

Lecture 29. Constituent Lidar (1)

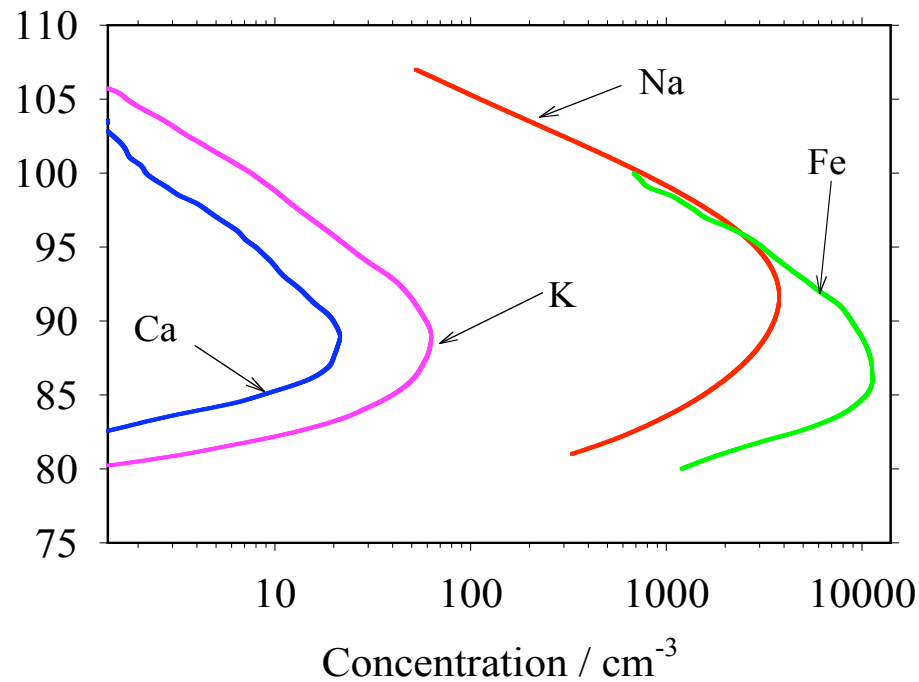
- ❑ Motivations to study atmosphere constituents
- ❑ Lidar detection of atmospheric constituents
(spectroscopic signatures to distinguish species)
- ❑ Metal atoms by resonance fluorescence lidar
- ❑ DIAL detection of molecules and pollutant
(DIAL Equation and Solution)
- ❑ Raman Lidar detection of molecules and pollutant
(Raman Equation and Solution)
- ❑ Summary

(Chapter 4 in our textbook "Laser Remote Sensing")

Motivations to Study Constituents

- ❑ Atmospheric constituents are referred to the trace gases that occur in relatively small but sometimes highly variable concentrations. In our class, constituents mean the atomic or molecular trace gases in the atmosphere, excluding aerosols and clouds.
- ❑ Atmospheric constituents include the metal atoms coming from meteor ablation (such as Na, Fe, K, Ca, Li, Mg, etc), the water vapor H_2O , ozone O_3 , carbon dioxide CO_2 , and many other molecular species coming from natural or anthropogenic sources, such as NO_x , CO, CFC, CH_4 , SO_2 , Cl_2 , HCl, NH_3 , etc. Some other species, like O and He in thermosphere and N_2^+ occurring in aurora, are also constituents that we may consider.
- ❑ In the middle and upper atmosphere (75–120 km), the metal atoms (such as Na, Fe, K, Ca, Li, Mg, etc) are excellent trace gases so that we can measure the temperature, wind, waves, and chemistry in this region through inquiring the spectrum of the atomic resonance fluorescence.
- ❑ In thermosphere (150 km and above), the O and He atoms could provide a trace to monitor the temperature and wind in thermosphere.
- ❑ N_2^+ could also help us to extend into thermosphere, but only possible in polar regions when aurora occurs.
- ❑ The best technique to achieve vertical profile of the constituent density, temperature and wind is the resonance fluorescence lidar technique.

Mesospheric Metal Atoms



These metal atoms are believed to come from meteor ablation.

	Central Wavelength λ_0 (nm)	Atomic Mass (10^{-26} kg)	A_{21} (10^8 s^{-1})	Doppler rms width σ_D (MHz)	Peak cross-section σ_0 (10^{-16} m^2)	Oscillator strength f
K (D_1)	770.1088	6.4923	0.382	267.90	13.42	0.3395
Na (D_2)	589.1583	3.8177	0.616	456.54	14.87	0.6411
Ca	422.793	6.6556	2.18	481.96	38.48	1.7516
Ca ⁺	393.777	6.6556	1.47	517.87	13.94	0.6820
Fe	372.0993	9.2738	0.163	463.79	0.944	0.0413

Motivations Cont'd

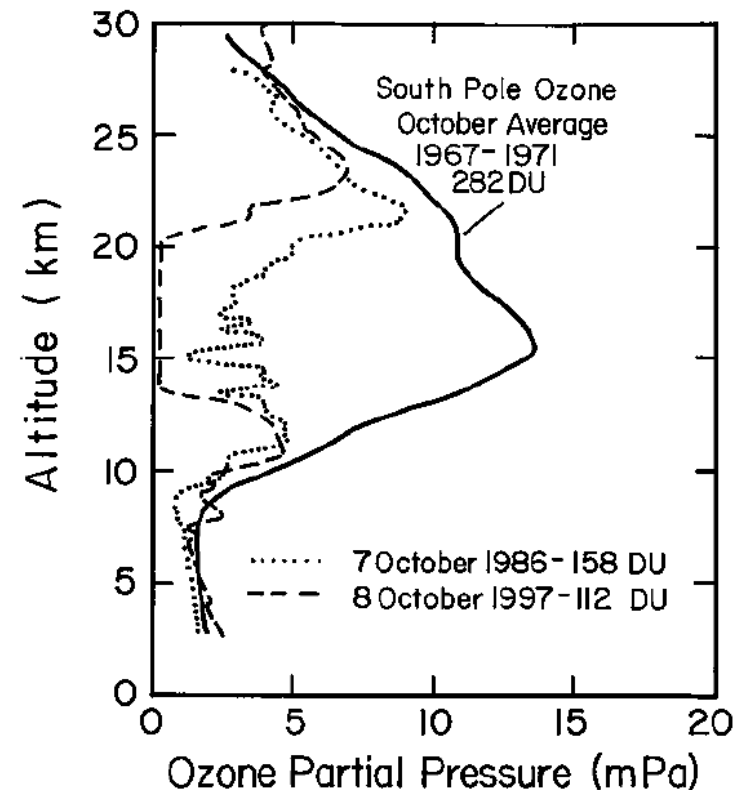
- ❑ The importance of water vapor in the atmosphere can hardly be overestimated. Water vapor is the most important greenhouse gas, much more effective than CO_2 . It governs the atmospheric water cycle which is the basis for life on earth, and it is a key component in atmospheric chemistry. The frequent occurrence of phase transitions from vapor to liquid water or ice crystals further enhances the importance of atmospheric humidity.
- ❑ Cloud formation and the various forms of precipitation certainly belong to the most important weather phenomena. The strong temperature dependence of the saturation vapor pressure in combination with vertical transport processes causes a large variability of the atmospheric humidity which exists on practically all scales from turbulence to global distribution.
- ❑ The observation capabilities for atmospheric water vapor are clearly insufficient. Most routine observations are still made using *in situ* sensors on radiosondes, either at small number of ground stations worldwide, or from aircraft, helicopters, balloons, or kites. All these have serious limitations especially for vertical profiling. Retrievals from spaceborne passive sensors (radiometer) can provide some information, but vertical resolution in particular is insufficient in view of the frequent occurrence of strong vertical gradients.
- ❑ Two lidar techniques can provide the required information on the water vapor vertical distribution with the necessary vertical and temporal resolution: Raman lidar and differential absorption lidar (DIAL).

Motivations Cont'd

❑ Majority of the atmospheric constituents considered here are related to air pollution and global climate change. Most of them are of natural or anthropogenic origin, but CFC (chlorofluorocarbons) are only generated by human activities. CFC is responsible to ozone depletion!

❑ Some of these gases play a crucial role in the earth's radiative balance and atmospheric chemistry, e.g., O_3 . Stratospheric ozone absorbs UV sunlight, so acts as a heating source in the stratosphere and a barrier to protect life on earth from harmful UV light. Tropospheric ozone is an important greenhouse gas due to its strong IR absorption band. Ozone is the main driver of the photochemical processes and contributes to the recycling of most of the natural and anthropogenic gases. Tropospheric ozone has direct effect on human health and causes significant losses in agriculture.

❑ Two lidar techniques can provide high resolution measurements of ozone: Raman lidar and DIAL (or Raman DIAL).



Pollutant Gases in Earth Atmosphere

Note: the absorption cross-sections of molecules are about 6 orders of magnitude smaller than the metal atoms such as Na, Fe, K .

Table 4.1 Absorption Cross Section of Pollutant Gases at Wavelengths Suitable for DIAL Measurement in the Troposphere

Molecule	Typical Wavelength	Laser (Examples)	Absorption Cross Section (10^{-18} cm^2)
Nitric oxide, NO	226.8 nm	Dye	4.6
Benzene, C ₆ H ₆	252.9 nm	Dye	5.7
Mercury, Hg	253.65 nm	Dye	3.3×10^4
Toluene, C ₇ H ₈	266.9 nm	Dye, Ti:Sa	2.8
Ozone, O ₃	266.0 nm	Dye, Nd:YAG-IV	9.49
	289.0 nm	Raman D ₂	1.59
	299.0 nm	Raman H ₂	0.42
Formaldehyde, CH ₂ O	286.5 nm	Dye, Ti:Sa	0.068
Sulfur dioxide, SO ₂	300.0 nm	Dye, Ti:Sa	1.3
Chlorine, Cl ₂	330.0 nm	Dye, XeCl + Raman cell	0.26
Nitrous acid, HONO	354.0 nm	Dye, Ti:Sa	0.50
Nitrogen dioxide, NO ₂	448.1 nm	Dye	0.69
Methane, CH ₄	3.270 μm	OPO	2.0
	3.391 μm		0.6
Propane, C ₃ H ₈	3.391 μm	OPO	0.8
Hydrogen chloride, HCl	3.636 μm	DF, OPO	0.20
Methane, CH ₄	3.715 μm	DF, OPO	0.002
Sulfur dioxide, SO ₂	3.984 μm	DF, OPO	0.42
Carbon monoxide, CO	4.709 μm	CO ₂	2.8
	4.776 μm		0.8
Nitric oxide, NO	5.215 μm	CO	0.67
	5.263 μm	CO ₂	0.6
Propylene, C ₃ H ₆	6.069 μm	CO	0.09
1,3-Butadiene, C ₄ H ₆	6.215 μm	CO	0.27
Nitrogen dioxide, NO ₂	6.229 μm	CO	2.68
Sulfur dioxide, SO ₂	9.024 μm	CO ₂	0.25
Freon-11, CCl ₃ F	9.261 μm	CO ₂	1.09
Ozone, O ₃	9.505 μm	CO ₂	0.45
	9.508 μm		0.9
Fluorocarbon-113, C ₂ Cl ₃ F ₃	9.604 μm	CO ₂	0.77
Benzene, C ₆ H ₆	9.621 μm	CO ₂	0.07
MMH, CH ₃ N ₂ H ₃	10.182 μm	CO ₂	0.06
Ethyl mercaptan, C ₂ H ₅ SH	10.208 μm	CO ₂	0.02
Chloroprene, C ₄ H ₅ Cl	10.261 μm	CO ₂	0.34
Monochloroethane, C ₂ H ₅ Cl	10.275 μm	CO ₂	0.12
Ammonia, NH ₃	10.333 μm	CO ₂	1.0
Ethylene, C ₂ H ₄	10.533 μm	CO ₂	1.19
Sulfur hexafluoride, SF ₆	10.551 μm	CO ₂	30.3

Table 4.1 Absorption Cross Section of Pollutant Gases at Wavelengths Suitable for DIAL Measurement in the Troposphere—(Continued)

Molecule	Typical Wavelength	Laser (Examples)	Absorption Cross Section (10^{-18} cm^2)
Trichloroethylene, C ₂ HCl ₃	10.591 μm	CO ₂	0.49
1,2-Dichloroethane, C ₂ H ₄ Cl ₂	10.591 μm	CO ₂	0.02
Hydrazine, N ₂ H ₄	10.612 μm	CO ₂	0.18
Vinyl chloride, C ₂ H ₃ Cl	10.612 μm	CO ₂	0.33
UDMH, (CH ₃) ₂ N ₂ H ₂	10.696 μm	CO ₂	0.08
Fluorocarbon-12, CCl ₂ F ₂	10.719 μm	CO ₂	1.33
Perchloroethylene, C ₂ Cl ₄	10.742 μm	CO ₂	0.18
1-Butene, C ₄ H ₈	10.787 μm	CO ₂	0.13
Perchloroethylene, C ₂ Cl ₄	10.834 μm	CO ₂	1.14

Lidar Detection of Constituents

Detection of constituents must be some kind of spectroscopy methods, i.e., spectral information is needed to identify special species – **fingerprints**. Usually, special laser frequency is required to perform such detection.

❑ **Metal atoms in the middle and upper atmosphere, Helium and N_2^+ in thermosphere:** density, abundance, temporal and spatial distributions, diurnal, seasonal and interannual variations; temperature, wind, waves

- resonance fluorescence lidar

❑ **Molecular species in lower stratosphere and troposphere:** H_2O , O_3 , NO_x , SO_2 , Cl_2 , C_6H_6 , C_7H_8 , VOC, HCl, SF_6 , NH_3 , etc

- Differential Absorption Lidar (DIAL)

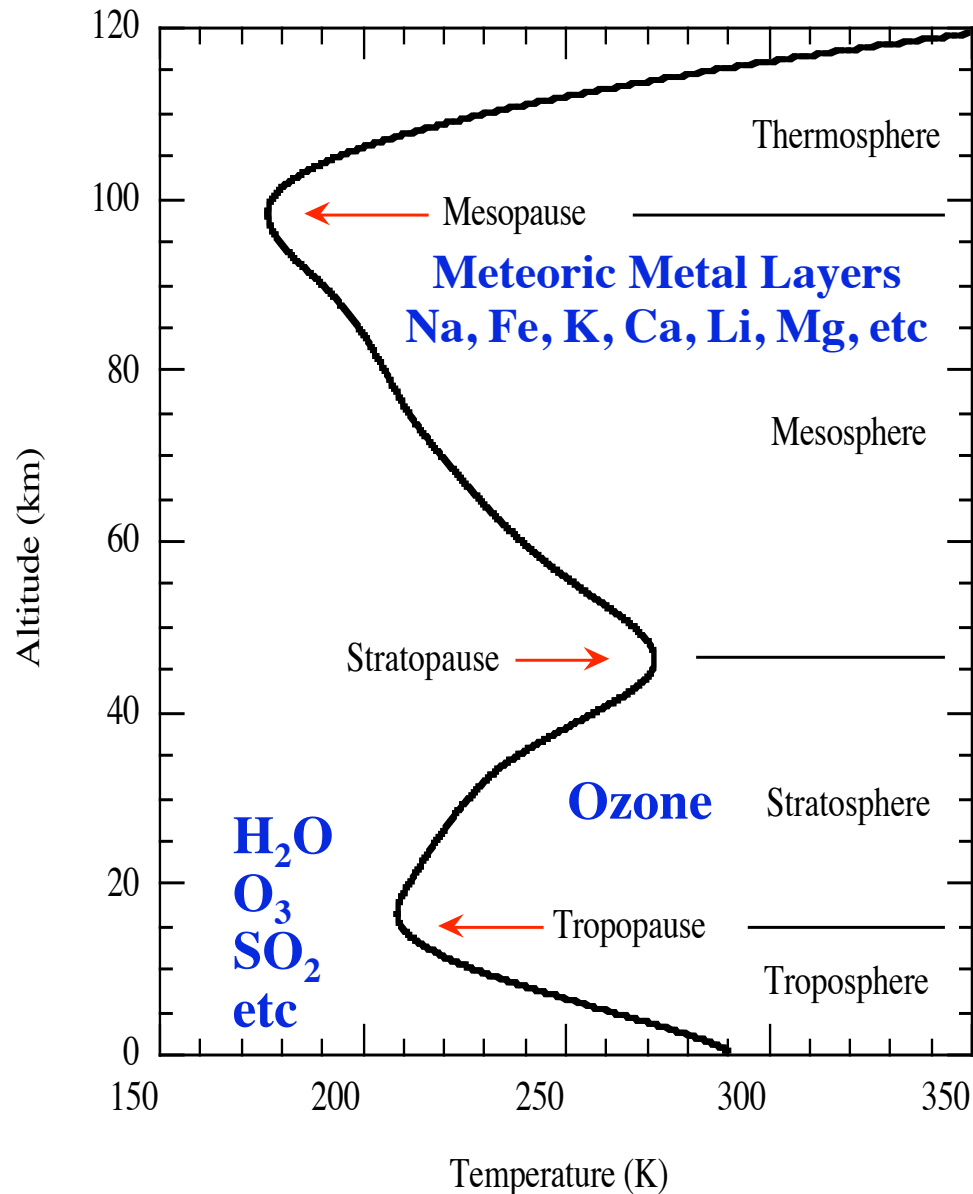
mainly Differential Absorption and Scattering Lidar (DAS)

- Raman Scattering Lidar

- Raman DIAL

- Multiwavelength DIAL

Constituent Lidar Techniques



- ❑ He and N₂⁺ in thermosphere: resonance fluorescence lidar
- ❑ O in thermosphere: resonance fluorescence lidar or DIAL from space
- ❑ Metal atoms in 75-120km: resonance fluorescence lidar (broadband or narrowband transmitter)
- ❑ Molecular species in lower stratosphere & troposphere: Differential absorption lidar (DIAL), Raman scattering lidar, Raman DIAL, Multi-channel DIAL

Resonance Fluorescence Lidar Equation

□ The fluorescence form of lidar equation:

$$N_S(\lambda, z) = \left(\frac{P_L(\lambda) \Delta t}{hc/\lambda} \right) \left(\sigma_{eff}(\lambda, z) n_c(z) R_B(\lambda) \Delta z \right) \left(\frac{A}{4\pi z^2} \right) \left(T_a^2(\lambda, z) T_c^2(\lambda, z) \right) \left(\eta(\lambda) G(z) \right) + N_B$$

□ Here, T_c is the transmission through the constituent layer, i.e., it is the light transmission after the extinction by constituent absorption.

$$T_c(z) = \exp\left(-\int_{z_{bottom}}^z \sigma_{eff}(\lambda, z') n_c(z') dz'\right) = \exp\left(-\int_{z_{bottom}}^z \alpha_c(\lambda, z') dz'\right)$$

□ Here, $\alpha_c(\lambda, z)$ is the extinction coefficient caused by the absorption.

$$\alpha_c(\lambda, z) = \sigma_{eff}(\lambda, z) n_c(z)$$

□ The Rayleigh scattering form of lidar equation:

$$N_R(\lambda, z_R) = \left(\frac{P_L(\lambda) \Delta t}{hc/\lambda} \right) \left(\sigma_R(\pi, \lambda) n_R(z_R) \Delta z \right) \left(\frac{A}{z_R^2} \right) T_a^2(\lambda, z_R) \left(\eta(\lambda) G(z_R) \right) + N_B$$

Solution for Resonance Fluorescence

□ Through Rayleigh normalization, we obtain the solution of the lidar equation (i.e., the constituent number density) as below

$$n_c(z) = n_R(z_R) \frac{N_S(\lambda, z) - N_B}{N_R(\lambda, z_R) - N_B} \cdot \frac{z^2}{z_R^2} \cdot \frac{4\pi\sigma_R(\pi, \lambda)}{\sigma_{eff}(\lambda)R_B(\lambda)} \cdot \frac{1}{T_c^2(\lambda, z)}$$

□ To introduce the lidar equation for DIAL, we make a format change to resonance fluorescence lidar equation using the relationship below

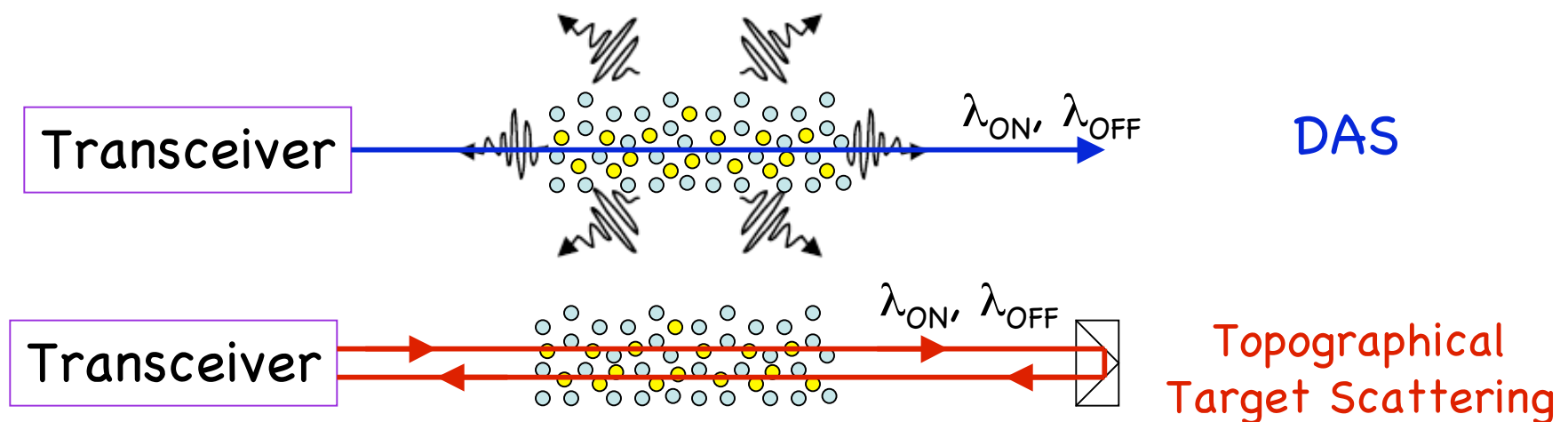
$$\beta_{resfluo}(\lambda, \lambda_L, R) = \frac{\sigma_{eff}(\lambda_L, R)}{4\pi} n_c(R) R_B(\lambda)$$

□ Therefore, the resonance fluorescence lidar equation can be written as

$$N_S(\lambda, z) = \left(\frac{P_L(\lambda)\Delta t}{hc/\lambda} \right) \left(\beta_{resfluo}(\lambda, z)\Delta z \right) \left(\frac{A}{z^2} \right) T_a^2(\lambda, z) \exp\left(-2 \int_{z_{bottom}}^z \sigma_{eff}(\lambda, z') n_c(z') dz' \right) \left(\eta(\lambda)G(z) \right) + N_B$$

Differential Absorption Lidar (DIAL)

- ❑ For the molecular species to be detected by DIAL, usually they have strong absorption, however, nearly none resonance fluorescence due to strong relaxation processes other than fluorescence (e.g., frequent collisions with surrounding atmosphere molecules can make molecules decay from excited states to ground state without giving fluorescence).
- ❑ Thus, in the lidar equation for DIAL, the influence of molecular species is in the extinction (atmosphere transmission) part, not in the backscatter part. In other words, the molecular absorption contributes to the extinction of light when incident light and scattered light propagate through atmosphere, while the return signals are from the scattering of laser light by air molecules and aerosols.



Lidar Equation for DIAL

□ DIAL lidar equation

$$P_S(\lambda, R) = P_L(\lambda) \left[\beta_{scatter}(\lambda, R) \Delta R \right] \left(\frac{A}{R^2} \right) \exp \left[-2 \int_0^R \bar{\alpha}(\lambda, r) dr \right] \\ \times \exp \left[-2 \int_0^R \sigma_{abs}(\lambda, r) n_c(r) dr \right] \left[\eta(\lambda) G(R) \right] + P_B$$

Extinction caused by interested constituent absorption

Extinction caused by other molecules and aerosols

□ Compared to resonance fluorescence, the main difference in DIAL is that the backscatter coefficient is from the elastic-scattering from air molecules and aerosols, not from the fluorescence of interested molecules.

$$\beta_{Scatter}(\lambda, R) = \beta_{aer}(\lambda, R) + \beta_{mol}(\lambda, R)$$

□ The parameter in the DIAL equation

$$\bar{\alpha}(\lambda, r) = \alpha_{aer}(\lambda, r) + \alpha_{mol}(\lambda, r) + \sigma_{IG}(\lambda, r) n_{IG}(r)$$

Aerosol Extinction

Air Molecule Extinction

Interference gas absorption

DIAL Equation Cont'd

❑ Notice that the constituent information is already included in the extinction part. If the lidar parameters and aerosol/air molecule backscatter and extinction are known, we can derive the constituent number density from the lidar equation directly.

❑ Unfortunately, most of these parameters are unknown. So the DIAL technique is to utilize two wavelengths - one tuned to strong molecular absorption and another one detuned off the absorption line. Thus, most of the parameters can be cancelled or estimated to a much better degree, allowing the constituent information to be derived more truthfully.

$$P_S(\lambda_{ON}, R) = P_L(\lambda_{ON}) \left[(\beta_{aer}(\lambda_{ON}, R) + \beta_{mol}(\lambda_{ON}, R)) \Delta R \right] \left(\frac{A}{R^2} \right) \exp \left[-2 \int_0^R (\alpha_{aer}(\lambda_{ON}, r) + \alpha_{mol}(\lambda_{ON}, r)) dr \right] \\ \times \exp \left[-2 \int_0^R \sigma_{IG}(\lambda_{ON}, r) n_{IG} dr \right] \exp \left[-2 \int_0^R \sigma_{abs}(\lambda_{ON}, r) n_c(r) dr \right] \left[\eta(\lambda_{ON}) G(R) \right] + P_B$$

$$P_S(\lambda_{OFF}, R) = P_L(\lambda_{OFF}) \left[(\beta_{aer}(\lambda_{OFF}, R) + \beta_{mol}(\lambda_{OFF}, R)) \Delta R \right] \left(\frac{A}{R^2} \right) \exp \left[-2 \int_0^R (\alpha_{aer}(\lambda_{OFF}, r) + \alpha_{mol}(\lambda_{OFF}, r)) dr \right] \\ \times \exp \left[-2 \int_0^R \sigma_{IG}(\lambda_{OFF}, r) n_{IG} dr \right] \exp \left[-2 \int_0^R \sigma_{abs}(\lambda_{OFF}, r) n_c(r) dr \right] \left[\eta(\lambda_{OFF}) G(R) \right] + P_B$$

Solution for DIAL Equations

□ To derive solution for DIAL equations, we take the ratio between the ON and OFF wavelength equations and take the logarithm of the ratio:

$$\ln \left[\frac{P_S(\lambda_{ON}, R) - P_B}{P_S(\lambda_{OFF}, R) - P_B} \right] = \ln \left[\frac{P_L(\lambda_{ON}) (\beta_{aer}(\lambda_{ON}, R) + \beta_{mol}(\lambda_{ON}, R)) \eta(\lambda_{ON})}{P_L(\lambda_{OFF}) (\beta_{aer}(\lambda_{OFF}, R) + \beta_{mol}(\lambda_{OFF}, R)) \eta(\lambda_{OFF})} \right]$$
$$- 2 \int_0^R [\alpha_{aer}(\lambda_{ON}, r) - \alpha_{aer}(\lambda_{OFF}, r)] dr$$
$$- 2 \int_0^R [\alpha_{mol}(\lambda_{ON}, r) - \alpha_{mol}(\lambda_{OFF}, r)] dr$$
$$- 2 \int_0^R [\sigma_{IG}(\lambda_{ON}, r) - \sigma_{IG}(\lambda_{OFF}, r)] n_{IG} dr$$
$$- 2 \int_0^R [\sigma_{abs}(\lambda_{ON}, r) - \sigma_{abs}(\lambda_{OFF}, r)] n_c(r) dr$$

□ Note: several factors have been eliminated from the equation: ΔR , A/R^2 , $G(R)$, as the ON and OFF wavelength laser lights are transmitted and received through the same transmitter and receiver, so share the same geometry factor and the same receiver aperture.

Solution for DIAL Cont'd

□ Take the differentiation of the equation, we obtain the number density of the constituent that we are interested in

$$n_c(R) = \frac{1}{2\Delta\sigma_{abs}} \frac{d}{dR} \left\{ \begin{array}{l} \ln \left[\frac{P_S(\lambda_{OFF}, R) - P_B}{P_S(\lambda_{ON}, R) - P_B} \right] \\ - \ln \left[\frac{P_L(\lambda_{OFF})\eta(\lambda_{OFF})}{P_L(\lambda_{ON})\eta(\lambda_{ON})} \right] \\ - \ln \left[\frac{\beta_{aer}(\lambda_{OFF}, R) + \beta_{mol}(\lambda_{OFF}, R)}{\beta_{aer}(\lambda_{ON}, R) + \beta_{mol}(\lambda_{ON}, R)} \right] \end{array} \right\} \quad \begin{array}{l} \text{---} \text{A} \\ \text{---} \text{B} \\ \text{---} \text{C} \end{array}$$

$$- \frac{1}{\Delta\sigma_{abs}} \left\{ \begin{array}{l} [\alpha_{aer}(\lambda_{ON}, R) - \alpha_{aer}(\lambda_{OFF}, R)] \\ + [\alpha_{mol}(\lambda_{ON}, R) - \alpha_{mol}(\lambda_{OFF}, R)] \\ + [\sigma_{IG}(\lambda_{ON}, R) - \sigma_{IG}(\lambda_{OFF}, R)]n_{IG} \end{array} \right\} \quad \begin{array}{l} \text{---} \text{D} \\ \text{---} \text{E} \\ \text{---} \text{F} \end{array}$$

□ Here, the $\Delta\sigma_{abs}$ is called the differential absorption cross-section

$$\begin{aligned} \Delta\sigma_{abs}(R) &= \sigma_{abs}(\lambda_{ON}, R) - \sigma_{abs}(\lambda_{OFF}, R) \\ &= \sigma_{abs}(\lambda_{ON}) - \sigma_{abs}(\lambda_{OFF}) \end{aligned}$$

DIAL Solution in Simple Case

□ In the case that the ON and OFF wavelengths have small separation, the laser power, lidar efficiency, aerosol/molecule backscatter coefficient and extinction coefficient are close to be the same for the ON and OFF wavelengths. Therefore, terms B-E are zero. Also, assume there is no interference gas present, so term F is zero. Then we have

$$n_c(R) = \frac{1}{2\Delta\sigma_{abs}} \frac{d}{dR} \left\{ \ln \left[\frac{P_S(\lambda_{OFF}, R) - P_B}{P_S(\lambda_{ON}, R) - P_B} \right] \right\}$$

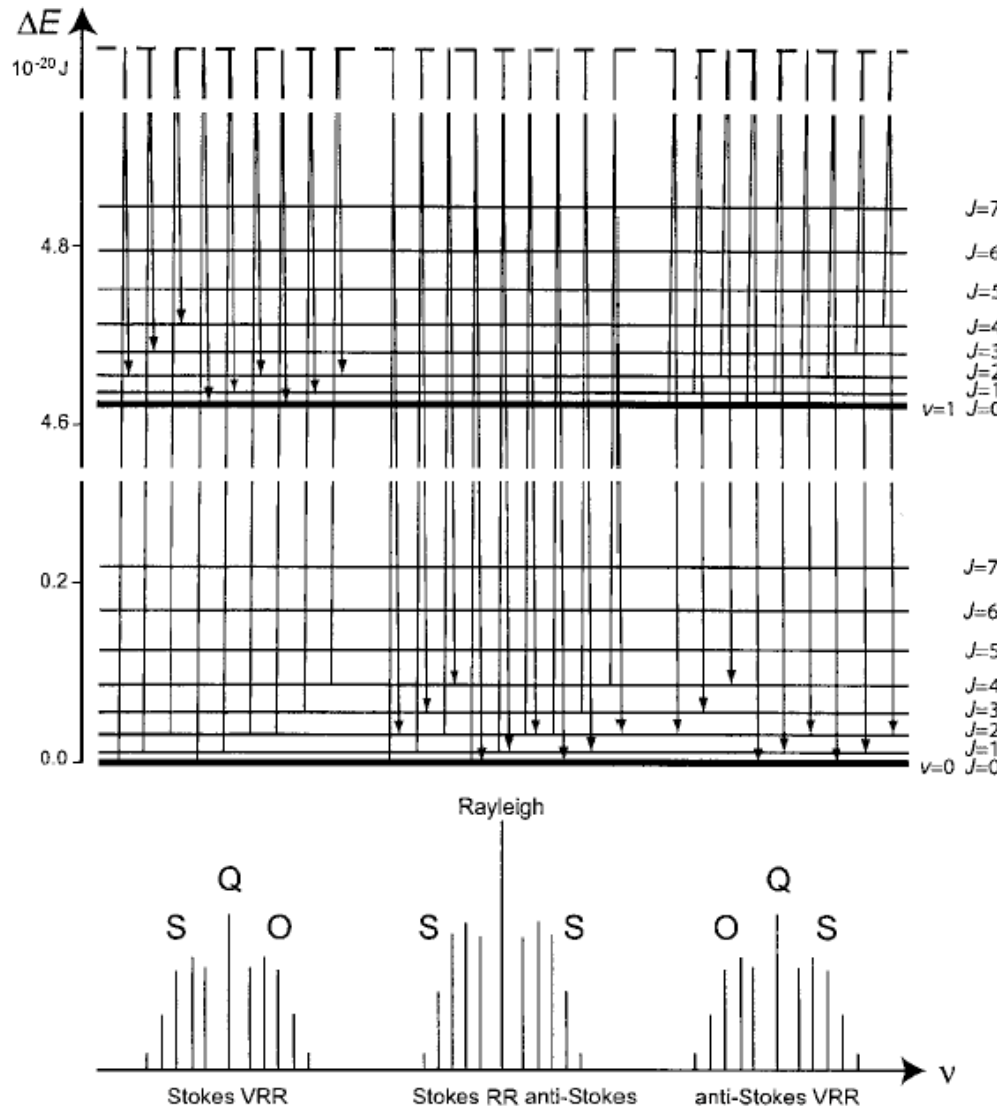
□ In practice, lidar signals are not recorded or analyzed as continuous functions, but rather as values in discrete range bins. Thus, the above solution should be expressed in terms of a range increment ΔR :

$$n_c(R) = \frac{1}{2\Delta\sigma_{abs}\Delta R} \ln \left[\frac{P_S(\lambda_{OFF}, R + \Delta R) - P_B}{P_S(\lambda_{ON}, R + \Delta R) - P_B} \cdot \frac{P_S(\lambda_{ON}, R) - P_B}{P_S(\lambda_{OFF}, R) - P_B} \right]$$

□ Number density average between range R_1 and R_2

$$n_c = \frac{1}{2\Delta\sigma_{abs}\Delta R} \ln \left[\frac{P_S(\lambda_{OFF}, R_2) - P_B}{P_S(\lambda_{ON}, R_2) - P_B} \cdot \frac{P_S(\lambda_{ON}, R_1) - P_B}{P_S(\lambda_{OFF}, R_1) - P_B} \right]$$

Raman Scattering (Inelastic)



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

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

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.

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

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

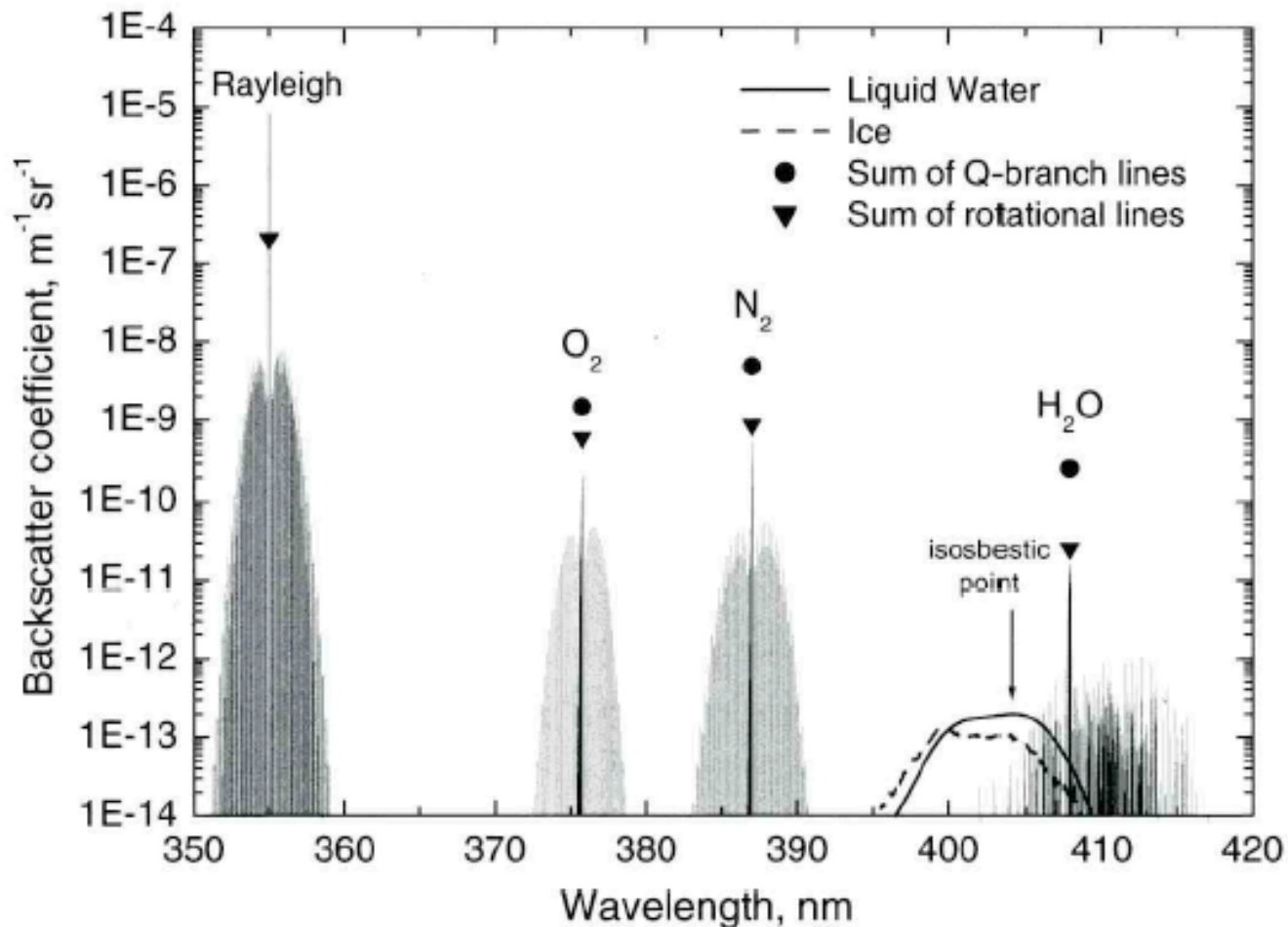


Fig. 9.2. Raman backscatter spectrum of the atmosphere for an incident laser wavelength of 355 nm, normal pressure, a temperature of 300 K, an N_2 and O_2 content of 0.781 and 0.209, respectively, and a water-vapor mixing ratio of 10 g/kg. The curves for liquid water and ice are arbitrarily scaled. The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

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

Extinction On the way up and on the way back

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

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

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

Constituent number density

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

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

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

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

$$\begin{aligned} r_m(R) &= \frac{M_c(R)}{M_{air}(R)} = \frac{M_c(R)}{M_{Ref}(R)} \frac{M_{Ref}}{M_{air}} = \frac{M_{Ref}}{M_{air}} \frac{m_c}{m_{Ref}} \frac{N_{cRa}(R)}{N_{RefRa}(R)} \\ &= \frac{M_{Ref}}{M_{air}} \frac{m_c}{m_{Ref}} \underbrace{\frac{\eta_{\lambda_{RefRa}}}{\eta_{\lambda_{cRa}}} \frac{\frac{d\sigma_{RefRa}}{d\Omega}(\pi, \lambda_0, \lambda_{cRa})}{\frac{d\sigma_{cRa}}{d\Omega}(\pi, \lambda_0, \lambda_{RefRa})}}_{\text{Calibration Constant } C} \frac{P_{cRa}(R, \lambda_{cRa})}{P_{RefRa}(R, \lambda_{RefRa})} \frac{\exp\left\{-\int_0^R \alpha(r, \lambda_{RefRa}) dr\right\}}{\exp\left\{-\int_0^R \alpha(r, \lambda_{cRa}) dr\right\}} \end{aligned}$$

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.

Summary

- ❑ Atmospheric constituents are important trace gases that are closely related to global climate change, air quality and pollution, atmosphere energy budget, atmospheric thermal structure, dynamics, and chemistry.
- ❑ Lidar techniques provide one of the best ways to monitor atmospheric constituents with high resolution and accuracy.
- ❑ Resonance fluorescence lidar, differential absorption lidar, and Raman lidar are the most promising techniques for constituent measurements, all providing spectral information to distinguish constituent species.
- ❑ DIAL involves lots of parameters in its lidar equation. For simple case where the ON and OFF wavelengths have small separation, the problem can be dramatically simplified. More considerations are required when dealing with other cases.
- ❑ The essential point for Raman lidar is to detect the specific spectra of interested species while avoiding 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.