Lecture 30. Constituent Lidar (2)
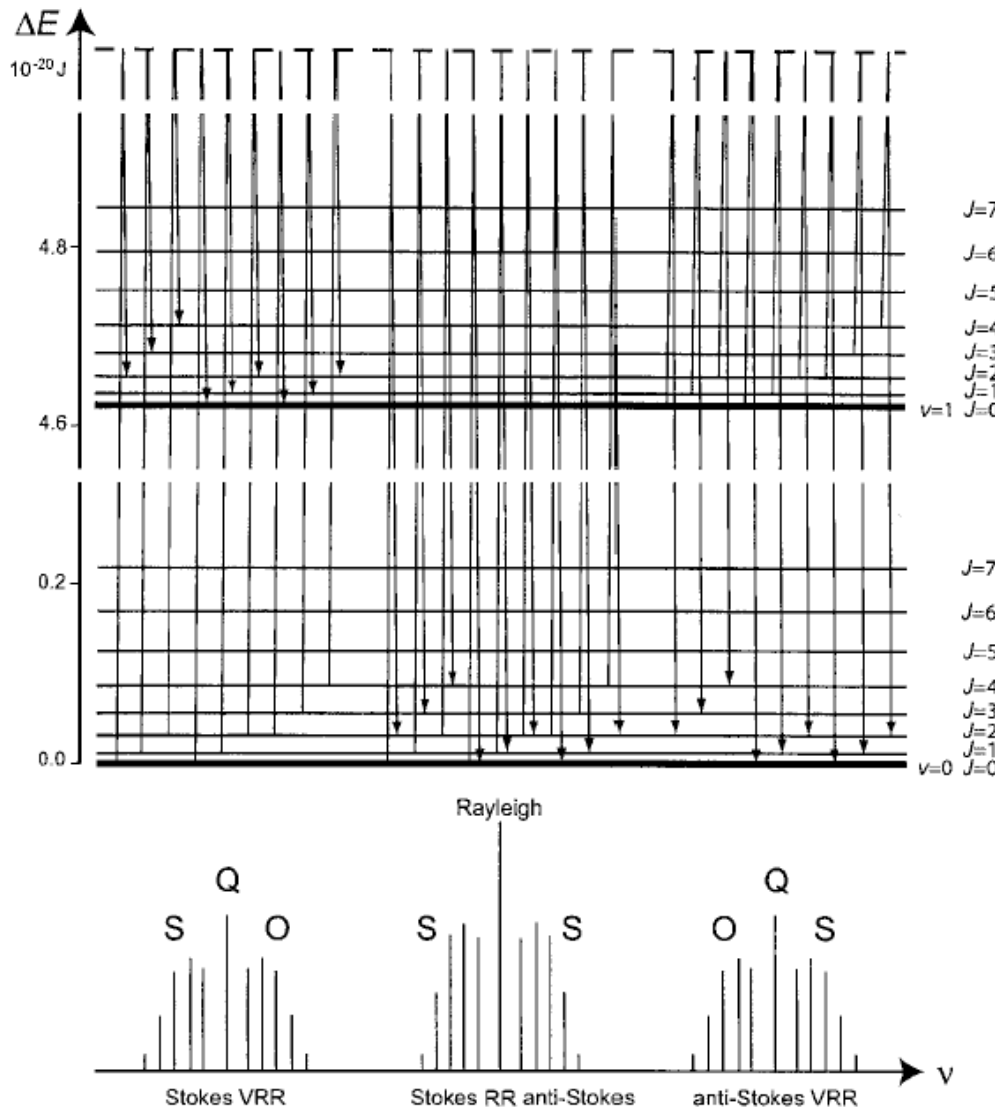
❑ Raman Scattering Lidar for Constituent Detection

(Example: Water Vapor Measurement)

❑ Raman DIAL for Constituent Detection

(Example: Ozone Measurement)

❑ Rotational Vibration-Rotational Raman DIAL

(RVR Raman DIAL)

❑ Summary

Raman Scattering (Inelastic)

Fig. 9.1. Vibration–rotation energy levels of the N_2 molecule, Raman transitions, and resulting spectrum.

$$\Delta k = k_i - k_s = \frac{\Delta E}{hc}$$

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

Wavenumber

The essential point for Raman lidar is to avoid the aerosol scattering in the Raman-shifted channel. Thus, only aerosol extinction will be dealt with in deriving constituent density.

Raman Scattering Frequency Shifts

❑ The scattering of incident radiation by atmospheric molecules involves both elastic and inelastic processes. (Wavenumber $k = 1/\lambda$)

❑ Elastic or Rayleigh (Cabannes) scattering is the scattering that the frequency of the scattered photon k_s is the same as the frequency of the incident photon k_i. In this case the molecule preserves its vibration-rotation energy level during the scattering process.

❑ Inelastic or Raman scattering processes lead to a change of the molecule's quantum state, and a change of the frequency of the scattered photon with respect to the incident photon frequency.

❑ If the molecule absorbs energy and transits to a higher energy level, the frequency of the scattered photon is decreased, so the wavelength is red-shifted. This is Stokes Raman scattering.

❑ If the molecule transfers energy to the scattered photon by decreasing its energy level, the frequency of the scattered photon is increased, so the wavelength is blue-shifted. This is anti-Stokes Raman scattering.

❑ The Raman frequency shift is $\Delta k = k_i - k_s = \Delta E/(hc)$

❑ Raman scattering cross-section is proportional to λ^{-4} (laser wavelength).
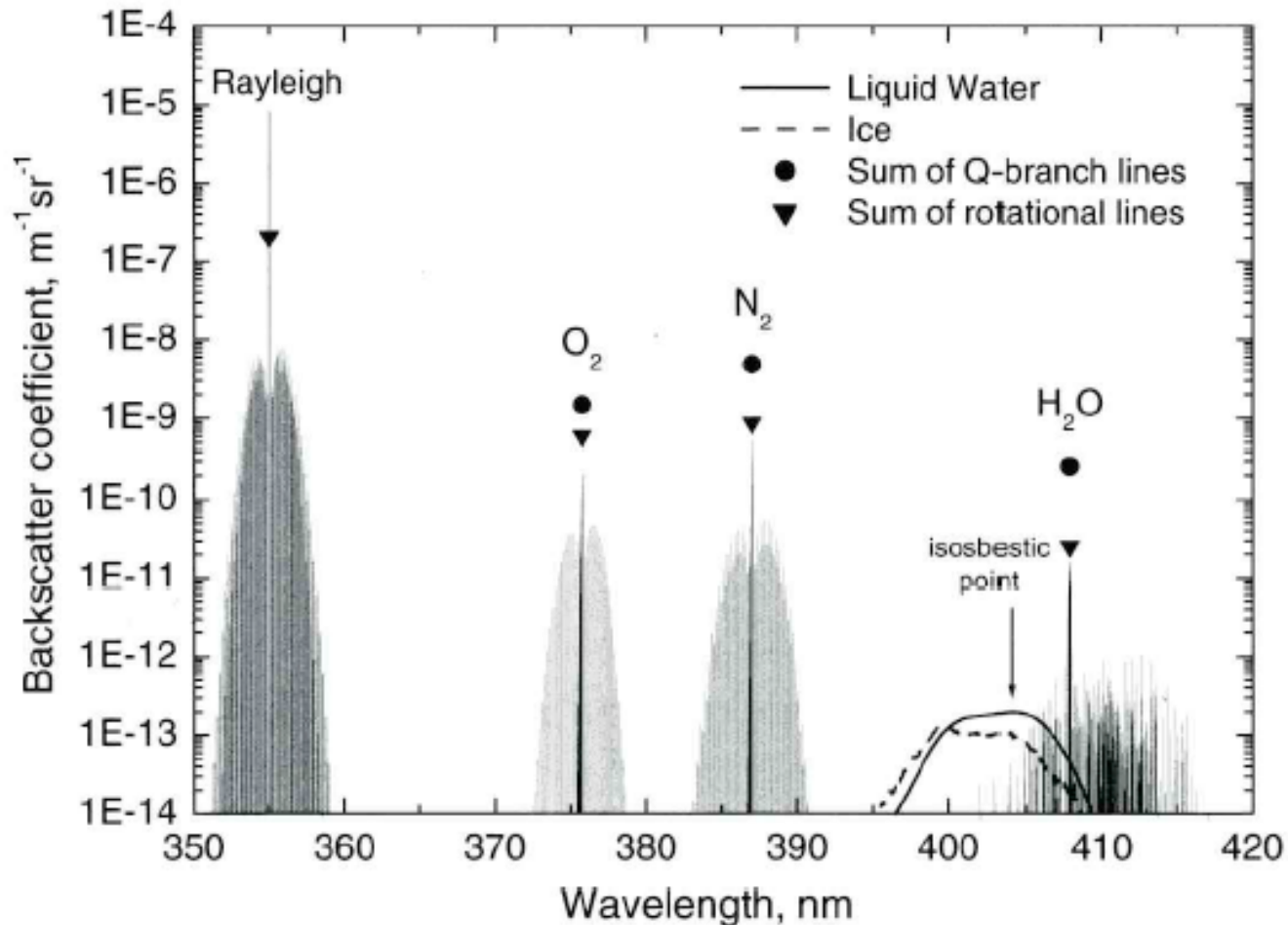
Raman Backscatter Spectrum

Fig. 9.2. Raman backscatter spectrum of the atmosphere for an incident laser wavelength of 355 nm, normal pressure, a temperature of 300 K, an N_2 and O_2 content of 0.781 and 0.209, respectively, and a water-vapor mixing ratio of 10 g/kg. The curves for liquid water and ice are arbitrarily scaled. The isosbestic point is discussed in Subsection 9.5.2.

Raman Lidar Equation

❑ The Raman lidar equation for the Raman scattering from the constituent interested and from the reference nitrogen N_2 or oxygen O_2

$$P_{cRa}(R,\lambda_{cRa}) = \frac{E_o \eta_{\lambda_{cRa}}}{R^2} O(R,\lambda_{cRa}) \beta_{cRa}(R,\lambda_0,\lambda_{cRa}) \exp\left\{-\int_0^R \left[\alpha(r,\lambda_0) + \alpha(r,\lambda_{cRa})\right] dr\right\}$$

Extinction On the way up and on the way back

$$P_{\mathrm{RefRa}}(R,\lambda_{\mathrm{RefRa}}) = \frac{E_o \eta_{\lambda_{\mathrm{RefRa}}}}{R^2} O(R,\lambda_{\mathrm{RefRa}}) \beta_{\mathrm{RefRa}}(R,\lambda_0,\lambda_{\mathrm{RefRa}}) \exp\left\{-\int_0^R \left[\alpha(r,\lambda_0) + \alpha(r,\lambda_{\mathrm{RefRa}})\right] dr\right\}$$

❑ The Raman backscatter coefficients from the constituent channel and from the reference molecule channel can be written as

$$\beta_{cRa}(R,\lambda_0,\lambda_{cRa}) = N_{cRa}(R) \frac{d\sigma_{cRa}}{d\Omega}(\pi,\lambda_0,\lambda_{cRa})$$

$$\beta_{\mathrm{RefRa}}(R,\lambda_0,\lambda_{\mathrm{RefRa}}) = N_{\mathrm{RefRa}}(R) \frac{d\sigma_{\mathrm{RefRa}}}{d\Omega}(\pi,\lambda_0,\lambda_{\mathrm{RefRa}})$$

Constituent number density

Reference molecule number density

Raman backscatter cross-section

Neither constituent nor reference channel includes aerosol backscattering!

Solution for Raman Lidar Equation

❑ Taking the ratio of the above two Raman lidar equations

$$\frac{P_{cRa}(R,\lambda_{cRa})}{P_{RefRa}(R,\lambda_{RefRa})} = \frac{\eta_{\lambda_{cRa}}}{\eta_{\lambda_{RefRa}}} \frac{N_{cRa}(R)\dfrac{d\sigma_{cRa}}{d\Omega}(\pi,\lambda_0,\lambda_{cRa})}{N_{RefRa}(R)\dfrac{d\sigma_{RefRa}}{d\Omega}(\pi,\lambda_0,\lambda_{RefRa})} \frac{\exp\left\{-\int_0^R \alpha(r,\lambda_{cRa})dr\right\}}{\exp\left\{-\int_0^R \alpha(r,\lambda_{RefRa})dr\right\}}$$

Here, E_0, R^2, $O(R)$, and $\alpha(r,\lambda_0)$ are already cancelled out

❑ Thus, the mixing ratio of the constituent in the atmosphere is given by

$$r_m(R) = \frac{M_c(R)}{M_{air}(R)} = \frac{M_c(R)}{M_{Ref}(R)}\frac{M_{Ref}}{M_{air}} = \frac{M_{Ref}}{M_{air}}\frac{m_c}{m_{Ref}}\frac{N_{cRa}(R)}{N_{RefRa}(R)}$$

$$= \frac{M_{Ref}}{M_{air}}\frac{m_c}{m_{Ref}}\frac{\eta_{\lambda_{RefRa}}}{\eta_{\lambda_{cRa}}} \frac{\dfrac{d\sigma_{RefRa}}{d\Omega}(\pi,\lambda_0,\lambda_{cRa})}{\dfrac{d\sigma_{cRa}}{d\Omega}(\pi,\lambda_0,\lambda_{RefRa})} \frac{P_{cRa}(R,\lambda_{cRa})}{P_{RefRa}(R,\lambda_{RefRa})} \frac{\exp\left\{-\int_0^R \alpha(r,\lambda_{RefRa})dr\right\}}{\exp\left\{-\int_0^R \alpha(r,\lambda_{cRa})dr\right\}}$$

Calibration Constant C

Solution Cont'd

❑ The calibration of Raman lidar data lies in several aspects:

(1) The ratio of reference molecule density in the air

(2) The lidar detector efficiency ratio at two wavelengths

(3) The effective Raman backscatter cross-section ratio

(4) Atmospheric transmission ratio, i.e., extinction coefficient difference

❑ Depending on the filter bandwidth, we have to take the average cross-section over the spectrum of the observed Raman band, weighted with the instrument's transmission function. It is also possible that we have to consider temperature dependence of the signal intensity distribution in the wings of the Raman bands.

❑ Regarding extinction coefficient at different wavelengths, it contains the extinction from aerosols and air molecules. Again, air molecules can be calculated from model data. For aerosols, we will introduce Angstrom exponent as we did earlier. This factor $a(R)$ is usually between 0-2, and normally 1. The error introduced by Angstrom factor is less than 10%.

$$\alpha(R) = \alpha_{aer}(R) + \alpha_{mol}(R)$$

$$\frac{\alpha_{aer}(\lambda_0)}{\alpha_{aer}(\lambda_{Ra})} = \left(\frac{\lambda_{Ra}}{\lambda_0}\right)^{a(R)}$$

Consideration on Raman Application

❑ In principle, the above Raman lidar approach is valid for measurements of any Raman-active gas with sufficiently high atmospheric concentration.

❑ The low Raman scattering cross sections require comparably high concentrations of the investigated atmospheric components. Accordingly, N_2, O_2, and H_2O as main constituent gases in air are of prime interest.

❑ Raman measurements do not require specific laser wavelengths. Due to the wavelength dependence λ^{-4}, shorter laser wavelengths are preferred. Laser wavelengths between 320-550 nm are best suited for Raman applications. Below 320 nm, O_3 absorption causes considerable attenuation (but the solar-blind region below 300 nm has also been used for Raman daytime). Above 550 nm, the Raman scattering cross section is much smaller but the light transmission through the atmosphere is much higher.

❑ Due to the low intensity of Raman backscatter signals, a high-power laser transmitter and a highly efficient receiving and detection system are required. Below is an example for water vapor Raman lidar.
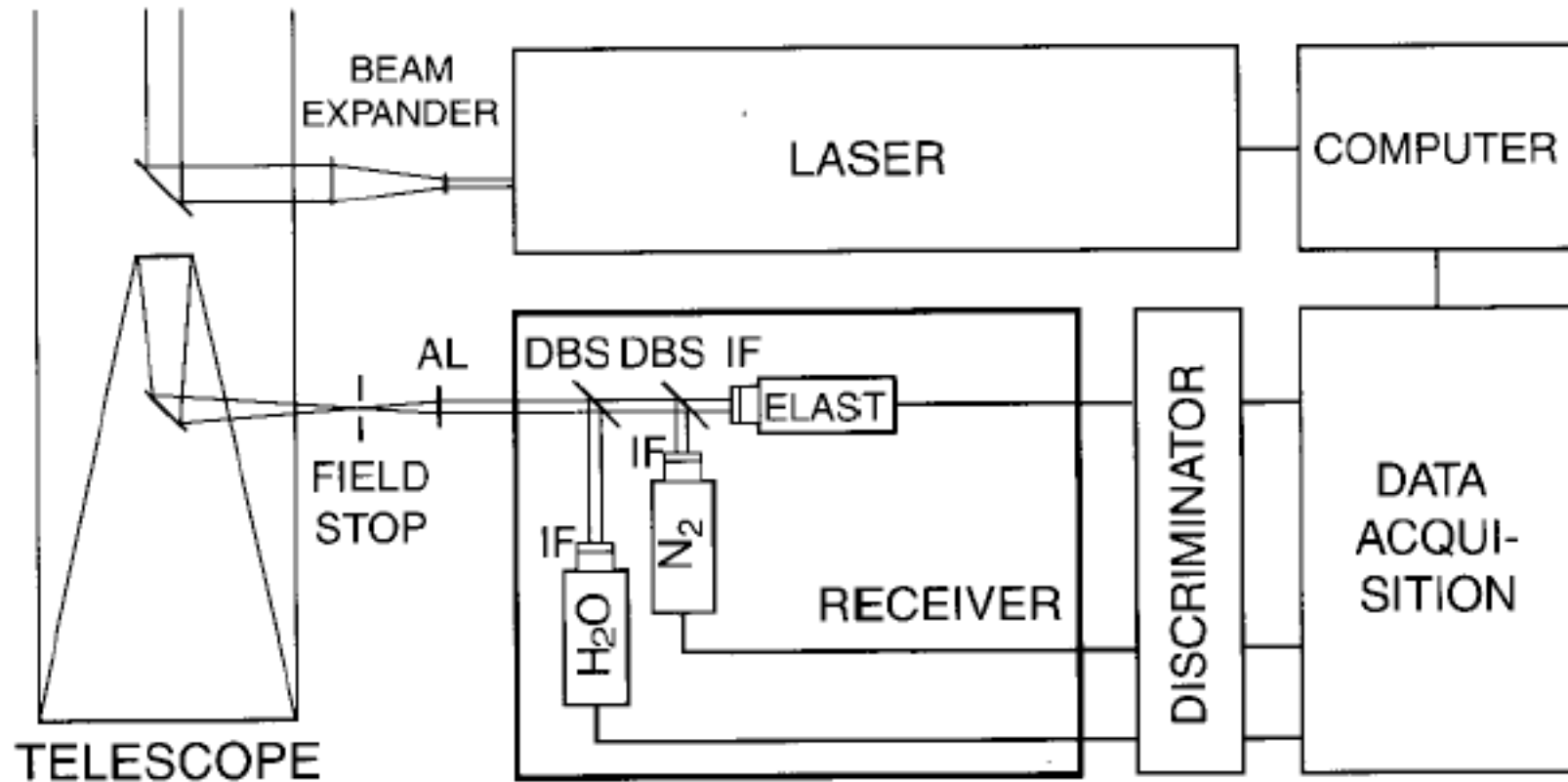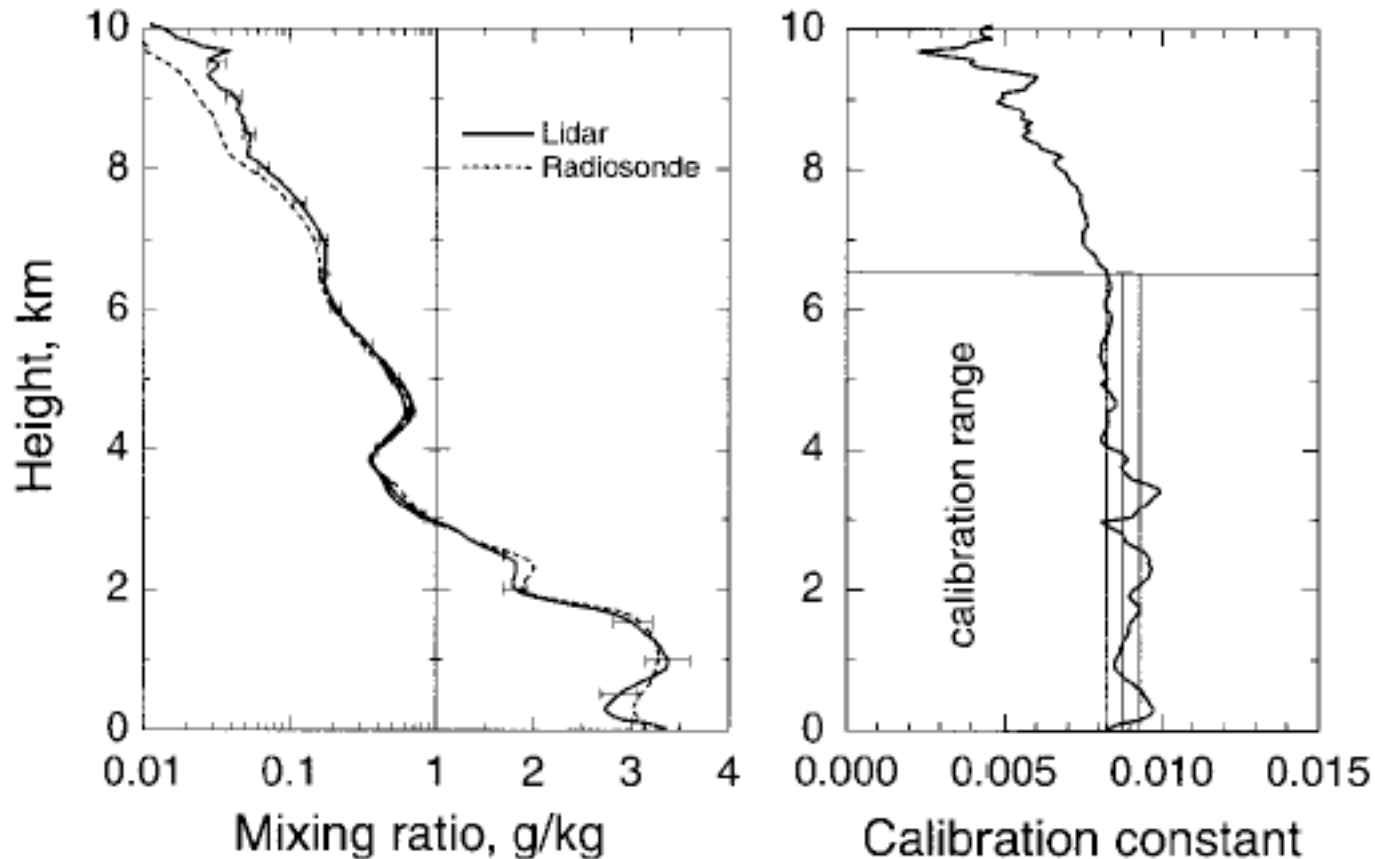
Water Vapor Raman Lidar Setup

Fig. 9.3. Typical setup of a water-vapor and aerosol Raman lidar. AL – achromatic lens, IF – interference filter, DBS – dichroic beam splitter.

Raman Water Vapor Results

□ Raman scattering lidar usually needs calibration with radiosonde or independent calibration by measuring or calculating the relevant system parameters or by using multichannel to measure the aerosol extinction and effective cross-sections.

Conventional DIAL Ozone Measurement
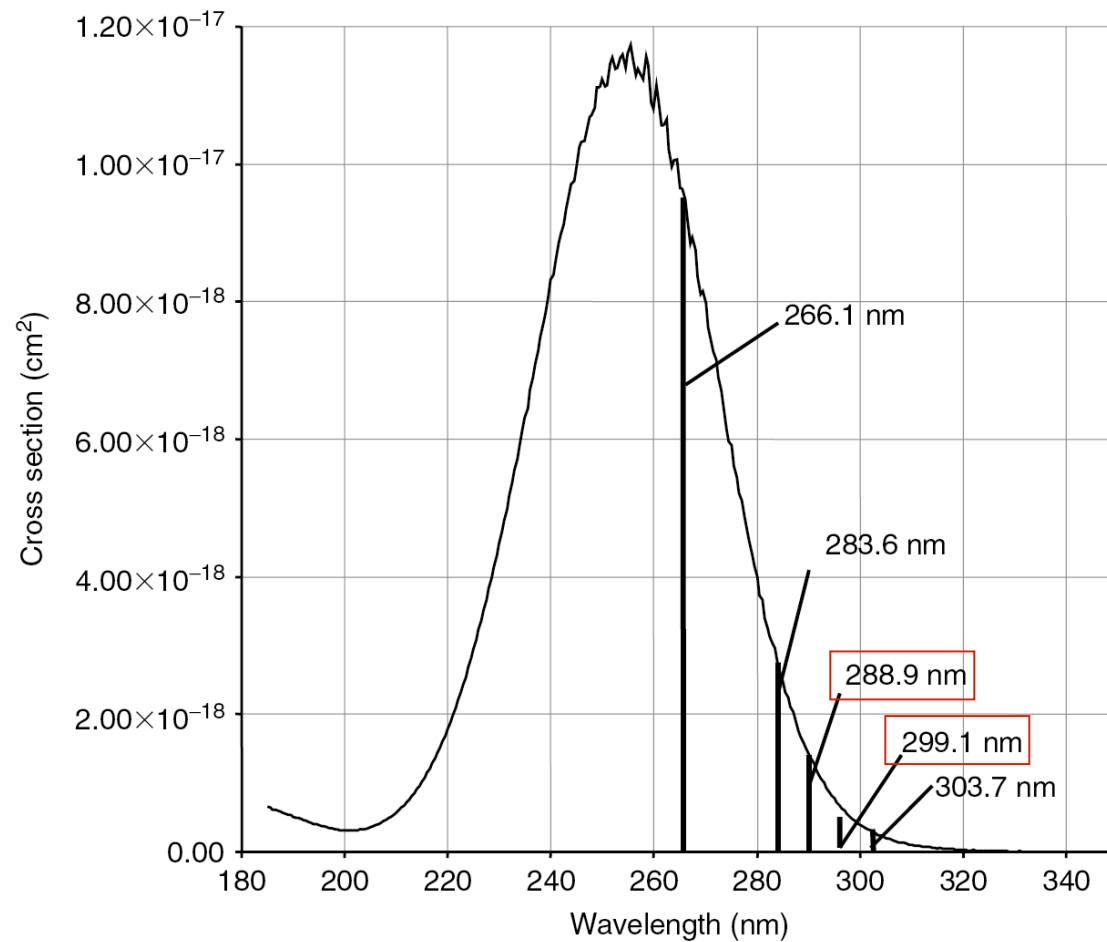
$$\lambda_{ON} = 288.9nm$$
$$\lambda_{OFF} = 299.1nm$$

Figure 4.1 Ozone absorption spectrum in the UV: the Raman shifted wavelengths given in Table 4.2 are highlighted in this figure.

Conventional DIAL Equations

$$P_S(\lambda_0^{ON}, R) = P_L(\lambda_0^{ON}) \left[\left(\beta_{aer}(\lambda_0^{ON}, R) + \beta_{mol}(\lambda_0^{ON}, R) \right) \Delta R \right] \left(\frac{A}{R^2} \right) \exp\left[-2 \int_0^R \left(\alpha_{aer}(\lambda_0^{ON}, r) + \alpha_{mol}(\lambda_0^{ON}, r) \right) dr \right]$$

$$\times \exp\left[-2 \int_0^R \sigma_{IG}(\lambda_0^{ON}, r) n_{IG} dr \right] \exp\left[-2 \int_0^R \sigma_{abs}(\lambda_0^{ON}, r) n_c(r) dr \right] \left[\eta(\lambda_0^{ON}) G(R) \right] + P_B$$

$$P_S(\lambda_0^{OFF}, R) = P_L(\lambda_0^{OFF}) \left[\left(\beta_{aer}(\lambda_0^{OFF}, R) + \beta_{mol}(\lambda_0^{OFF}, R) \right) \Delta R \right] \left(\frac{A}{R^2} \right) \exp\left[-2 \int_0^R \left(\alpha_{aer}(\lambda_0^{OFF}, r) + \alpha_{mol}(\lambda_0^{OFF}, r) \right) dr \right]$$

$$\times \exp\left[-2 \int_0^R \sigma_{IG}(\lambda_0^{OFF}, r) n_{IG} dr \right] \exp\left[-2 \int_0^R \sigma_{abs}(\lambda_0^{OFF}, r) n_c(r) dr \right] \left[\eta(\lambda_0^{OFF}) G(R) \right] + P_B$$

DIAL Solution

$$n_c(R) = \frac{1}{2 \Delta \sigma_{abs}} \frac{d}{dR} \left\{ \ln\left[\frac{P_S(\lambda_{OFF}, R) - P_B}{P_S(\lambda_{ON}, R) - P_B} \right] - \ln\left[\frac{P_L(\lambda_{OFF}) \eta(\lambda_{OFF})}{P_L(\lambda_{ON}) \eta(\lambda_{ON})} \right] - \ln\left[\frac{\beta_{aer}(\lambda_{OFF}, R) + \beta_{mol}(\lambda_{OFF}, R)}{\beta_{aer}(\lambda_{ON}, R) + \beta_{mol}(\lambda_{ON}, R)} \right] - 2\left[\alpha_{aer}(\lambda_{ON}, R) - \alpha_{aer}(\lambda_{OFF}, R) \right] - 2\left[\alpha_{mol}(\lambda_{ON}, R) - \alpha_{mol}(\lambda_{OFF}, R) \right] - 2\left[\sigma_{IG}(\lambda_{ON}, R) - \sigma_{IG}(\lambda_{OFF}, R) \right] n_{IG} \right\}$$

Introducing large error when large aerosol gradient or IG exists
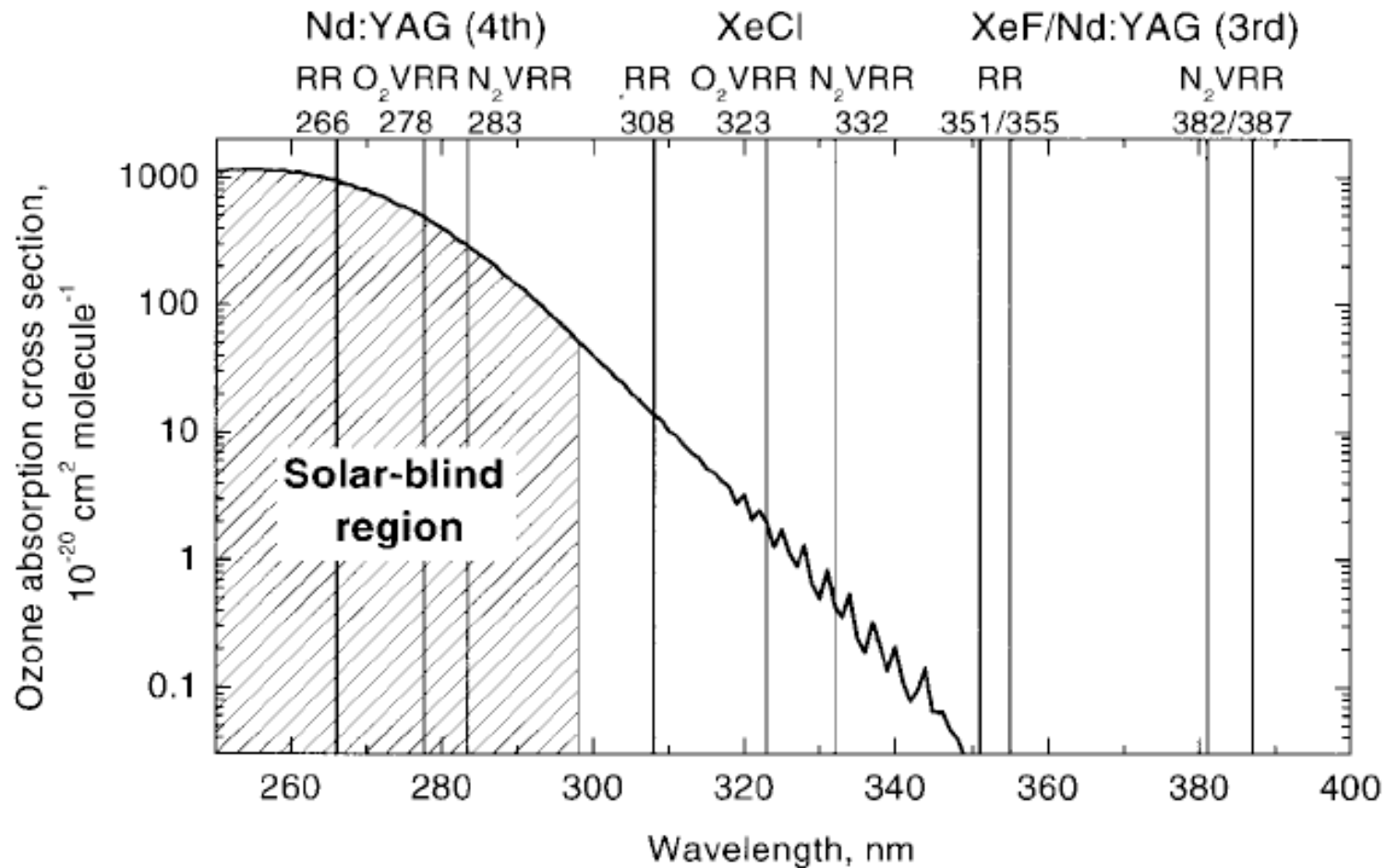
Ozone Raman DIAL

Fig. 9.5. Ozone absorption cross section and wavelengths applied in the ozone Raman DIAL technique for upper tropospheric and stratospheric measurements ($\lambda > 300$ nm) and for boundary-layer measurements in the solar-blind region ($\lambda < 300$ nm).

Raman DIAL Equations

❑ For the Raman reference channels (e.g., from N_2 Raman scattering),

$$P_S(\lambda_{\text{Ref}}^{ON}, R) = P_L(\lambda_0^{ON})\left[\beta_{Raman}(\lambda_0^{ON}, \lambda_{\text{Ref}}^{ON}, R)\Delta R\right]\left(\frac{A}{R^2}\right)$$

$$\times \exp\left[-\int_0^R \left(\alpha_{aer}(\lambda_0^{ON}, r) + \alpha_{aer}(\lambda_{\text{Ref}}^{ON}, r) + \alpha_{mol}(\lambda_0^{ON}, r) + \alpha_{mol}(\lambda_{\text{Ref}}^{ON}, r)\right)dr\right]$$

$$\times \exp\left[-\int_0^R \left(\sigma_{IG}(\lambda_0^{ON}, r) + \sigma_{IG}(\lambda_{\text{Ref}}^{ON}, r)\right)n_{IG}dr\right]$$

$$\times \exp\left[-\int_0^R \left(\sigma_{abs}(\lambda_0^{ON}, r) + \sigma_{abs}(\lambda_{\text{Ref}}^{ON}, r)\right)n_c(r)dr\right]\left[\eta(\lambda_{\text{Ref}}^{ON})G(R)\right] + P_B$$

$$P_S(\lambda_{\text{Ref}}^{OFF}, R) = P_L(\lambda_0^{OFF})\left[\beta_{Raman}(\lambda_0^{OFF}, \lambda_{\text{Ref}}^{OFF}, R)\Delta R\right]\left(\frac{A}{R^2}\right)$$

$$\times \exp\left[-\int_0^R \left(\alpha_{aer}(\lambda_0^{OFF}, r) + \alpha_{aer}(\lambda_{\text{Ref}}^{OFF}, r) + \alpha_{mol}(\lambda_0^{OFF}, r) + \alpha_{mol}(\lambda_{\text{Ref}}^{OFF}, r)\right)dr\right]$$

$$\times \exp\left[-\int_0^R \left(\sigma_{IG}(\lambda_0^{OFF}, r) + \sigma_{IG}(\lambda_{\text{Ref}}^{OFF}, r)\right)n_{IG}dr\right]$$

$$\times \exp\left[-\int_0^R \left(\sigma_{abs}(\lambda_0^{OFF}, r) + \sigma_{abs}(\lambda_{\text{Ref}}^{OFF}, r)\right)n_c(r)dr\right]\left[\eta(\lambda_{\text{Ref}}^{OFF})G(R)\right] + P_B$$

Solution for Raman DIAL Equations

❑ From the two Raman reference channel equations, we obtain the number density of the constituent that we are interested in

$$
n_c(R) = \frac{1}{\Delta\sigma_{abs}} \frac{d}{dR}
\begin{cases}
\ln\left[\dfrac{P_S(\lambda_{\mathrm{Ref}}^{OFF},R) - P_B}{P_S(\lambda_{\mathrm{Ref}}^{ON},R) - P_B}\right] & \text{A} \\[2ex]
-\ln\left[\dfrac{P_L(\lambda_0^{OFF})\eta(\lambda_{\mathrm{Ref}}^{OFF})}{P_L(\lambda_0^{ON})\eta(\lambda_{\mathrm{Ref}}^{ON})}\right] & \text{B} \\[2ex]
-\ln\left[\dfrac{\beta_{Raman}(\lambda_{\mathrm{Ref}}^{OFF},R)}{\beta_{Raman}(\lambda_{\mathrm{Ref}}^{ON},R)}\right] & \text{C} \\[2ex]
-\Delta\alpha_{aer}(R) & \text{D} \\[2ex]
-\Delta\alpha_{mol}(R) & \text{E} \\[2ex]
-\Delta\sigma_{IG}(R)n_{IG} & \text{F}
\end{cases}
$$

❑ Here, the Δ expressions consist of four terms each

$$
\Delta\xi = \xi(\lambda_0^{ON}) + \xi(\lambda_{\mathrm{Ref}}^{ON}) - \xi(\lambda_0^{OFF}) - \xi(\lambda_{\mathrm{Ref}}^{OFF})
$$

with

$$
\xi = \sigma_{abs}, \alpha_{aer}, \alpha_{mol}, \sigma_{IG}
$$

Solution in Ozone Case

❑ Term B can be measured and it is range-independent, so the derivative is zero,

❑ Term C is only concerned about molecule Raman scattering, so can be calculated.

❑ Term D will be determined through using the Raman channel at OFF wavelength and introducing Angstrom exponent.

❑ Term E is concerned about molecule Rayleigh scattering, so can be be calculated from atmosphere temperature and pressure.

❑ Term F can be minimized through choosing proper wavelengths, thus, can be ignored.

Ozone Comparison
GSFC Lidar vs STOIC Reference

LEGEND
6/28/91
6/29/91
7/3/91
STOIC Ref. — —

ALTITUDE (KM)
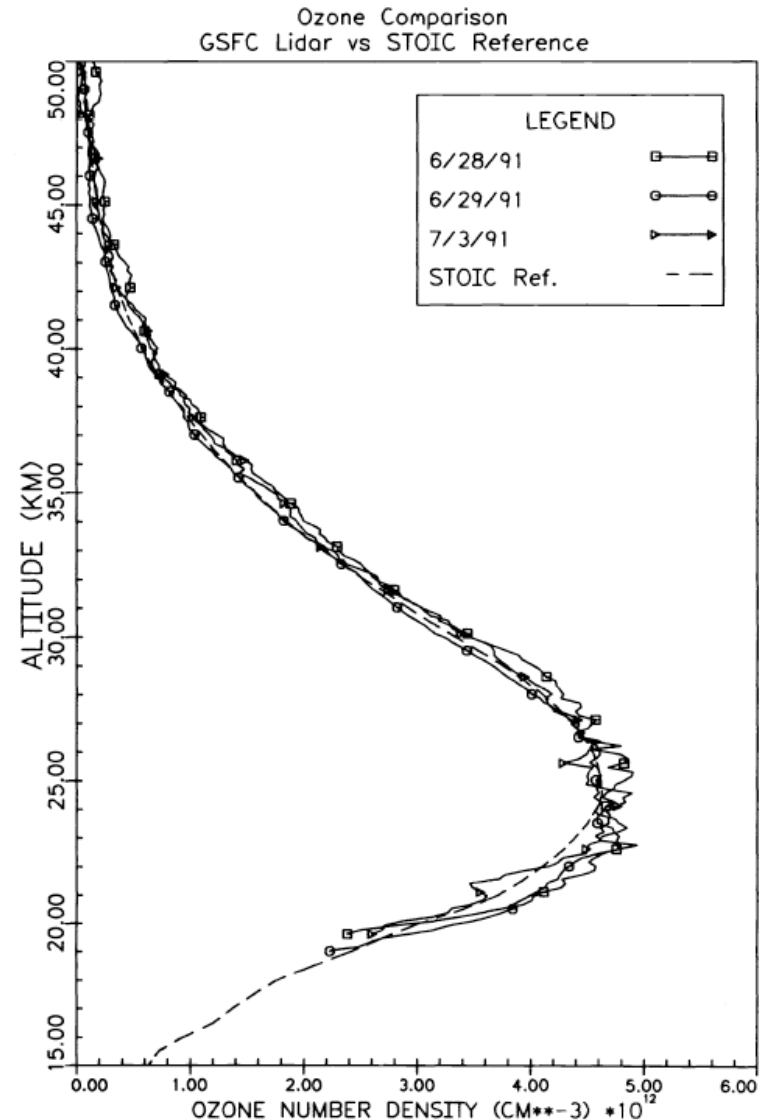
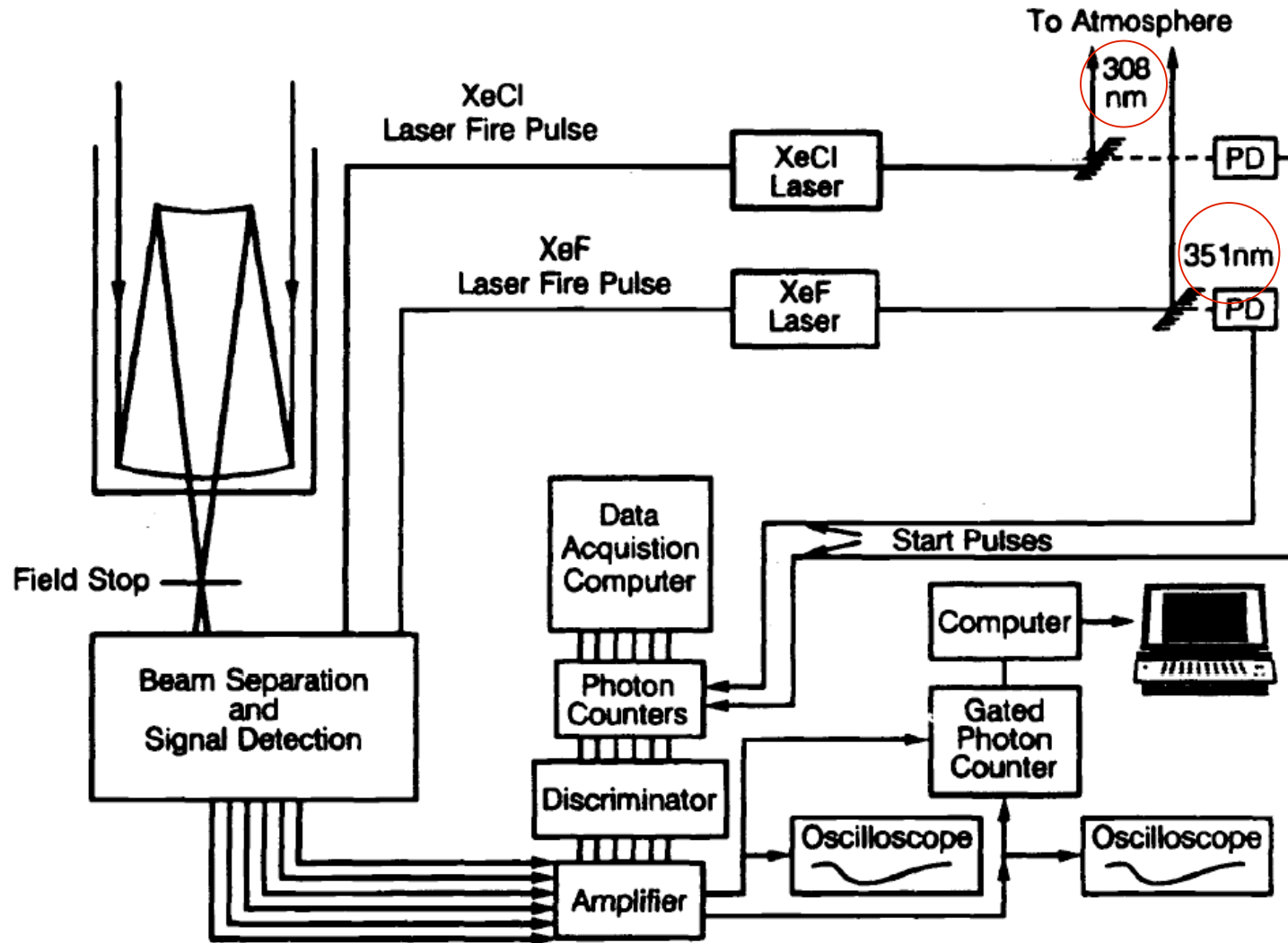OZONE NUMBER DENSITY (CM**-3) *10^{12}

Fig. 6 GSFC lidar ozone profiles taken at JPL-TMO during June and July 1991 using the mechanical chopper.

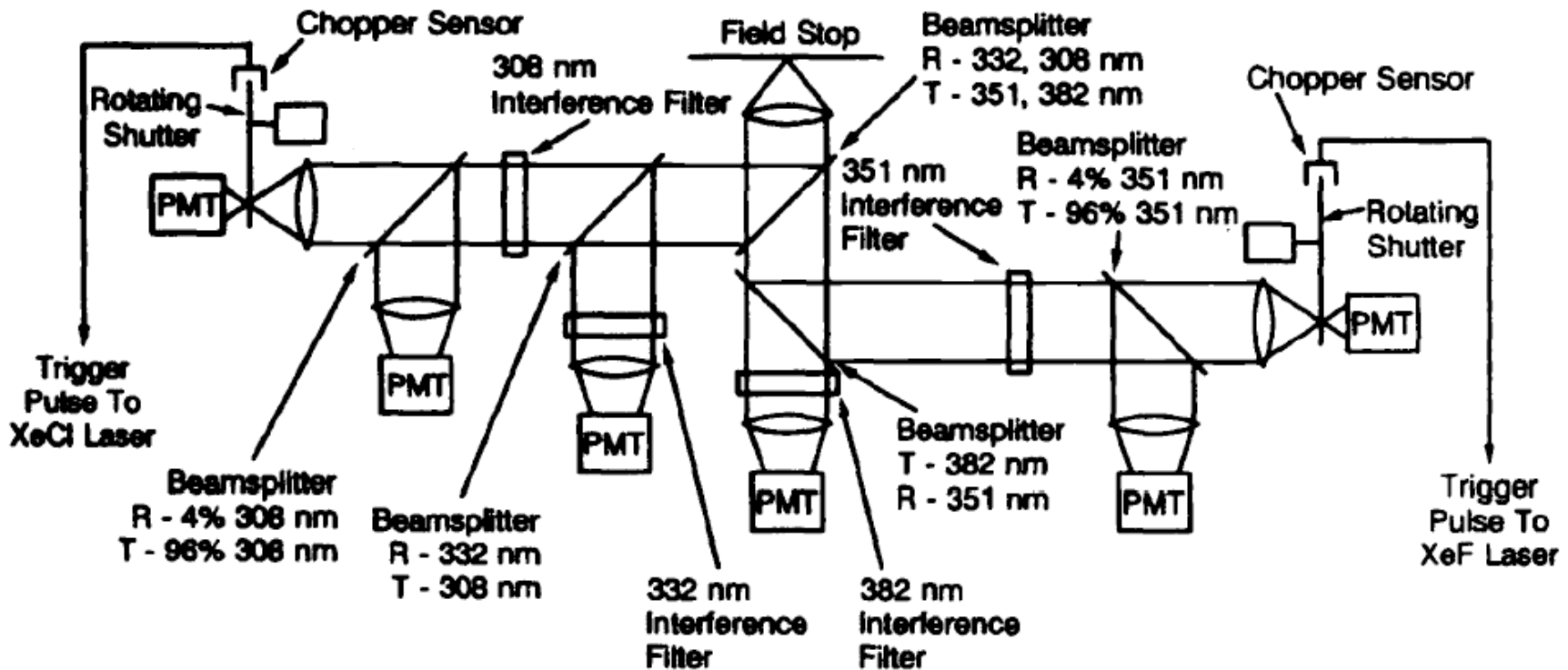# Ozone Raman DIAL Instrumentation

Return Signals –
    On-line: 332 nm (N_2 Raman scattering from 308 nm)
    Off-line: 382 nm (N_2 Raman scattering from 351 nm)

Ozone Raman DIAL Receiver

Rotational Vibrational-Rotational (RVR) Raman DIAL with Single Laser

Table 1. Parameters of the Conventional Raman DIAL and the RVR Raman DIAL's[a]

| Lidar | On-Resonance | | Off-Resonance | | | |
	Raman Wavelength (nm)	λ_L (nm)	Raman Wavelength (nm)	λ_L (nm)	$\Delta\lambda$ (nm)	$\Delta C_{O_3}^{abs}$ (10^{-24} m^2)
O_2 RVR Raman DIAL	307	308	323	308	16	11.7
N_2 RVR Raman DIAL	307	308	332	308	25	12.3
Raman DIAL	332	308	387	355	79	12.4

[a] $\Delta\lambda$, maximum spectral separation of the signals used for the measurements. Differential ozone absorption cross sections ($\Delta C_{O_3}^{abs}$) are calculated from Ref. 13 ($T = 226$ K). Wavelength values are rounded to full nanometers.

The RVR Raman DIAL measurement yields the numbers $N(\lambda, z)$ of lidar return photons from distance z at the rotational Raman wavelength λ_R of molecular oxygen and nitrogen and at the vibrational–rotational Raman wavelength λ_{VR} of O_2 or N_2, if light of the primary wavelength λ_L is transmitted. When absorption by particles and trace gases other than ozone is neglected, a condition satisfied for cirrus measurements in the free troposphere,[3] the RVR Raman DIAL ozone molecule number density $n(z)$ in the single-scattering approximation is given by

RVR Raman DIAL

$$n(z) = RVRN - RVRM - RVRP, \qquad (1)$$

where

$$RVRN = \frac{(\mathrm{d}/\mathrm{d}z)\ln[N(\lambda_{\mathrm{VR}}, z)/N(\lambda_{\mathrm{R}}, z)]}{C_{\mathrm{O_3}}^{\mathrm{abs}}(\lambda_{\mathrm{R}}, T) - C_{\mathrm{O_3}}^{\mathrm{abs}}(\lambda_{\mathrm{VR}}, T)},$$

$$RVRM = \frac{\alpha_{\mathrm{mol}}^{\mathrm{sca}}(\lambda_{\mathrm{R}}, z) - \alpha_{\mathrm{mol}}^{\mathrm{sca}}(\lambda_{\mathrm{VR}}, z)}{C_{\mathrm{O_3}}^{\mathrm{abs}}(\lambda_{\mathrm{R}}, T) - C_{\mathrm{O_3}}^{\mathrm{abs}}(\lambda_{\mathrm{VR}}, T)},$$

$$RVRP = \frac{\alpha_{\mathrm{par}}^{\mathrm{sca}}(\lambda_{\mathrm{R}}, z) - \alpha_{\mathrm{par}}^{\mathrm{sca}}(\lambda_{\mathrm{VR}}, z)}{C_{\mathrm{O_3}}^{\mathrm{abs}}(\lambda_{\mathrm{R}}, T) - C_{\mathrm{O_3}}^{\mathrm{abs}}(\lambda_{\mathrm{VR}}, T)}.$$

Here $C_{\mathrm{O_3}}^{\mathrm{abs}}(\lambda, T)$ is the ozone absorption cross section at temperature T, and $\alpha_{\mathrm{mol}}^{\mathrm{sca}}(\lambda, z)$ and $\alpha_{\mathrm{par}}^{\mathrm{sca}}(\lambda, z)$ are the Rayleigh extinction and the single-scattering particle extinction coefficient, respectively. Similar expressions, RDN, RDM, and RDP, have been derived for conventional Raman DIAL.[4]

[Reichardt et al., Applied Optics, 39, 6072-6079, 2000]
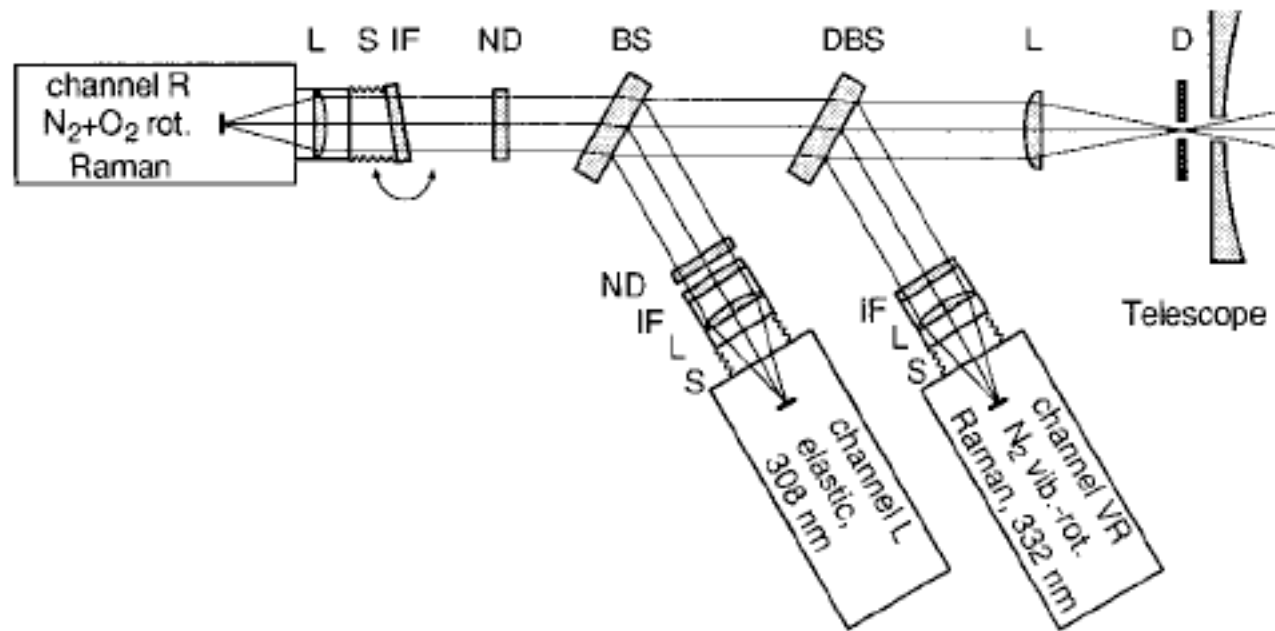
Single-Laser RVR Raman DIAL

Fig. 3. RVR Raman DIAL receiver: D, diaphragm; L, lens; DBS, dichroic beam splitter; BS, beam splitter; ND, neutral-density filter; IF, interference filter; S, flexible shield. Atmospheric rotational Raman, elastic, and N_2 vibrational–rotational Raman backscattering signals are detected in channels R, L, and VR. The center wavelength of the channel-R interference filter can be tuned by rotating the filter around the vertical axis.

Summary

❑ The essential point for Raman lidar is to avoid the aerosol scattering in the Raman-shifted channel. Thus, only aerosol extinction will be dealt with in deriving constituent density. Aerosol extinction can be safely estimated by introducing Angstrom exponent. The error introduced by Angstrom uncertainty is much less than the lidar ratio or backscatter coefficient.

❑ Combination of Raman and DIAL can effectively remove the influence from aerosol or interference gases.

❑ More combination and approaches using DIAL and Raman are on the way to solve practical constituent detection problems.

❑ Again, spectroscopy is the key to guide the laser wavelength selection and DIAL/Raman considerations.