



**Remote Sensing  
of the  
Atmosphere by  
Resonance  
Raman LIDAR**

**Arthur J. Sedlacek, David Harder, King P. Leung,  
Peter B. Zuhoski, Jr., D. Burr, Carl L. Chen**

**December, 1994**

Safeguards, Safety & Nonproliferation Division  
Department of Advanced Technology  
Brookhaven National Laboratory  
Upton, NY 11973

This paper was prepared for the Optical Remote  
Sensing of the Atmosphere Sixth Topical Meeting,  
Salt Lake City, Utah, February 6-10, 1995

This work was performed under the auspices of the U.S. Department of Energy by  
Brookhaven National Laboratory under Contract No. DE-AC02-76CH00016.

**SSN**

SAFEGUARDS, SAFETY, AND NONPROLIFERATION DIVISION  
DEPARTMENT OF ADVANCED TECHNOLOGY  
Brookhaven National Laboratory  
Building 197C  
P.O. Box 5000  
Upton, New York 11973-5000

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

## ABSTRACT

Poster Paper Submitted To  
Optical Remote Sensing Of The Atmosphere  
February 6-10, 1995  
Salt Lake City, Utah  
Sponsored by the  
Optical Society of America

Remote Sensing of the Atmosphere by Resonance Raman LIDAR - A. Sedlacek,  
D. Harder, K. Leung, P. Zuhoski, D. Burr, and C.L. Chen

When in resonance, Raman scattering exhibits strong enhancement ranging from four to six orders of magnitude. This physical phenomenon has been applied to remote sensing of the atmosphere. With a 16 inch Cassegrain telescope and spectrometer/CCD-detector system, 70-150 ppm-m of SO<sub>2</sub> in the atmosphere has been detected at a distance of 0.5 kilometer. This system can be used to detect/monitor chemical effluence in the atmosphere by their unique Raman fingerprints. Experimental result together with detailed resonance Raman and atmospheric laser propagation effects will be discussed.

### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**MASTER**

## Remote Sensing of the Atmosphere by Resonance Raman LIDAR

Arthur J. Sedlacek\*, David Harder, King P. Leung, Peter B Zuhoski, Jr., D. Burr, Carl L. Chen

Brookhaven National Laboratory  
Department of Advanced Technology  
Upton, NY 11973  
\*516-282-2404

### I. INTRODUCTION

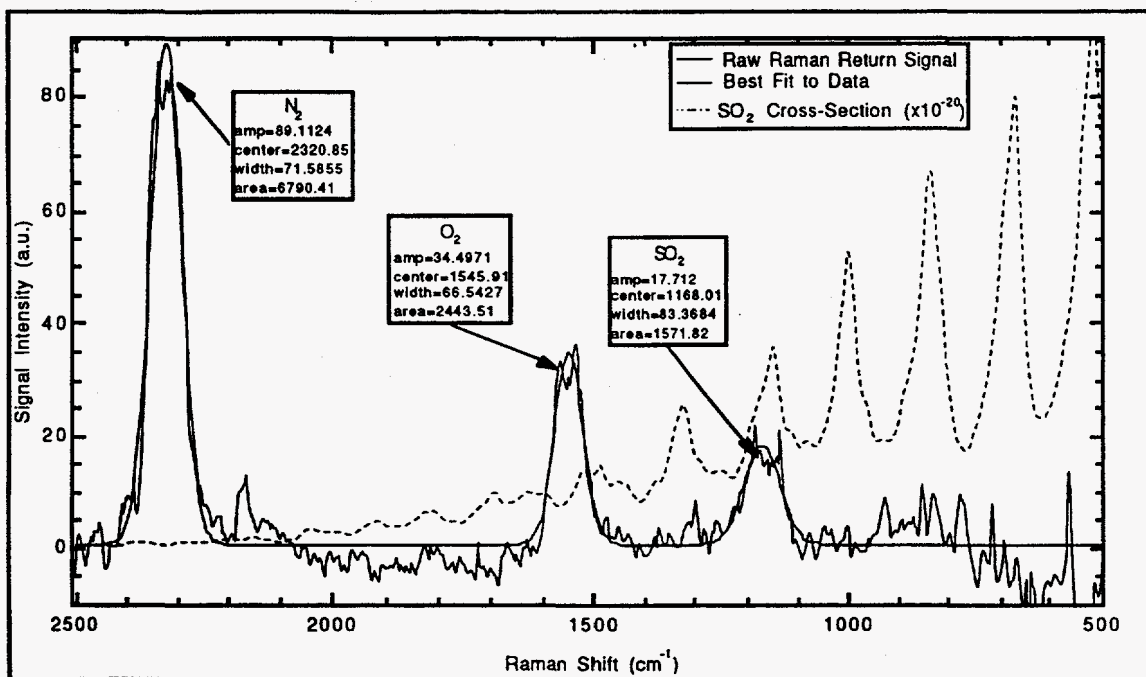
With our increased environmental awareness has come the need for technologies that can detect, identify and monitor pollutants and, where necessary, verify their destruction. This need is evidenced by the recent creation of the Clean Air Act Amendments (CAAA), of which the Title III-Hazardous Air Pollutants (HAP) amendments mandate the complete revision and expansion of the earlier Clean Air Act (CAA), section 112.<sup>1</sup> As was pointed out by Grant, Kagann and McClenny,<sup>2</sup> optical remote sensing technologies are expected to play a very important role in insuring that various facilities are in compliance with the Maximum Achievable Control Technology (MACT) standards for the reduction of HAP emissions that are called for in section 301 of Title III. Unfortunately, however, many of these technologies have varying detection and applicability characteristics which often dictate the conditions under which one can use the sensor to detect, identify or monitor a chemical species. Some of the advantages<sup>3-8</sup> that a Raman-based pollution sensor possess are: (1) very high selectivity (chemical specific fingerprints), (2) independence from the excitation wavelength (ability to monitor in the solar blind region), (3) chemical mixture fingerprints are the sum of its individual components (no spectral cross-talk), (4) near independence of the Raman fingerprint to its physical state (very similar spectra for gas, liquid, solid and solutions), and (5) insensitivity of the Raman signature to environmental conditions (no quenching, or interference from water). The detection of atmospheric components using Raman backscattering of laser radiation dates back to the pioneering work of Leonard<sup>9</sup> in 1967. In that study, he used a pulsed N<sub>2</sub> gas laser at 337.1 nm to generate Raman return signals from N<sub>2</sub> and O<sub>2</sub>. Further investigations performed by Cooney<sup>10</sup>, Inaba and Kobayasi<sup>11,12</sup>, Melfi<sup>13,14</sup> and others<sup>15</sup> during the early 1970s pushed the envelope of performance for a Raman LIDAR. However, due to the lack of tunable UV laser sources, these early investigations were not able to take advantage of near-resonance enhancement<sup>16</sup> of the Raman cross-section which occurs when the excitation frequency approaches an electronically excited state of the molecule<sup>6,17-19</sup>. The enhancement of the scattering cross-section can be quite large, often approaching 4 to 6 orders of magnitude. This improvement in the cross-section, in conjunction with the global advantages of Raman spectroscopy cited earlier and the availability of frequency-tunable, all solid-state UV laser systems and high sensitivity/low noise multichannel detectors, provides a promising optical open-path platform for the remote atmospheric sensing. In this paper, we will discuss the active technique of resonance Raman LIDAR for the remote detection gaseous chemicals.

### II. EXPERIMENTAL

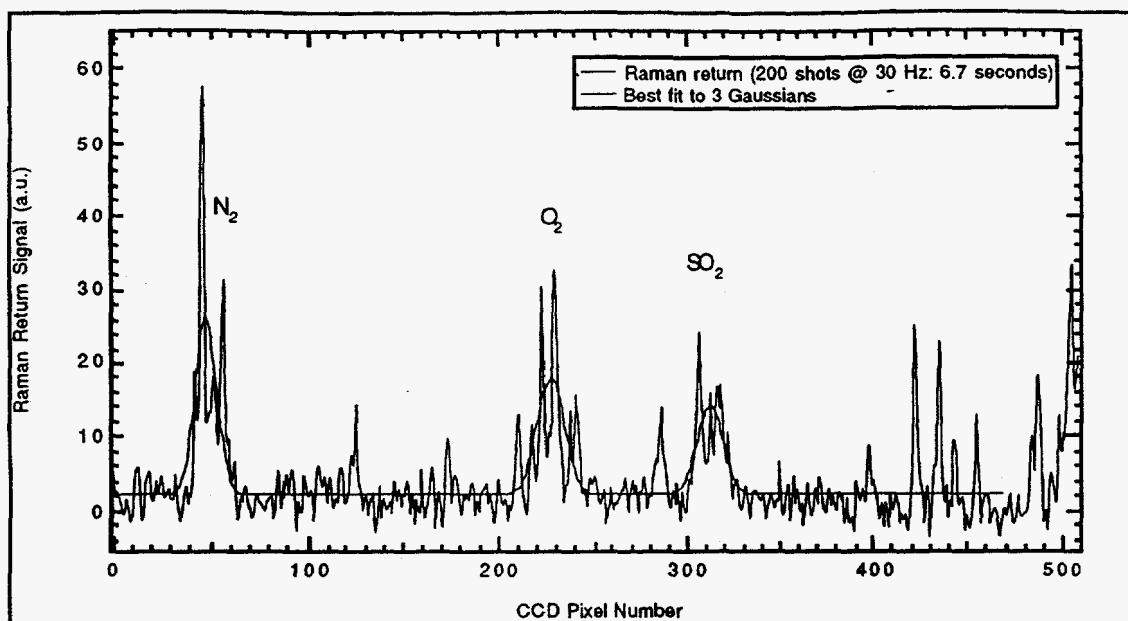
The BNL resonance Raman chemical sensor is typical of most Raman LIDAR configurations. It is composed of three main subsystems: (i) frequency tunable laser system and beam transmitter, (ii) signal receiver telescope and spectral fingerprinting detection unit, and (iii) equipment control and data acquisition/processing subsystem. All timing aspects of this system are based on a single master oscillator which provides triggering to the laser and gate delay timing to the detector circuitry. Following the laser trigger from the master oscillator, the 6 mm diameter, 300 nm laser beam (of 3-4 ns duration) was expanded to a diameter of 100 mm via a 1:16 beam expander prior to exiting the trailer. The laser used for the current set of experiments was the all solid-state, completely tunable Spectra-Physics 730 MOPO system. All return signals were collected by a 16 inch Cassegrain telescope and focused onto the slits of a single grating spectrometer (1200 grooves/mm) and then detected by an EG&G intensified CCD (charge-coupled device) camera for spectral fingerprinting. In order to avoid the possibility of charge saturation of pixels by the unwanted Rayleigh-return, and to prevent charge spill-over to the Raman channels, a pre-disperser was employed for the preferential removal of the Rayleigh signal return. The SO<sub>2</sub> resonance Raman and N<sub>2</sub> and O<sub>2</sub> Raman return signals were typically averaged over 10<sup>4</sup> laser pulses. However, it should be noted that as few as 200 laser pulses were necessary to distinguish the SO<sub>2</sub> resonance Raman return (see below). Collected signals were then exported over to a Sun SparcStation model 10 for initial spectral analysis and display.

### III. RESULTS AND DISCUSSION

Shown in Figure 1 is a sample of the resonance Raman return signal from  $\text{SO}_2$  along with the Raman return signals from atmospheric nitrogen and oxygen. These data were averaged over  $10^4$  laser pulses with a nominal pulse energy of 3-5 mJ, and a CCD intensifier gate width of 20 ns. Since this gate width corresponds to a 6 meter sampling length and the exhaust plume diameter was estimated to be 2 meters, the signal strengths of the nitrogen and oxygen return signal were nominally 3-times larger than would be measured with a range resolution of 2 meters ( $\sim 6.5$  ns).



A significant advantage of the resonance Raman chemical sensor is the presence of the atmospheric nitrogen and oxygen return signals in the same scan, therefore providing self-calibration of the concentration with signal intensity. This self-calibration is accomplished by comparing the integrated areas under the respective return signals for the knowns ( $\text{N}_2$  and  $\text{O}_2$ ) and the unknowns (in the present case  $\text{SO}_2$ ), and using their respective scattering cross-sections to derive the unknown concentration(s) from the known concentrations for atmospheric nitrogen and oxygen. The Raman scattering cross-sections for these two atmospheric species as a function of laser excitation wavelength is documented in the literature<sup>10</sup>. For the specific case of  $\text{SO}_2$ , the resonance Raman scattering cross-section has been measured at 300 nm<sup>15</sup>. In order to check the accuracy of these field measurements, two calculations have been performed: the first one examining the ratio of the corrected  $\text{N}_2$  return signal to the corrected  $\text{O}_2$  return signal and the second one calculating the  $\text{SO}_2$  concentration based upon signal strength, scattering cross-sections and known concentration of atmospheric nitrogen. Also shown in Figure 1 is the result of a non-linear curve fit to the experimental data which assumed that the return signals had Gaussian lineshapes. The best fit curve was then used to calculate the respective areas under the  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{SO}_2$  return signals. By using the known concentrations, measured areas, scattering cross-sections, and correcting for ozone absorption it was found that the ratio of  $\text{N}_2$  molecules to  $\text{O}_2$  molecules was 3.31. The known ratio is 3.73. This immediately provides an initial estimate of the accuracy of  $\sim 10\%$  for the return signal. A similar analysis between atmospheric nitrogen and the released chemical  $\text{SO}_2$ , revealed a concentration of  $\sim 120$  ppm of  $\text{SO}_2$ . This analysis includes corrections for self-absorption of the  $\text{SO}_2$  return signal within the plume (see the dotted line in Figure 1) and ozone attenuation over the 500 meter pathlength. At a laser repetition rate of 30 Hz, this signal required only 6.7 seconds to collect with a signal-to-noise sufficient to allow curve fitting to be performed and the relevant Raman return signals identified.



#### IV. CONCLUSIONS

We have discussed recent experimental results using a resonance Raman based LIDAR system as a remote pollution sensor. This spectroscopy has the fundamental advantage that it is based on optical fingerprints that are unique to each molecular species and are insensitive to environmental perturbations or excitation frequency. By taking advantage of resonance enhancement, the inelastic scattering cross-section can increase anywhere from 4 to 6 orders of magnitude translating into increased sensing range or lower detection limits. The availability of frequency-agile UV lasers, high gain low noise multichannel detectors and other state-of-the-art technologies now allows the phenomenon of resonance-enhanced Raman spectroscopy to be fully exploited as a remote chemical sensor platform. Since many chemicals have electronic transitions in the UV/VIS, it is expected that many will have pronounced resonance enhancements.

#### References:

1. Lee, B., *J. Air Waste Manage. Assoc.* **41**, 16 (1991).
2. Grant, W. B., Kagann, R. H. and McClenny, W. A., *J. Air Waste Manage. Assoc.* **42**, 18 (1992).
3. Measures, R. M., *Laser Remote Chemical Analysis*, in *Chemical Analysis Series Vol. 94*, R. M. Measures, Ed., John Wiley and Sons: New York 1988.
4. Hendra, P., Jones, C. and Warnes, G., *Fourier Transform Raman Spectroscopy: Instrumentation and Chemical Applications*, Ellis Horwood: New York 1991.
5. Grasselli J. G. and Bulkin B. J., *Analytical Raman Spectroscopy*, John Wiley and Sons: New York 1991.
6. Carey, P. R., *Biochemical Applications of Raman and Resonance Raman Spectroscopies*, Academic Press: New York 1982.
7. Schrötter, H. W. and Klöckner H. W., *Raman Spectroscopy of Gases and Liquids in Topics in Current Physics*, A. Weber, Ed., Springer-Verlag: New York 1979.
8. Long D. A., *Raman Spectroscopy*, McGraw-Hill: New York 1977.
9. Leonard, D. A., *Nature* **216**, 142 (1967).
11. Kobayasi, T and Inaba, H, *Opto-Electron.* **2**, 45 (1970); Kobayasi, T and Inaba, H, *Proc. IEEE* **58**, 1568 (1970).
12. Inaba, H and Kobayasi, T, *Opto-Electron.* **4**, 101 (1972).
13. Melfi, S. H, Lawrence, J. D. and McCormick M.P.M., *Appl. Phys. Lett.* **15**, 295 (1969)
14. Melfi, S.H., *Appl. Opt.* **11**, 1605 (1972).
15. For example see: Penny, C.M., Morey, W.W., St. Peters, R. L., Silverstein, S.D., Lapp, M., and White, D.R., *NASA Report, NASA-CR-132363*, Sept. 1973; Penny, C.M and Silverstein, S.D. *General Electric Report, GE-72CRD150*, May 1972.
16. Rosen, H, Robrish, P., and Chamberlain, O., *Appl. Opt.* **14**, 2701 (1975).
17. Rousseau, D. L., Friedman, J. M. and Williams, P. F., *Raman Spectroscopy of Gases and Liquids in Topics in Current Physics*, A. Weber, Ed., Springer-Verlag: New York 1979.
18. Asher, S. A., *Ann. Rev. Phys. Chem.* **39**, 537 (1988).
19. Ziegler, L. D. and Albrecht, A. C., *J. Chem. Phys.* **70**, 2634 (1979).