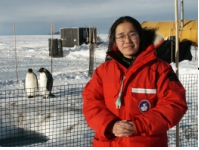


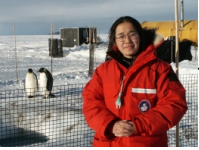
Lecture 43. Constituent Lidar (3)

- ❑ 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)
 - Laser induced Fluorescence, White-light lidar, Freq. comb
- ❑ Summary



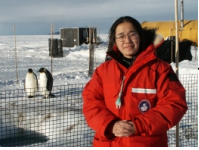
Motivations to Study Constituents

- ❑ 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 Fe, Mg, Na, K, Ca, Li, Ni, Al, AlO, etc), hydroxyl radical OH, water vapor H₂O, ozone O₃, carbon dioxide CO₂, and many other molecular species coming from natural or anthropogenic sources, such as NO_x, CO, CFC, CH₄, SO₂, Cl₂, HCl, NH₃, etc. Some other species, like O and He in thermosphere, and N₂⁺ occurring in aurora, are also constituents that we may consider. There could be organic molecules as well.
- ❑ 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.

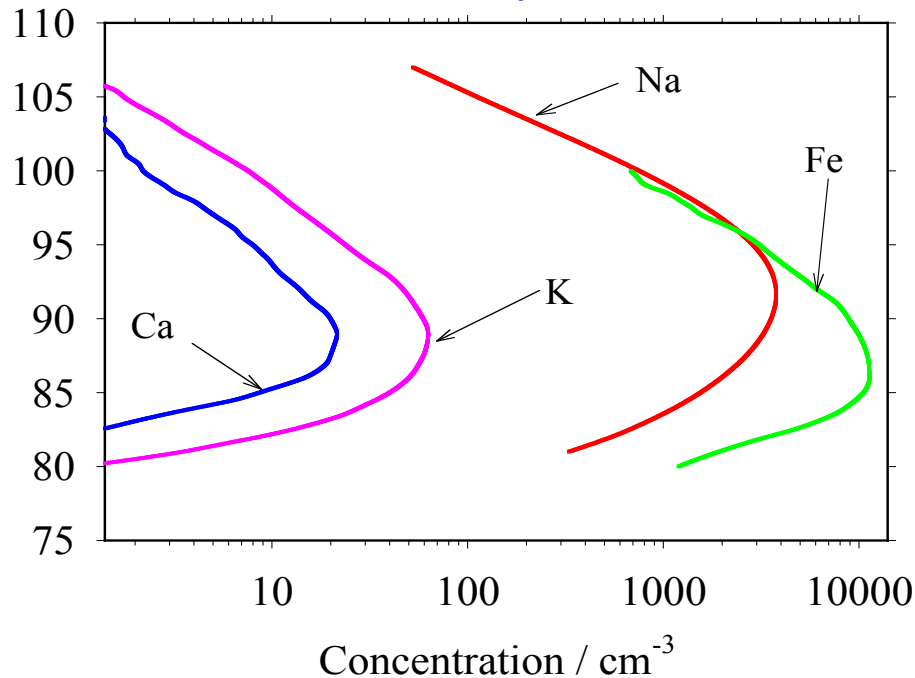


Motivations to Study Constituents

- ❑ In the middle and upper atmosphere (75–120–200 km), the metal atoms (such as Na, Fe, K, Ca, Li, Mg, Ni, 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 discoveries of neutral metal Fe, Na and K atoms well into the thermosphere by lidar observations at McMurdo and other locations in the world provide a new potential for extending lidar detection of neutral atmosphere wind, temperature and species into the thermosphere, especially at thermospheric altitudes 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.

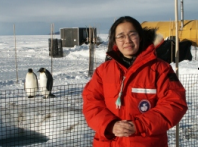


Mesospheric Metal Atoms

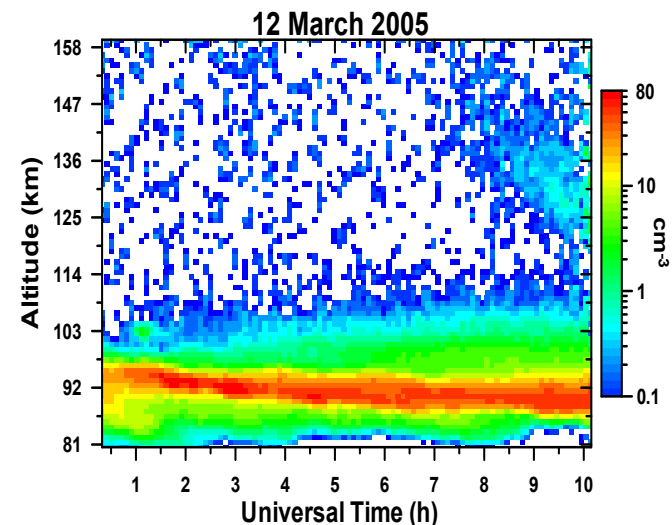
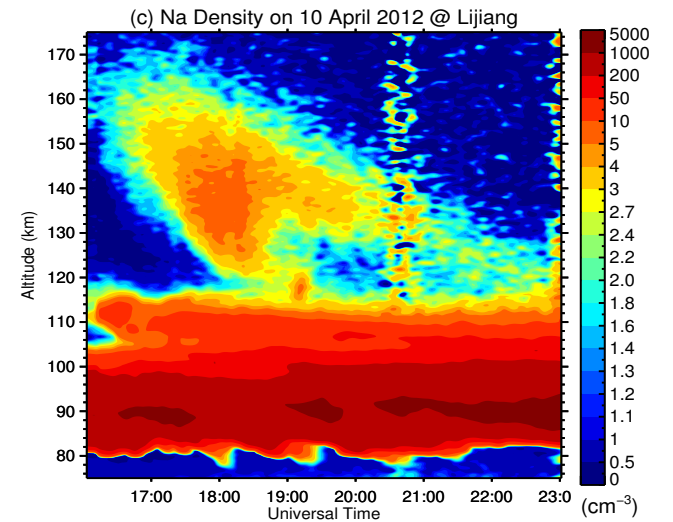
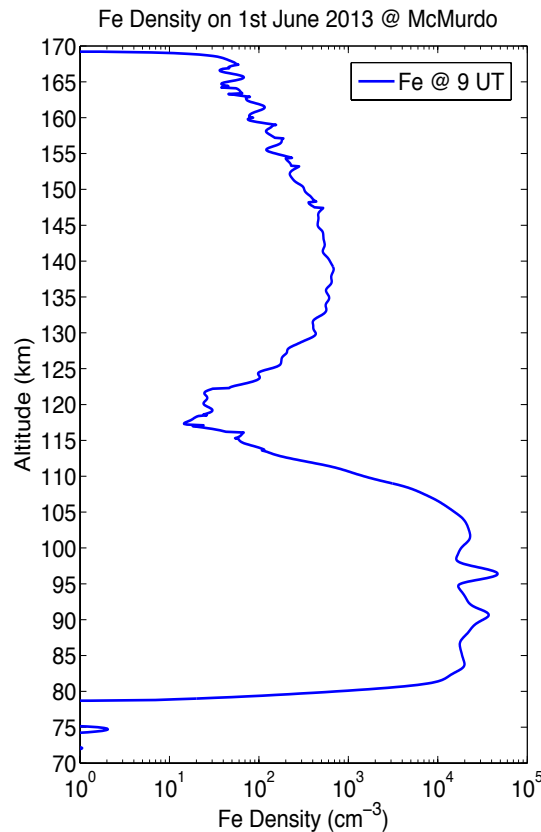
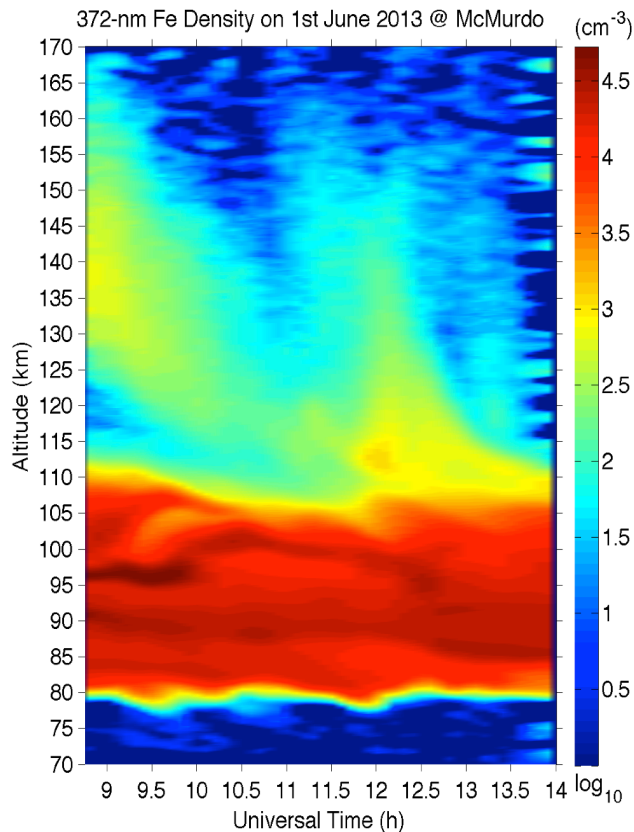


These metal atoms are believed to come from meteor ablation.

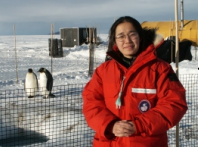
	Central Wavelength λ_0 (nm)	Atomic Mass (10^{-26} kg)	A_{21} (10^8 s^{-1})	Doppler rms width σ_D (MHz)	Peak cross-section σ_0 (10^{-16} m^2)	Oscillator strength f
K (D_1)	770.1088	6.4923	0.382	267.90	13.42	0.3395
Na (D_2)	589.1583	3.8177	0.616	456.54	14.87	0.6411
Ca	422.793	6.6556	2.18	481.96	38.48	1.7516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



Thermospheric Metal Atoms

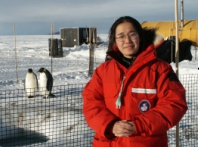


Recent lidar observations at McMurdo, Antarctica and other locations in the world have discovered neutral metal layers (Fe, Na, & K) at thermospheric altitudes to nearly 200 km [e.g., Chu et al., 2011, 2013, 2015; Friedman et al., 2013; Gao et al., 2015]



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 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).

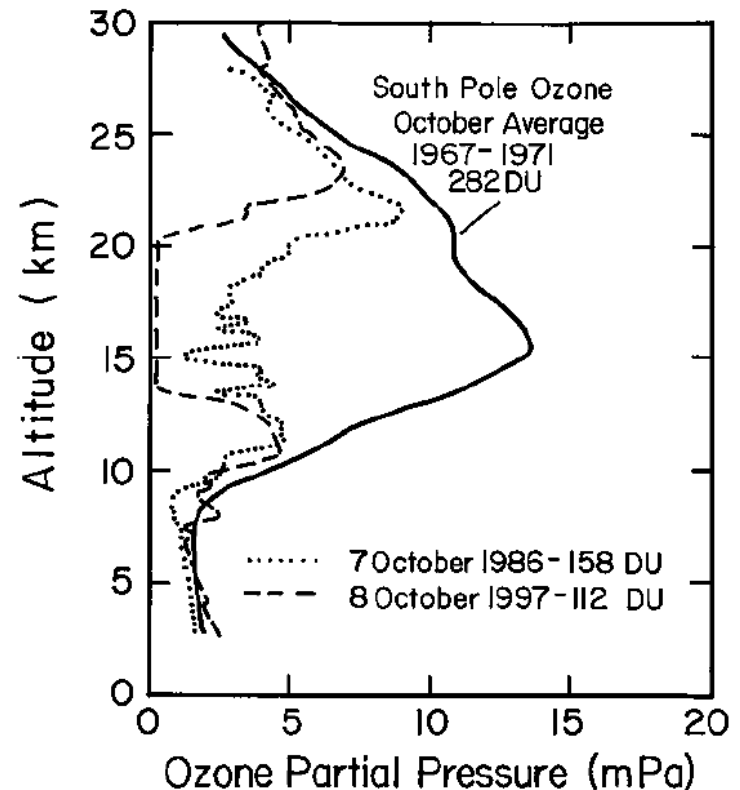


Table 4.1 Absorption Cross Section of Pollutant Gases at Wavelengths Suitable for DIAL Measurement in the Troposphere

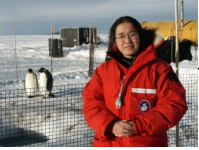
Molecule	Typical Wavelength	Laser (Examples)	Absorption Cross Section (10^{-18} cm^2)
Nitric oxide, NO	226.8 nm	Dye	4.6
Benzene, C ₆ H ₆	252.9 nm	Dye	5.7
Mercury, Hg	253.65 nm	Dye	3.3×10^4
Toluene, C ₇ H ₈	266.9 nm	Dye, Ti:Sa	2.8
Ozone, O ₃	266.0 nm	Dye, Nd:YAG-IV	9.49
	289.0 nm	Raman D ₂	1.59
	299.0 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

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—(Continued)

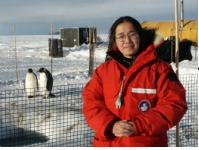
Molecule	Typical Wavelength	Laser (Examples)	Absorption Cross Section (10^{-18} cm^2)
Trichloroethylene, C ₂ HCl ₃	10.591 μm	CO ₂	0.49
1,2-Dichloroethane, C ₂ H ₄ Cl ₂	10.591 μm	CO ₂	0.02
Hydrazine, N ₂ H ₄	10.612 μm	CO ₂	0.18
Vinyl chloride, C ₂ H ₃ Cl	10.612 μm	CO ₂	0.33
UDMH, (CH ₃) ₂ N ₂ H ₂	10.696 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



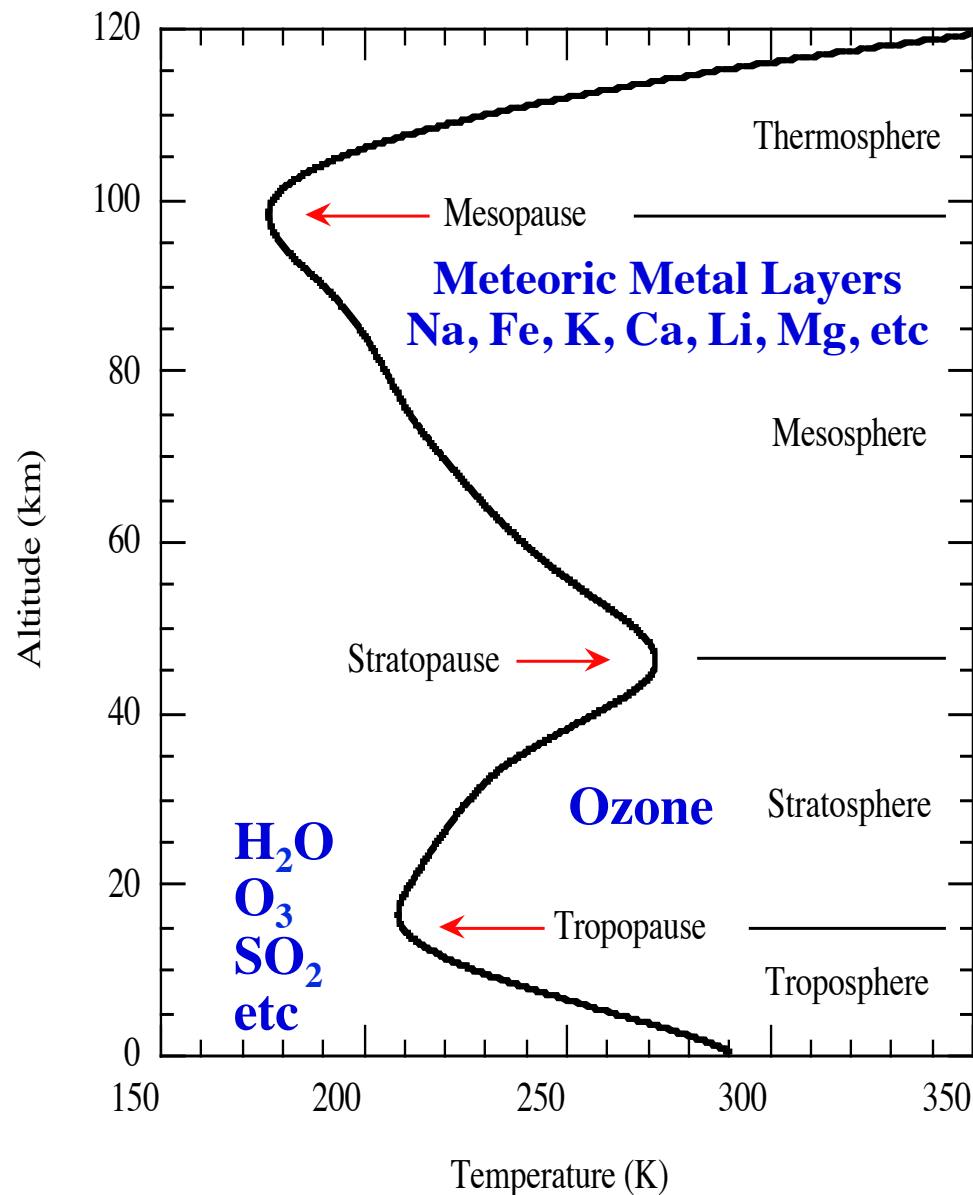
Lidar Detection of Constituents

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.

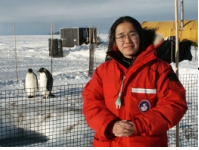
- ❑ **Metal atoms in the middle and upper atmosphere, Helium, O and N_2^+ in thermosphere:** density, abundance, temporal and spatial distributions, diurnal, seasonal and interannual variations; temperatures, winds, waves
 - resonance fluorescence lidar, two-photon absorption/fluorescence
- ❑ **Molecular 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 possibilities:**
 - Laser-induced-fluorescence lidar
 - White-light lidar, laser frequency comb, etc.



Constituent Lidar Techniques



- Fe, He and N₂⁺ in thermosphere: resonance fluorescence lidar
- O in thermosphere: resonance fluorescence lidar or DIAL from space
- Metal atoms in 75–120 km: resonance fluorescence lidar (broadband or narrowband transmitter)
- Molecular species in lower stratosphere & troposphere: DIAL, Raman scattering lidar, Raman DIAL, Multi-channel DIAL, multi-channel Raman DIAL, LIF, white-light, freq. comb lidar, ...



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.

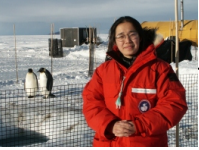
$$T_c(z) = \exp\left(-\int_{z_{bottom}}^z \sigma_{eff}(\lambda, z') n_c(z') dz'\right) = \exp\left(-\int_{z_{bottom}}^z \alpha_c(\lambda, z') dz'\right)$$

- 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

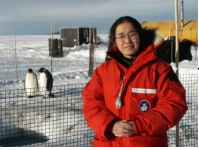
$$n_c(z) = n_R(z_R) \frac{N_S(\lambda, z) - N_B}{N_R(\lambda, z_R) - N_B} \cdot \frac{z^2}{z_R^2} \cdot \frac{4\pi\sigma_R(\pi, \lambda)}{\sigma_{eff}(\lambda)R_B(\lambda)} \cdot \frac{1}{T_c^2(\lambda, z)}$$

□ 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.

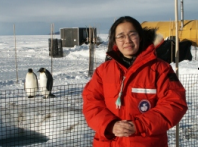
□ Resonance fluorescence lidars only work for certain conditions, e.g., the density cannot be too large (insufficient transmission through the entire layer) or too small (insufficient fluorescence signal levels).

□ 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 [Collins et al., GRL, 2015].

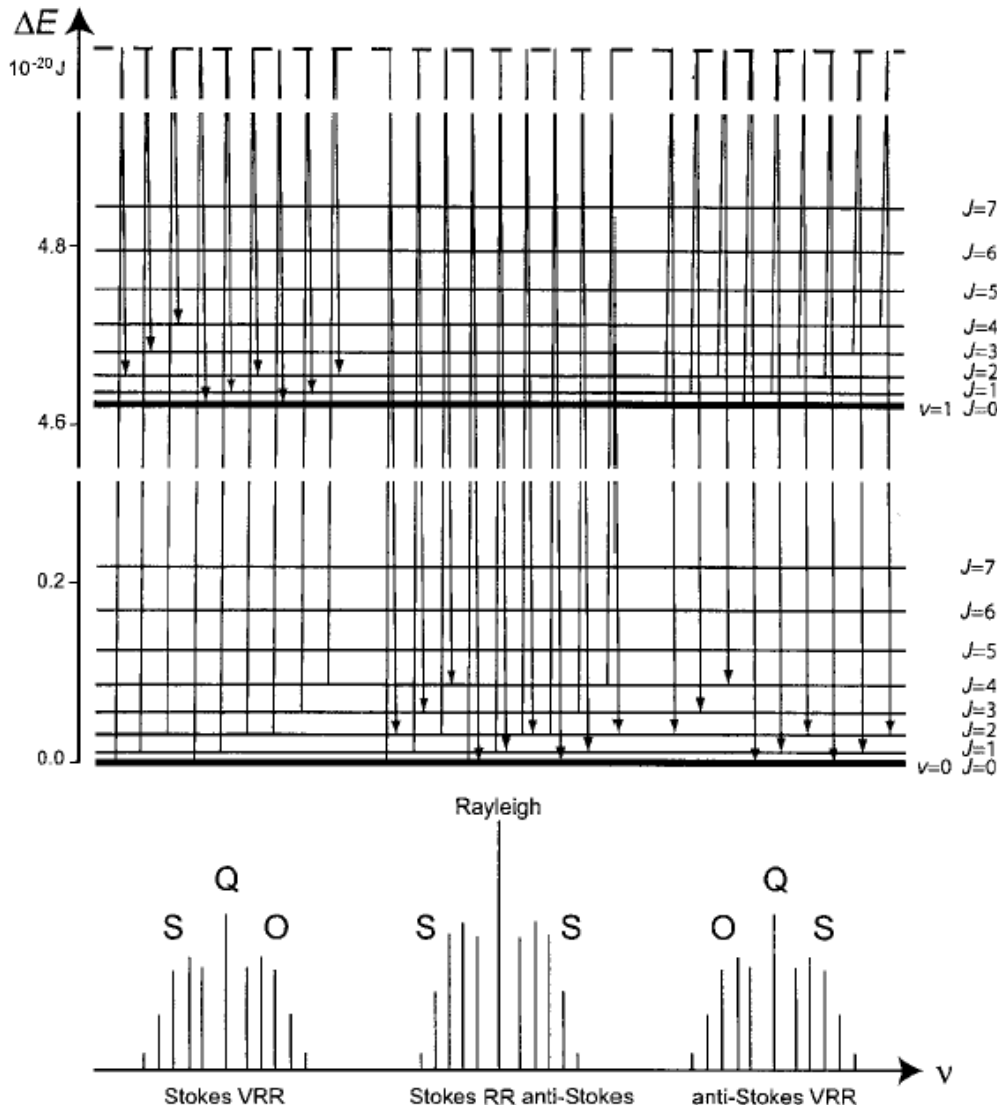


Raman Scattering Lidar

- ❑ 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.



Raman Scattering (Inelastic)



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

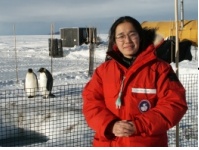
$$k = \frac{1}{\lambda}$$

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.

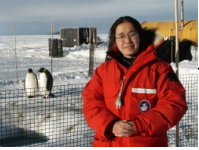
$$\Delta v = 0, \pm 1 \text{ and } \Delta J = 0, \pm 2,$$

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).^{1,5}



Raman Backscatter Spectrum

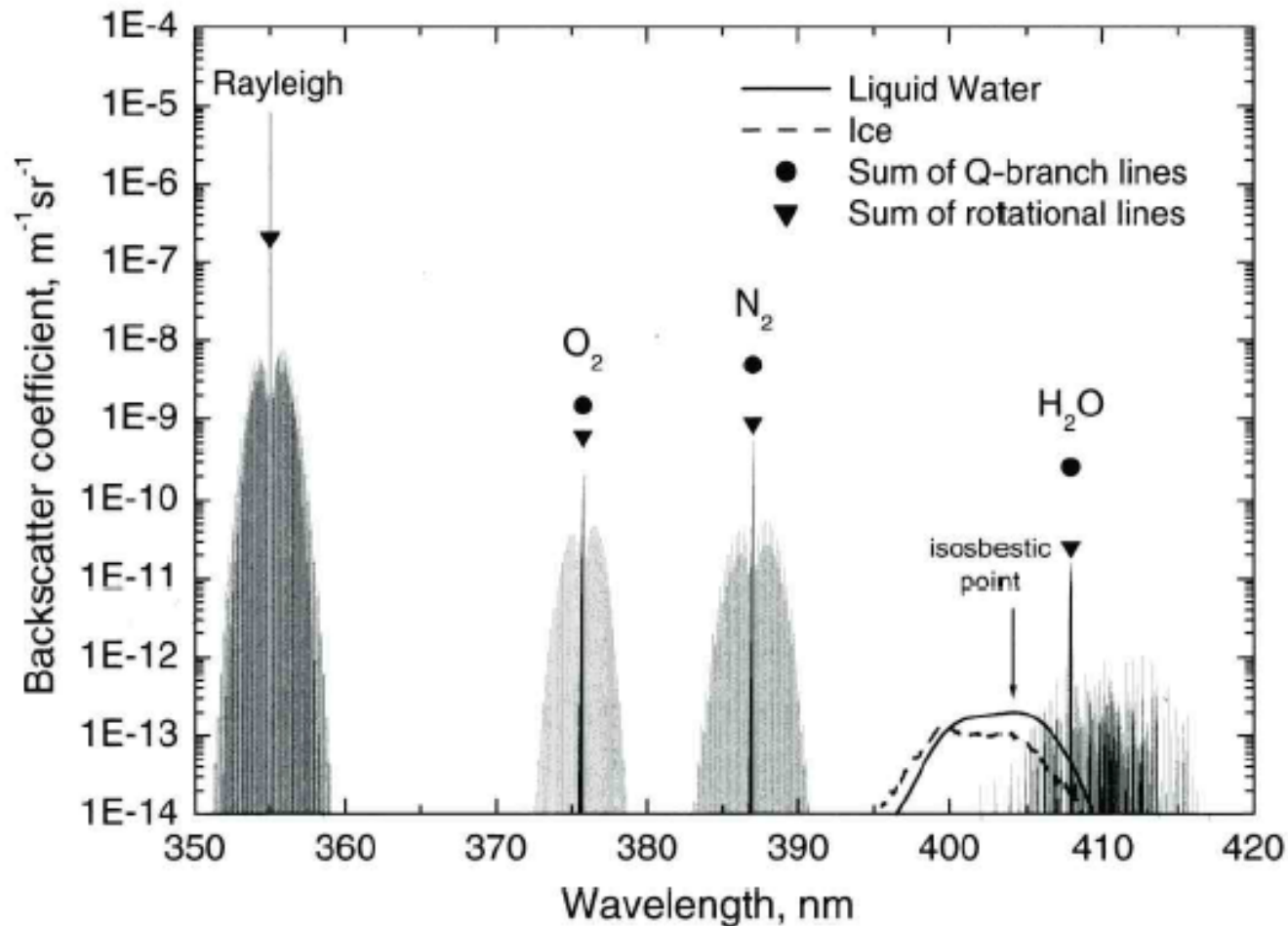
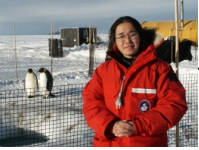


Fig. 9.2. Raman backscatter spectrum of the atmosphere for an incident laser wavelength of 355 nm, normal pressure, a temperature of 300 K, an N_2 and O_2 content of 0.781 and 0.209, respectively, and a water-vapor mixing ratio of 10 g/kg. The curves for liquid water and ice are arbitrarily scaled. The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

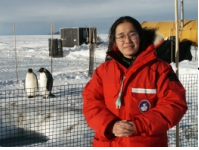


Raman Lidar

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 ₂ O (vapor), VRR (+ reference gas, VRR)	0–12 km (night) [16, 47] 0–5 km (day) [11, 47]
Extinction coefficient	N ₂ or O ₂ , VRR or RR	0–30 km (night) [48]
Backscatter coefficient	(+ elastic signal for back- scatter and lidar ratio)	0–10 km (day) [49]
Lidar ratio		
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 ₂ O (liquid), VRR (+ reference gas, VRR)	0–4 km (night) [34]

[Ulla Wandinger, Raman Lidar chapter, 2005]



Fundamentals of Raman Scattering

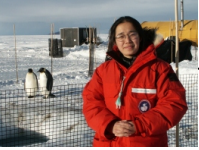
□ Raman scattering is an inelastic scattering and the Raman shift is characteristic for the scattering molecule. Using wavenumber $\tilde{\nu}=1/\lambda$, the Raman shift is given by

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

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 $\tilde{\nu}_{\text{vib}}$ 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	$\tilde{\nu}_{\text{vib}}$ 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]



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

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

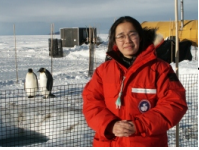
Constituent number density

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

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

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

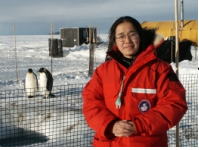
Here, E_0 , R^2 , $O(R)$, and $\alpha(r, \lambda_0)$ are already cancelled out

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

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

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

Calibration Constant **C**



Solution Cont' d

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

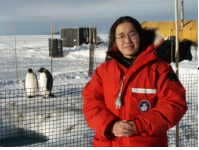
- (1) The ratio of reference molecule density in the air
- (2) The lidar detector efficiency ratio at two wavelengths
- (3) The effective Raman backscatter cross-section ratio
- (4) Atmospheric transmission ratio, i.e., extinction coefficient difference

❑ 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. 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%.

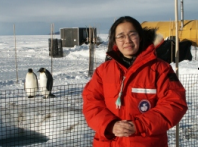
$$\alpha(R) = \alpha_{aer}(R) + \alpha_{mol}(R)$$

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



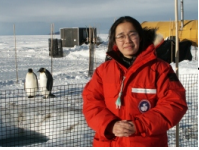
Considerations on Raman Applications

- ❑ 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 allow 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

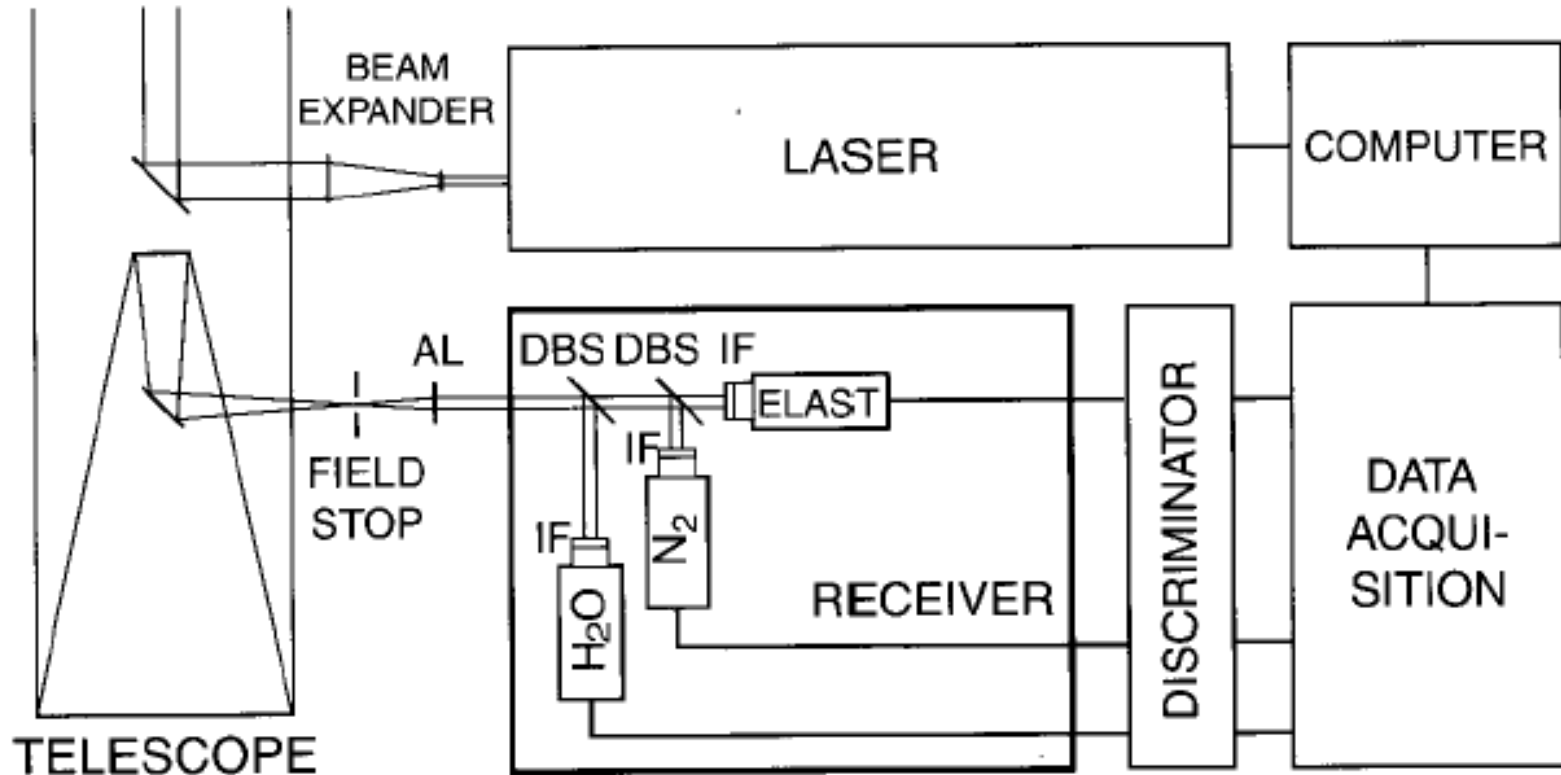
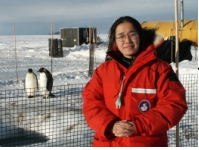
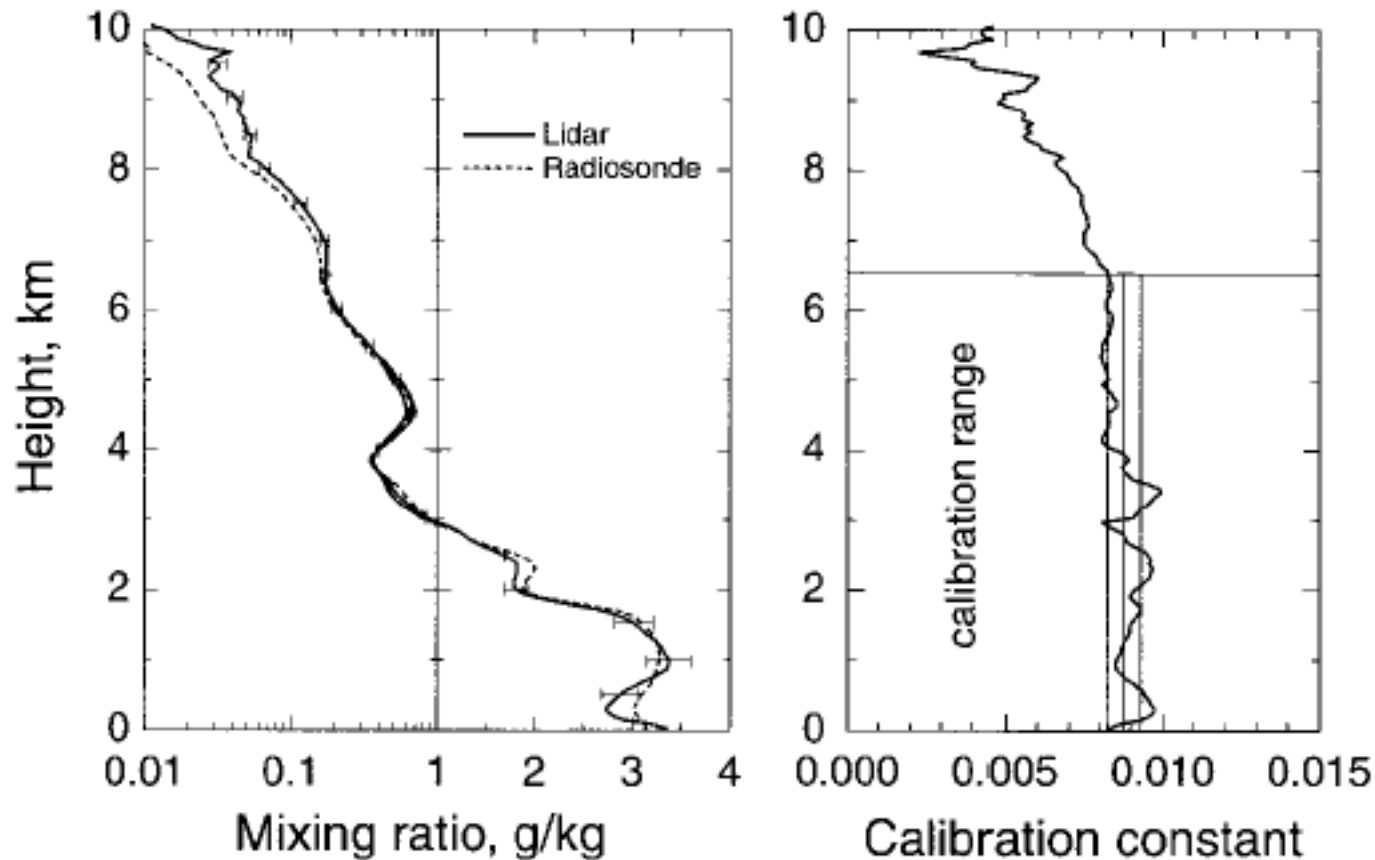


Fig. 9.3. Typical setup of a water-vapor and aerosol Raman lidar. AL – achromatic lens, IF – interference filter, DBS – dichroic beam splitter.

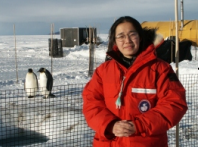
❑ Mixing ratio: two Raman channels: one is the return from the gas of interest and another is the return of a reference gas (N₂ or O₂).



Water Vapor Results by Raman Lidar

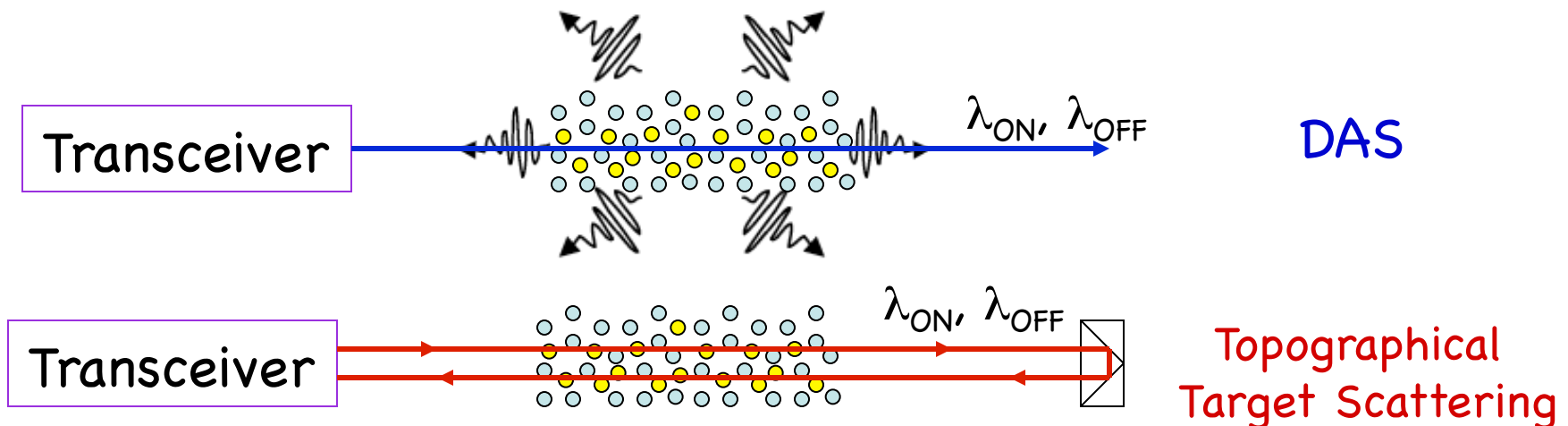


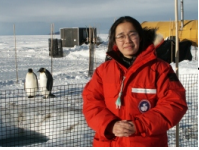
❑ Raman scattering lidar usually needs calibration with radiosonde or independent calibration by measuring or calculating the relevant system parameters or by using multichannel to measure the aerosol extinction and effective cross-sections.



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

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

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.

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

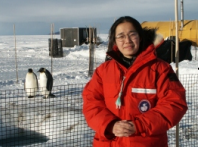
□ The parameter in the DIAL equation

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

Aerosol Extinction

Air Molecule Extinction

Interference gas absorption



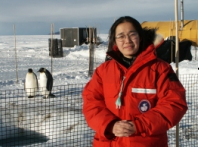
DIAL Equation Cont' d

□ 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.

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

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

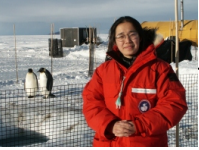


Solution for DIAL Equations

□ 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

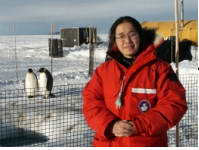
Take the differentiation of the equation, we obtain the number density of the constituent that we are interested in

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

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

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

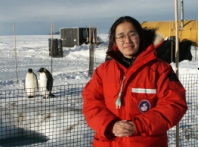
$$n_c(R) = \frac{1}{2\Delta\sigma_{abs}} \frac{d}{dR} \left\{ \ln \left[\frac{P_S(\lambda_{OFF}, R) - P_B}{P_S(\lambda_{ON}, R) - P_B} \right] \right\}$$

□ 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

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



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. Laser induced fluorescence, white-light lidar, and laser frequency comb provide new potentials for detecting various constituents.
- ❑ 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.