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REMOTE SENSING OF ATMOSPHERIC CHEMICAL CONTAMINATION

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ABSTRACT

Use of LIDAR sensor systems for atmospheric characterization is becoming an established technology. At ARL/PSU, we have developed and demonstrated several systems capable of measuring water vapor profiles, aerosol distribution and temperature profiles from ground level up through the troposphere. We are currently developing a prototype system which will go aboard a Navy ship to undergo sea tests during the next year, prior to full scale deployment. This system will be used to predict radar system performance by providing real time computation of RF refractivity from profiles of temperature and water vapor for modeling of RF ducting conditions. We have examined the potential use of Raman scattering measurements to detect the spectra of several atmospheric pollution species and various chemical agents. A previous approach demonstrated for lidar measurements of atmospheric pollutants and chemical agents involved the use the SPR-DIAL technique with about sixty of the CO_2 laser lines in the 10 μm region of the spectrum. An evaluation of the current techniques available for remote sensing of chemical agents has been prepared. The active lidar combined with passive optical remote sensing techniques hold great promise as the basis of a mobile sensor system for measurement of pollution episodes and for remote detection of covert manufacture and employment of chemical warfare agents.

INTRODUCTION

Remote sensing, detection and profiling, of chemical species in the atmosphere has been a long term goal and promise of the lidar techniques. There have been many efforts during the past twenty years which have contributed to this goal. However, the research efforts to manufacture reliable and stable lasers, to develop techniques, and prepare the detector and filter technology has delayed much progress toward the autonomous instrument which would be useful in many applications of lidar. Most researchers have been fully involved in the development of laboratory research investigations and have moved from one topic to another in an amazingly broad range of research topics. The time has come to push the research instruments from the laboratory and into several useful applications. This process requires that the several PhD scientists and graduate students usually associated with lidar instruments must be replaced with automated control sub-systems which will operate the lidar and produce the desired data products.

The application of laser remote sensing to measurement of chemical species in the atmosphere, whether these result from pollution sources, accidental release of hazardous vapor from industrial processes, or from the release of toxic chemicals in the battlefield environment, appears to be ready for major advancement. The techniques which show the most promise for active sensing are the vibrational Raman scattering and DIAL (DIfferential Absorption Lidar) or SPR-DIAL (Spectral Pattern Recognition - DIAL) techniques. For application to contamination of surfaces and possibly for plumes or clouds, the lidar fluorescence technique will also have application.

LIDAR BACKGROUND

During the past twenty years, researchers at several laboratories have demonstrated that lidar has special capabilities for remote sensing of many different properties of the atmosphere. In this description, our application of the Raman scattering techniques to obtain profiles of water vapor and temperature in the lower atmosphere is briefly described. The first Raman measurements of atmospheric properties with lidar were carried out in the late 1960's by Leonard (1967) and Cooney (1968). Two years later, Melfi, et al. (1969) and Cooney (1970, 1971) showed that it was possible to measure water vapor using the Raman lidar technique. A significant contribution was made by Inaba and Kobayasi (1972) which suggested several species that could be measured using vibrational Raman techniques. While the early tests (Melfi et al., 1969, Cooney 1970, 1971 and Strauch et al., 1972) showed that it was possible to measure the water vapor with limited range and accuracy, recent investigations have demonstrated significant improvements. Particularly, the investigations of Vaughan et al. (1988), Melfi et al. (1989), Whiteman et al. (1992) and Philbrick et al. (1992) have demonstrated rather convincingly that the Raman technique has an excellent capability for making accurate water vapor measurements. A most useful review of the Raman and DIAL lidar techniques applied to the water vapor measurement has been prepared by Grant (1991). The measurements of water vapor during the daytime have been demonstrated using the fourth harmonic of the Nd:YAG laser. At this wavelength, the measurements of N_2 and H_2O are contaminated, at least to a small degree, by the absorption of O_3 in the lower troposphere. However, we have found that an adequate correction can be obtained from the use of the measured Raman signals of the N_2 and O_2 compared to the known mixing ratio, and this results in a measured profile of O_3 in the range from the surface to 3 km.

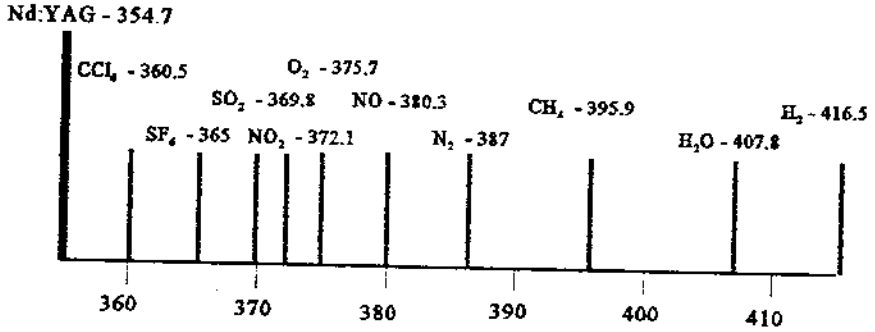

Figure 1. Locations of several Raman lines that are available from the 3rd harmonic of Nd:YAG.

At tropospheric altitudes, the Raman N_2 profile allows the determination of the profile of the extinction. The advantage in using the Raman signals in the lower atmosphere is clear from the profiles shown above. Figure 1 shows a representation of the locations for several species which can be measured using the vibrational Raman technique. These are only a sample of the many species that can be measured using the technique. To enable the selection of any vibrational Raman line, we are combining the Acousto-Optical Tunable Filter (AOTF) technology (Pustovoit, 1994) with our lidar development to measure the spectral signatures of atmospheric chemical species. An idea of the wide range of species which can be measured with the technique can be gathered from consideration of the descriptions of Measures (1992) and Inaba and Kobayasi (1972). Only the first Stokes vibrational states are considered, since the simple molecules have large vibrational energy state separation and the anti-Stokes lines are not normally populated at atmospheric temperatures. The Raman H_2O signal measured as a ratio to the Raman N_2 signal provides a profile which is proportional to the water vapor concentration. The N_2 fraction of the atmospheric profile is known, thus the atmospheric profile of most any species present in sufficient concentration can be obtained. The error caused by the extinction differences between the backscatter wavelengths is small (few percent) and can be corrected using the results from multiple wavelengths.

The rotational Raman technique for temperature measurements was reported by Cooney in 1972. A double grating monochrometer was used by Arshinov, et al. to measure the rotational Raman spectrum in 1983. Hauchecorne, et al. (1992) and Nedeljkovic, et al. (1993) demonstrated the capability to measure the temperature using narrow-band filter technology in the upper troposphere and lower stratosphere. We are making use of the rotational Raman envelop of several lines which pass through a narrow band filter. The molecular species of the atmosphere, principally N_2, O_2 and to some degree H_2O, contribute to the envelop of lines on either side of fundamental laser wavelength. In our case, we measure the lines in the rotational states at the 530 and 528 nm filter bands. The envelop shape is determined by the population of the rotational states under the temperature distribution of the gas in the volume, which is illuminated by the doubled Nd:YAG laser at 532 nm. There are rotational envelops on both the long and short wavelength sides of the fundamental exciting frequency, however we have chosen to work on the short wavelength, higher energy, side of the distribution in case there is any excitation from fluorescent transitions. The ratio between the intensities of the two filter bands is used to directly determine the temperature. We use a method of comparison of a rawinsonde balloon measurements with the measured results to develop a calibration curve based upon an empherical fit. With the measured temperature profile and a ground based measurement of the surface pressure, the profiles of the structure properties, density, pressure and temperature are available from the calculations based upon the hydrostatic equation and the ideal gas law. The calculated profile of density can be used to obtain the N_2 profile to place an absolute density on the water vapor from the ratio of vibrational Raman signals.

LAMP LIDAR INSTRUMENT

The LAMP lidar which was developed at PSU during the past several years has focused on the application of Raman vibrational and rotational scattering results [Philbrick, 1994]. Measurements have been carried out during several campaign periods which demonstrate the performance of Raman lidar techniques compared to standard rawinsonde balloon payload measurements. The investigation has included water vapor and molecular nitrogen profiles determined from the 1st Stokes vibrational Raman transitions from laser wavelengths of 532 nm, 355 nm and 266 nm. The profiles of the N_2 vibrational Raman scatter provide true extinction measurements in the lower atmosphere. Water vapor profiles are determined from the ratio of signals measured at the following wavelength pairs: 660/607, 407/387 and 294/283. The fact that the profile is determined from a signal ratio removes most of the factors which would result in errors in the profiles and makes the technique preferred for many applications. The temperature structure has been measured using the rotational Raman scattering in the region of anti-Stokes wavelengths between 526 and 532 nm. Figure 2 shows an example of a water vapor, rotational Raman temperature profile and the calculated atmospheric refractivity for the LAMP lidar. Measurements have been carried out for evaluation of the performance which have proven the capability of Raman lidar to measure the profiles of atmospheric structure properties and water vapor in the lower atmosphere during night conditions. Also, the daytime measurement capability has been demonstrated using the "solar blind" region from the 266 nm fourth harmonic of Nd:YAG. Many examples of results from the LAMP lidar are available, the LAMP has proven to be a versatile research instrument (see references 18 - 20). The lessons learned from the LAMP have been used to design and build two more recent lidars, LAPS and LARS. The LAPS instrument is intended to be a prototype for an operational meteorological instrument. The LARS is a research instrument that has volume scanning capability and it will be used to study cloud micro-physics and pollution plumes.

LAPS LIDAR INSTRUMENT

A sensor capable of measuring profiles of atmospheric properties has been prepared. The Lidar Atmospheric Profile Sensor (LAPS) instrument is currently undergoing tests of its automated operation to determinate its performance under a wide range of meteorological conditions. The instrument measures the water vapor profile based on the vibrational Raman scattering and the temperature profile based on the rotational Raman scattering. These measurements provide real-time profiles of RF refractivity. Profiles are obtained each 5 minutes with a vertical resolution of 75 meters from the surface to 7 km. The prototype instrument, which includes several sub-systems to automate and monitor the operation, has been designed to provide the real-time measurements of profiles. The instrument includes an X-band radar which detects aircraft as they approach the beam and automatically protects a 6 degree cone angle around the beam. The instrument incudes self calibration, performance testing and built-in-tests to check many functions.

In addition to the water vapor and temperature profiles, the true extinction and ozone profiles are also measured. By comparing the molecular profiles of the N_2 Raman and rotational Raman with the neutral atmosphere gradient, the extinction profile can be obtained. The day time measurements of water vapor are determined using the solar blind ultraviolet wavelengths. The ratio of the N_2 and O_2 vibrational Raman measurements on the slope of the Hartley band of ozone provides a DIAL measurement of the ozone profile in the lower atmosphere, up to 3 km. Initial results from the instrument are presented. Eventual deployment of the LAPS instrument will provide results to test and improve the optical propagation models of the atmosphere.

ACOUSTO-OPTICAL TUNABLE FILTER

Remote sensing systems with high spectral resolution in the visible and near-IR regions can provide the sensitivity and discrimination against interferents to monitor the hazardous chemical vapors in the background environment. Due to their compact size, ruggedness and relatively narrow spectral resolution, Acousto-Optical Tunable Filters (AOTF) which can be used to select the Raman line of a species of interest, or it can be used to provide a tunable narrow band filter for the on and off line detection of a DIAL instrument in synchronization with the laser source. To date, several AOTF devices have been designed which make high quality measurements in portions of the wavelength range of interest, however, none of the instruments thus far designed have been able to achieve both the ultra high resolution required for narrow band discretionary measurement and combine the frequency agile operational characteristics and physical features which could fully leverage the potential of these devices. Current state of the art AOTF instruments are capable of achieving spectral resolution of 10 cm^{-1} at selected visible wavelengths (less than 0.3 nm at 500 nm), but not over a wide range that would include the infrared spectrum that would serve the environmental applications envisioned. The advantages in light through-put, frequency agility, ruggedness and resolution have

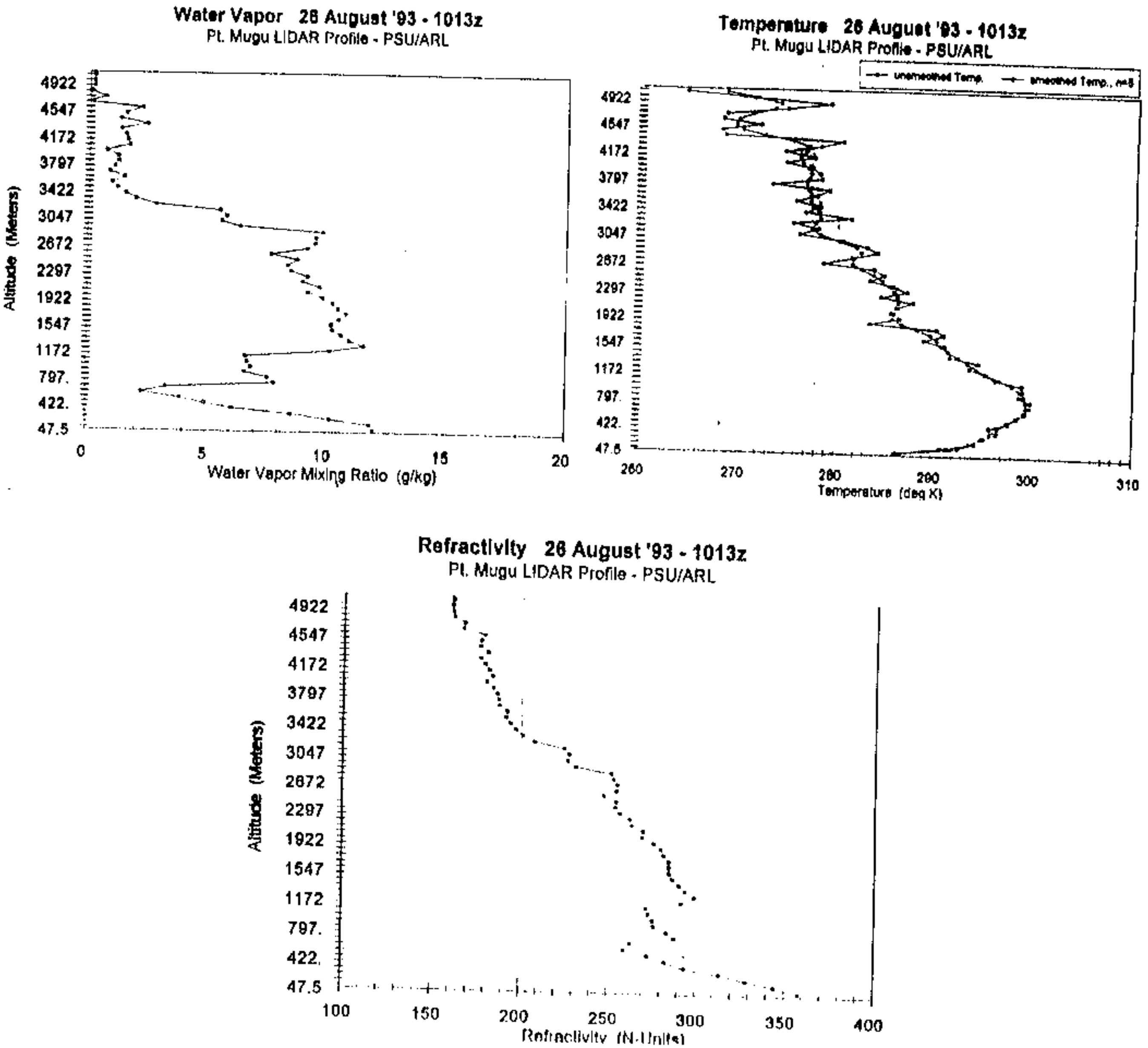

Figure 2. Example of the LAMP lidar results from a test at Point Mugu CA during 1993. The lidar measured profiles for water vapor and temperature have been used to calculate the refractivity during a period of RF ducting.

drawn attention to this technique. The rich spectral signatures of many chemical species of interest in the infrared region from 8 to 12 μm make it very attractive to develop the AOTF capability in this wavelength region as a filter to accompany development of an OPO laser in this same wavelength region.

LIDAR FOR CHEMICAL SPECIES

During the early 1980's, SPR-DIAL lidar systems were developed for remote detection of chemical agents and other chemical species using as many as sixty wavelengths of the CO_2 laser by researchers at GTE Sylvania (now EEO, Inc.) and by SRI. These instruments depended upon the differential absorption of the gas species of interest at the multiple wavelengths between 8 and 12 μm to identify the species of interest and to discriminate against background gases. The work on these techniques has continued at a low level effort but many different chemical species have been identified which can be detected with the technique. The 8-12 μm range provides a rich fingerprint for many chemicals of interest in pollution studies and it contains spectral features which are unique to the nerve agents and blister agents which are of concern in military battlefields. The development of an OPO tunable laser source in this wavelength region will provide major advances for future remote sensing of chemical species.

The DIAL techniques require precise knowledge of the wavelength and line shape to be effective in quantifying the species and its concentration. In the early investigations of remote detection of chemical species, the use of Raman scatter was considered to be a primary approach. However, the development of the potential of the technique has proceeded slowly until the last few years. At present, the Raman technique has progressed to the point that detection of the concentrations of most species at the parts per million level is possible for ranges out to about 5 km. When the DIAL and Raman techniques are compared, each is found to have advantages and disadvantages for particular applications. Table I shows the characteristics of DIAL and Raman instruments which can easily be assembled using off the shelf technology. In Table II, the detectable concentration for DIAL and Raman measurements of NO_2 and SO_2 at ultraviolet and visible wavelengths are compared. The calculations are based upon modeling and simulation programs that have been developed by several graduate students in the PSU Lidar Laboratory during the past several years.

Much work has gone into the DIAL technique because on first glance the absorption cross sections are larger that the Raman scattering cross sections. The early demonstrations of Raman measurements suffered from the hardware and the techniques employed. With current photon counting capabilities, the Raman measurement for minor chemical species is very attractive. We have been able to demonstrate the capabilities of the Raman technique in the background of the boundary layer aerosols and light tropospheric clouds, as well as, in the near field where telescope form factors become important. Generally, the Raman and DIAL techniques are capable of providing a quantitative profile based upon the fact that absolute detector sensitivity, telescope form factor, laser power variation and many other factors are cancelled from the equations because we are using a ratio measurement. However the DIAL technique still requires stringent controls on the dependence of laser line-width and wavelength control to obtain useful measurements. Therefore, we believe that the Raman technique will have a stronger role in the remote sensing

Table I. Characteristics of Raman and DIAL lidar instruments for measurements of chemical species.

	Raman	DIAL
Laser	Nd:YAG (2 or 3)	OPO or $Ti:Al_2O_3$
Energy	400 or 150 mj	50 mj
Pulse Length	6 ns	100 ns
Pulse Rate	20 Hz	20 Hz
Telescope	60 cm	60 cm
Detector Eff.	5 %	5 %

Table II. Comparison of expected measurement by Raman and DIAL techniques of a chemical plume at 1 km range with 10 minute integration for SO_2 and NO_2 (cross sections based on Measures, 1992).

RAMAN	NO_2	SO_2
Shift (cm -1)	1320	1151.5
Wavelength (nm)	572.2 or 372.1	566.7 or 369.8
Cross Sect($cm^2 sr^{-1}$)	8.2 or 42 $\times 10^{-30}$	2.7 or 14 $\times 10^{-30}$
Concentration (S/N = 10)	0.05 ppm	0.02 ppm
DIAL	NO_2	SO_2
Wavelength (nm)	448.2	300.1
Cross Sect (cm^2)	0.2 $\times 10^{-18}$	1.0 $\times 10^{-18}$
Concentration (S/N = 10)	4 ppm	2 ppm

measurement technologies in the future. While demonstrations by several researchers have shown the potential of lidar to measure many properties of the atmosphere, there have been few efforts to develop the lidar techniques sufficiently for them to be used for routine measurements. The research lidars generally require attentive interaction by highly specialized personnel to obtain useful measurements and thus the investigations have been generally limited to short and intensive measurement periods. The transition of the technical capability of lidar to operational applications in meteorological data collection, atmospheric physics investigations, studies of the environment, investigations of radiative transport and global climate analysis requires that instrumentation be improved and automated. The efforts that have been undertaken with the LAPS instrument represent a start in that direction.

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