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REMOTE DETECTION OF TRACE EFFLUENTS USING RESONANCE RAMAN SPECTROSCOPY: FIELD RESULTS AND EVALUATION

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ABSTRACT

Resonance Raman spectroscopy (RRS) possesses many characteristics that are important for detecting, identifying and monitoring chemical effluents. Raman scattering is a coherent, inelastic, two-photon scattering process where an exciting photon of energy hν promotes a molecule to a virtual level and the subsequently emitted photon is shifted in frequency in accordance with the rotational-vibrational structure of the irradiated species, thereby providing a unique fingerprint of the molecule. Under resonance enhancement, the Raman scattering cross-sections have been observed to increase up to 6 orders of magnitude above the normal scattering cross-sections, thereby providing the practical basis for a remote chemical sensor. Some of the other advantages that a Raman sensor possesses are: (1) very high selectivity (chemical specific fingerprints), (2) independence of the spectral fingerprint on 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 or solutions), (5) no absolute calibration is necessary because all Raman signals observed from a given species can be compared with the Raman signal for N_2, whose concentration is known very accurately, and (6) insensitivity of the Raman signature to environmental conditions (no quenching, or interference from water vapor). In this presentation, the technology of resonance Raman spectroscopy as applied to the detection of narcotics production activities will be presented along with some recent experimental results.

I. INTRODUCTION

The remote detection of narcotic manufacturing and/or its trafficking has the potential to either help truncate the distribution of the contraband within the U.S. or to lower the its flow across the border by providing an early detection/warning that such illicit activities are underway. In an effort to create such an early detection device [1], Brookhaven National Laboratory has been developing a remote chemical sensor based upon the phenomenon of resonance Raman spectroscopy. Some of the advantages [2-16] that a Raman-based LIDAR (Light Detection And Ranging) system 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 [3] in 1967. In that study, he used a pulsed N_2 gas laser at 337.1 nm to generate Raman return signals from N_2 and O_2. Further investigations performed by Cooney [9,10], Inaba and Kobayasi [4,8], Melfi [10,11] and others [12-16] during the early 1970s pushed the envelope of performance for a Raman light detection and ranging (LIDAR) system. However, due to the lack of tunable UV laser sources, these early investigations were not able to take advantage of near-resonance enhancement [17] of the Raman cross-section which occurs when the excitation frequency approaches an electronically excited state of the molecule [2,18-21]. 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

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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 remote atmospheric sensing. In this paper, we will discuss the active technique of resonance Raman LIDAR for the remote detection of gaseous chemicals and present some recent experimental data.

II. EXPERIMENTAL

The BNL resonance Raman chemical sensor is typical of most Raman LIDAR configurations. [2-17] As depicted in Figure 1, 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.

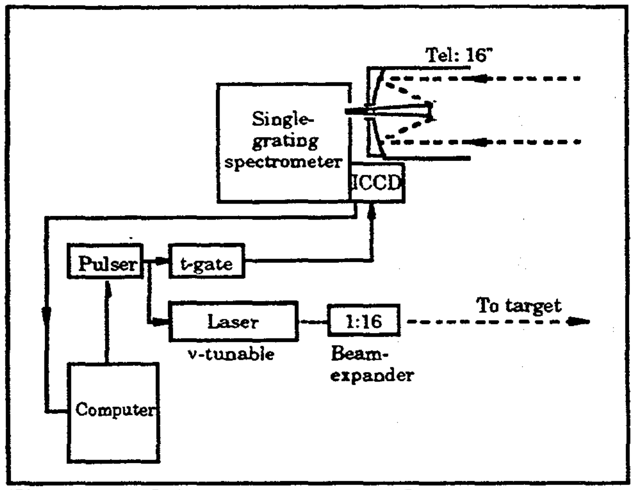

Figure 1: Schematic of BNL Resonance Raman Chemical Sensor

All timing aspects of this system were based on a single master oscillator which provided triggering to the laser and gate delay timing to the detector circuitry. Following a trigger pulse to the laser the 6-mm diameter, 300-nm laser beam (of 3-4 ns duration) output 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, minimally tunable Spectra-Physics 730 MOPO system. This laser system provided output energies at this wavelength of 3-5 mJ/pulse. All return signals were collected by a 16-inch Cassegrainian telescope and focused onto the slits of a pre-disperser/single-grating spectrometer (1200 grooves/mm) and then detected by a time-gated, blue-enhanced 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, the pre-disperser (McPherson) was employed for the preferential removal of this elastic Rayleigh return. The collected SO_2 resonance Raman and N_2 and O_2 Raman return signals were typically averaged over 10,000 laser pulses. However, it should be noted that as few as 200 laser pulses were sufficient to establish the presence of SO_2 via its resonance Raman fingerprint, along with the N_2 and O_2 Raman return signals, from the baseline (see below). Collected signals were displayed and then stored on the PC for later spectral analysis.

III. RESULTS AND DISCUSSION

Shown in Figure 2 is an example of the signal quality that was achieved with this system. Specifically, the resonance Raman return signal from SO_2 along with the normal Raman return signals from atmospheric nitrogen and oxygen can be clearly discerned in this spectrum. These data were averaged over 10,000 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 approximately a 6 meter sampling length, which was much larger than the plume diameter used for the release of the SO_2 (~2m), the signal strengths of the nitrogen and oxygen return signal were nominally 3-times larger than would be measured with an optimized range resolution of 2 meters (~6.5ns).

In addition to collecting a vibrational fingerprint from the interrogated chemicals, the resonance Raman chemical sensor has the other distinct advantage that every spectrum collected will also contain return signals from atmospheric nitrogen and oxygen, therefore providing a concentration calibration for the chemical of interest. [2-17] This self-calibration is accomplished by comparing the integrated areas under the respective return signals for the knowns (N_2 and O_2) and the unknown(s) (in the present case 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 are well documented in the literature [18]. For the specific case of SO_2, the resonance Raman scattering cross-section has been measured at 300 nm [19]. In order to check the accuracy of these field measurements, two calculations have been performed: the first one examining the ratio of the corrected N_2 return signal to the corrected O_2 return signal and the second one calculating the SO_2 concentration based upon signal strength, scattering cross-sections and known concentration of atmospheric nitrogen. Also shown in Figure 2 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 N_2, O_2 and SO_2 return signals. By using the known concentrations, measured integrated signals, and their respective scattering cross-sections, it was found that the ratio of N_2 molecules to O_2 molecules was 3.31. Comparison of this measured ratio to the documented ratio of 3.73, [3] an estimated accuracy of ~ 10% for the BNL remote resonance Raman sensor is established. A similar analysis between atmospheric nitrogen and the released chemical SO_2, revealed that our system's estimate of the sulfur dioxide concentration was to within about 15% of its actual value. One potential source for this discrepancy can be traced back to the accuracy of the measured SO_2 Raman cross-section.[19] Further analysis will be required to resolve the origin of this discrepancy in its entirety.

Since the BNL resonance Raman LIDAR collects the vibrational fingerprints of the interrogated molecules, an evaluation of the state-of-the-art pattern recognition algorithms has been undertaken. At present, this effort has focused upon Artificial Neural Networks (ANNs) using Multi-Layer Perceptron (MLP) architecture along with a pre-processing filter. A two neuron-based ANN, in conjunction with the preprocessing filter, was able to achieve an accuracy of 100% for identifying the presence/absence of SO_2 from spectra collected prior to and during the chemical release. In addition to this, we are also examining the potential of other pattern recognition algorithms such as Partial Least Squares (PLS). Based upon these results, it is expected that the successful application of pattern recognition algorithms, such as ANNs, to the detection, identification and ultimately quantification, of resonance Raman return signals will result in a new, previously unattainable, level of sensitivity for this remote sensing platform.

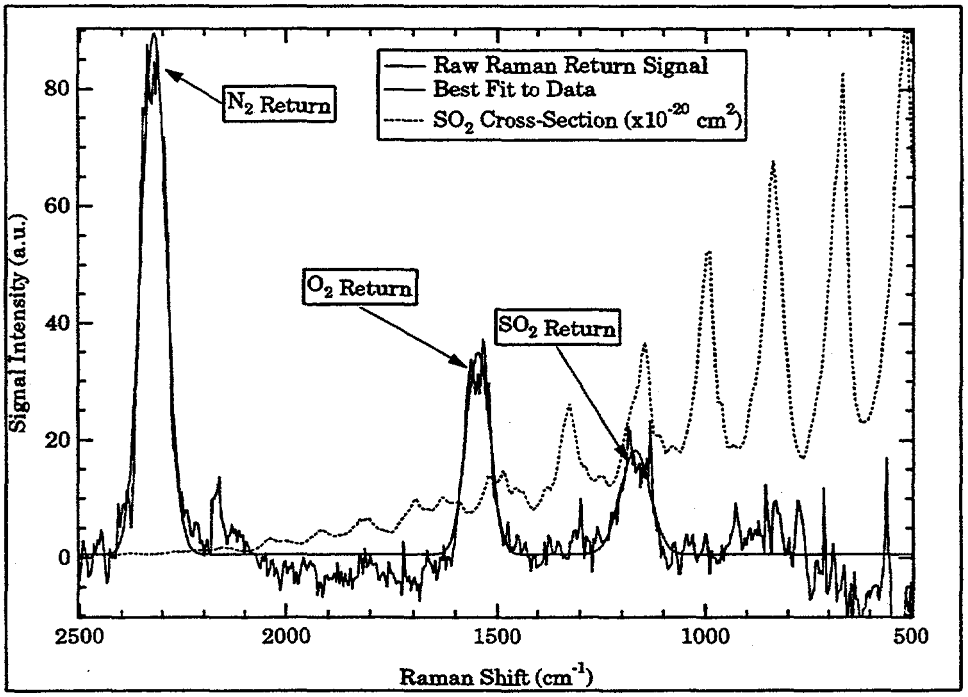

Figure 2: Resonance Raman Return Signal

IV. COMPARISON WITH PREVIOUS RAMAN LIDARS

A comparison of these results with those obtained employing normal Raman scattering LIDAR is instructive in that it shows what improvements can be expected when the Raman LIDAR platform is configured to take advantage of the resonance-enhanced phenomenon and provides guidance as to those paths that might further improve the sensitivity of the technique. In addition to choosing SO_2 because of its large resonance enhanced scattering cross-section, the choice of this chemical species also affords a reasonably large database of studies that employed normal Raman to detect sulfur dioxide.

The initial interest in Raman LIDAR during the late 1960s and early 1970s stemmed from a growing national consciousness about the environment and the pollution that was destroying it. In these early studies, then state-of-the-art Raman LIDAR platforms (also housed in mobile trailers/vans) were built and tested in an effort not much different than what is being undertaken today; that is, to evaluate the performance of the technique, and push the technique to the technical limits available. The detection of atmospheric components using Raman backscattering of laser radiation dates back to the pioneering work of Leonard[3] in 1967. In that study, he used a pulsed N_2 gas laser at 337.1 nm to generate Raman return signals from N_2 and O_2. Further investigations performed by Inaba and Kobayasi [4-8] Cooney [9,10], Melfi, [11,12] Hirschfeld [13,14] and others [14-17] during this time pushed the performance envelope of Raman LIDAR. Some of the work relevant to the present discussion was that of Inaba and Kobayasi [4-8] in their classic studies of Raman "Radar" in 1972, which was followed by the equally qualified investigations orchestrated by both Hirschfeld [13,14] and co-workers in 1973, and Melfi [11,12] and co-workers in the same year, and the work of Poultney et al. [16] which followed 4 years later. All these studies used a Ruby laser, either at the fundamental laser wavelength (694.6 nm) or its doubled frequency (347.3 nm), except for the 1972 study by Nakahara et al. who used a frequency-double Nd:YAG laser (532 nm). Collected in Table I are the relevant system parameters that defined the LIDAR unit and its performance. It should be remembered that these early investigations were not able to take advantage of near-resonance enhancement [20] of the Raman scattering cross-section because of the technical limitations associated with the lasers. [20,21]

A cursory examination of Table 1 shows immediately that in the detection of SO_2, the BNL resonance Raman chemical sensor is able to detect a lower concentration of this chemical species at a lower average laser power, using a smaller aperture but at a distance nominally twice that of the previous systems. A quantitative performance comparison to these systems reveals that the BNL system is nearly two orders-of-magnitude more sensitive towards SO_2 detection.

Table 1:

System Parameter	**This Work**	**Nakahara, et al.**	**Hirschfeld**	**Melfi**	**Poultney**
Average Laser Power (W)	0.150	0.56	0.40	~1.25	~1.0
Receiver Aperture Diameter (cm)	38	50	90	61	60
Conc. of SO_2 detected (ppm.m)	~70	~1000+	300	800	1000
Stand-off Distance (km)	0.5	0.2	0.2-0.4	0.21 (slant)	0.3

V. CONCLUSIONS AND PROGNOSIS

We have discussed recent experimental results using a resonance-Raman-based LIDAR system as a remote chemical sensor. This spectroscopy has the fundamental advantage that it is based on optical fingerprints that are insensitive to environmental perturbations. By taking advantage of resonance enhancement, which can be as large as 4 to 6 orders-of-magnitude, an increased sensing range for a given chemical concentration or lower detection limit for a given stand-off distance can be realized. The success discussed above can in part be traced back to the use of new state-of-the-art technologies which, only recently, have allowed 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 spectral region, it is expected that many will have pronounced resonance enhancements. Laboratory measurements of the scattering cross-section for various solvents and solutes important in the manufacture of narcotics are presently underway.

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