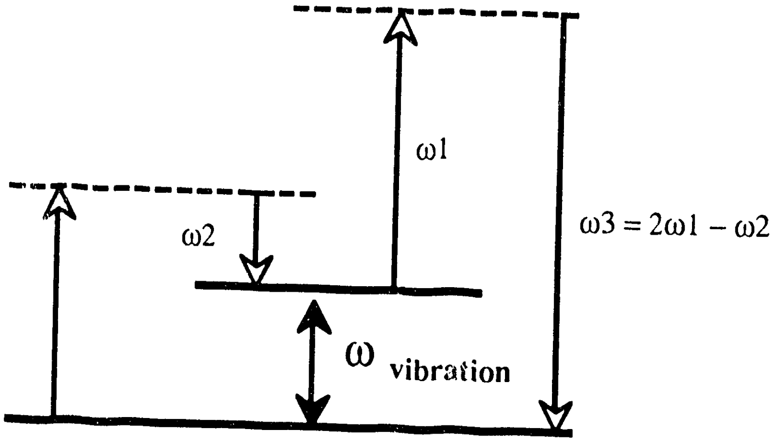

Figure 2.1. Schematic energy level diagram for CARS. ω_1 is the pump beam frequency; ω_2 is the Stokes probe frequency; $\omega_{\text{vibration}}$ is the frequency of the vibrational transition; ω_3 frequency of the CARS signal beam.

If the phase mismatch, Δk, is zero, the intensity of the CARS signal, I_3, at ω_3 is related to the CARS susceptibility χ_{CARS} , the sampling extent, l, and the intensity of the pump beam, I_1, at ω_1 and the intensity of the probe beam I_2, at ω_2.

$$I_3 \propto l^2 \, |\chi_{\text{CARS}}|^2 \, I_1^2 \, I_2 \qquad (2.1)$$

Several practical points arise from this equation. First, the signal is highly dependent on the square of the pump beam intensity. This gives rise to the non-linearity of the phenomenon. The second point regards the magnitude of χ_{CARS}. From the intensity relationship above, one can see that it too affects the magnitude of the CARS signal quadratically. Analysis of this term , shows that it is directly proportional to the Raman cross section and the molecular density. Thus, the intensity of the CARS signal is proportional to the square of the Raman cross section and density. χ_{CARS} is also dependent on the resonant susceptibility of all the neighboring resonances of the molecule as well as the non-resonant susceptibility. This means that the CARS line shape is complex as well as concentration dependent.

The phase matching condition ($\Delta k=0$) is important as well. When this is so, the signal builds constructively over the length in which the wave mixing occurs (l). The result of this constructive interference is a coherent signal along the direction of propagation (unlike Raman scattering which is isotropic). The angle at which the CARS signal is emitted relative to the incident laser beams is generally in the forward direction to the incident beams as defined by the phase matching criterion. It depends upon the wave vectors for the two incident beams as follows:

$$2\vec{k}_{pump} = \vec{k}_{probe} + \vec{k}_{CARS} \tag{2.2}$$

The simplest way to satisfy this phase matching criterion is for the incident beams to be colinear in which case the CARS beam is emitted in the same direction of propagation as the incident beams. However, a number of other arrangements are possible in which the phase matching occurs.

2.3 CARS Equipment

In a CARS experiment, either cw- or pulsed lasers may be used. The pump laser is a narrow-band high-power laser. The probe laser can be a broad band-laser in which case the frequency range accessed is limited to the bandwidth of the laser. It can also be a narrow-band laser which is tuned across the frequency range of interest. In this case, the data acquisition time is limited by the rate of scan of the probe laser. A wide range of lasers can be used to accomplish all of these arrangements. The frequency of the input lasers required is determined by the vibrational frequencies, ω_{vib} of the molecules being probed

$$\omega_{pump} = \omega_{probe} + \omega_{vib} \tag{2.3}$$

For the purposes of remote detection, one may assume that the vibrational frequency range of interest is 400 to 3000 cm^{-1}. For this range of frequencies, it is possible to calculate the probe and output wavelengths, ω_2 and ω_3, respectively which are associated with a particular pump laser wavelength. The results of this calculation are shown for several potential pump lasers and one solid-state, tunable probe laser in Figure 2.2. It can be seen from this figure that a variety of solid-state laser sources are available for use as either pump or probe excitation sources. In addition, it is possible to cover the range of required probe frequencies using a tunable dye laser.

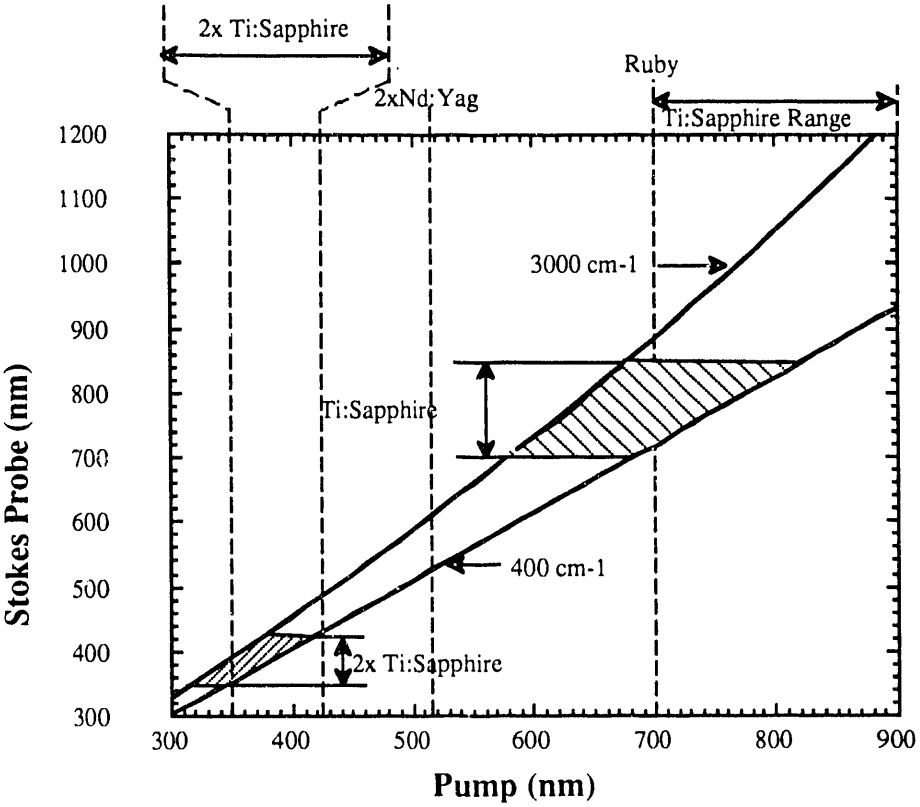

Figure 2.2. Stokes probe wavelength vs. pump laser wavelength for vibrational modes of 400 cm^{-1} and 3000 cm^{-1}. The positions of several solid-state laser wavelengths as well as the tunable range of Ti-Sapphire and frequency-doubled Ti-Sapphire lasers are indicated for reference.

The choice of excitation lasers depends upon several factors. The range of a remote detection device will depend in large measure on the transmission characteristics of the excitation and signal beams in the atmosphere. Bands of high transmission exist throughout the visible and near infrared which will allow for minimal absorption of the radiation. At wavelengths less than 900 nm, the transmittance is quite high in the region of 400 to 650 nm. For example, at a zenith angle of 0° (looking straight up) the transmittance over one air mass (i.e., the amount of air through which the light passes in going through the atmosphere) ranges from approximately 60% to 80%. A second consideration, in the choice of the laser is the sensitivity which one might expect. This depends on several factors including the frequency and pulse energy of the incident light. These sensitivity considerations will be discussed below. A final consideration in the selection of lasers is the ease of use, mobility and robustness of the system. In this respect, dye lasers are less desirable than solid state lasers.

Detection equipment for a CARS system consists of a monochromater or prism arrangement and a detector such as photomultiplier for scanning systems or a CCD array. The detection equipment should be capable of providing frequency resolution of the CARS signal to on the order of a few cm^{-1}. Such equipment is readily available and is easily fielded. It can also be quite small. In a discussion of Raman spectroscopy presented recently, Carrabba described a detection system which should be adequate for a CARS system which was on the order of 6"-12" in diameter.[3] The spectral range from the CARS signal is blue shifted from the pump frequency by a small amount as shown in Table 2.1. Further, all three beams (pump, probe, and signal) are spatially separated so that filtration of the pump and probe is not required.

Table 2.1. Wavelength of CARS output for various pump wavelengths.

λ_{Pump} (nm)	λ_{CARS} (nm)	
	$\omega_{vib} = 3000\ cm^{-1}$	$\omega_{vib} = 400\ cm^{-1}$
350	316.74	345.17
400	357.14	393.70
500	434.78	490.20
550	472.10	538.16
600	508.47	585.94
650	543.93	633.53
700	578.51	680.93
750	612.24	728.16
800	645.16	775.19
850	677.29	822.05

2.4 CARS Sensitivity

The detection limits of CARS has been variously estimated to range from 0.1% (Eckbreth [2]) to on the order of 10^{14} molecules/cm^3 (4 ppm at STP) [4]. Nibler and Knighten [2] estimate a detection limit of 10^{-3}% in gases. In part, this wide range is probably due to variations in experimental details to which the CARS output signal is particularly sensitive as will be seen.

For the purposes of a remote sensing application, Eckbreth's estimate [2] is probability conservative. In making his calculation, he assumed that the CARS measurement was performed with a single pulse of a frequency doubled Nd:YAG laser with a beam energy of 100 mJ, and a probe input energy of 25 mJ which could be obtained from a dye laser. He also assumed a spatial resolution of 1 mm and that only a single vibrational state was involved (Q(18) of N_2). The Raman cross section for this state is 3.7×10^{-31} cm^2/sr. Finally, he assumed a molecular density associated with N_2 at 2000 K and 70% concentration. For these conditions, he calculated that the CARS signal would be on the order of 2×10^4 photons. In an actual CARS experiment on room temperature nitrogen, Rakestraw et al. [5], report a signal level of 2.5×10^4 counts for an input power of 30 mJ. The CARS signal is proportional to the square of the pump power as well as the square of the molecular density. The former means that for room temperature nitrogen Eckbreth's estimate [2] should be increased by about a factor of seven to 1.4×10^5. Similarly, to account for the power differences, Rakestraw's data should be scaled by a factor of 11 to 2.8×10^5 counts or about a factor of 2 higher than Eckbreth's estimate [2] For an estimate of a remote sensing application, Eckbreth's estimate [2] will be used as a basis.

To estimate what kind of detection limits one might expect using CARS we assume that a minimal signal of 100 counts in a peak characteristic of a molecule is necessary. This assumes that the signal-to-noise ratio is estimated from the square root of the signal and neglects solar background. Using the above discussion as a basis, a hypothetical CARS signal can be calculated by scaling Eckbreth's estimate [2] for power, molecular density, sampling extent and Raman cross section which would be anticipated in a remote system. Each of these parameters has a dramatic effect on the sensitivity. The assumed system parameters are as follows:

> Laser Wavelength. In order to maximize the range, a minimum in atmospheric absorbance is desirable. As can be seen from Figure 2.2, the entire visible region is accessible using available lasers. A pump laser operating at 400 nm would require a probe laser range of 455 to 406 nm to access the vibrations in the frequency range of 3000 to 400 cm^{-1}. The resulting CARS signal would be in the wavelength range of 357 to 393 nm. Under conditions of excellent visibility and zenith angle of zero, roughly 60% of the pump energy, 60-70% of the probe energy and 45-60% of the CARS signal could be

transmitted through the entire atmosphere. Eckbreth considered a pump frequency of 532 nm. Using a pump at 400 nm will increase the cross section by a factor of 3.

Laser Power. For a pump laser, Eckbreth considered a frequency doubled Nd-YAG laser operating at 100 mJ/pulse with a pulse duration of 10^{-8} s with a 1 mrad beam divergence. The pump intensity for this arrangement was 5 x 10^9 W/cm^2. We will assume a 40 mJ pump laser operating with the same pulse duration and a divergence of 0.6 mrad. These specifications are available using a Ti:Sapphire laser. Assuming only 60% transmission of this beam, gives a calculated intensity of 3.4 x 10^9 W/cm^2, reducing the pump intensity by a factor of 0.68. For a Stokes probe, a broad band laser was assumed with an energy of 25 mJ/pulse. We will assume this is also achievable.

Raman Cross Section. Eckbreth [2] used the cross section for nitrogen in his calculation. For many compounds, the cross section is much higher. In particular, the Raman cross sections measured for agents and simulants can be much higher as seen in Table 2.2. It can be seen from this table, when compared to other chemicals of interest, nitrogen has with two exceptions a much smaller cross section. For the sake of calculation, we will assume a cross section of an order of magnitude higher than that of nitrogen.

Table 2.2. Raman cross section for nitrogen and various agents and simulants as neat liquids at 514.5 nm. Data on nitrogen scaled from Eckbreth [2], and on agents and simulants from Christensen.[6] normalized cross sections are relative to the value of nitrogen

Species	Cross Section (x 10^{30} cm^2/sr)	Normalized Cross Section
N_2	0.37	1
DMMP	12	32
DIMP	7.4	20
GB	6.0	16
GA	7.6	21
VX	0.1	0.3
HD	0.08	0.2

Sampling Extent. Eckbreth [2] assumed a sampling extent of 1 mm since he was interested in a high degree of spatial resolution for combustion diagnostics. For remote sampling this degree of resolution is not necessary. A sampling extent of 1cm should be easily achievable without degrading the power density excessively.

Consideration of the four factors discussed above has the net effect of changing the signal level considerably. Each of the factors discussed affects the signal quadratically. Thus, the combined effect is an increase in the anticipated signal by a factor of 4 x 10^4. This means that for a chemical present in high concentration (70%) at STP with a Raman cross section of 0.9 x 10^{-29} cm^2/sr at 400 nm roughly 6 x 10^9 counts should be expected from a single pulse. Assuming 60% atmospheric attenuation of the signal would result in a signal level of 2.5 x 10^9 counts. Since the signal is dependent on the square of the density, this result can be scaled to give a sensitivity of ~ 150 ppm. This neglects background considerations as well as problems which may be encountered in achieving phase matching.

2.5 CARS vs. Raman Spectroscopy

The advantages and disadvantages of CARS vs conventional Raman spectroscopy have been listed by Nibler and Knighten [2]. Those relevant to remote sensing application are as follows :

Advantages of CARS relative to Raman :

a. Higher signal levels ~ 10^5 Raman with no resonance enhancement.

b. Fluorescence is avoided in CARS since the CARS signal is Stokes shifted relative to the pump and probe beams. In Raman fluorescence problems must be avoided or one must compensate for them.[7]

c. Resonance enhancement is possible for both CARS and Raman. For Raman, the incident light frequency must approach the electronic resonance frequency. In resonance enhanced CARS, either the pump or the CARS signal need be near the resonance. This will in itself increase the sensitivity of resonance enhanced CARS over resonance enhanced Raman since the path length of the UV light can be reduced by a factor of 2. This factor enters into the sensitivity in an exponential fashion. A second point to bear in mind in this respect is the fact that χ_{CARS}, which is proportional to the Raman cross section, affects the intensity of the CARS signal quadratically. Thus, increases in the Raman cross section due to resonance enhancement will be magnified in CARS relative to their effects on the Raman sensitivity.

d. Lower signal divergence which in turn means higher collection efficiencies. The signal divergence of CARS is on the order of mrad and is ~ 10^{-4} Raman values which is scattered over 4π sr. Thus, not only is the signal higher for CARS (see advantage a., above), but more of the signal can be collected.

Disadvantages of CARS relative to Raman:

a. CARS signal is dependent on the square of the molecular density. As we have seen, this limits the detection capability for a non-resonance enhanced system to about 150 ppm for a remote system. Resonance enhanced Raman (UV-Raman) can potentially detect lower concentrations, but the range is much reduced due to attenuation of the UV [1].

b. Optical damage due to the focusing of high powered lasers is a possibility with CARS, however, in optically transparent media such as air, this should not be a problem.

c. A tunable laser source is required for CARS. With recent advances in solid state lasers, this is not nearly the difficulty that it was in 1979. Rapidly tunable, pulsed solid-state lasers such as Ti:Sapphire appear to be state-of-the-art.

d. CARS signals are strongly dependent on laser intensity and phase matching. The required laser intensity for large CARS signals is well within state-of-the-art laser technology. Phase matching is a real issue for CARS which will have to be addressed in basing, and system designs.

From the above, it is evident that for species present in even relatively low concentrations (150 ppm) CARS offers distinct advantages over Raman spectroscopy conducted at the same frequency. A comparison of UV-Raman with a lower frequency CARS system is a bit less clear cut since the cross section increase for resonance enhanced Raman compensates for the inherently higher CARS signal levels. Range still an issue since the CARS system can operate in a range of high atmospheric transmission. For a resonance enhanced Raman system, the frequency of the laser is fixed by the electronic spectrum of the molecules being analyzed for and is for the most part limited to the UV. This raises a second difficulty with resonance enhanced Raman. Data obtained by Sedlacek et al.[8] is illustrative of the sensitivity of the cross section and band shape to excitation frequency. A five nanometer difference in excitation wavelength can result in more than a factor of four difference in signal, for example. Unless resonances exist for all molecules of interest within a narrow frequency band, multiple UV laser frequencies will have to be used to observe the resonance-enhanced spectra. As with CARS, the necessity to scan over a range of wavelengths complicates and lengthens the data acquisition process and some of the inherent simplicity of UV

Raman relative to CARS is lost. Changes in band shape with excitation frequency also means that care must be taken in assembling a cross section library to insure that data is available for all molecules of interest at the planned measurement frequency not just at the peak of the resonance enhancement.

3. CONCLUSIONS

The assessment of CARS technology from the standpoint of its use as a remote sensing technology leads to the conclusion that the technique has the potential for further development in this area. Sensitivities on the order of 100-200 ppm appear to be achievable within the state-of-the-art for CARS technology. Its use in a variety of environments and particularly as a tool for combustion diagnostics show promise for the technique in a remote sensing application. It appears to offer many advantages over both conventional Raman spectroscopy as well as resonance enhanced Raman spectroscopy in this respect.

Of course, issues such as equipment design, long-distance phase-matching of pump and probe beams and appropriate basing for the technology are still to be addressed. These issues are currently under consideration in DNA-funded work being undertaken by DESE Research. In addition, for a particular application, model systems must be developed along with a compound identification methodology. These issues have both generic and application specific components.

ACKNOWLEDGEMENT

The author would like to thank J. Veligdan for his comments on the manuscript. In addition, the assistance of DESE Research in allowing the use of some of the material presented herein is appreciated.

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