Lecture 37. Constituent Lidar (1)
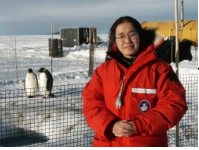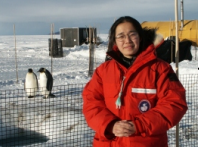
❑ Motivations to study atmosphere constituents

❑ Lidar detection of atmospheric constituents

(spectroscopic signatures to distinguish species)

➢ Metal atoms by resonance fluorescence lidar

➢ Raman Lidar detection of molecules and pollutant

(Raman Equation and Solution)

➢ DIAL detection of molecules and pollutant
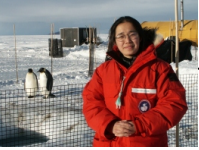
(DIAL Equation and Solution)

❑ Summary

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), hydroxyl radical OH, 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.

❑ Although they are usually referred to as "minor species", they are very important to the climate and weather on the Earth as well as to human's health and survival on the Earth.

❑ Some of these constituents provide tracers for lidar to monitor thermal structure and wind dynamics of the whole atmosphere.

Motivations to Study Constituents

❑ 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.

❑ The discovery of neutral metal Fe atoms well into the thermosphere by lidar observations at McMurdo provides a new potential for extending lidar detection of neutral atmosphere wind, temperature and species into the thermosphere, especially in the altitude range of 100–200 km.

❑ O and He atoms could be used as tracers to monitor the temperature and wind in the thermosphere. Atomic O itself is one of the most important minor species in the atmospheric chemistry.

❑ N_2^+ could also help 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.
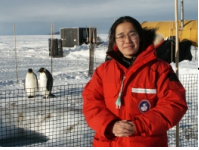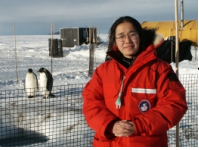
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Mesospheric Metal Atoms
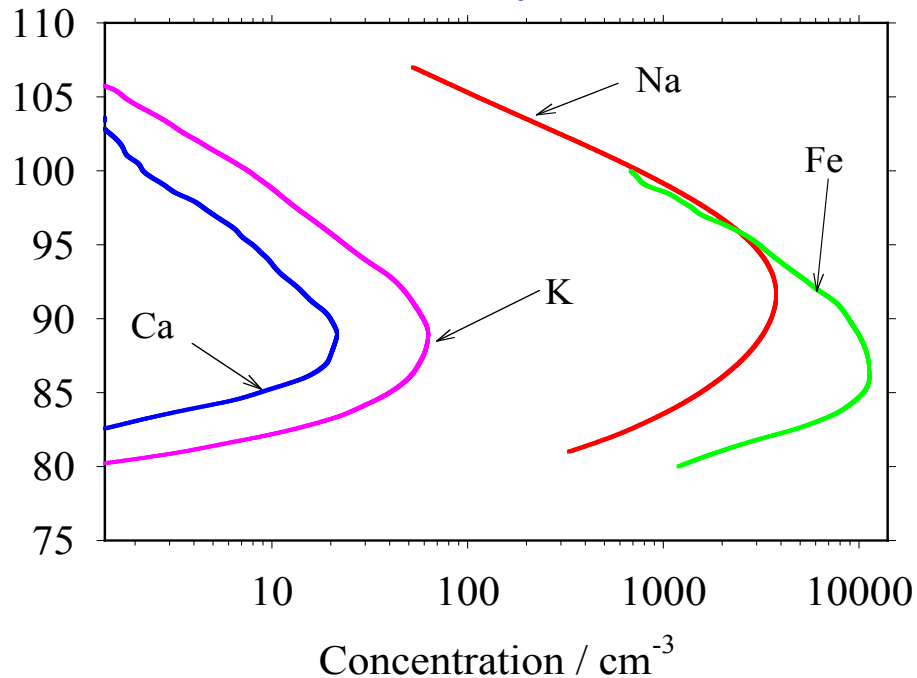
These metal atoms are believed to come from meteor ablation.

	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).

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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 for 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).
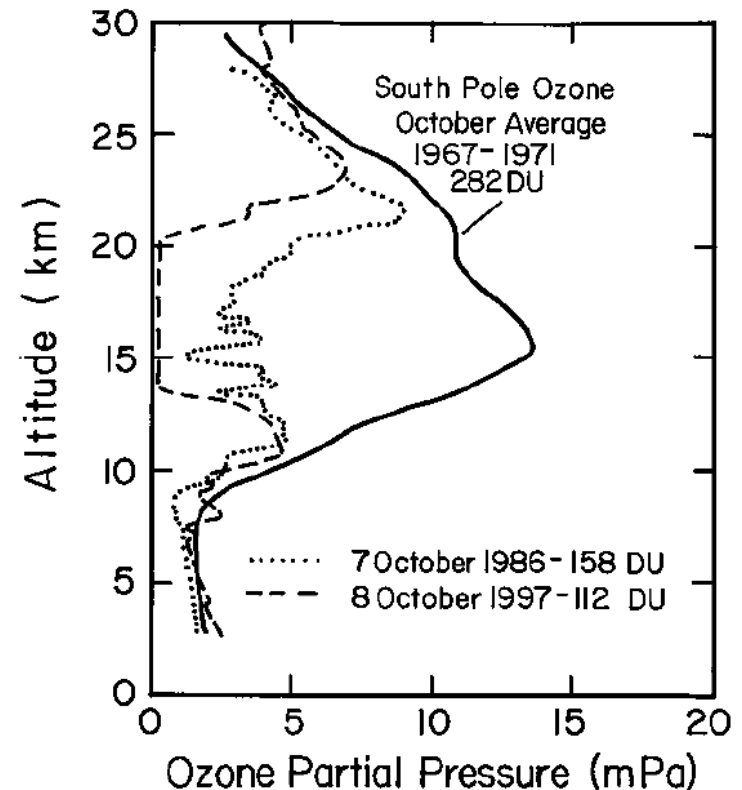
Pollutant Gases in Earth Atmosphere

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

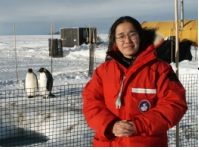| Molecule	Typical Wavelength	Laser (Examples)	Absorption Cross Section $(10^{-18}\,cm^2)$
Nitric oxide, NO	226.8 nm	Dye	4.6
Benzene, C_6H_6	252.9 nm	Dye	5.7
Mercury, Hg	253.65 nm	Dye	3.3×10^4
Toluene, C_7H_8	266.9 nm	Dye, Ti:Sa	2.8
Ozone, O_3	266.0 nm	Dye, Nd:YAG-IV	9.49
	289.0 nm	Raman D_2	1.59
	299.0 nm	Raman H_2	0.42
Formaldehyde, CH_2O	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	$3.270\,\mu m$	OPO	2.0
	$3.391\,\mu m$		0.6
Propane, C_3H_8	$3.391\,\mu m$	OPO	0.8
Hydrogen chloride, HCl	$3.636\,\mu m$	DF, OPO	0.20
Methane, CH_4	$3.715\,\mu m$	DF, OPO	0.002
Sulfur dioxide, SO_2	$3.984\,\mu m$	DF, OPO	0.42
Carbon monoxide, CO	$4.709\,\mu m$	CO_2	2.8
	$4.776\,\mu m$		0.8
Nitric oxide, NO	$5.215\,\mu m$	CO	0.67
	$5.263\,\mu m$	CO_2	0.6
Propylene, C_3H_6	$6.069\,\mu m$	CO	0.09
1,3-Butadiene, C_4H_6	$6.215\,\mu m$	CO	0.27
Nitrogen dioxide, NO_2	$6.229\,\mu m$	CO	2.68
Sulfur dioxide, SO_2	$9.024\,\mu m$	CO_2	0.25
Freon-11, CCl_3F	$9.261\,\mu m$	CO_2	1.09
Ozone, O_3	$9.505\,\mu m$	CO_2	0.45
	$9.508\,\mu m$		0.9
Fluorocarbon-113, $C_2Cl_3F_3$	$9.604\,\mu m$	CO_2	0.77
Benzene, C_6H_6	$9.621\,\mu m$	CO_2	0.07
MMH, $CH_3N_2H_3$	$10.182\,\mu m$	CO_2	0.06
Ethyl mercaptan, C_2H_5SH	$10.208\,\mu m$	CO_2	0.02
Chloroprene, C_4H_5Cl	$10.261\,\mu m$	CO_2	0.34
Monochloroethane, C_2H_5Cl	$10.275\,\mu m$	CO_2	0.12
Ammonia, NH_3	$10.333\,\mu m$	CO_2	1.0
Ethylene, C_2H_4	$10.533\,\mu m$	CO_2	1.19
Sulfur hexafluoride, SF_6	$10.551\,\mu m$	CO_2	30.3

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—(Continued)
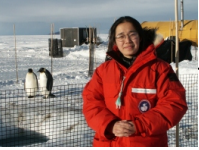
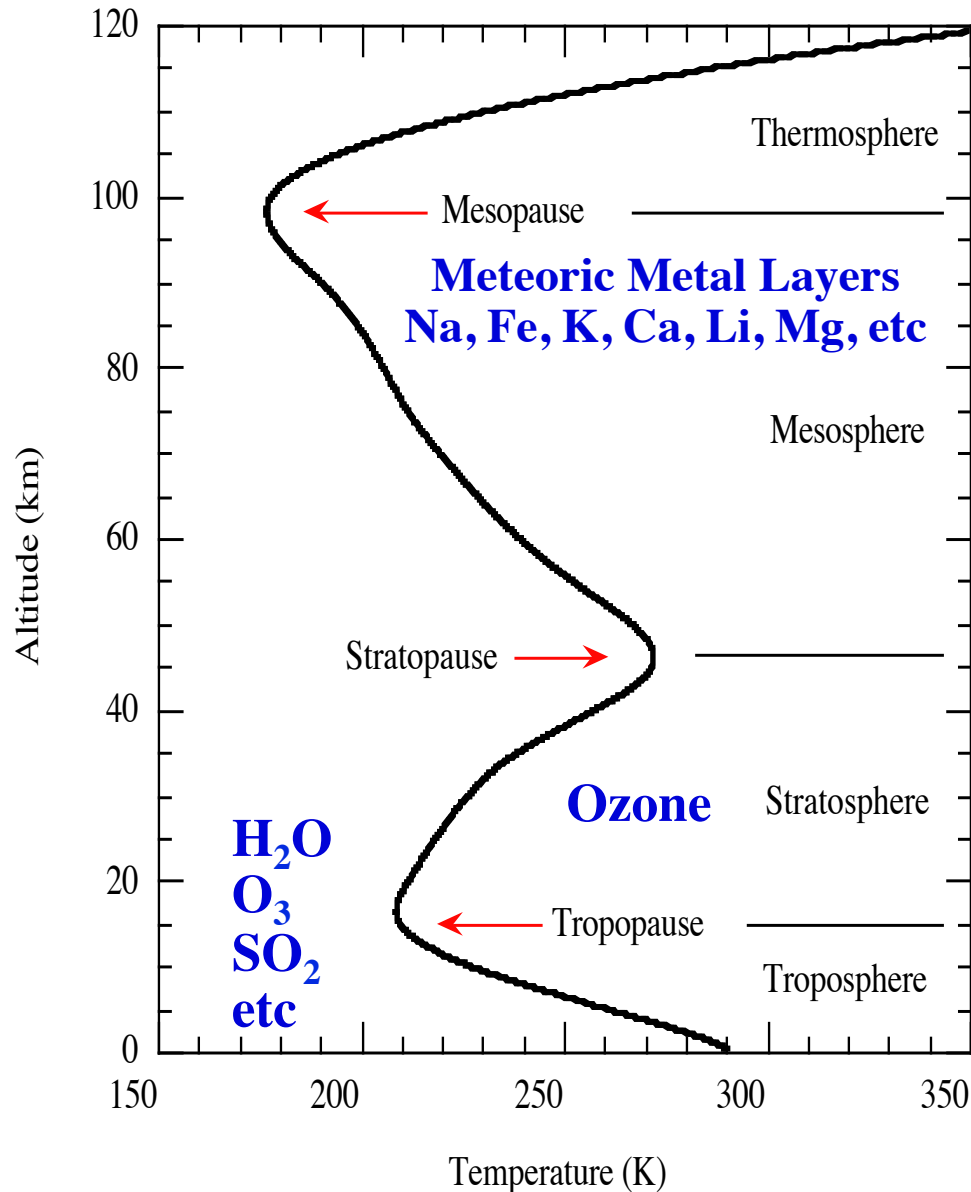| Molecule	Typical Wavelength	Laser (Examples)	Absorption Cross Section $(10^{-18}\,cm^2)$
Trichloroethylene, C_2HCl_3	$10.591\,\mu m$	CO_2	0.49
1,2-Dichloroethane, $C_2H_4Cl_2$	$10.591\,\mu m$	CO_2	0.02
Hydrazine, N_2H_4	$10.612\,\mu m$	CO_2	0.18
Vinyl chloride, C_2H_3Cl	$10.612\,\mu m$	CO_2	0.33
UDMH, $(CH_3)_2N_2H_2$	$10.696\,\mu m$	CO_2	0.08
Fluorocarbon-12, CCl_2F_2	$10.719\,\mu m$	CO_2	1.33
Perchloroethylene, C_2Cl_4	$10.742\,\mu m$	CO_2	0.18
1-Butene, C_4H_8	$10.787\,\mu m$	CO_2	0.13
Perchloroethylene, C_2Cl_4	$10.834\,\mu m$	CO_2	1.14

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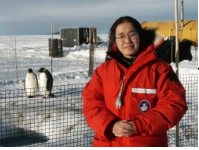
❑ Metal atoms in the middle and upper atmosphere, Helium, O and N_2^+ in thermosphere: density, abundance, temporal and spatial distributions, diurnal, seasonal and interannual variations; temperature, wind, waves

- 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
- Multiwavelength Raman DIAL

❑ New possibility: White-light lidar, laser frequency comb, etc.

Constituent Lidar Techniques

H$_2$O
O$_3$
SO$_2$
etc

Ozone

Meteoric Metal Layers
Na, Fe, K, Ca, Li, Mg, etc

Thermosphere

Mesopause

Mesosphere

Stratopause

Stratosphere

Tropopause

Troposphere

Altitude (km)

Temperature (K)

❑ Fe, He and N$_2^+$ 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 …

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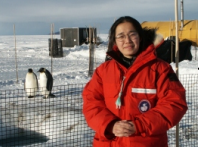
$$T_c(z) = \exp\left(-\int_{z_{bottom}}^{z}\sigma_{eff}(\lambda,z')n_c(z')\mathrm{d}z'\right) = \exp\left(-\int_{z_{bottom}}^{z}\alpha_c(\lambda,z')\mathrm{d}z'\right)$$

❑ 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:

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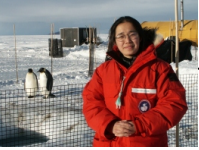
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Solution for Resonance Fluorescence

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

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

❏ Therefore, once the atmosphere number density $n_R(z_R)$ at the Rayleigh normalization altitude z_R is known, then the constituent number density will be determined from this solution.

❏ $n_R(z_R)$ is usually taken from an atmosphere model or independent measurement. Since atmosphere number density is relatively stable, such calibration is usually good within 10% accuracy.

❏ Detection of Ca^+ and Ca is a challenging task but essential to study the differential ablation of meteoroid. Nickel (Ni) can also be detected by lidar now [Collins et al., CEDAR, 2014].
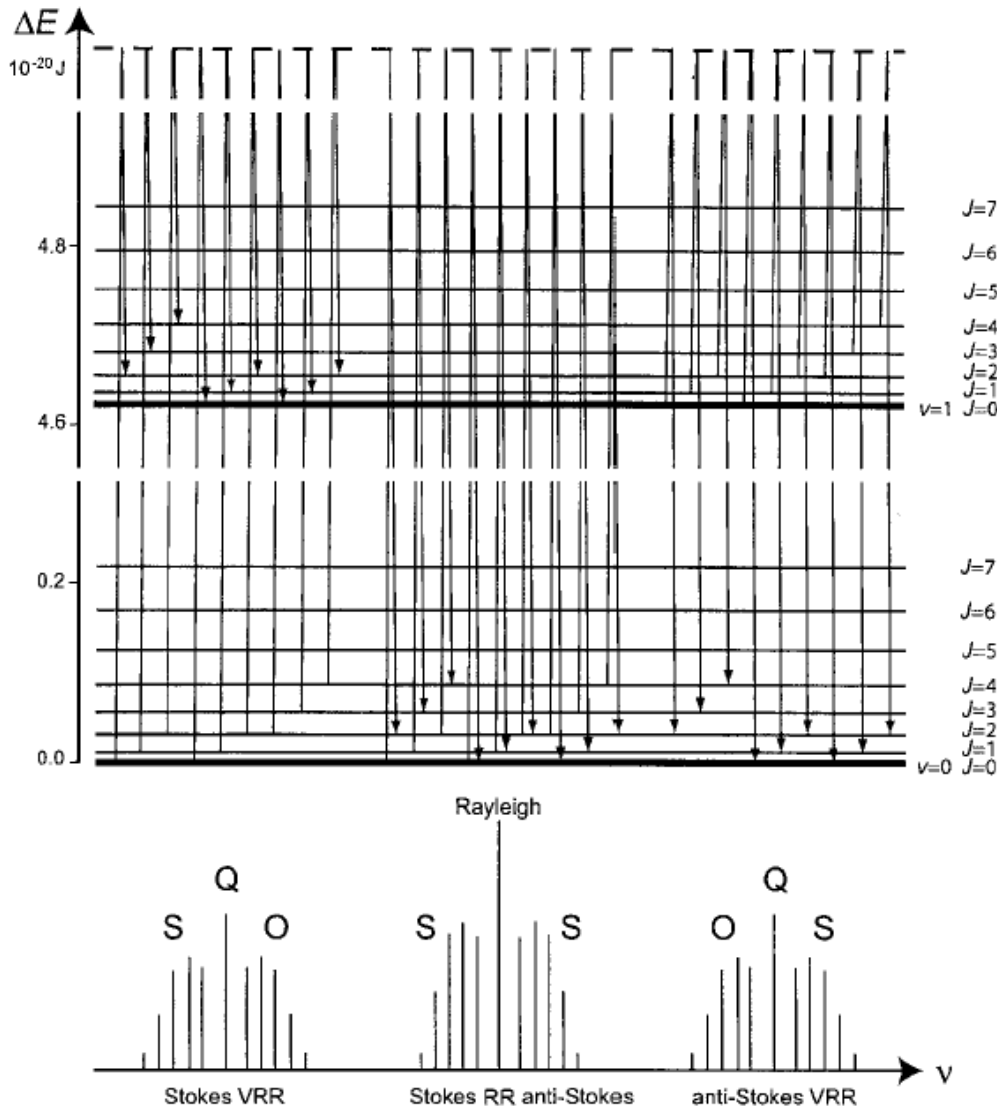
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Introduction of Raman Lidar

❑ Raman scattering is a very powerful spectroscopy tool to study many molecular structures and spectroscopy. As a result, the Raman lidar is very useful in constituent detection in the lower atmosphere. A good chapter describing Raman lidar is given by Dr. Ulla Wandinger of Leibniz Institute for Tropospheric Research, Germany. A scanned PDF of this chapter can be found at our class website.

❑ Raman lidars have become widely used instruments in atmospheric research, which have low demands concerning spectral purity of the emitted laser light and frequency stabilization of the receiver. However, it suffers from the low cross sections of Raman scattering and thus from the comparably small signal-to-noise ratios of the measurements.

❑ Raman measurements do not require specific laser wavelengths. Because of the wavelength dependence of the Raman scattering cross-section which is proportional to λ^{-4}, shorter laser wavelengths are preferred. Attenuation of the laser light by gas absorption, especially ozone, can be avoided if wavelengths longer than 320 nm are chosen. However, the solar-blind region below 300 nm has also been used for Raman lidar. Concerning measurement range, wavelengths of 320-550 nm are best suited for Raman applications.

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Raman Scattering (Inelastic)

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

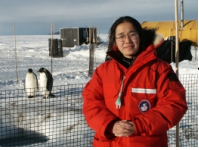$$\Delta k = k_i - k_s = \frac{\Delta E}{hc}$$

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

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.

$$\Delta v = 0, \pm 1 \text{ and } \Delta J = 0, \pm 2,$$

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Raman Scattering Frequency Shifts

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

❑ 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) 14
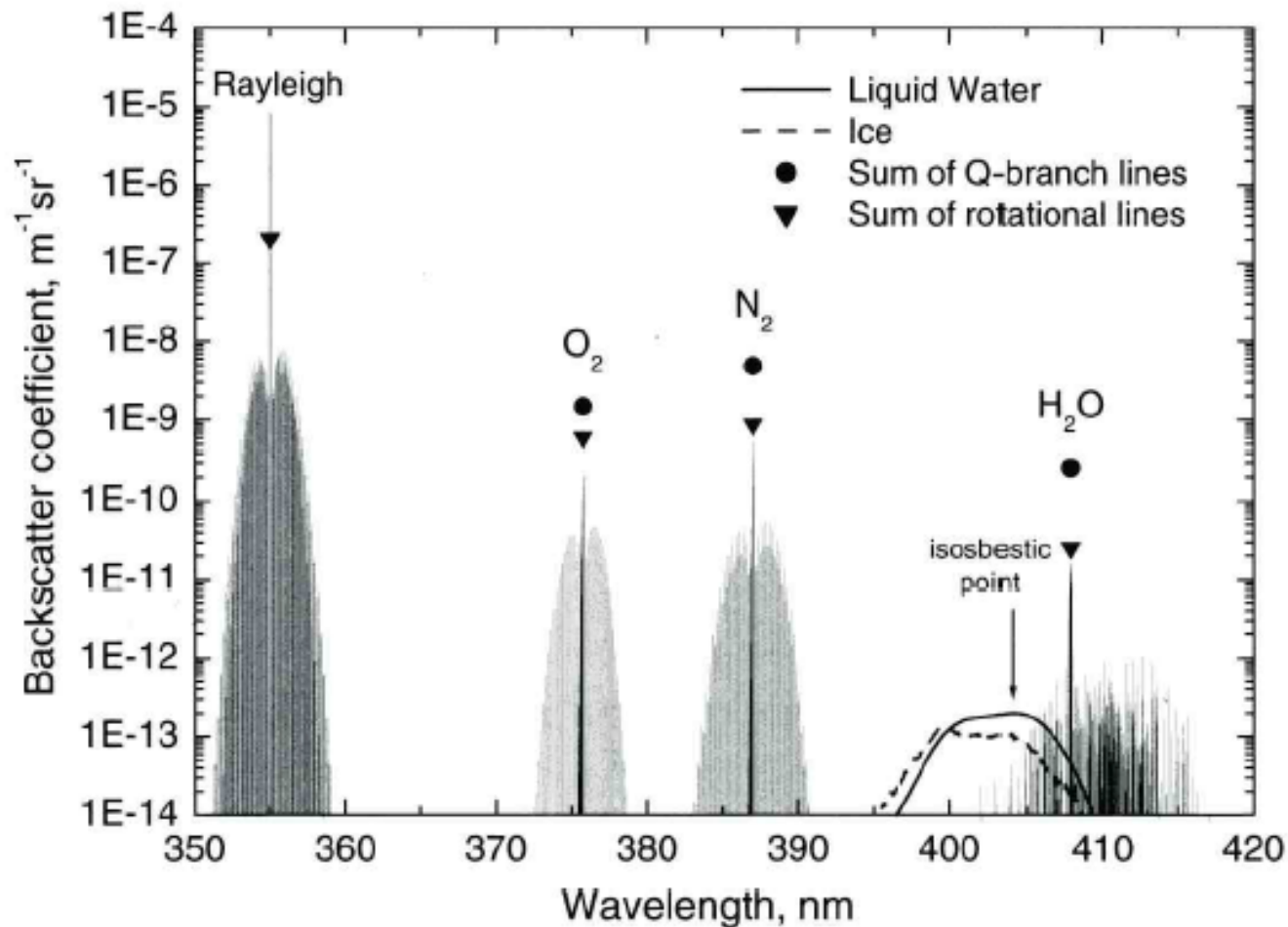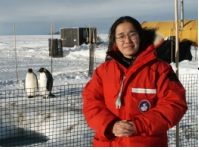
Raman Backscatter Spectrum

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.
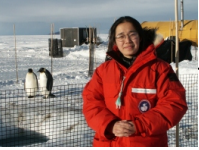
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Raman Lidar

Table 9.1. Overview of Raman lidar techniques. VRR – vibration–rotation Raman band, RR – rotational Raman band, SB – solar-blind spectral region

Measured quantity	Interacting molecule, Raman band used	Typical achievable measurement range
Water-vapor mixing ratio	H_2O (vapor), VRR (+ reference gas, VRR)	0–12 km (night) [16, 47] 0–5 km (day) [11, 47]
Extinction coefficient Backscatter coefficient Lidar ratio	N_2 or O_2, VRR or RR (+ elastic signal for back-scatter and lidar ratio)	0–30 km (night) [48] 0–10 km (day) [49]
Temperature	N_2 and/or O_2, RR	0–40 km (night) [19, 40] 0–12 km (day) [19]
Ozone concentration (Raman DIAL)	N_2 and/or O_2, VRR-VRR or RR-VRR	3–20 km (night) [46] 0–3 km (day SB) [29]
Other trace-gas concentrations	Specific gas, VRR (+ reference gas, VRR)	0–1 km (day and night) [32]
Liquid water	H_2O (liquid), VRR (+ reference gas, VRR)	0–4 km (night) [34]

[Ulla Wandinger, Raman Lidar chapter, 2005]
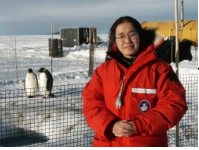
Fundamentals of Raman Scattering

❑ Raman scattering is an inelastic scattering and the Raman shift is characteristic for the scattering molecule. Using wavenumber $\tilde{\nu}=1/\lambda$, the Raman shift is given by

$$\Delta\tilde{\nu} = \tilde{\nu}_1 - \tilde{\nu}_s = \frac{\Delta E}{hc_0}$$

Where ΔE is the energy difference between the molecular energy levels involved in the Raman scattering.

Table 9.2. Molecular constants for the calculation of Raman frequency shifts of nitrogen and oxygen. The values for $\tilde{\nu}_{vib}$ consider an anharmonicity correction for the transition from the ground state to the first excited vibrational state (see Ref. [53], p. 125 and 182)

Gas	$\tilde{\nu}_{vib}$ cm^{-1}	B_0 cm^{-1}	B_1 cm^{-1}	D_0 cm^{-1}
N_2	2330.7	1.98957 [59]	1.97219 [59]	5.76×10^{-6} [59]
O_2	1556.4	1.43768 [58]	1.42188 [61]	4.85×10^{-6} [58]

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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

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

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

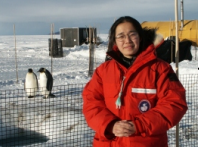$$\beta_{cRa}(R,\lambda_0,\lambda_{cRa}) = N_{cRa}(R) \frac{d\sigma_{cRa}}{d\Omega}(\pi,\lambda_0,\lambda_{cRa})$$

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

Constituent number density

Reference molecule number density

Raman backscatter cross-section

Neither constituent nor reference channel includes aerosol backscattering!

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Solution for Raman Lidar Equation

❑ Taking the ratio of the above two Raman lidar equations

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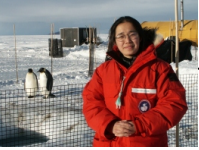frac{\exp\left\{-\int_0^R \alpha(r,\lambda_{cRa})dr\right\}}{\exp\left\{-\int_0^R \alpha(r,\lambda_{RefRa})dr\right\}}$$

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

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

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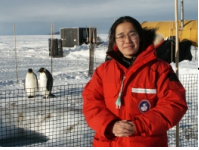
Calibration Constant C

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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. Air molecules can be calculated from model data. For aerosols, we will introduce Angstrom exponent. This factor a(R) is usually between 0-2, and normally 1. The error introduced by Angstrom factor is less than 10%.
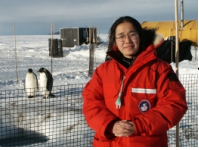
$$\alpha(R) = \alpha_{aer}(R) + \alpha_{mol}(R)$$

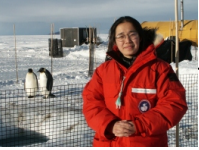$$\frac{\alpha_{aer}(\lambda_0)}{\alpha_{aer}(\lambda_{Ra})} = \left(\frac{\lambda_{Ra}}{\lambda_0}\right)^{a(R)}$$

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Considerations on Raman Applications

❑ 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.

Raman Lidar Technical Requirements

❑ Raman lidar has low Raman scattering cross section, so a high-power laser transmitter and a highly efficient receiving and detection system are required.

❑ Laser: no specific wavelength is needed, but ideal wavelengths are between 320 and 550 nm

❑ Beam expander: is to reduce the laser beam divergence in order to llow for a narrow telescope field of view, which will help to suppress background light and increase SNR. Usually go from 1 mrad to 0.1 mrad.

❑ Telescope: usually 0.5-1 m in diameter

❑ Receiver optics:

❑ Detectors and DAQ:

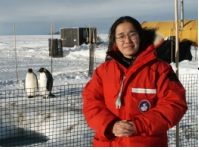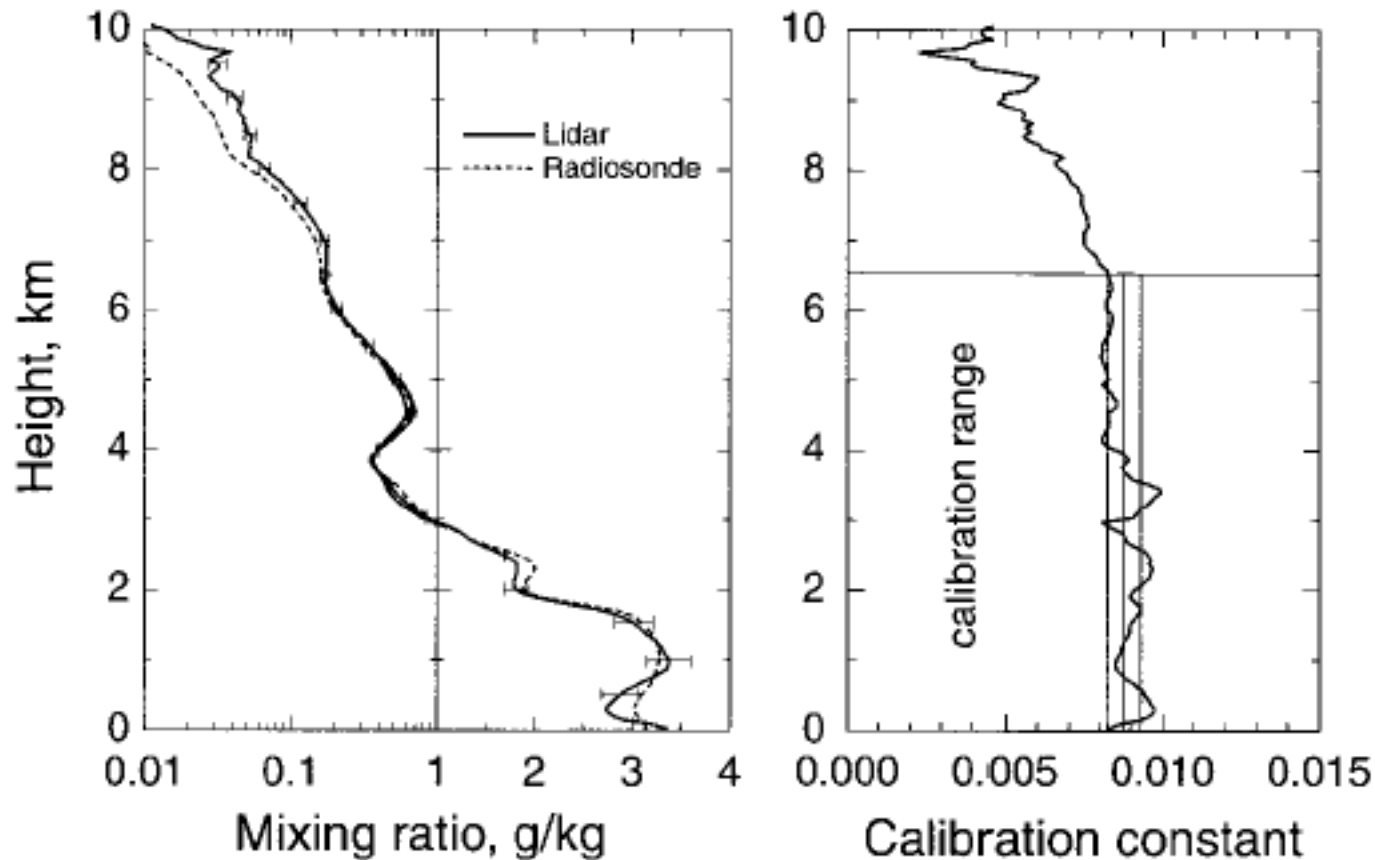# Water Vapor Raman Lidar Setup
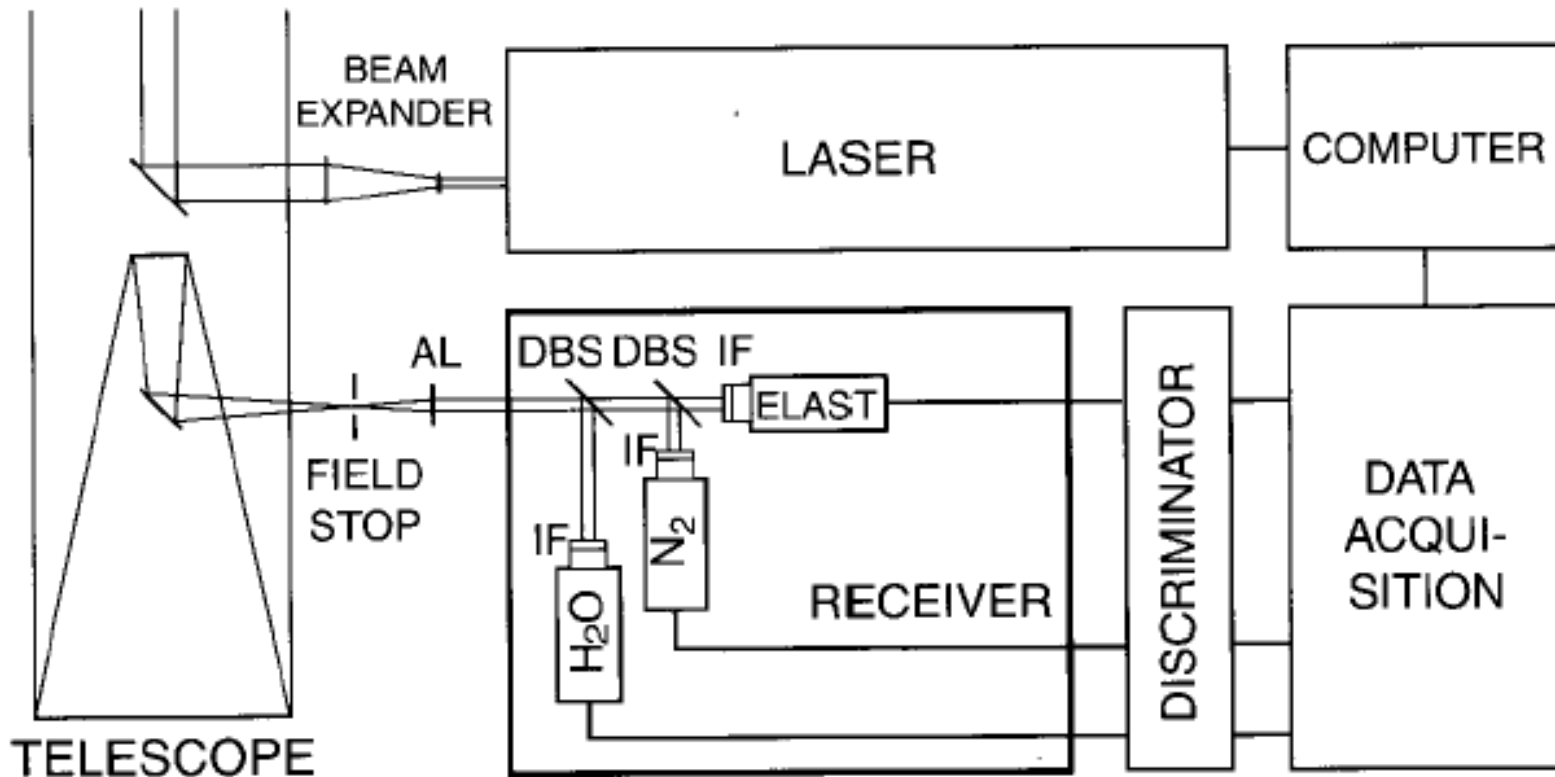
Fig. 9.3. Typical setup of a water-vapor and aerosol Raman lidar. AL – achromatic lens, IF – interference filter, DBS – dichroic beam splitter.
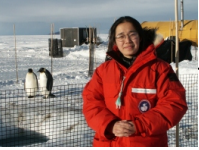
❑ Mixing ratio: two Raman channels: one is the return from the gas of interest and another is the return of a reference gas (N2 or O2).
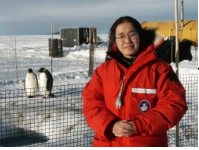
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Water Vapor Results by Raman Lidar

□ 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.

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.
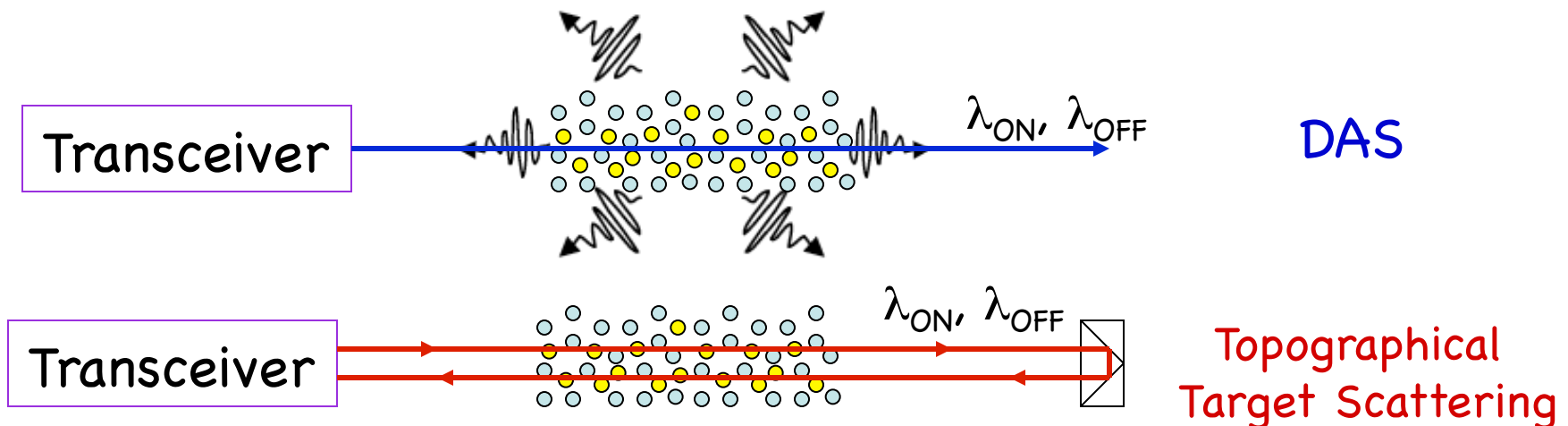
Lidar Equation for DIAL

❑ DIAL lidar equation

$$P_S(\lambda,R) = P_L(\lambda)\left[\beta_{scatter}(\lambda,R)\Delta R\right]\left(\frac{A}{R^2}\right)\exp\left[-2\int_0^R \overline{\alpha}(\lambda,r)dr\right]$$

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

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.

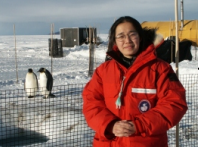$$\beta_{Scatter}(\lambda,R) = \beta_{aer}(\lambda,R) + \beta_{mol}(\lambda,R)$$

❑ The parameter in the DIAL equation

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

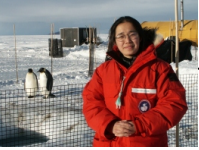Aerosol Extinction   Air Molecule Extinction   Interference gas absorption

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.

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

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

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

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

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:

$$
\ln\left[\frac{P_S(\lambda_{ON},R)-P_B}{P_S(\lambda_{OFF},R)-P_B}\right] = \ln\left[\frac{P_L(\lambda_{ON})\big(\beta_{aer}(\lambda_{ON},R)+\beta_{mol}(\lambda_{ON},R)\big)\eta(\lambda_{ON})}{P_L(\lambda_{OFF})\big(\beta_{aer}(\lambda_{OFF},R)+\beta_{mol}(\lambda_{OFF},R)\big)\eta(\lambda_{OFF})}\right]
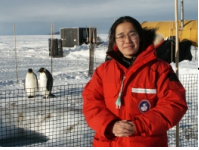$$

$$
-2\int_0^R\big[\alpha_{aer}(\lambda_{ON},r)-\alpha_{aer}(\lambda_{OFF},r)\big]dr
$$

$$
-2\int_0^R\big[\alpha_{mol}(\lambda_{ON},r)-\alpha_{mol}(\lambda_{OFF},r)\big]dr
$$

$$
-2\int_0^R\big[\sigma_{IG}(\lambda_{ON},r)-\sigma_{IG}(\lambda_{OFF},r)\big]n_{IG}\,dr
$$

$$
-2\int_0^R\big[\sigma_{abs}(\lambda_{ON},r)-\sigma_{abs}(\lambda_{OFF},r)\big]n_c(r)dr
$$

❑ Note: several factors have been eliminated from the equation: ΔR, A/R², G(R), as the ON and OFF wavelength laser lights are transmitted and received through the save transmitter and receiver, so share the same geometry factor and the same receiver aperture.
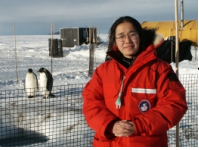
Solution for DIAL Cont'd

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

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

$$
-\ln\left[\frac{P_L(\lambda_{OFF})\eta(\lambda_{OFF})}{P_L(\lambda_{ON})\eta(\lambda_{ON})}\right] \quad \text{B}
$$

$$
\left. -\ln\left[\frac{\beta_{aer}(\lambda_{OFF},R)+\beta_{mol}(\lambda_{OFF},R)}{\beta_{aer}(\lambda_{ON},R)+\beta_{mol}(\lambda_{ON},R)}\right]\right\} \quad \text{C}
$$

$$
-\frac{1}{\Delta\sigma_{abs}} \left\{ \left[\alpha_{aer}(\lambda_{ON},R)-\alpha_{aer}(\lambda_{OFF},R)\right] \right. \quad \text{D}
$$

$$
+\left[\alpha_{mol}(\lambda_{ON},R)-\alpha_{mol}(\lambda_{OFF},R)\right] \quad \text{E}
$$

$$
\left. +\left[\sigma_{IG}(\lambda_{ON},R)-\sigma_{IG}(\lambda_{OFF},R)\right]n_{IG}\right\} \quad \text{F}
$$

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

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

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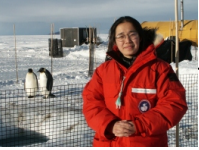
$$n_c(R) = \frac{1}{2\Delta\sigma_{abs}} \frac{d}{dR}\left\{\ln\left[\frac{P_S(\lambda_{OFF},R) - P_B}{P_S(\lambda_{ON},R) - P_B}\right]\right\}$$

❑ 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

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

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.

❑ 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.