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# Atmospheric laser spectroscopy for remote sensing of chemical distribution in the environment

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**Abstract :** Spectroscopy is an established methodology for identification of chemicals. This method uses absorption or scattering characteristics of species. Atmospheric laser spectroscopy utilizes the method of remote sensing to identify chemicals in the surrounding air. This spectroscopy technique locates chemical in the atmosphere, as well as provides temporal information of distribution/location of chemical. Raman scattering exploited through this spectroscopy technique, results into Raman Lidar. This works as optical radar that uses spectroscopy technique for measurement of chemicals in the atmosphere and quantifies the spatial distribution of individual atmospheric molecular trace constituents. This paper presents Laser radiation technique used for chemical sensing based on Raman scattering that uses wavelength-dependent interaction between electromagnetic radiation and matter. The report incorporates the calculation of backscattering cross-section of atmospheric gas molecules for different excitation wavelengths such as 308,355,514, and 532 nm. This paper also presents the result and comparison of the Raman cross sections of various molecules present in the atmosphere such as $N_2$,$O_2$, CO, $CO_2$, $SO_2$, $CH_4$, NO, $H_2O$, $N_2O$ and $NH_3$relative to that of $N_2$. In above mentioned gases water vapour is one of the most important components as well as one of the most difficult to quantify due to its high variability on short time and space scales.Therefore, a high interest in obtaining water vapor profiles is manifested in the meteorological and remote sensing scientific world all around the globe. We will conclude with different analysis of profile measurements of atmospheric water vapour using the Raman Spectroscopic Lidar.

**Keywords :** Spectroscopy, Raman Lidar, chemical sensing, backscattering cross-section, Raman scattering cross-sections, Laser radiation technique.

## Introduction

Now a days sophisticated Lidar (Light Detection and Ranging) remote sensing system are used to study many different aspects of the atmosphere and its chemical distribution in the environment[1].The interaction between electromagnetic radiation and target of interest such as air molecules, dust particles, water vapour and other entities result in the form of scatter and absorption which are necessary for active remote sensing. This effect is know as Rayleigh scattering which is well understood, both from a theoretical and an experimental perspective[2,4]. For studying of gases, Rayleigh scattering is a powerful tool[3]. The Rayleigh cross section is valid for small spherical particles compared to the wavelength of the scattered light[5,6]. It involves important concepts such as the definition of the scattering cross section, the depolarization of a dielectric non-spheric particles (King correction factor), and radiating dipole oscillation.[7]

In recent years, sensors have been developed to detect lower concentration of chemical species for air pollution and presence of hazardous chemicals monitoring[8,9]. The detection and characterization of molecular gases in a given sample is a relatively difficult challenge[10,11]. Herein, a technique for studying gaseous samples is presented which uses Raman spectroscopy[12]. It is very important practical tool for quickly identifying molecules[14]. Only a single wavelength is required by Raman scheme. The Raman lines of a molecule are shifted from the laser pump frequency by the characteristic vibrational frequencies of the molecule. These vibrational frequencies are specific and allow interference-free detection of many important molecules. Weak inelastic scattering of light is used by Raman Lidar technique to detect atmospheric molecules[13]. A Raman Lidar operates by emitting a pulsed laser beam, usually in the ultraviolet or near ultraviolet, into the atmosphere. Atmospheric gases such as nitrogen, oxygen and water vapour interact with the light via the Raman scattering process, causing light of longer wavelength to be scattered[15,16]. It has become optical fingerprint of the chemicals in the environment.

The atmospheric water is a key parameter for climate study[17]. Global warming has direct influence on precipitation therefore to determine atmospheric stability vertical distribution of moisture is very important[18]. Different measurement techniques are used to measure water mixing content. Raman Lidar is well known established technique for measurement for atmosphere species concentration determination. We can determine water vapour mixing through backscattering Raman signal from water vapour and nitrogengases[19-24]. Raman Lidar provides simultaneous measurements of both the photomultiplier analog output voltage and photon counts[25]. The Lidar system currently works on three channel at the third harmonic of ND:YAG which includes water vapour channel at 408nm, nitrogen channel at 387nm and elastic backscattered signals at 355nm. Range resolved remote sensor have significant effects on our knowledge of the boundary layer[26]. Total of 10 hours sample data is taken and analysed with gluing technique so that it can be combined into an entire profile.

## Experimental

### 1. Calculation and plotting of backscattering Rayleigh-Scattering Cross-Section

The scattering of light is the redirection of light that happens when electromagnetic wave encounters the scattering particles or molecules i.e. obstacles. The discrete particle as interacts with electromagnetic wave, particle's electron orbit which constitute molecules gets anxious periodically with the same frequency (vo) as that of electric field of the incident wave. Because of oscillation induced dipole moment occur due to periodic separation of charge within the molecule. The oscillating induced dipole moment is manifest as a source of EM radiation, thereby resulting in scattered light. The particleemits the identical frequency of the incident light which is referred to as elastic scattering.

Two theoretical frameworks are required to categorized the light scattering theory. One of this is Rayleigh scattering which applicable to small non-absorbing and spherical particles. Other one is of Mie scattering that fringes general spherical scattering solution of no particle size limitation. Accordingly, Mie scattering theory has no size limitation therefore may be used for describing most spherical particle scattering system, which include Rayleigh scattering also. Due to more complexity of Mie scattering formulation , Rayleigh scattering theory is generally preferred. The criteria for Rayleigh scattering is that a<<1 and |m| a<<1, where ais the dimensionless size parameter given somewhere else.

Laser light interact with the molecule present in atmosphere which results in backscattering of the laser propagation suffering from Rayleigh scattering.

The cross-section for Rayleigh scattering can be calculated from other literature survey found somewhere else[27].

Altitude dependent molecular backscattering coefficient can be found as:

$$B_m(z) = \frac{9\pi^2 ({\eta_{air}}^2 - 1)^2 (6 + 3\gamma)}{\lambda^4 {N_S}^2 ({\eta_{air}}^2 + 2)^2 (6 - 7\gamma)} (N_S) \frac{T_O P(z)}{P_O T(z)} \qquad (1)$$

Where, $N_S$ = molecular number density

$\eta_{air}$ = refractive index

depolarization of the air

$N_S$ =2.547 x $10^{25}$ $m^{-3}$ for standard atmospheric pressure and temperature

The ratio*((*$6 + 7\gamma$ *)/*$(6 - 7\gamma$ *))*is often called the 'King correction factor'.

Ref[1]gives the effective King correctionfactors, which approximate air as a single species (Bates1984),

## 2. Calculation and plotting of Raman Scattering Cross-Section for different gases at different excitation wavelength

The laser radiation is inelastic scattering when Raman scattering is involves from molecules and is observed with a frequency shift characteristic of the molecule (and with a known backscattering cross-section). Raman scattering are of two types that occurred simultaneously i.e. the Stokes process which shifts the wavelength to upper ones, and the anti Stokes one which shifts the wavelengths to lower values. In this scheme one photon is reemitted with less (Stokes) or more (anti Stokes) energy than the incoming one. The interaction between the exciting radiation and the electric dipole moment of the molecule results in scattering. It induces a change in the rotational or/and vibrational states of the molecule.

The interaction life time is very small, and smaller than $10^{-14}$s. The study of the Raman spectrum allows the simultaneous measurement of a wide variety of components and the absolute measurement of their mixing ratio. This process has a very low efficiency (cross-sections about $10^{-32}$–$10^{-28}$ $cm^2$ $molecule^{-1}$), and can be improved by working in the UV, at shorter wavelengths, because the Raman differential cross-section is proportional to $\lambda^{-4}$.

The expression for the total Raman backscattering cross-section of a Stokes shifted vibrational-rotational Raman band υj is given by [Inaba and Kobayashi, 1969]:

$$\frac{\partial\sigma}{\partial\Omega}(V_o) = \frac{(2\pi)^4}{45} \frac{(V_o - V_j)^4 {b_j}^2}{1 - \exp\left(\frac{-hcV_j}{KT}\right)} \left((45[\![a')]\!]^2 j + (7y')^2 j\right) \qquad (2)$$

$${b_j}^2 = \frac{h}{8\pi^2 CV_j} = \frac{6.626 \times 10^{-34} \times 10000}{8 \times (3.14)^2 \times 3 \times 10^{10} \times 2331} = 1.2 \times 10^{-45}$$

Where,

υj [cm-1] = frequency of the $j_{th}$vibrational mode of the molecule.

bj = zero amplitude of this $j_{th}$vibrational mode

T [K] = temperature.

aj and γj = isotropic and anisotropic parts of the polarizability tensor derived with respect to the normal coordinates and k is the Boltzmann constant respectively.

At atmospheric temperature most molecules are in their vibrational ground state υ = 0 (and also the electronic one). The Stokes bands will then be much more important than the anti-Stokes ones. In addition, each vibrational line gives rise to a closely spaced band of lines corresponding to different transitions in the rotational quantum number. Thus, the laser excitation of the O2, N2 and H2O atmospheric molecules due to the laser beam will give essentially the Stokes type transition υ 0–>1. For a given excitation wavelength, the Raman scattering will provide a shifted spectra characteristic of the excited molecule. The wavenumber k [cm-1] is defined by:

$$\lambda = \frac{c}{v} = \frac{1}{k}$$

And the Raman shift Δk is given by

$$\Delta k = kL - kR$$

where kL [cm-1] is the laser pump wavenumber and kR [cm-1] is the Raman shifted wavenumber. The Raman shifts from the exciting wavelength are the following: 2331 cm-1 for N2 and 3652 cm-1 for H2O. The related Raman shifted wavelength λR [cm] is

$$\lambda_R = \frac{\lambda_L}{1 - \Delta k . \lambda_L}$$

Where Δk [cm-1] is the Raman shift, λL [cm] is the laser pump wavelength.

## 3. Calculation of water vapour mixing ratio in atmosphere.

Lidar techniques which is commonly used for water vapour measurement are DIAL and Raman. Among these DIAL demand sophisticated and an expensive tuneable laser source and is less appropriate for ground based operation because of attenuation of the laser beam due to humid air near the ground which results in limiting the operational range. Consequently, Raman principle is used by most of the ground based experimental water vapour Lidarswhich has lower laser requirements and offers better reliability.The major limitation of Raman Lidars is the low level of the Lidar signals, which makes daytime operation more difficult.

Raman Lidar system in the NARL, Gadanki (13.5°N, 79.2°E, 375 m AGL), was developed to provide measurements of lower and middle tropospheric water vapour mixing ratios and aerosol scattering profiling. It is achieved with high temporal and spatial resolution. NARL Lidar utilizes an Nd: YAG laser that operates at the third-harmonic wavelength (355 nm) consisting of a narrow-field-of-view, coaxial, three-channel, fibre-optic coupled system that uses narrow bandpass filters to measure backscattered radiation at 355nm and Raman scattered radiation from N2 molecules at 387 nm and water vapour molecules at 407 nm. It operates Licel Transient Recorders (available online at http://www.licel.com/index.html) for data acquisition that can simultaneously obtain both analog (AD) and photon counting (PC) signals, thereby expanding the dynamic range of thedetection system.

Generally, the Lidar was operated at one or two-minute time integration with 30m vertical resolution (range gate). An integration of 150000 laser shots constitutes a meaningful photon count profile. This forms the raw data signal. It corresponds to a time span of 60 sec. A Lidar signal integrated over 569 min time span is shown in Figure [3-6].

For a ground-based Lidar system, the backscattered light usually has large dynamic range. Photon-counting mode has the capability to measure weak signal from high altitude, while Analog-to-Digital mode with better linearity is good at measuring strong signal at low altitude. Atmospheric return signal is measured in both Analog-to-Digital and Photon Counting modes and combined into an entire profile by using a gluing algorithm. A method for gluing atmospheric return signal is developed and tested. For the Photon Counting signal, the saturation characteristics are analysed to calculate the coefficients for correction. Then the Analog-to-Digital and Photon Countingsignals are glued by a weighted average process. Results show the glued signal is reliable at both low and high altitudes.

The gluing algorithm is one of the essential issues to be considered for improving measurement accuracy of various atmospheric parameters One method is to find regressions coefficient from two measurement modes to convert AD data to PC data and replace the saturated PC data with the converted AD data.

This paper used gluing method to solve the problems mentioned above. Firstly, the Relationship between original data of AD and PC is analysed and the linear region is calculated. Secondly, the unit of AD data is converted into photon counting rates and is used to correct the saturated PC data according to the relationship obtained by curve-fitting. At last, the gluing signal is calculated by the weighted average method.The glue coefficients (slope and intercept), determined from the regression, are used to convert the ADsignal into a PC signal by using the equation

$C=m'D + b'$

where, C is the virtual photon count rates, D is thecorrected analog signal, $m'(1/m)$ is the slope, andb'$(-b/m)$ is the intercept.

## Result and Conclusion:

Temperature and pressure data were obtained from **NOAA READY** site to calculate the altitude profile of molecular number density using given equations. Data collected corresponds to New Delhi, India, ( Lat: 28.58 Lon: 77.20 elevation: 211 m ).Wavelength such as 532,514,355 and 308 nm were used to derive the altitude profile of molecular backscattering coefficient which is shown in Fig 1.

The differential Raman cross section of various molecules present in the atmosphere such as $N_2$, $O_2$,CO, $CO_2$, $SO_2$, $CH_4$, NO, $H_2O$, $N_2O$ and $NH_3$ relative to that of $N_2$as a reference gas using different excitation wavelength laser light is calculated and plotted which is shown in figure [2].

To calculate the differential Raman cross section of $N_2$ which is taken as a reference gas for other atmospheric gases, molecular constants for the calculation of Raman scattering cross sections of nitrogen is taken from somewhere else[16]. Moreover, the relative ratio between different gases as compared to standard $N_2$ gas is taken from table given in[29].

Various gases Raman cross section is plotted with various excitation wavelength as given in literature which is shown in fig2.

Data were obtained during a 10 hours' period. Results are shown for a single 1-minute averaged data run. We have analysed 569 ASCII text files through MATLAB. The MATLAB code was applied to derive the gluing coefficient, gluing region, glued region, normalisation of water vapour and Rayleigh Mie signals by N2 signals. This code is available in the report submitted to IASc-INSA-NASI SRFP-2016 by Mr. Ketan Gupta.The abscissa gives the counting signal strength in units of MHz The upper trace is for the Rayleigh-Mie signal at 355 nm, the intermediate trace is for the 387 nm N2 Raman signal, and the lower trace is for the 407 nm water vapour Raman signal. The 407nm signal has been scaled for display on the graph. Ratio of the water vapour signal to N2 signal and Rayleigh-Mie signal to N2 signal for the data is shown in Figure 6.

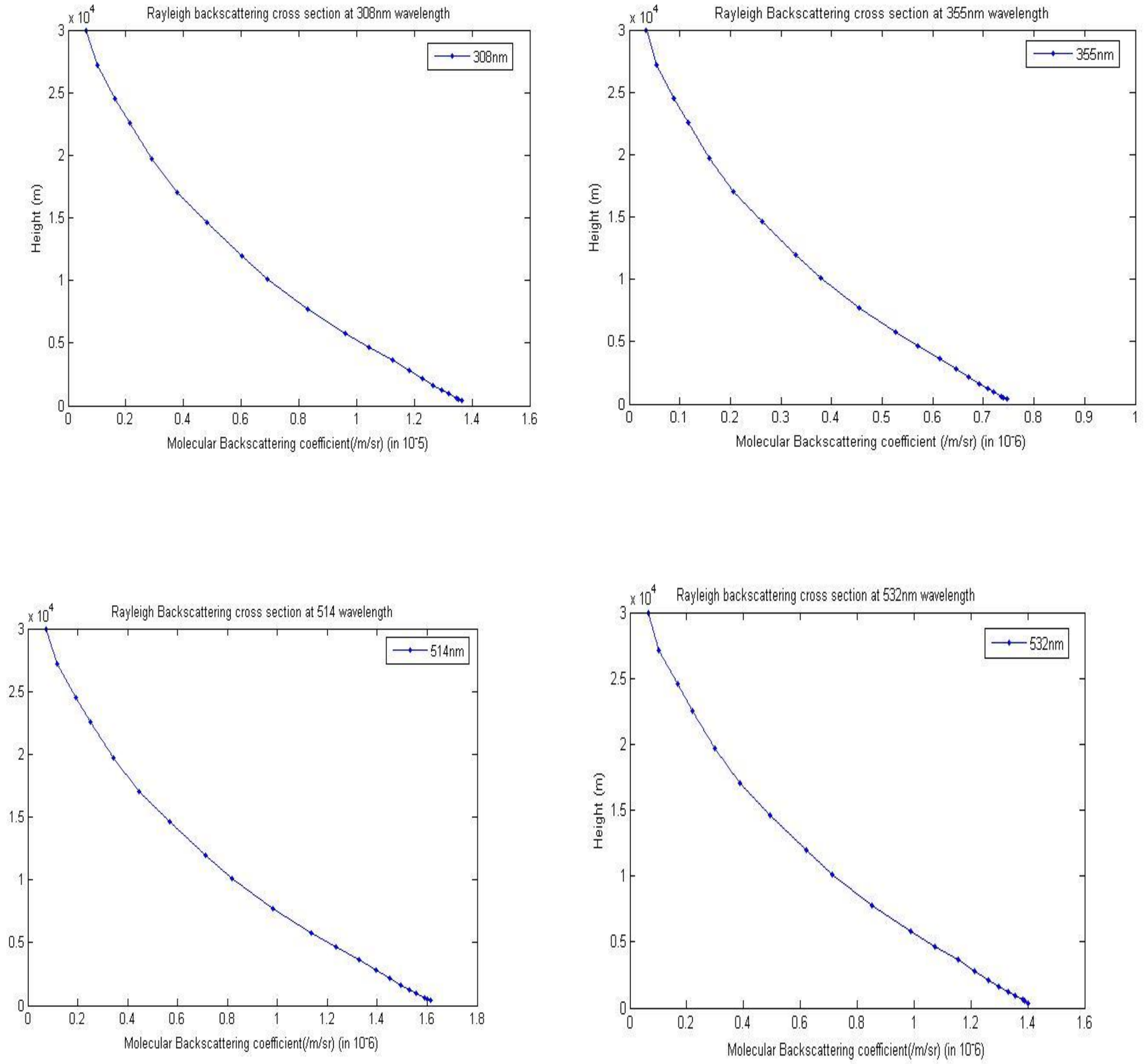
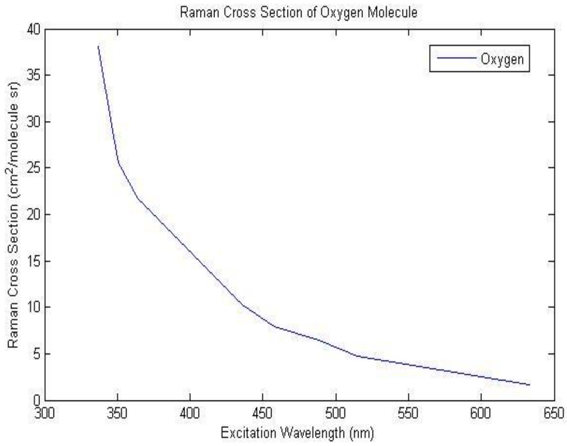
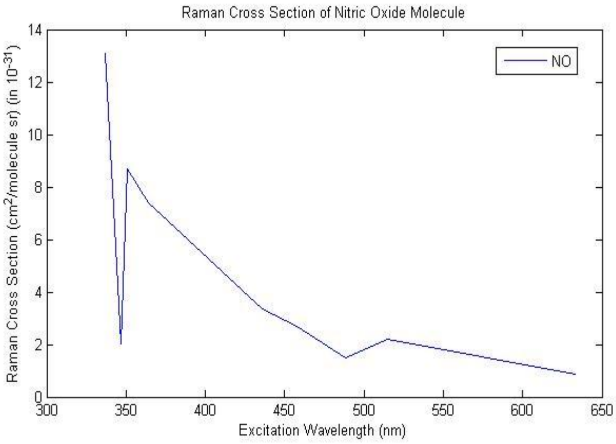


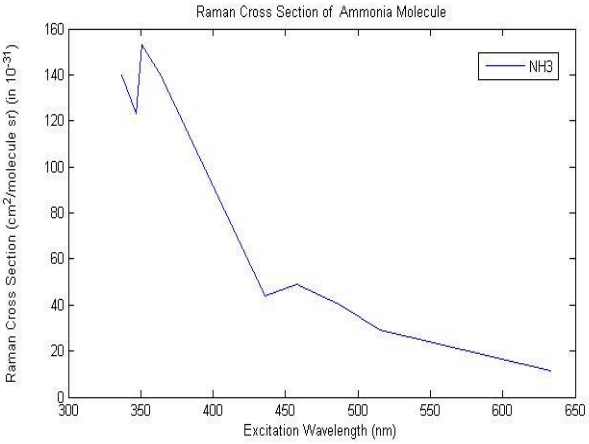
**Fig1: Molecular backscattering coefficient at different altitude distribution for various wavelength**

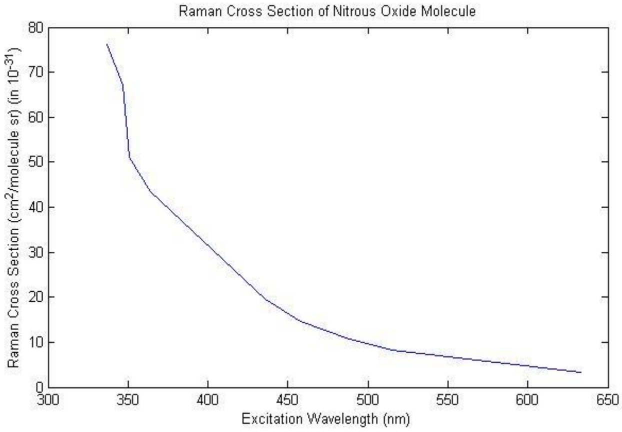
The Lidar system developed by NARL Gadanki is used to acquire data for testing the proposed gluing method. Deviation of AD data is much smaller than PC data because AD data becomes noisy in the case of weak signal with small value. In addition, deviation increases below cloud layer. However, in the cloud region at the height of 5km to 7km, deviation decreases.

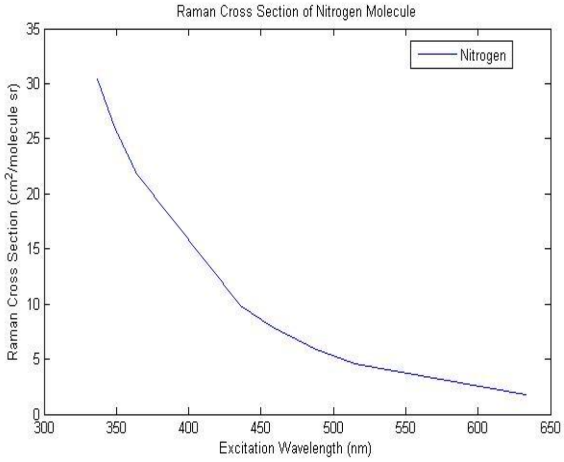
A gluing method is proposed and tested in this paper. Original AD data and PC data are used to calculate the relationship by curve-fitting and to correct PC data. A linear region is determined to obtain a linear relationship to change AD data to PC unit. Finally, the glued signal is calculated by weighted average. Results show the gluing method can correct the saturated PC data. Comparison in cloud region indicates that strong signal keeps the reliability after gluing. This method can be used for gluing PC data and AD data in Lidar systems for measuring various atmospheric parameters.

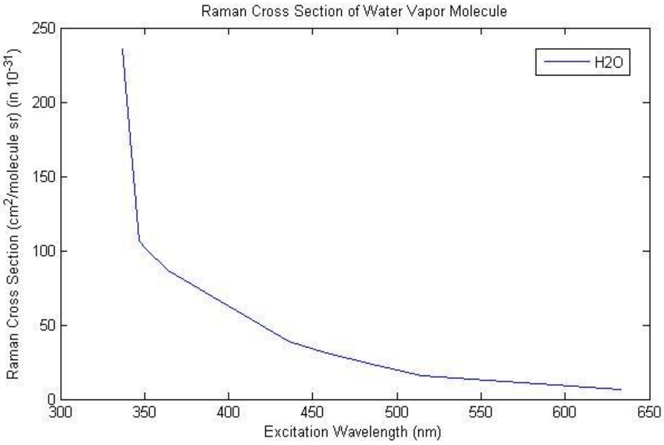

Raman Cross Section of Oxygen Molecule
Oxygen
Raman Cross Section (cm$^2$/molecule sr)
0
5
10
15
20
25
30
35
40
300
350
400
450
500
550
600
650
Excitation Wavelength (nm)


Raman Cross Section of Nitric Oxide Molecule
NO
Raman Cross Section (cm$^2$/molecule sr) (in $10^{-31}$)
0
2
4
6
8
10
12
14
300
350
400
450
500
550
600
650
Excitation Wavelength (nm)


Raman Cross Section of Ammonia Molecule
NH3
Raman Cross Section (cm$^2$/molecule sr) (in $10^{-31}$)
0
20
40
60
80
100
120
140
160
300
350
400
450
500
550
600
650
Excitation Wavelength (nm)


Raman Cross Section of Nitrous Oxide Molecule
Raman Cross Section (cm$^2$/molecule sr) (in $10^{-31}$)
0
10
20
30
40
50
60
70
80
300
350
400
450
500
550
600
650
Excitation Wavelength (nm)


Raman Cross Section of Nitrogen Molecule
Nitrogen
Raman Cross Section (cm$^2$/molecule sr)
0
5
10
15
20
25
30
35
300
350
400
450
500
550
600
650
Excitation Wavelength (nm)


Raman Cross Section of Water Vapor Molecule
H2O
Raman Cross Section (cm$^2$/molecule sr) (in $10^{-31}$)
0
50
100
150
200
250
300
350
400
450
500
550
600
650
Excitation Wavelength (nm)

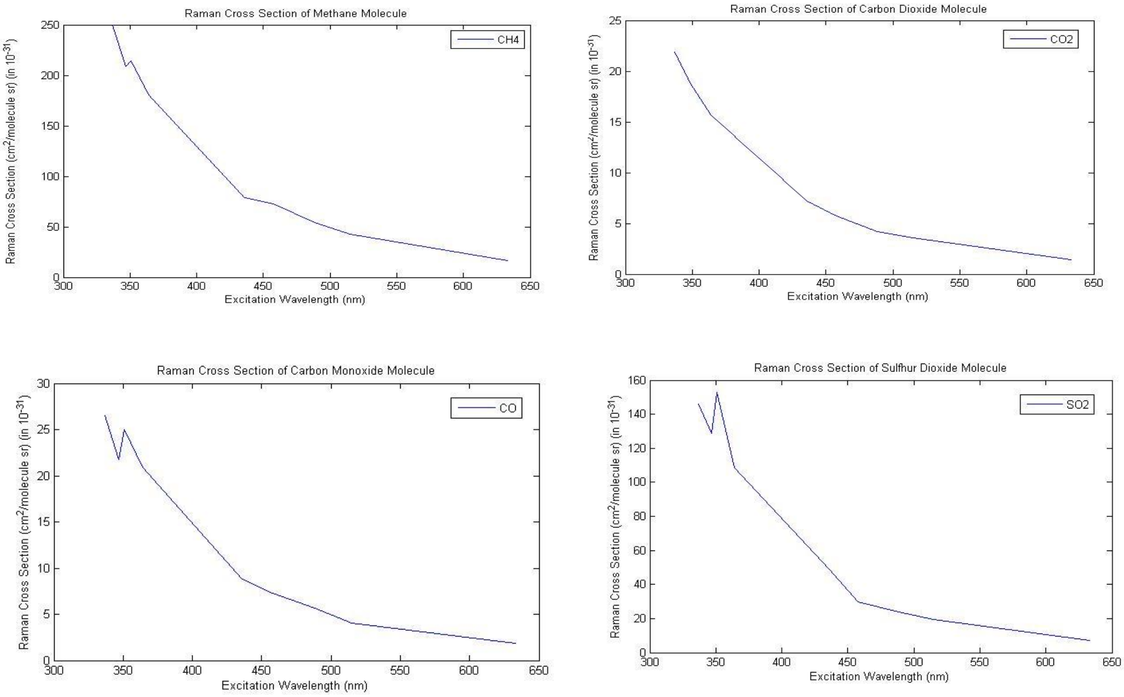


**Fig2: Raman Cross Section at various wavelength for different gases**

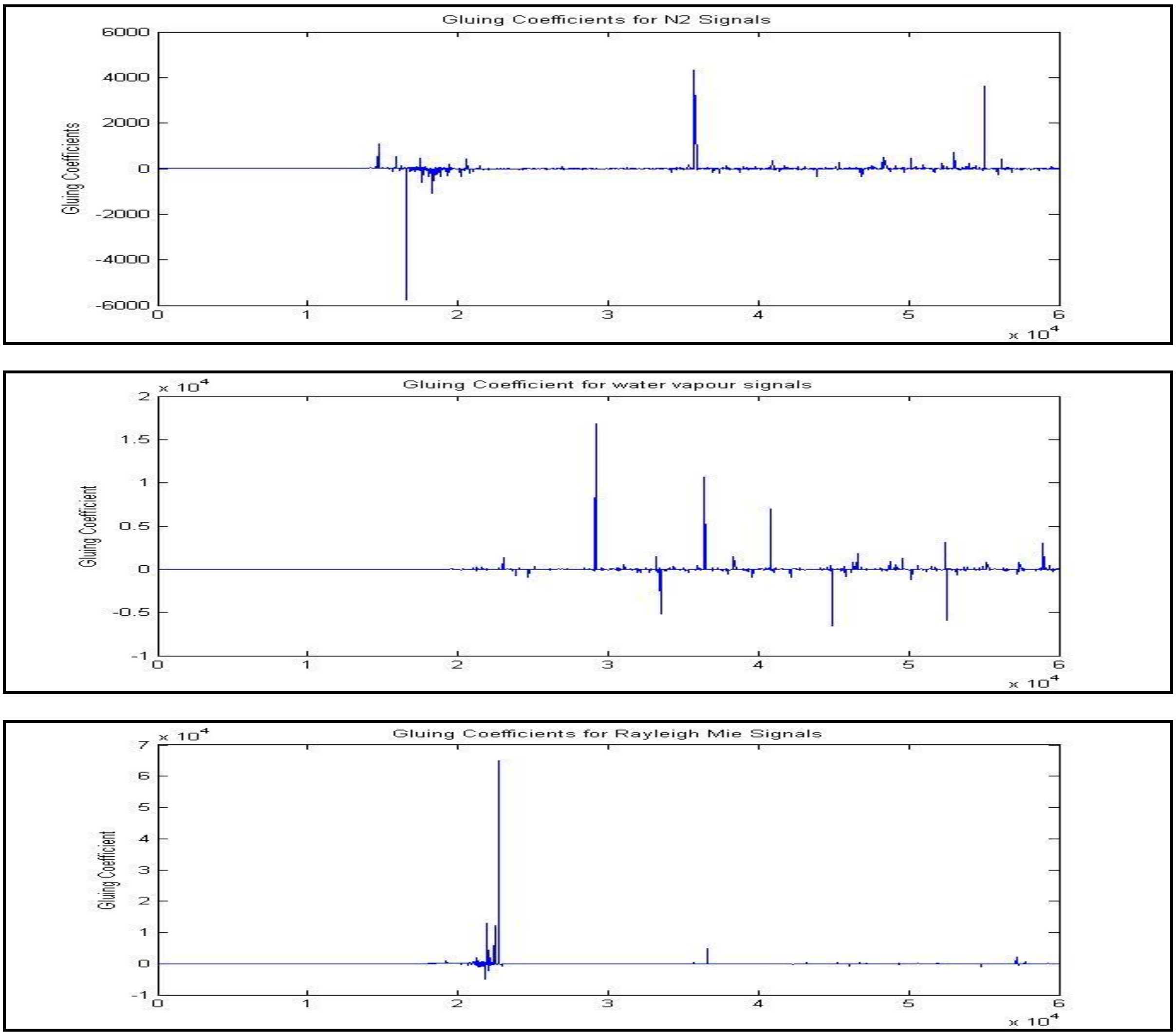


**Fig3: Gluing Coefficient for N2,water vapour and Rayleigh Mie Signals**

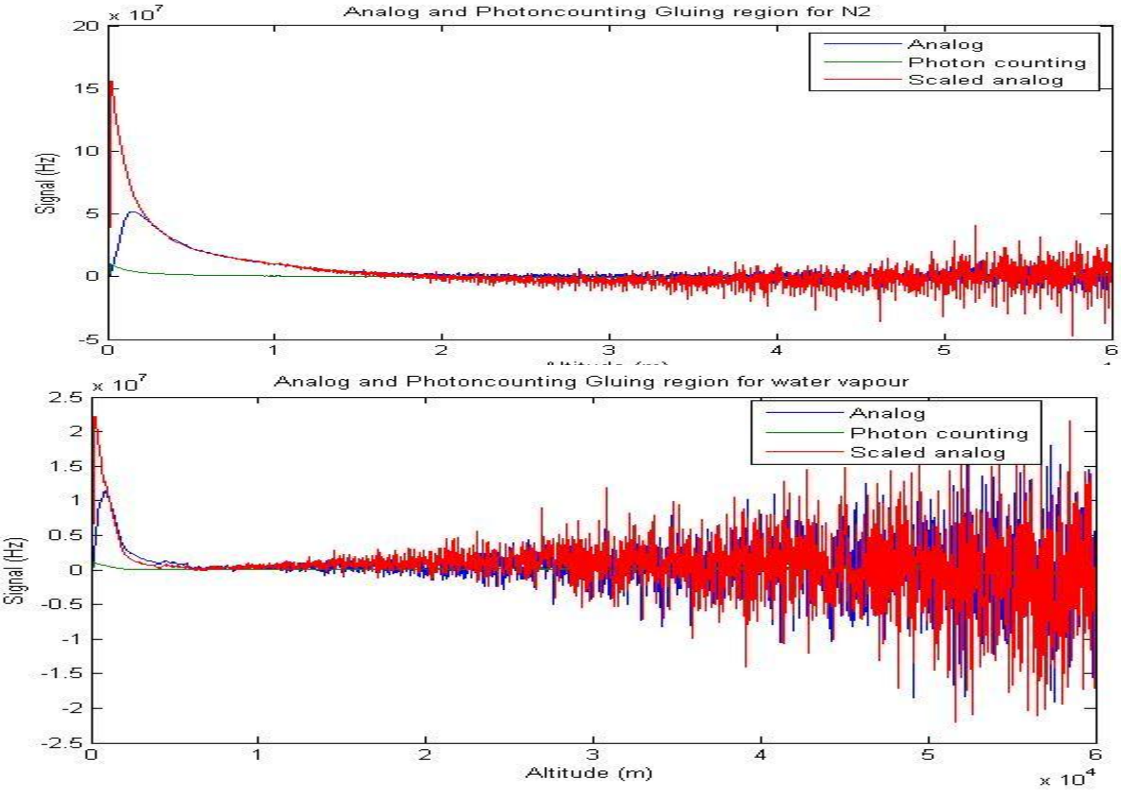
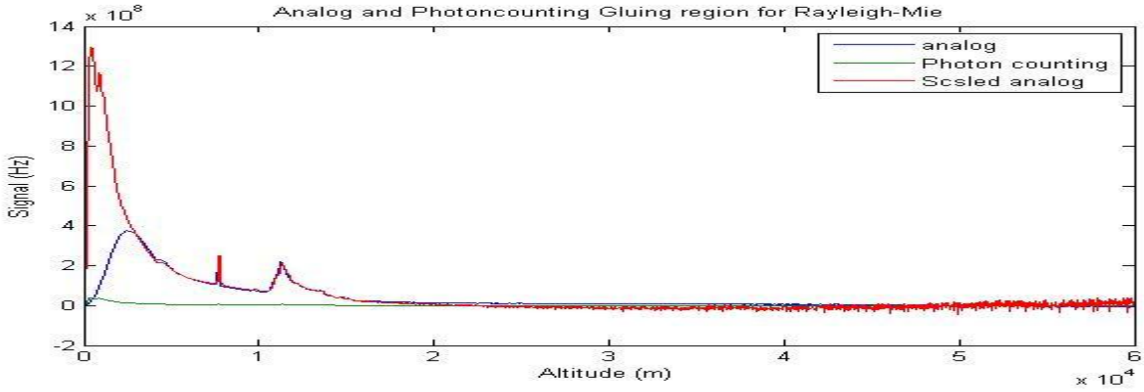


Fig4: Gluing region for N2, water vapour and Rayleigh Mie Signals



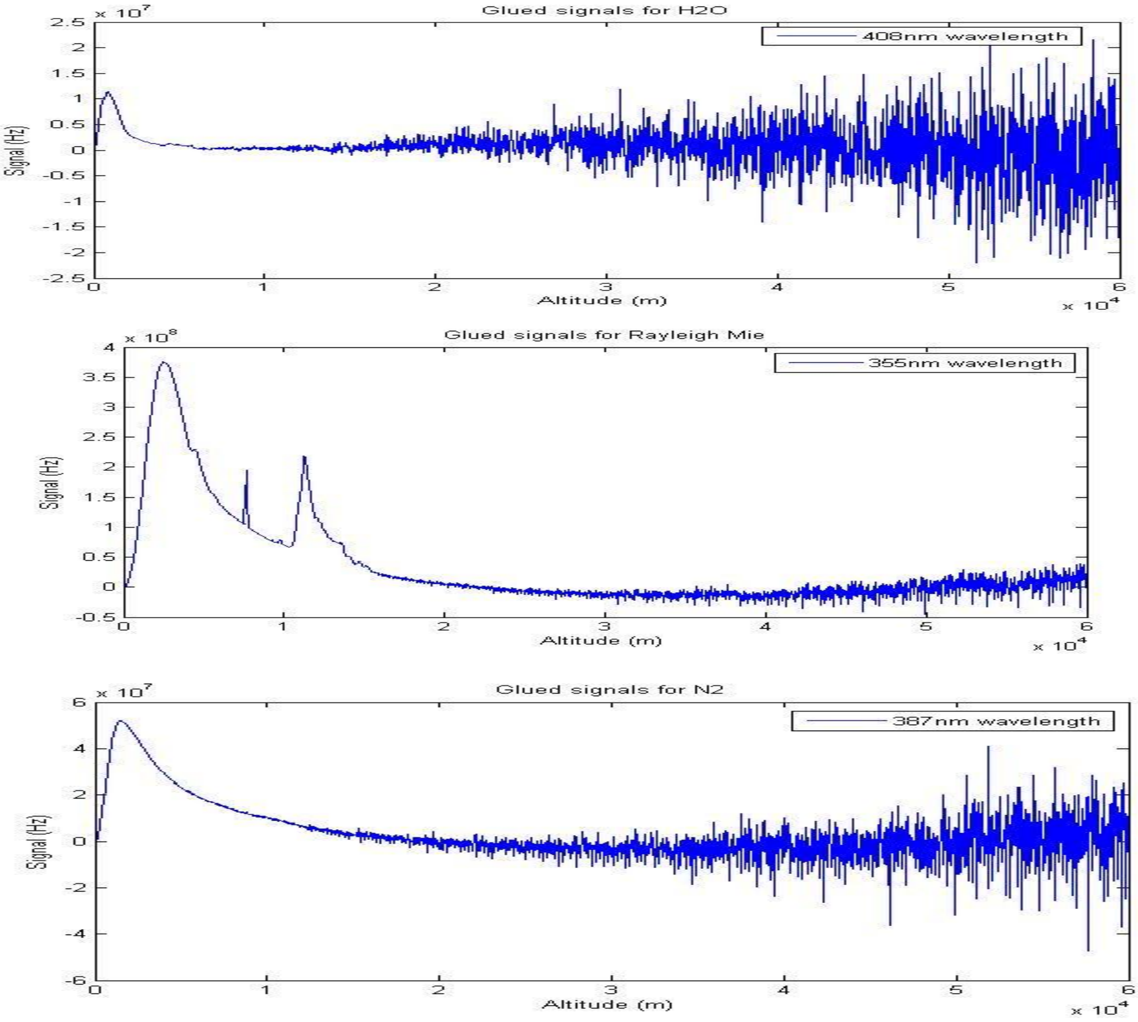
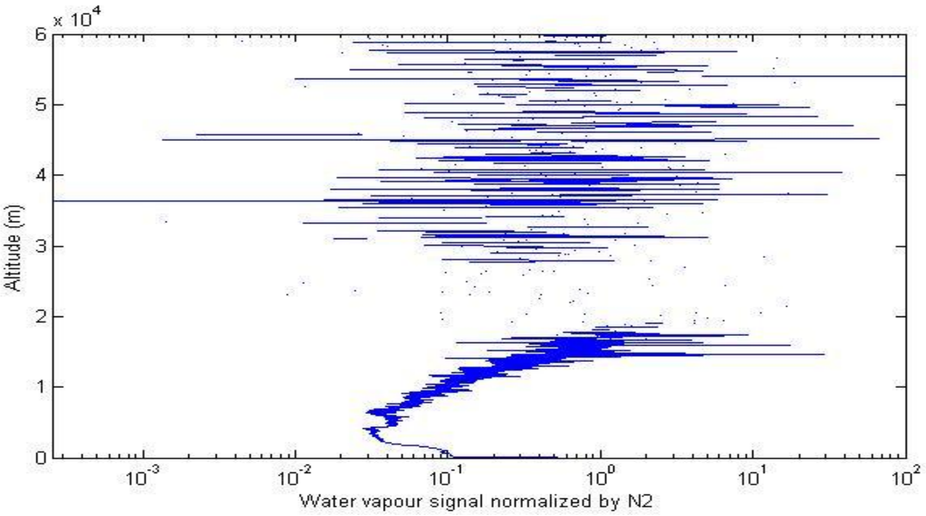


**Fig5: Glued signals for N2, water vapour and Rayleigh Mie Signals**



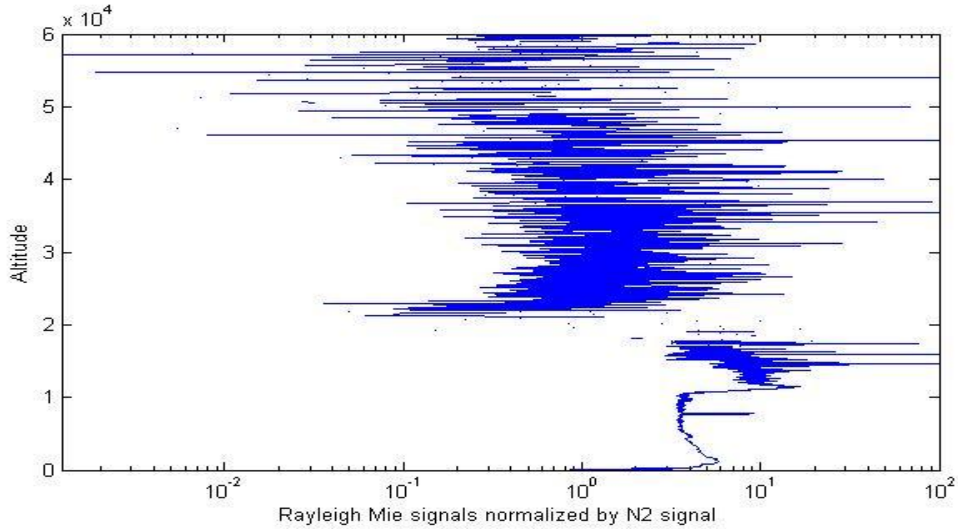


**Fig6: Normalized water vapour and Rayleigh Mie signals by N2 signals**

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