Efficiency Assessment of Single Cell Raman Gas Mixture for DIAL Ozone Lidar

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Abstract. The conversion efficiency and flexibility of using single Raman cell with mixture of high-pressure Raman active gases H_2 and CH_4 has been tested and reported in this study. Though the higher conversion efficiency could be achieved with independent gases, the pre-mixed gas combination could emit a coaxial beam of two wavelengths 288.4nm, 299.1nm with total conversion efficiency of about 45% along with the residual 266nm coaxial beam. However, a suitable gas mixing ratio needs to be selected to avoid carbon particle formation inside the cell which attenuates the laser energy. In the present case a volume mixing ratio of 2:1 (H_2+CH_4) at a total cell pressure of 18bar is found optimum for the generation of required wavelengths with almost equal energies. This configuration of generating coaxial beam of multiple SRS with a single Raman cell greatly reduces the optical configuration and make the DIAL system compact for mobile operations for ozone profiling.

Keywords: Stimulated Raman Scattering · Raman cell · Mixture of gases · Ozone absorption.

1 Introduction

Differential Absorption Lidar (DIAL) technique has been extensively used by various authors for the determination of the vertical profiles of atmospheric gases. Out of various gaseous species, ozone in the lower and upper atmosphere has been one of the major greenhouse gases being observed owing to its great influence on earth's radiation budget as well as environmental impacts. Though several gas constituents are present in the real atmosphere, most of the gaseous species doesn't require vertical profiling due to their well-mixed chemical activity in the surface layers [1].

High resolution profiling of ozone concentrations in the free troposphere requires suitable wavelengths in the ozone absorption UV band to be transmitted into the atmosphere. However, the selection of optimum wavelengths depends on various factors like the availability of the laser source emitting required wavelengths, maximum altitude of interest, laser attenuation in the day light when transmitted and also the temperature conditions. Moreover the aerosol back scattering and extinction coefficients in the second and third terms in the DIAL equation are highly dependent on the pair of wavelengths transmitted to the atmosphere. Thus, the most convenient spectral region for monitoring ozone in the troposphere with the differential–absorption technique was found to be between 250 and 300 nm. Within this band, the optimal ozone measurement can be achieved when $\frac{\Delta\sigma_{O_3}}{\Delta\lambda}$ is maximized.

Stimulated Raman Scattering (SRS) in the Raman cell filled with high pressure Raman active gases like Hydrogen (H_2), Deuterium (D_2), Methane(CH_4), Nitrogen (N_2) and Carbon Dioxide (CO_2) excited with intense UV laser has been widely used to generate the λ_{ON} and λ_{OFF} to estimate the profiles of Ozone concentrations in DIAL technique. Among these, the combination of CH_4 and H_2 is found best suitable to generate two spatially separated wave lengths of 288.4nm and 299.1nm, respectively. Several researchers used these two wavelengths to measure Ozone, as the former (strong O_3 absorption) has an absorption cross section nearly 3 times as large as the later(weak O_3 absorption), and both wavelengths can be generated reliably (and much more cost-effectively than dye or tunable cavity lasers) using SRS in high-pressure Raman cells [2]. This report explains the performance characteristics of the single Raman cell to produce the optimum energy conversion efficiency of 288.4nm (CH_4) and 299.1nm (H_2) with different mixing ratios under different total cell pressure and laser excitation energy.

2 SRS Technique

SRS is a coherent nonlinear optical mixing process that mainly dependent on the laser spectral linewidth, input laser intensity and the interaction length of the Raman active medium [3]. SRS technique is used to generate the required frequency (wavelength) range above and below the range of laser pump frequency by passing through some nonlinear medium like H_2 or CH_4.

3 Experimental setup

The block diagram of the Raman cell setup is shown in in Figure 1. This system utilizes a stable Nd:YAG laser (LOTIS TII LS-2138N) to generate the fourth harmonic laser beam of 266nm at 100 Hz that is steered through the Raman cell filled with high pressure Raman active gases to generate required ON and OFF wavelengths of laser output. This fourth harmonic of 266nm laser beam diameter of ∼5mm with a beam divergence of <1.5mrad and pulse duration of 10ns is then steered to the Raman cell using two high reflectance UV grade 266nm mirrors. Note that the optical path loss after reflection from two reflecting mirrors is about 10% of input laser energy. Further, a double convex lens of 75cm focal length is placed in front of the cell to focus the laser beam at about 50cm which is almost center of the length of Raman cell. This is done to achieve maximum energy density required for SRS to happen with high pressure gaseous mixture present in the cell and produce maximum conversion efficiency of required wavelengths. Addition of lens induced another 10% loss of laser energy resulting in a total loss of 20% of laser energy from the source to the entrance of the cell.

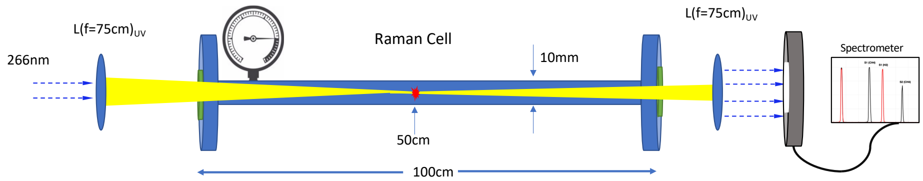

Fig. 1. Block diagram of the Raman cell setup used in this work.

The Raman cell is a stainless steel hollow tube of about 100 cm length and outer diameter of about 12mm and inner diameter of 10mm to facilitate the 5mm diameter laser beam pass through the cell without hitting the inner walls. The outer edges of the cell are made such that high transmission UV grade optical windows can be fixed to seal the cell leak proof for high pressure gas filling. A high pressure gas valve is fixed at the cell inlet and end of the cell to control the gas inflow and outflow. A pressure gauge of 0-70bar is fixed at the inlet position of the cell to monitor the total cell pressure. The SRS output from the cell is further collimated using another 75cm focal length Plano convex lens and focused on to the spectrometer detector for further visualization and recording.The total setup is fixed on the optical bench for safety and stability.

4 Results and Discussion

In general, the SRS of Raman active medium excited with high energy laser generates higher order stokes lines in addition to the required wavelengths. Depending on our required wavelengths, other orders need to be suppressed to maximize the conversion efficiency of required wavelengths. The SRS spectrum of H_2 and CH_4 at 20bar excited with 25mJ laser beam is shown in Figure 2a. Here the second order stokes of 314nm (CH_4) and 342nm (H_2) can be noticed along with the required first order stokes 288.4nm (CH_4) and 299.1nm (H_2).

The conversion efficiency (η) of the Raman shifted line is measured as the ratio of the intensity of the particular Raman shifted line ($I_{\lambda S}$) to the sum of intensities of all lines in the output spectrum measured at the exit of the Raman cell.

$$\eta = \frac{I_{\lambda S}}{I_{266} + \sum_{S=1}^{n} I_{Sn}} \times 100\% \tag{1}$$

Where I_{266} is the intensity of residual 266nm line in the output spectrum, S=1,2,3... n is the order of stokes line and I_{Sn} is the intensity of n-stoke line.

The conversion efficiency of independent gases H_2(299.1nm) and CH_4 (288.4nm) are estimated initially with variable pressure and laser energy and shown in

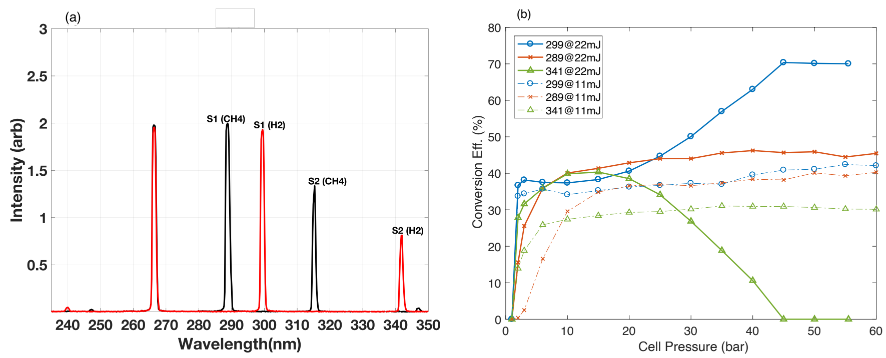

Fig. 2. (a) SRS spectrum of pure CH_4 and H_2 at 20bar excited with 25mJ quadrupled 266nm laser. (b) Conversion efficiency of pure H_2 and CH_4 (lower CE of 299.1nm in at low pressure is owing to high S2). Intensities of 314nm are low, hence not shown.

Fig. 2b. It can be noticed that H_2 could exhibit SRS at a relatively low pressure of 3bar compared to CH_4 which starts SRS at 9bar. Further, the maximum conversion efficiency of both gases is found lower at lower laser energy (11mJ) compared to higher laser energy (22mJ). Moreover, at lower energy (11mJ), the intensity of second stokes remained unchanged with increasing pressure. With laser energy of 22mJ, the efficiency of first stokes of H_2 becomes higher (40%) than second stokes at 20bar, however the total cell pressure of 45bar is required to achieve maximum efficiency of first stokes (70%) while the second stokes is completely suppressed. Similarly, the maximum conversion efficiency (42%) of CH_4 first stokes is achieved at about 25bar with nearly constant efficiency at higher pressures. It is interesting to see that the second stokes for CH_4 is not visible with higher (22mJ) laser input. Though, higher conversion efficiency of independent H_2 and CH_4 gases can be achieved but it is necessary to use two independent Raman cells to generate these two wave lengths that makes the optical configuration of DIAL system complex.

Further, the single cell configuration is used to estimate the conversion efficiency of mixed gas H_2+CH_4 filled with varying pressure and laser energy. The conversion efficiency of 299.1nm (H_2) and 288.4nm (CH_4) with mixing ratio of 2 under varying pressure and energy is shown in Figure 3b. It is to be noted here that, with all input laser energies (18mJ, 24mJ and 25mJ) the efficiency of 299.1nm gradually decreases with increasing pressure while 288.4nm gradually increases with pressure. At certain pressure the intensity(efficiency) of both wavelengths become nearly equal. It can be noted here that the pressure of nearly equal intensity (efficiency) decreases with decreasing laser energy whereas the total conversion efficiency increases. Thus, with H_2:CH_4 mixing ratio of 2, the total conversion efficiency (288.4+299.1nm) of 52% is achieved with 18mJ input laser energy at 13bar. However, the total conversion efficiency of 45% is achieved at 18bar with 18mJ input energy when the intensity of both first stokes lines is nearly equal. Further, the efficiency with a mixing ratio of 1.5 is measured

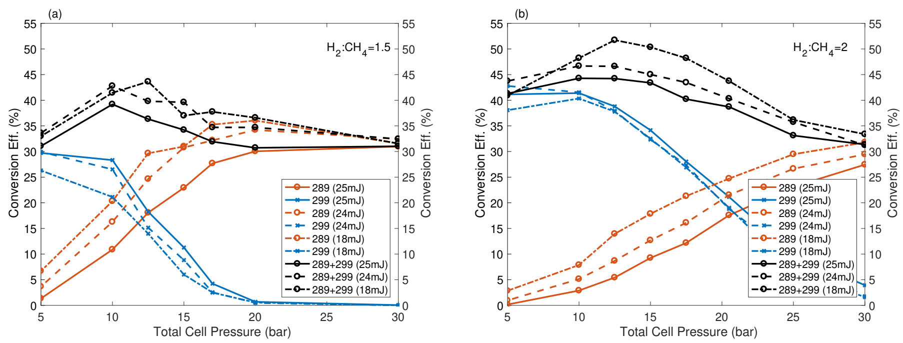

Fig. 3. The conversion efficiency of 299.1nm (H_2) and 288.4nm (CH_4) with mixing ratios of (a) R=1.5 and (b) R=2 under varying pressure and laser energy.

and shown in Figure 3a. With this mixing ratio, the total conversion efficiency is found slightly less than the mixing ratio 2 with similar input energies and pressure. The maximum total conversion efficiency is found to be about 42% at 13bar.

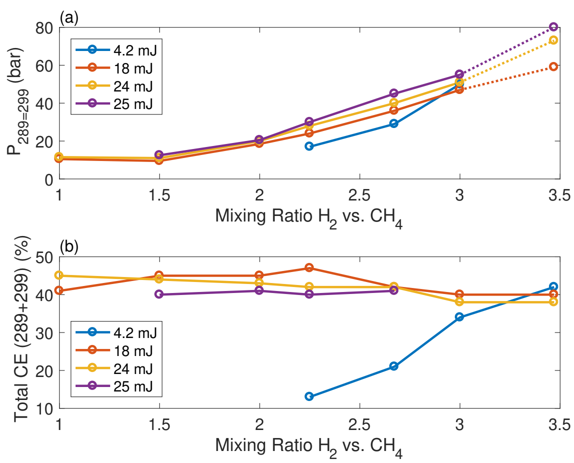

Fig. 4. (a) The total cell pressure vs. mixing ratio when the intensity of both wave lengths 288.4nm and 299.1nm become nearly equal. (b) The total conversion efficiency achieved with each mixing ratio when wavelengths are equal.

Similarly, the conversion efficiency of different mixing ratios with varying pressure and laser energy is estimated and the consolidated picture is shown in Figure 4. One can observe that higher cell pressure and higher laser input energy is required for higher H_2:CH_4 mixing ratios to achieve near equal intensities of two wavelengths. Further, while comparing the total conversion efficiency achieved with each mixing ratio when two wave lengths are equal shows that the H_2:CH_4 mixing ratio of 2:1 with a total cell pressure of 18bar and laser input energy of 18mJ is found best suitable for the generation of two wavelengths with nearly equal intensity.

5 Conclusion

A compact single Raman cell system has been set up to achieve the coaxial beam of SRS wavelengths CH_4 (288.4nm) and H_2(299.1nm) with maximum possible conversion efficiency. The conversion efficiency of CH_4 and H_2 Raman shift intensities under different laser energies and total cell pressure with individual gases and mixture of gases is observed. While the individual gases are used, with a laser energy of 25 mJ, the maximum conversion efficiency of first stokes of about 70% for H_2 and 42% for CH_4 can be achieved. The conversion efficiency of 288.4nm and 299.1nm with H_2: CH_4 mixing ratio of 1(50%:50%) at a total cell pressure of 21bar could generate near equal intensities of ON and OFF wavelengths, however the optical windows were damaged due to carbon formation inside the cell after few hours[4]. The detailed investigation on the carbon formation inside the cell is yet to be carried out.

Further, several combinations were tested and found that the higher mixing ratios require higher total cell pressure to generate similar conversion efficiency at lower mixing ratios with lower cell pressure. However, it is found that the laser input energy of higher than 4.2mJ is required to get reasonable conversion efficiency. Altogether, a mixing ratio of 2:1 ($H_2 : CH_4$) at 18bar total cell pressure is found best suitable to generate 45% optimum energy conversion efficiency with an output energy of 14mJ of wavelength pair 288.4nm and 299.1nm that can be used for DIAL ozone lidar profiling.

References

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