Measurement of tropospheric CO_2 and aerosol extinction profiles with Raman lidar

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Received August 16, 2007

A prototype Raman lidar was designed for monitoring tropospheric CO_2 profile and other scientific investigations. The third harmonic of Nd:YAG laser (354.7-nm wavelength) was used as stimulated light source to provide nighttime measurements. Filter with high rejection ratio performance was used to extract CO_2 Raman signals from Rayleigh-Mie scattering signals effectively. To improve the real time monitoring function, a two-channel signal collection system was designed to collect CO_2 and N_2 Raman scattering signals simultaneously. The N_2 Raman scattering signals were used to retrieve aerosol extinction coefficient. Typical features of CO_2 concentration profile and aerosol extinction coefficient in Hefei were presented. The mixing ratio of atmospheric CO_2 in Hefei can reach about $360 - 400$ ppmv.

OCIS codes: 010.1290, 010.3640, 010.1120, 010.1110.

During the last decade, a rising concern for the influence of human activity upon the environment has been developed. More and more advanced techniques in various domains of environmental quality monitoring were proposed. The flow analysis methods are applied for the solving of routine or research analytical problems. On the other hand, special attention has been paid to the domain of remote sensing. Lidars provide an active remote sensing technique to probe atmospheric regions with high spatial and temporal resolution inaccessible to other instruments. Differential absorption lidar (DIAL) is a powerful instrument for atmospheric CO_2 profile sensing due to abound absorption lines existing in infrared spectrum band. DIAL potentially offers several advantages for remote CO_2 sensing. Taczak *et al.* reported their research on atmospheric CO_2 measurement with differential absorption technique in 1998. A narrow-linewidth, continuously and smoothly tunable 2.066-μm Ho:YLF laser was used as light source for their lidar[1]. Menzies *et al.* presented optimum sounding wavelengths for lower-troposphere measurements of CO_2[2]. Koch *et al.* built a differential absorption lidar to measure CO_2 concentration in the atmosphere, whose transmitter was a pulsed single-frequency Ho:Tm:YLF laser at 2.05-μm wavelength, and coherent heterodyne detection was used to improve the sensitivity of the DIAL[3]. Abshire *et al.* used laser sounder for remotely measuring atmospheric CO_2 concentrations from space orbit and obtained the CO_2 total column[4]. At the same time, Raman technique shows a great deal of promise in atmospheric CO_2 measurement. Whiteman obtained the mixing ratio of CO_2 concentration from 1 to 5 km altitude[5]. Recently, a prototype Raman lidar system for atmospheric CO_2 profile monitoring was developed in China[6,7]. This paper describes a Raman lidar system that is capable of measuring the atmospheric CO_2 concentration profile with sufficient reliability to allow continuous nighttime operation.

Assuming no multi-scattering, the Raman lidar equation is given by

$$S_{\mathrm{Ram},x}(z) = \frac{k_x(z)}{z^2}\sigma_{\mathrm{Ram},x}(\pi) \times n_x(z) \times q(\lambda_0, z_0, z) \times q(\lambda_{\mathrm{Ram},x}, z_0, z), \quad (1)$$

where x stands for CO_2 or N_2, $\sigma_{\mathrm{Ram},x}(\pi)$ is the backscatter cross section for species x caused by Raman scattering, $n_x(z)$ is the number density for species x as a function of height z, and $q(\lambda_0, z_0, z)$ is the atmospheric transmittance from the lidar at height from z_0 to z at output wavelength λ_0 (354.7 nm) and is equal to

$$\exp(-\int_{z_0}^{z} \alpha(\lambda_0, z')\mathrm{d}z'), \quad (2)$$

where $\alpha(\lambda_x)$ is the volume extinction coefficient at wavelength λ_x. $q(\lambda_{\mathrm{Ram},x}, z_0, z)$ is the atmospheric transmittance from the lidar at height from z_0 to z at wavelength $\lambda_{\mathrm{Ram},x}$. k_x is a scale constant for channel x that accounts for the system optical efficiency, the telescope receiver area, the photomultiplier tube (PMT) spectral efficiency, and the laser output energy. The vibrational Raman scattering provides distinct wavelength shifts for specific vibrational energy states of the molecules. When 354.7-nm wavelength light was used as stimulated source, the CO_2 Raman shift spectrum is at 371.66 nm with 1388-cm^{-1} pertinent shift wave number. N_2 is used as reference medium for its constant proportion to dry air in low troposphere, and thus the N_2 Raman return signals are used as an equivalent of the mass of dry air. The N_2 Raman shift spectrum is at 386.7 nm with 2330.7-cm^{-1} pertinent shift wave number.

The atmospheric CO_2 mixing ratio, which is the mass of CO_2 divided by the mass of dry air in a given volume, is a function of height z, and can be expressed as

$$w_{CO_2}(z)=\frac{n_{CO_2}(z)}{n_{dry}(z)}\frac{M_{CO_2}(z)}{M_{dry}(z)}, \tag{3}$$

where M refers to the respective molecular weight. The mixing ratio can be determined from the lidar data by using the Raman-shifted signals from CO_2 and N_2,

$$w(z)=C_w\Delta q^w(z_0,z)\frac{S_{CO_2}(z)}{S_{N_2}(z)},$$

$$C_w=\frac{k_{N_2}}{k_{CO_2}}\frac{\sigma_{N_2}(\pi)}{\sigma_{CO_2}(\pi)}\frac{M_{CO_2}}{M_{dry}}\frac{n_{N_2}}{n_{dry}},$$

$$\Delta q^w(z_0,z)=\frac{q(\lambda_{N_2},z_0,z)}{q(\lambda_{CO_2},z_0,z)}, \tag{4}$$

where C_w is the system calibration constant, and $\Delta q^w(z_0,z)$ is the transmission correction function for atmospheric CO_2 mixing ratio.

The mixing ratio is proportional to the ratio of Raman signal of CO_2 to that of N_2 with the exception of the transmission correction term $\Delta q^w(z_0,z)$. The transmission $q(\lambda_{N_2},z_0,z)$ and $q(\lambda_{CO_2},z_0,z)$ differ primarily as a result of the λ^{-4} dependence of Rayleigh scattering by air molecules and the λ^{-1} dependence of Mie scattering by aerosol extinction. The US standard atmosphere mode of middle latitude and the extinction profile in Hefei are used to conduct simulation. The differential transmission correction curve has been simulated as shown in Fig. 1. The curve for aerosol free represents the differential transmission caused by Rayleigh scattering alone, as shown by the solid line. The 3% effect between the ground and 5-km altitude is clearly seen. The values of differential transmission correction under quite light and dense haze conditions are 3.5% and 6% between 0 and 5 km, respectively. A value of differential transmission caused by the US standard atmosphere mode of middle latitude conditions produces an additional 4% correction between 0 and 5 km. The calibration constant C_w can be determined by comparison with the data of radiosonde simultaneously.

The Raman lidar system for monitoring atmospheric CO_2 profile designed at our institute in Hefei is composed of a frequency-tripled Nd:YAG laser transmitter which transmits at the wavelength of 354.7 nm with 50-mJ energy and 20-Hz repetition rate, an optical telescope receiver which is of quasi Cassegrain with 35-cm diameter, and various signal-processing and data acquisition

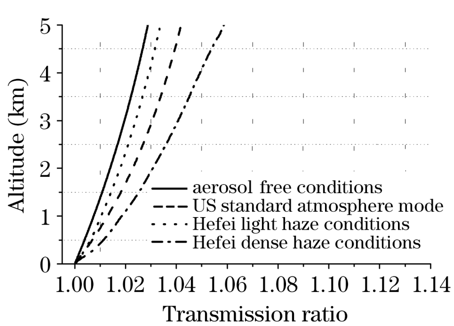

Fig. 1. Transmission correction curves for CO_2 mixing ratio calculations.

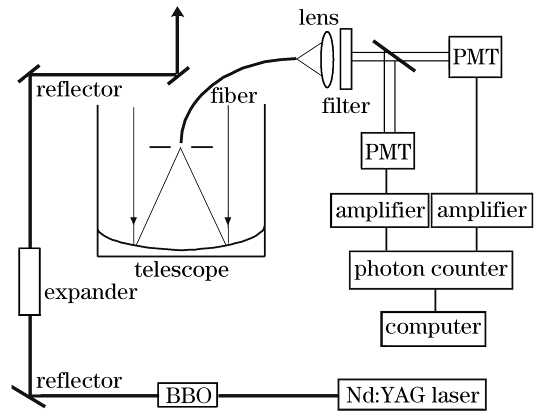

Fig. 2. Scheme of the Raman lidar system.

electronics. After being expanded and reflected, laser beams are conducted into atmosphere, the signals including elastic scattering signals (Mie and Rayleigh scattering) and Raman non-elastic signals (N_2, CO_2 and other gases Raman scattering) are collected by telescope. As indicated in Fig. 2, the data acquisition system consists of two channels which can obtain the N_2 and CO_2 Raman scattering signals simultaneously. The collected signals are introduced into narrow band filters via fiber and into photoelectron multiple tube and amplifier sequentially, at last photons could be counted by a photon counter. All reflective surfaces of the telescope are coated with aluminum and high-reflective medium film, so that the reflection is maximized in the used wavelength range. The output laser beam and the quasi Cassegrain telescope are aligned in coaxial mode. The interference filters in the Raman lidar systems is a key element for extracting pertinent Raman shift signals effectively. The interference filters must provide a high rejection ratio at the transmitted wavelength because the Raman shift backscattering signals are $3-4$ orders of magnitude less than the Rayleigh-Mie ones. Considering the mixing ratio of CO_2 in low atmosphere, the Raman channel interference filters are designed so that the transmission would be $10-12$ orders of magnitude at the transmitted wavelength less than that at the Raman-shifted wavelength, offering essentially complete rejection of the Rayleigh-Mie backscattering signals.

The parameters of filter at different wavelengths are also given in Table 1. Interference filters are produced by Barr Associates. The detectors are 9214B (Electron tubes) photomultiplier tubes which offer a 12-stage linear focus dynode chain with a usable gain of 7×10^7. The tubes are normally operated at fixed voltages of 1250 V. The amplifier is Phillips 6954 with a usable gain of 20 and band width range from 100 kHz to 1.5 GHz. In order to obtain the Raman backscattering photon effectively, we acquire data in photon counting (PC) modes instead of analog-to-digital (AD). The photon counter is MCA-3 P7882 which offers a counting rate capability in excess of 200 MHz.

Raman scattering signals shown in Fig. 3 can provide rude intensities of CO_2 and N_2 in the lower atmosphere. In order to avoid high background radiation effect, the Raman lidar was only operated in nighttime. Data

Table 1. Narrow Band Filter Parameters for CO_2 Raman Signal Measurement

	Requiring Index	Tested or Simulated Value	Remarks
Peak Transmission	> 45%	64%	OD: Optical Density
Center Wavelength	371.66 − 371.78 nm	371.71 nm	Incident Angle 0°
FWHM (nm)	0.4 + / − 0.1 nm	0.46 nm	Tested Value
200 − 1100 nm	OD 5	OD 5	Tested Value
375.4 nm	OD > 7	OD 7.4	Simulated Value
386.7 nm	OD > 7	OD 10.3	Simulated Value
580 nm	OD > 7	OD 23.6	Simulated Value
607.4 nm	OD > 7	OD 27.8	Simulated Value
354.7 nm	OD > 12	OD 20.5	Simulated Value
532.1 nm	OD > 12	OD 17.8	Simulated Value

processing of Raman lidar consists of background-subtracted, adjacent smoothing and range-squared correction, differential transmission correction and determination of calibrated constant. The calibrated constant is important for Raman lidar system, which is often compared with the radiosonde or other instruments. After calibration of the Raman lidar, we can obtain the CO_2 mixing ratio profile in atmosphere, and thus obtain the absolute concentration by the unit conversion. LI-7500 CO_2/H_2O analyzer is applied to calibrate the constant for the atmospheric CO_2 monitoring Raman lidar. It is estimated that an uncertainty in the value of constant contributes an error of less than 5% for the CO_2 measurements. The capability of this Raman lidar for monitoring atmospheric CO_2 profile is discussed under different weather conditions. The range of minimum detectable concentration can reach 45 − 90 ppmv for 20000 shots at 1.5-km altitude under different weather conditions[8]. The total error of Raman lidar can be estimated by the error propagation formulas, as shown in Fig. 4. Figure 5 indicates the atmospheric CO_2 mixing ratio profile with differential transmission corrections. The accuracy and stabilization of measuring decay with the increase of detecting range because of the decrease of signal-to-noise ratio (SNR), especially from 1.6 to 2.4-km altitude. Aerosol extinction influences measurement results significantly and can reach about 13 ppmv.

Aerosol extinction effects would influence the detectable capability of Raman lidar significantly. Generally, in order to compute aerosol extinction analytically, a knowledge of the exact nature of the aerosols that are responsible for the extinction is required. However, the dispersion and distribution of aerosol will be influenced

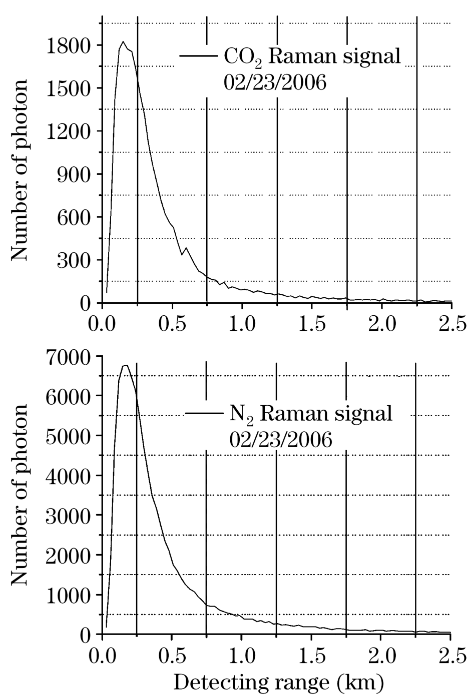

Fig. 3. CO_2 and N_2 backscattering Raman signals with 20000 shots accumulated in 16 min.

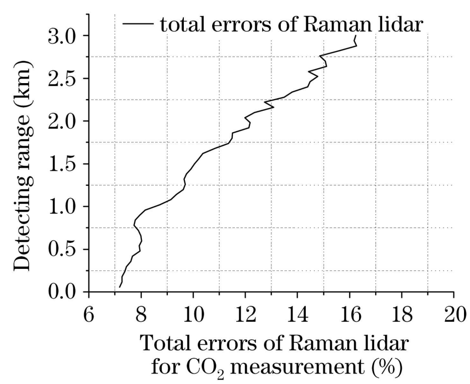

Fig. 4. Total errors of Raman lidar for CO_2 measurement with 20000 shots accumulated and laser energy of 50 mJ.

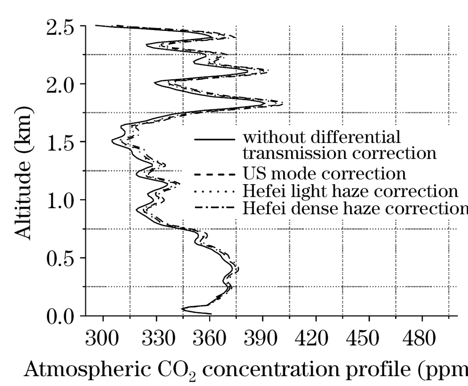

Fig. 5. Atmospheric CO_2 concentration profiles obtained with Raman lidar in Hefei with differential transmission correction. The laser energy is 50 mJ with 20000 shots accumulated in 16 min and 30 m spatial resolution. Date: 03/02/2006.

by weather conditions and it is difficult to determinate the aerosol extinction exactly with the above method. Klett and Fernald methods were often used in application of lidar retrieving the aerosol extinction coefficient. For the Raman lidar system, another approach for calculation of aerosol extinction coefficient is feasible. One may use the Raman vibrational[9] from N_2 or O_2 to calculate the round-trip atmospheric extinction, when vibrational Raman scattering occuring at the laser wavelength for the outgoing path and at the Raman shifted wavelength for the return path.

When the wavelengths of the lasers are typically used in the Raman lidar, atmospheric absorption by ozone and other gases is negligible. Thus aerosol extinction is determined by the total amount of light scattered into all directions. The aerosol extinction can be expressed by

$$\alpha_{\mathrm{p}}(\lambda_0, z) = \frac{1}{1+(\frac{\lambda_{\mathrm{N}_2}}{\lambda_0})^{-\gamma}} \left\{ \frac{\mathrm{d}}{\mathrm{d}z} \left[\ln \frac{n_{\mathrm{N}_2}(z)}{S(\lambda_{\mathrm{N}_2}, z) \times z^2} \right] - \alpha_{\mathrm{m}}(\lambda_0, z) \left[1 + \left(\frac{\lambda_{\mathrm{N}_2}}{\lambda_0} \right)^{-4} \right] \right\}, \quad (5)$$

where the subscriptions "p" and "m" stand for aerosol particles and atmospheric molecules, respectively, λ_{N_2} is the wavelength of Raman scattering light for N_2 molecules, and λ_0 is the exciting wavelength. The parameter γ is the index of aerosol extinction versus wavelength that can be expressed by

$$\frac{\alpha_{\mathrm{p}}(\lambda_0, z)}{\alpha_{\mathrm{p}}(\lambda_{\mathrm{N}_2}, z)} = (\frac{\lambda_{\mathrm{N}_2}}{\lambda_0})^{\gamma}, \quad (6)$$

where γ may vary approximately from 0 to 2, depending on the nature of the aerosols, and is a function of range. Aerosol extinction coefficient can be retrieved from N_2 vibrational Raman signals as shown by Eq. (5). It should be noted that the Eq. (5) neglected the influence of overlap function which could be considered as unity. However, in practice it is quite difficult to quantify the lidar channel overlap function sufficiently well. In the overlap region, the signal may be changing rapidly, small errors in quantifying the overlap function can introduce large errors in the derived aerosol extinction. For this reason, calculations of aerosol extinction are typically performed on the portion of the lidar profile that is fully overlapped. Aerosol extinction coefficient with different scanning modes in Hefei is indicated in Fig. 6. The dispersion character of aerosol can be observed from the graph.

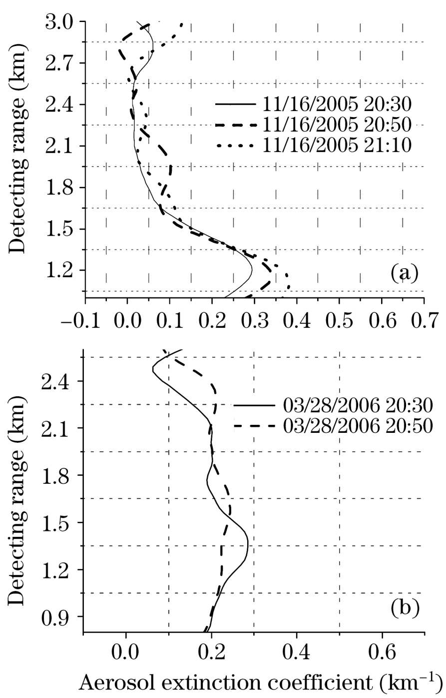

Fig. 6. Aerosol extinction coefficient retrieved by N_2 Raman signal in Hefei. (a) Vertical scanning mode; (b) horizontal scanning mode.

In conclusion, the Raman lidar system can realize the performence of monitoring atmospheric CO_2 concentration. The high performance of narrow band filters has significant contribution to extract the desired signals from Rayleigh-Mie scatter signals. The N_2 Raman scattering signals can be used to retrieve the aerosol extinction coefficient. The third channel will be added in the system to collect the Rayleigh-Mie elastic scattering signals which can be combined with N_2 Raman scattering signals to retrieve the aerosol backscattering ratio and aerosol extinction simultaneously. In over two years of experiment in laboratory, the Raman lidar has shown itself to be a reliable, valuable tool for study of atmospheric CO_2 in lower atmosphere.

Measuring the tropospheric CO_2 concentration profile has many conceivable error sources, including possible interference from other trace gas species, the effects of temperature, clouds, aerosols, and turbulence in the path, changes of surface reflectivity, variability of dry air density caused by changes in atmospheric pressure, water vapor, and topographic height. Some research indicates that the photon pile up correction needs to be considered. Work towards this goal is in progress.

This work was supported by National High Technology Development Program of China under Grant No. 2002AA135030. P. Zhao's e-mail address is peitaozhao@163.com.

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