



Chap.7. Raman Systems

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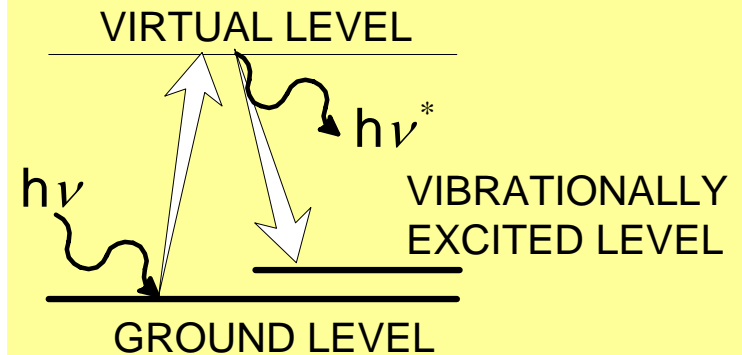
MEASUREMENTS:

- Direct: Concentration of chemical species in the atmosphere such as

SO₂, NO, CO, H₂S, C₂H₄, CH₄,
H₂CO, H₂O, N₂, O₂...

- Indirect: Temperature, Humidity, α , β , S_M

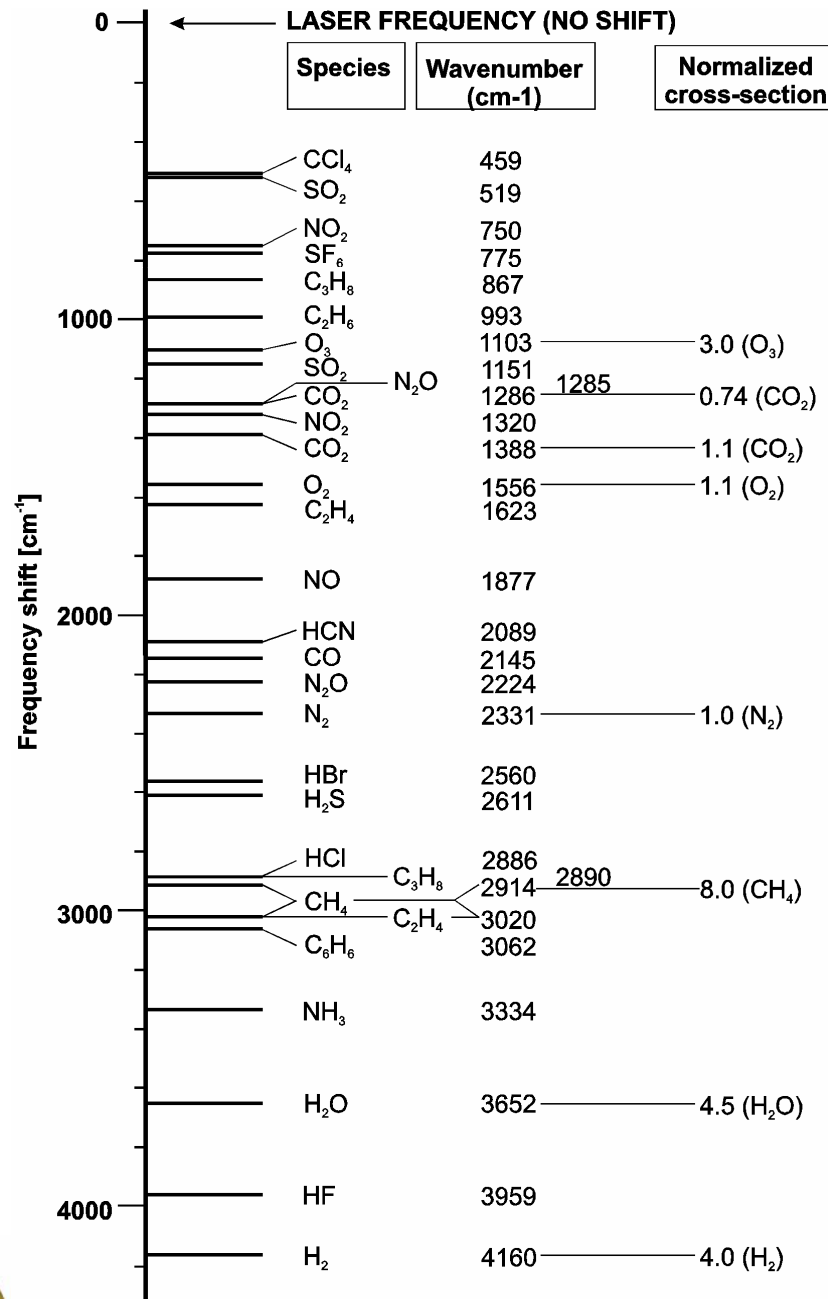
INELASTIC INTERACTION



LASER TYPES:

- Ruby ($\lambda = 694.3 \text{ nm}, 347.2 \text{ nm}$)
- N₂ ($\lambda = 337 \text{ nm}$)
- Nd:YAG ($\lambda = 1060 \text{ nm}, 532 \text{ nm}, 266 \text{ nm}$)
- Excimer ($\lambda \sim 350 \text{ nm}$)

RAMAN LIDAR



OPERATIONAL PRINCIPLE

- 1) In contrast to elastic systems, the return wavelength, λ_R , is shifted from the incident one, λ_0 .
- 2) Wavelength shift, κ , depends on each molecular species.

$$\lambda_R = \frac{\lambda_0}{1 - \kappa\lambda_0}$$

- 3) Very faint returns.

- *requires photon counting*
- *very often, night-time operation*

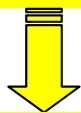
Fig. ADAPTED FROM: Inaba, H. Detection of Atoms and Molecules by Raman Scattering and Resonance Fluorescence. In *Laser Monitoring of the Atmosphere*, Hinkley, E. D., Ed.; Springer-Verlag: New York, 1976; Chap. 5, 153-236.

RAMAN LIDAR

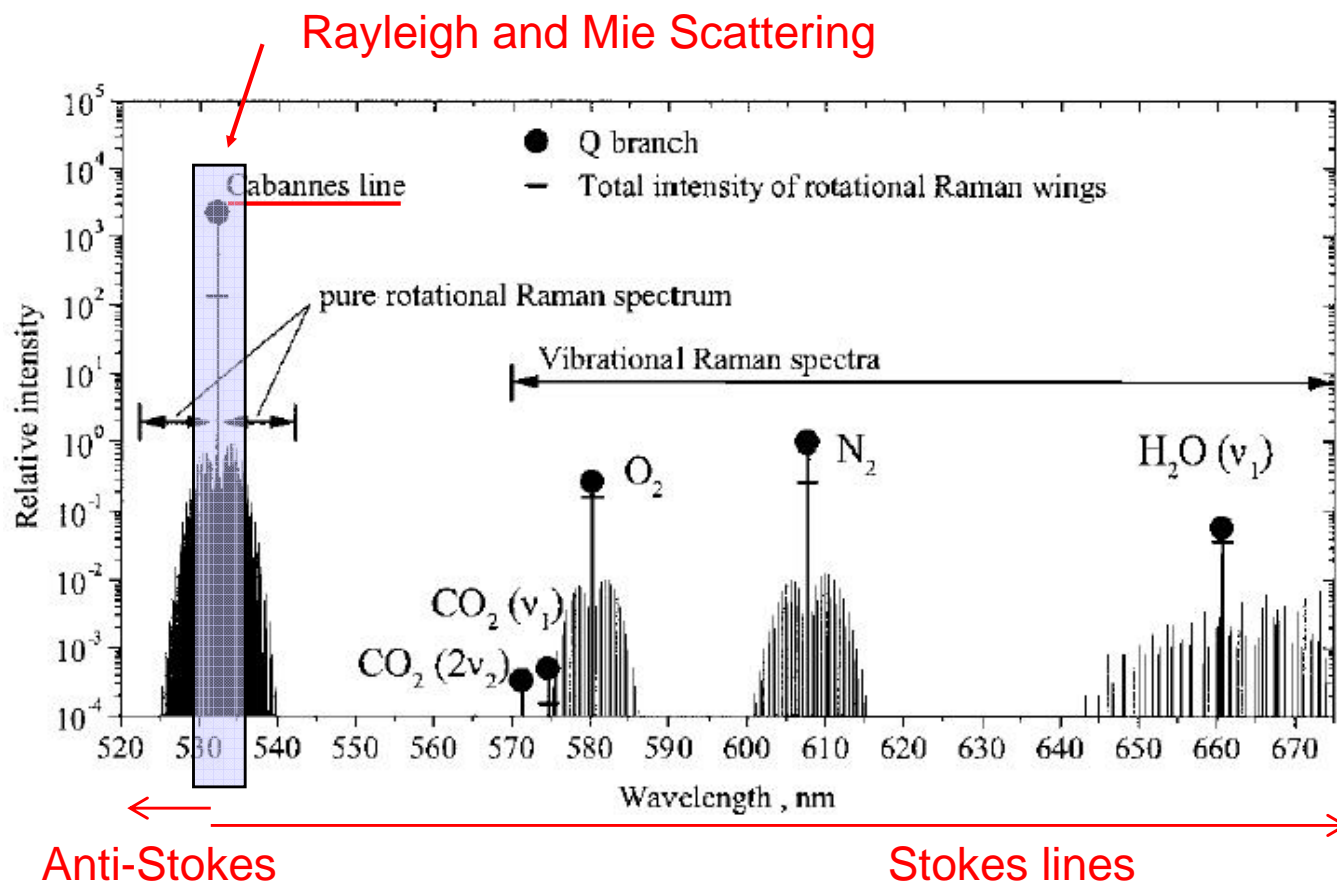
RAMAN SPECTRUM CHARACTERISTICS

The Raman shift, κ :

- 1) does not depend on the excitation wavelength λ_0 and,
- 2) it is specific of the chemical species



- A) Laser need **not** be tunable
- B) The Raman spectrum is characteristic of each molecule
- C) Conveys **temperature** info.

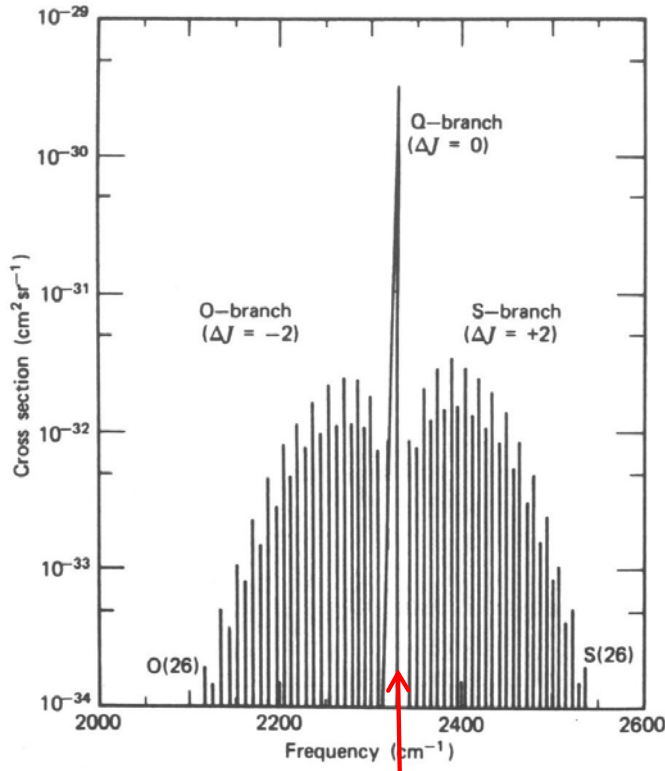


Overview of the lidar backscatter signals for 532-nm laser excitation wavelength.

Fig. SOURCE: Behrendt, A., et al., "Combined Raman lidar for the measurement of atmospheric temperature, water vapor, particle extinction coefficient, and particle backscatter coefficient", *Appl. Opt.* **41** (36), 7657-7666, (2002).

RAMAN LIDAR

KEY CONCEPTS



Common Raman shifts:

N ₂	2331 cm ⁻¹	H ₂ O	3654 cm ⁻¹
O ₂	1556 cm ⁻¹		

Fig. SOURCE: Inaba, H. Detection of Atoms and Molecules by Raman Scattering and Resonance Fluorescence. In *Laser Monitoring of the Atmosphere*, Hinkley, E. D., Ed.; Springer-Verlag: New York, 1976; Chap. 5, p.162.

1) Raman components

- *Stokes lines*
 - molecule gains energy from the radiation field
 - scattered radiation is at $\lambda_R > \lambda_0$
- *Anti-Stokes lines* ($\lambda_R < \lambda_0$)

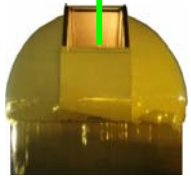
2) Motivation for the “wavenumber” concept (with κ , the Raman shift):

$$\frac{1}{\lambda_R} = \frac{1}{\lambda_0} - \kappa, \quad \kappa [\text{cm}^{-1}]$$

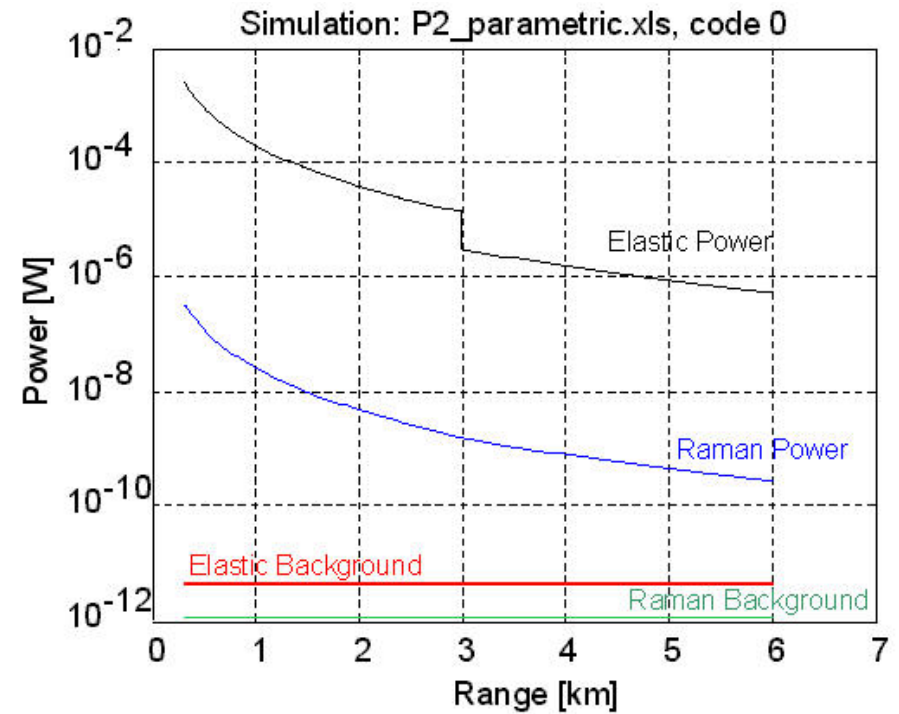
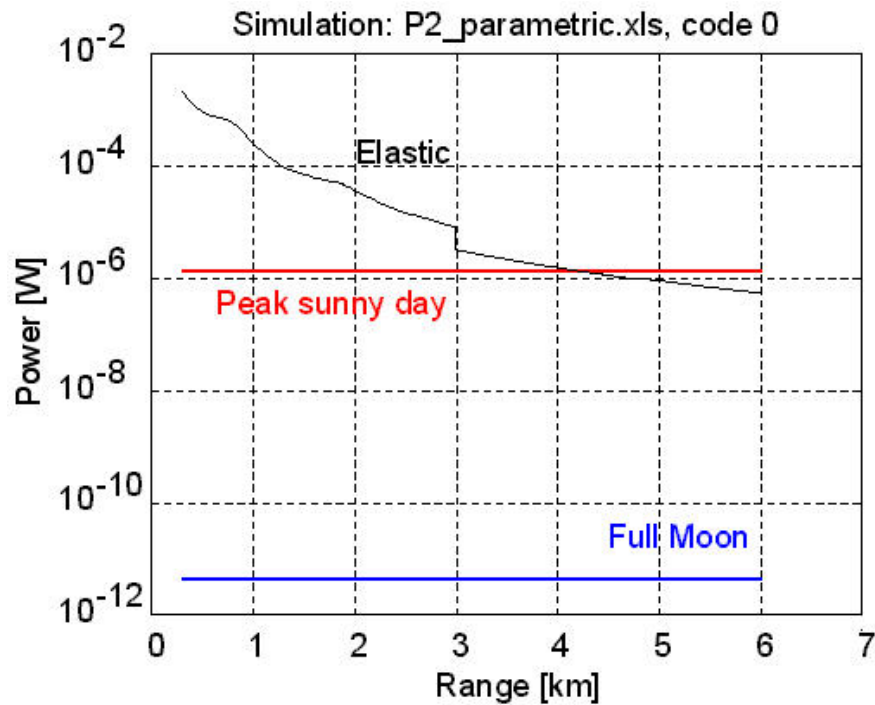
3) Raman cross-sections

- *dependency* $\propto \lambda^{-4}$

$$\left. \frac{d\sigma(\pi)}{d\Omega} \right|_{\text{Raman}} \approx 10^{-3,-4} \left. \frac{d\sigma(\pi)}{d\Omega} \right|_{\text{Ray}}$$

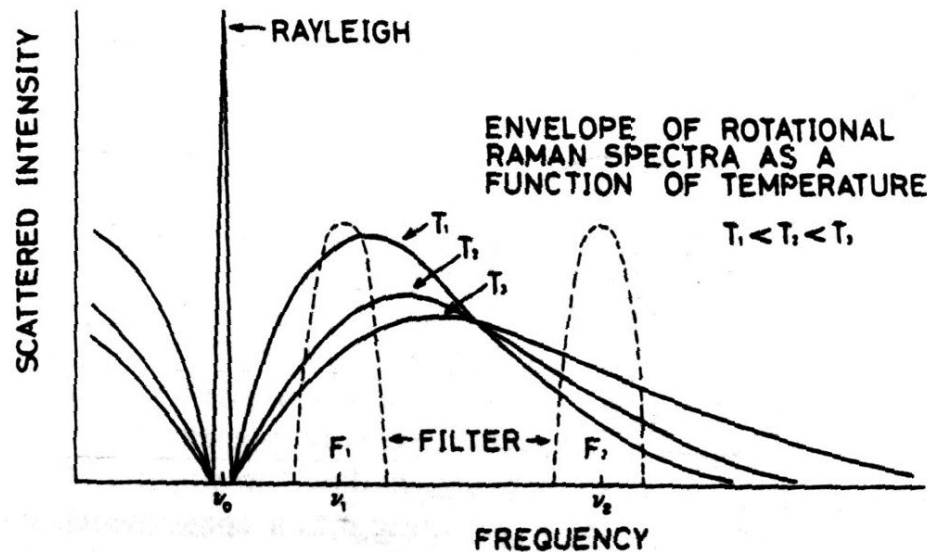


RAMAN LIDAR LINK-BUDGET



CATEGORY	PARAMETER	VALUE (CODE 0)	UNITS
LASER	Energy	160	mJ
	PRF	20	Hz
TELESCOPE	Primary lens diameter	0,2032	m
ELASTIC CHANNEL	PHOTODIODE, Multiplication factor	150	no units
	PHOTODIODE, Excess-noise factor	4,5	no units
RAMAN CHANNEL	INTERFERENCE FILTER, bandwidth	3	nm
	PMT, Multiplication factor	3,00E+06	no units
	Anode dark current	1	nA
ATMOSPHERE	Anode radiant sensitivity	3,00E+04	A/W
	Visibility margin	39,12	km
	Lidar ratio, SM	25	sr
	Boundary-layer height	3	km
	System operation (question 2)	night-time	

TEMPERATURE MEASUREMENT (I)



KEY

Raman signatures are direct measures of the relative populations among the internal molecular modes

- (In thermal equilibrium) → fundamental def. of temperature

METHODS

1) Rotational Raman (RR)

- Comparison of the *envelope shape* of all the lines
- *Intensity ratio* of selected spectral regions of the band

Suitable for atmospheric profiling

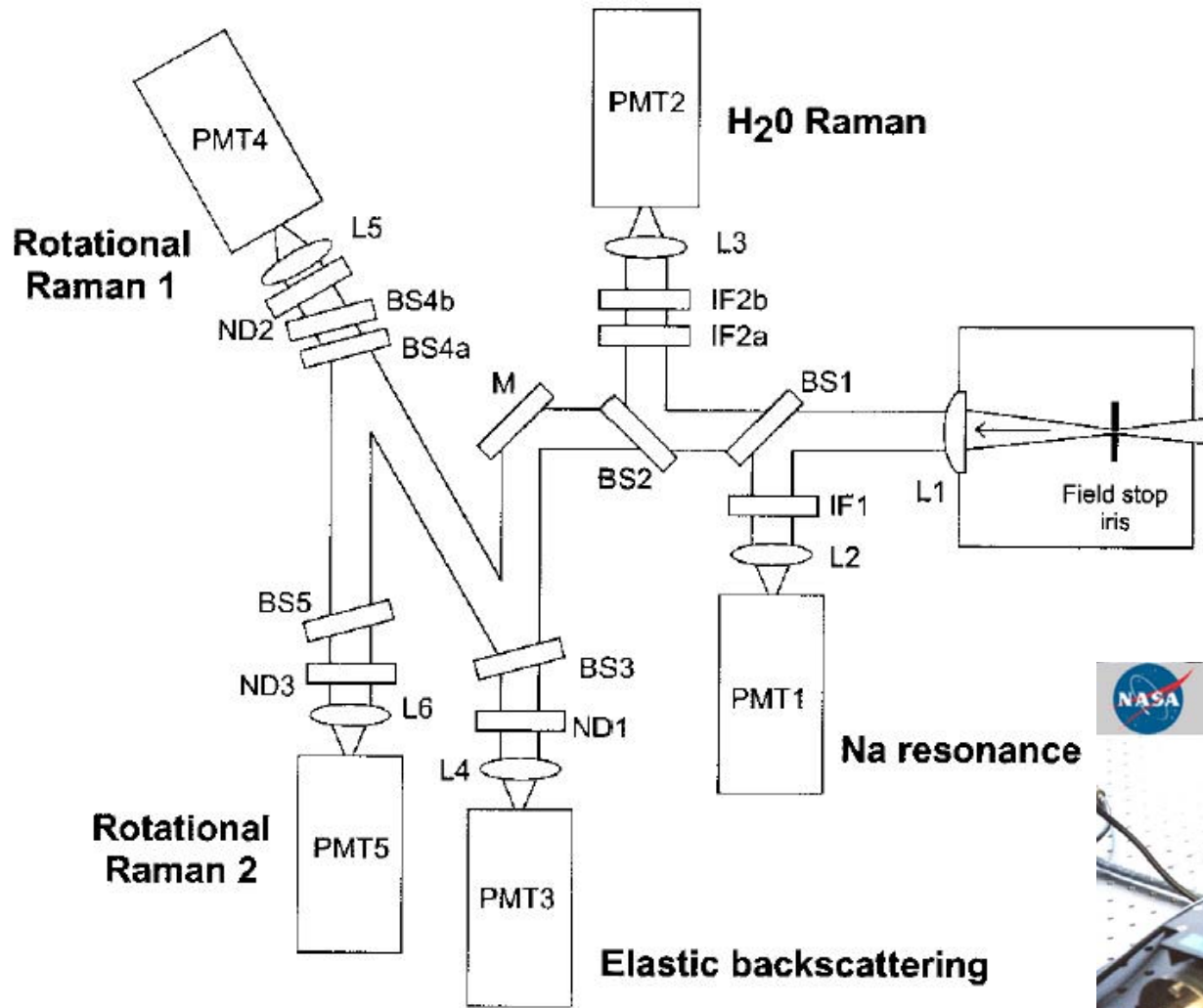
2) Vibrational Raman (VR)

- +
- *Intensity ratio between Stokes and anti-Stokes components*
- *Width of a specific Q-branch*

Suitable for high-temperature diagnostics (e.g. flames)

Fig. SOURCE: Inaba, H. Detection of Atoms and Molecules by Raman Scattering and Resonance Fluorescence. In *Laser Monitoring of the Atmosphere*, Hinkley, E. D., Ed.; Springer-Verlag: New York, 1976; Chap. 5, 153-236.

TEMPERATURE MEASUREMENT (II)



RASC (GKSS) lidar

- 1) T (temperature)
- 2) WV (water vapor mixing ratio)
- 3) α , β , S_M
- 4) RH (humidity)

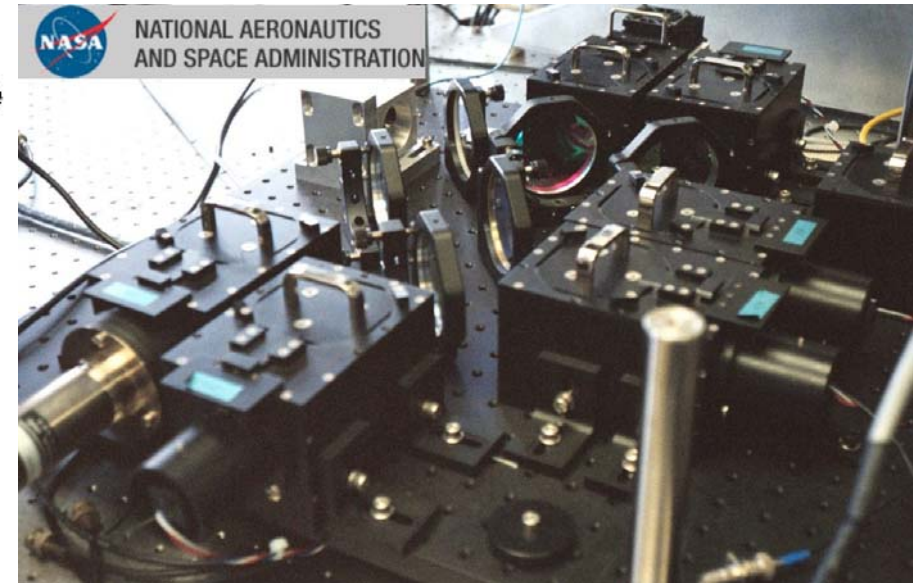
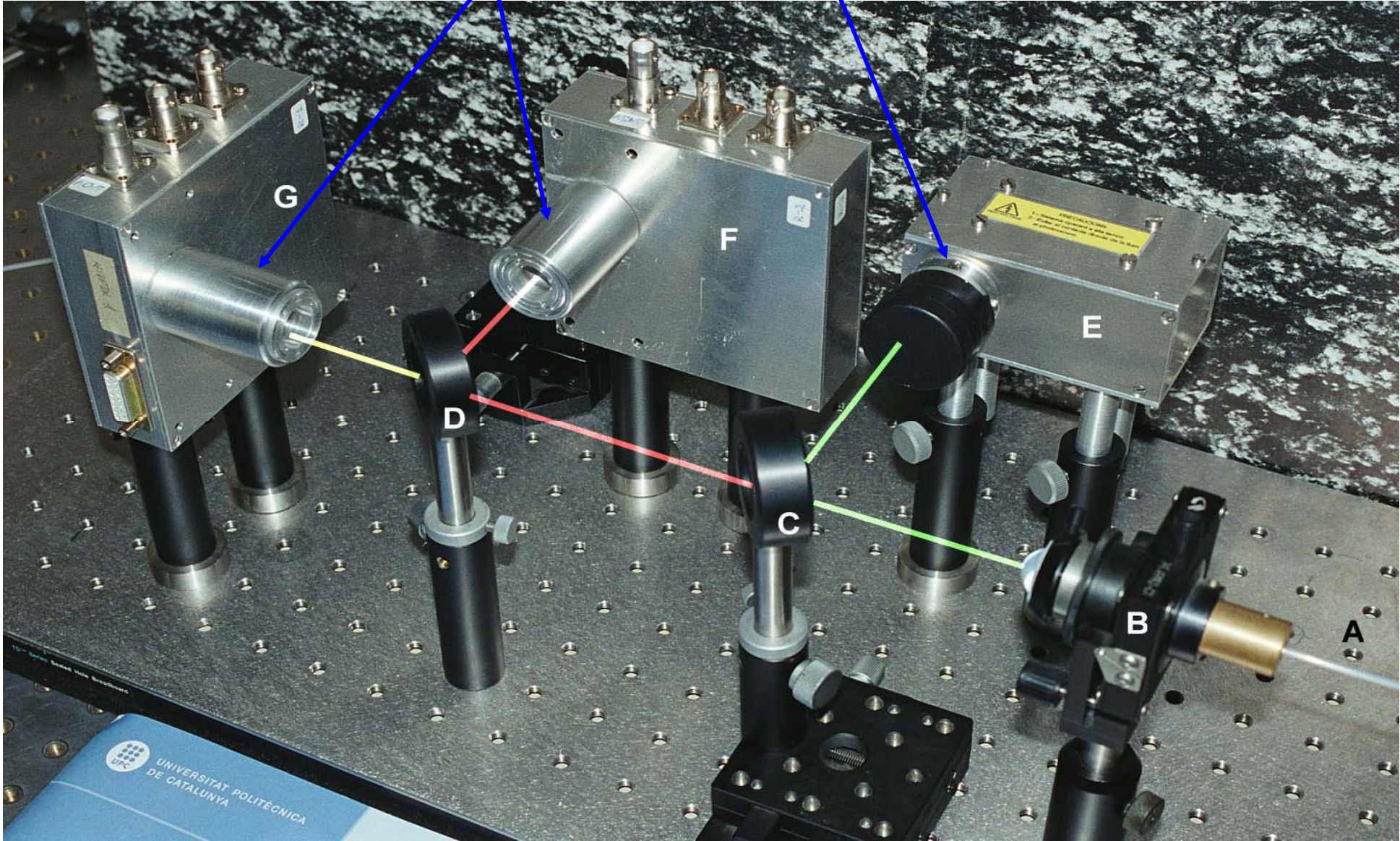


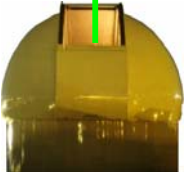
Fig. SOURCE: Behrendt, A., et al., "Combined Raman lidar for the measurement of atmospheric temperature, water vapor, particle extinction coefficient, and particle backscatter coefficient", *Appl. Opt.* 41 (36), 7657-7666, (2002).

UPC POLYCHROMATOR TEST LAYOUT



LIDAR (LASER RADAR)

DEP. OF SIGNAL THEORY AND COMMUNICATIONS



TEMPERATURE MEASUREMENT (III)

DISCUSSION PARAMETERS (RASC lidar LAYOUT)

Wavelength (nm) ^b	Parameter	BS1	BS2	BS3	BS4a and BS4b Combined	BS5	IF2a and IF2b Combined
	AOI (°)	45	45	5.8	7.4	5.5	0
	CWL (nm)			532.25	530.70	529.20	660.3
	FWHM (nm)			0.74	0.55	1.20	2.6
589 (s)	ρ	>0.95					
660	τ	≈0.70					≈0.3
	ρ		>0.95				
532.11 (p or s)	τ	≈0.80	≈0.85	0.83	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁸
	ρ			0.11			
530.70	τ	≈0.80	≈0.85		0.38	<2 × 10 ⁻⁴	
	ρ			>0.95			
529.20	τ	≈0.80	≈0.85			0.75	
	ρ			>0.96	>0.96		

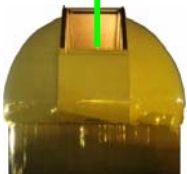
^aAOI, angle of incidence; CWL, central wavelength; FWHM, full width at half maximum; ρ , reflectivity; τ , transmission. Transmission values $\tau < 10^{-3}$ are estimations by the manufacturer.

^bs, perpendicular polarized; p, parallel polarized.

Note:

ND filters are used to cope with saturation effects in the RR channels in the lower troposphere (correction of photon-counter receiver dead-time effects).

Tab. SOURCE: Behrendt, A., et al., "Combined Raman lidar for the measurement of atmospheric temperature, water vapor, particle extinction coefficient, and particle backscatter coefficient", *Appl. Opt.* 41 (36), 7657-7666, (2002).



TEMPERATURE MEASUREMENT (IV)

Specific RR Temperature approaches:

Use of two RR channels with opposite temperature dependency

- + 3rd RR channel (isosbestic point) as reference or,
- combine them to obtain a temperature-indep. reference

$$Q(T) = \frac{N_{RR2}(T)}{N_{RR1}(T)}$$

$$N_{ref}(z) = N_{RR1}(z) + cN_{RR2}(z)$$

- calibrate $Q(T)$ with a radiosonde
 - find c for minimum temp. variation

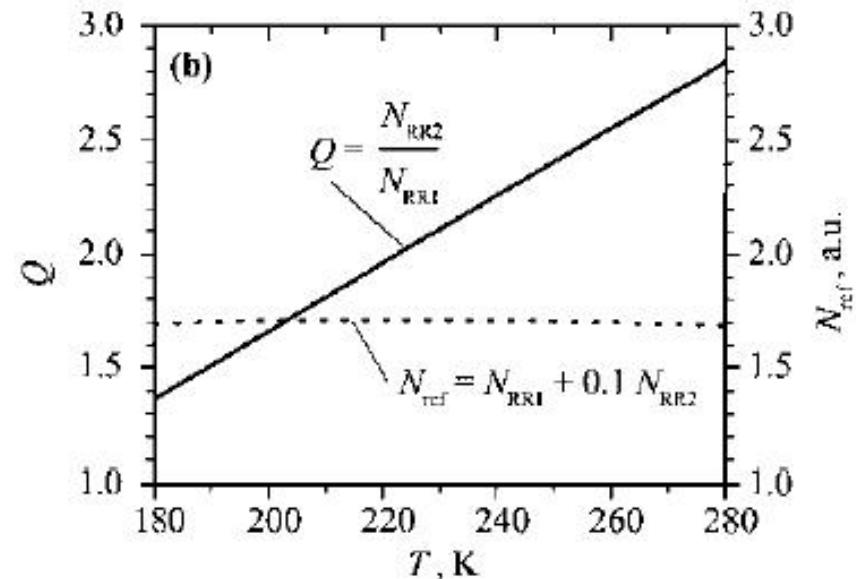
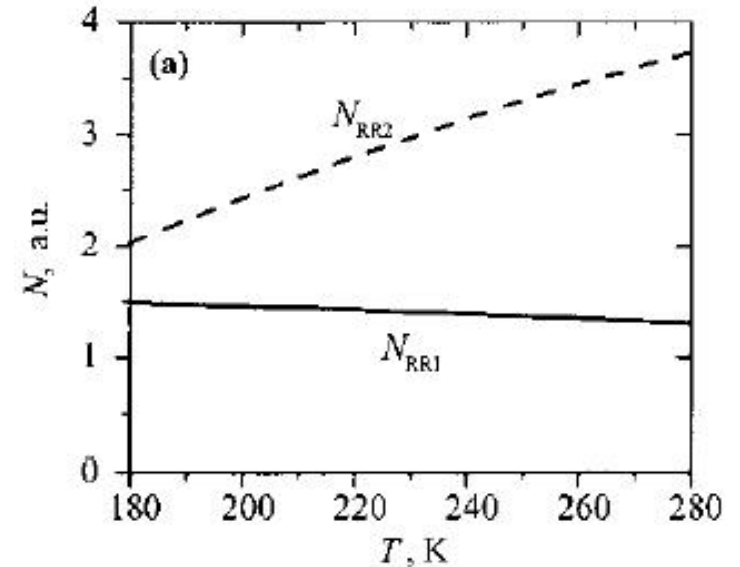
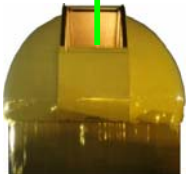
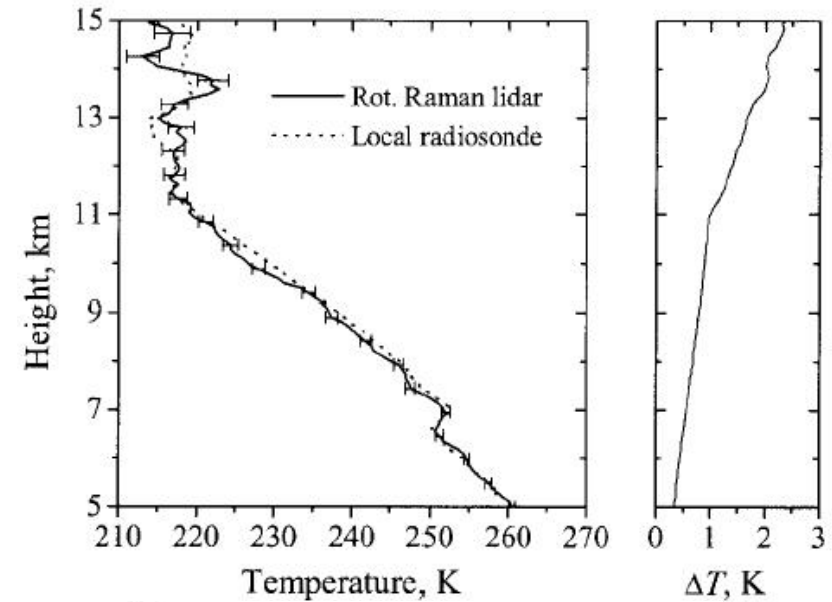
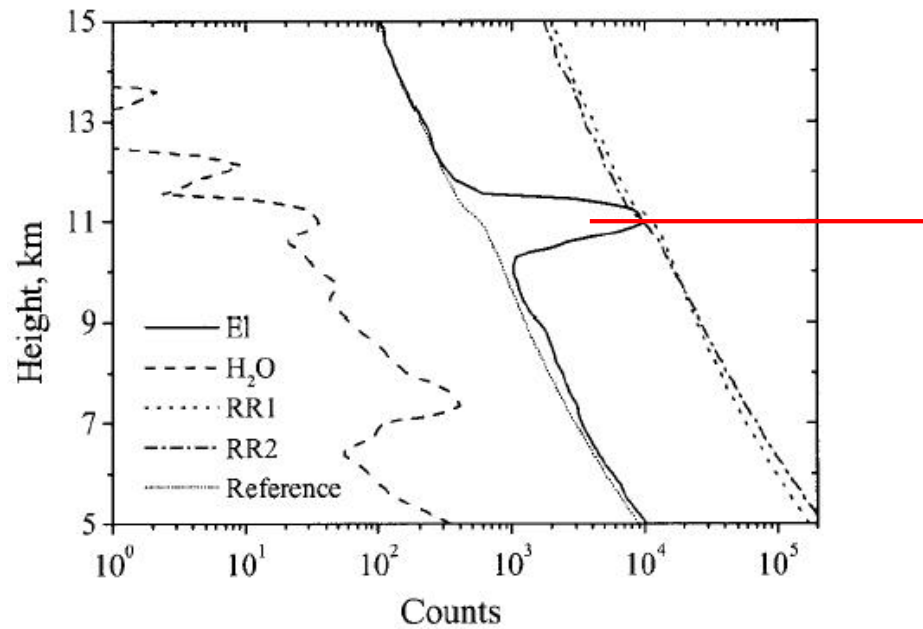


Fig. SOURCE: Behrendt, A., et al., "Combined Raman lidar for the measurement of atmospheric temperature, water vapor, particle extinction coefficient, and particle backscatter coefficient", *Appl. Opt.* **41** (36), 7657-7666, (2002).



TEMPERATURE MEASUREMENT (V)



Problem: Elastic cross-talk with the RR channel

Action: Calibrate on a cirrus cloud using

$$Q(T) = \frac{N_{RR2}(T)}{N_{RR1}(T) - \epsilon N_{El}(z)}$$

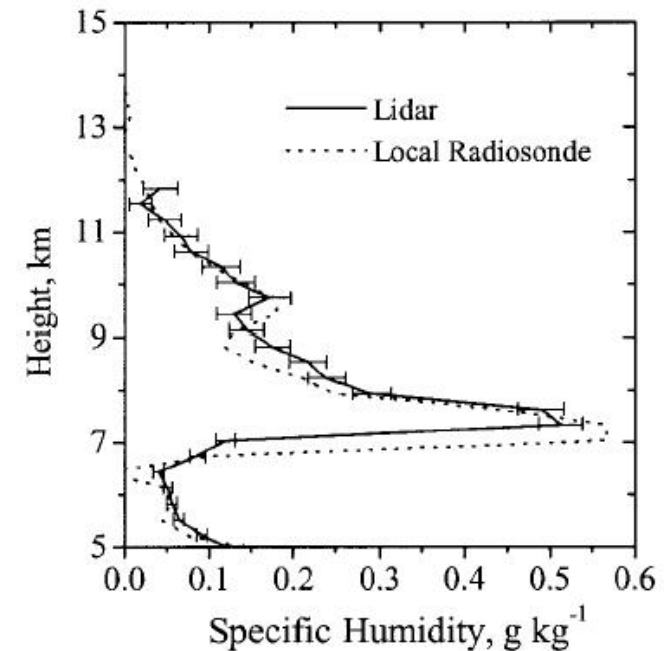


Fig. SOURCE: Behrendt, A., et al., "Combined Raman lidar for the measurement of atmospheric temperature, water vapor, particle extinction coefficient, and particle backscatter coefficient", *Appl. Opt.* **41** (36), 7657-7666, (2002).

CONCEPTS:

1) The absolute concentration of each molecular species can be performed by comparing the Raman backscattered intensity with that of the Raman line from N₂ which occupy the same volume.

1A) Raman-backscattered signal:

$$P_{\lambda_R}(R) = K_{\lambda_R} \frac{O(R)}{R^2} F_R(T, \Delta\lambda_R) \left[N_R(R) \frac{d\sigma_{\lambda_R}(\pi)}{d\Omega} \right] \times \exp \left\{ - \int_0^R \left[\alpha_{\lambda_0}^{tot}(\xi) + \alpha_{\lambda_R}^{tot}(\xi) \right] d\xi \right\}$$

1B) (Oversimplified) Gas-to-N₂ normalised ratio

N₂-normalised cross section

$$\frac{P_{\lambda_X}(R)}{P_{\lambda_N}(R)} = \frac{O_X(R) F_X(T, \Delta\lambda_X) N_X(R)}{O_N(R) F_N(T, \Delta\lambda_N) N_N(R)} \left[\frac{d\sigma_{\lambda_X}(\pi)/d\Omega}{d\sigma_{\lambda_N}(\pi)/d\Omega} \right] \frac{\xi(\lambda_X)}{\xi(\lambda_N)} \Delta\tau(\lambda_X, \lambda_N, R),$$

solve for N_x(R)

known (US-std model, radiosonde)

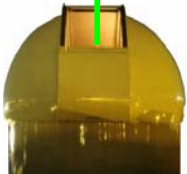
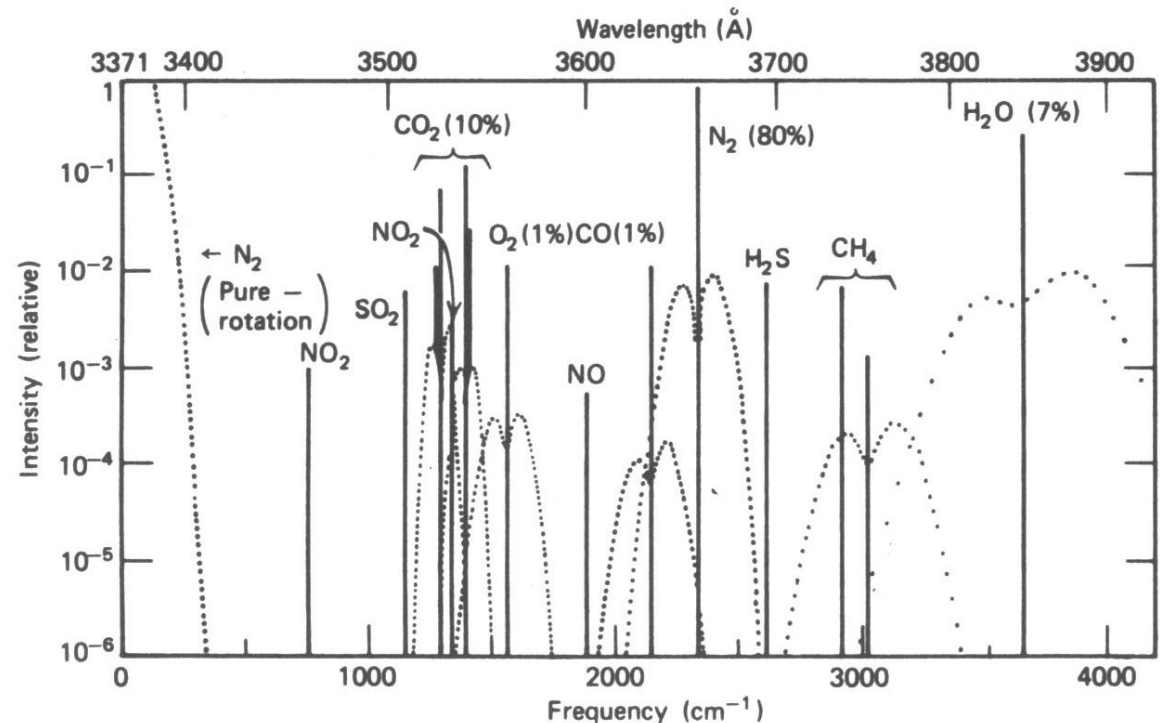
where $\Delta\tau(\lambda_X, \lambda_N, R) = \exp \left\{ - \int_0^R \left[\alpha_{\lambda_X}^{tot}(\xi) - \alpha_{\lambda_N}^{tot}(\xi) \right] d\xi \right\}$

1C) (Estimation of the) **Differential Transmission term:**

- *Molecular extinction* → *US-std. atmosphere model + radiosonde*
- *Aerosol extinction* → *Cooperative elastic-Raman channel (N2)*
 - Only in hazy conditions (See Elastic-Raman inversion Sect. in Chap.7)
- *Angström coefficient* → *E.g. Sun photometer calibration*

2) The (VR) spectrum is preferred to the (RR)

- *RR lines of major atmospheric constituents overlap,*
- *large Rayleigh-Mie cross-talk.*
- *In contrast, VR cross-sections are usually lower than RR ones.*



MOLECULAR SPECIES (GAS) DETECTION (III)

SOME MEASUREMENT EXAMPLES

- Fig.1 Raman spectroscopy from the **ordinary atmosphere**
- Fig.2 Molecular species in an **oil smoke plume**

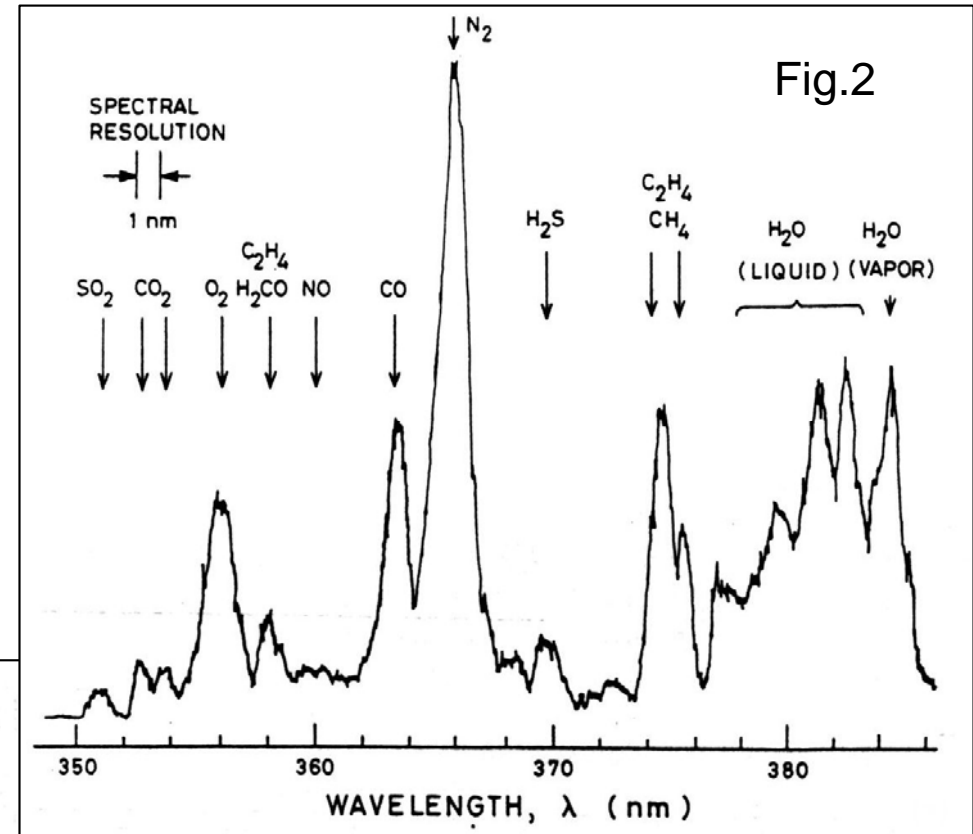
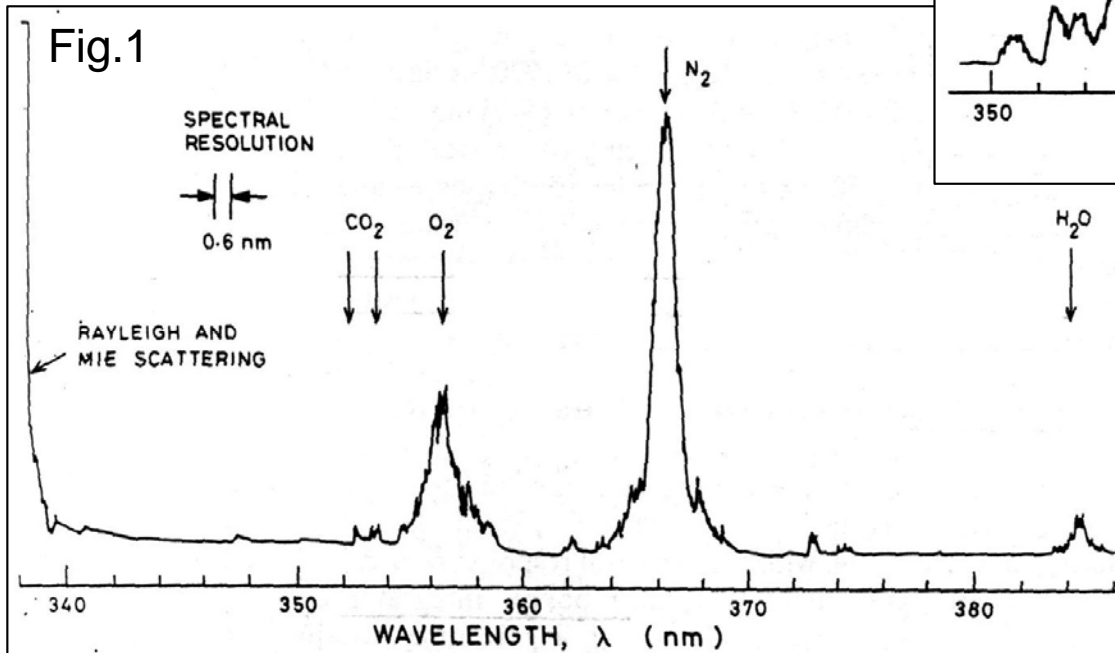
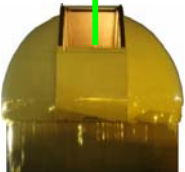


Fig. SOURCE: Inaba and Kobayasi, Opto-Electron 4, 101 (1972).



WATER-VAPOR (WV) KEYS:

- *Influences convective stability (likelihood of storm initiation)*
- *Most active green-house gas*
 - it absorbs terrestrial radiation more strongly than does CO₂
- *Water-vapor mixing ratio (w)*

$$w = \frac{MW_{H_2O}}{MW_{DryAir}} \frac{N_{H_2O}(R)}{N_{DryAir}(R)} \approx \frac{MW_{H_2O}}{MW_{DryAir}} \frac{N_{H_2O}(R)}{N_{N_2}(R)/0.78} \approx 0.485 \frac{N_{H_2O}(R)}{N_{N_2}(R)}$$

- where MW_x stands for molecular weight (≈ 18 g/mol for H₂O and ≈ 28.94 g/mol for dry air) and N_x stands for molecule number concentration.

- *Importance of the mixing ratio:*
 - It is conserved in atmospheric processes that do not involve condensation or evaporation
 - Serves well as a tracer of the movement of air parcels in the atmosphere

DERIVATION FROM THE RAMAN CHANNELS

From Eq.(1B) in Slide 12

$$\frac{P_{\lambda_H}(R)}{P_{\lambda_N}(R)} = \frac{O_H(R) F_H(T, \Delta\lambda_R) N_H(R)}{O_N(R) F_N(T, \Delta\lambda_R) N_N(R)} \left[\frac{d\sigma_{\lambda_H}(\pi)/d\Omega}{d\sigma_{\lambda_N}(\pi)/d\Omega} \right] \frac{\xi(\lambda_H)}{\xi(\lambda_N)} \Delta\tau(\lambda_H, \lambda_N, R)$$

and the definition of the mixing ratio (w)

$$w = 0,485 \underbrace{\frac{O_N(R)}{O_H(R)} \left[\frac{d\sigma_{\lambda_N}(\pi)/d\Omega}{d\sigma_{\lambda_H}(\pi)/d\Omega} \right] \frac{\xi(\lambda_N)}{\xi(\lambda_H)}}_{\text{System's calibration factor, } k^*(R)} \underbrace{\frac{F_N(T, \Delta\lambda_N)}{F_H(T, \Delta\lambda_H)}}_{\text{Temperature-dependent ratio}} \underbrace{\frac{P_H(R)}{P_N(R)} \Delta\tau(\lambda_N, \lambda_H, R)}_{\text{Measurement factor}}$$

– where $P_x(R)$ are background-subtracted quantities.

In summary,

$$w = k_L^*(R) \frac{F_N(T, \Delta\lambda_N)}{F_H(T, \Delta\lambda_H)} R_w(R) \Delta\tau(\lambda_N, \lambda_H, R) \quad R_w = \frac{P_H(R)}{P_N(R)}$$

WATER-VAPOR MEASUREMENT (III)

EXAMPLE

- In the UV ($\lambda_L=355$ nm), Raman channels: $\lambda_N=387$ nm, $\lambda_H=408$ nm

$$w = k_{355}^*(R) \frac{F_N(T, \Delta\lambda_N) P_H(R)}{F_H(T, \Delta\lambda_H) P_N(R)} \Delta\tau(\lambda_N, \lambda_H, R) \quad k_{355}^* \approx 0.22 \frac{O_N(R) \xi(\lambda_N)}{O_H(R) \xi(\lambda_H)}$$

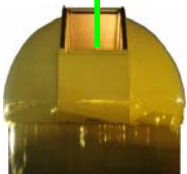
SPECIES	kappa (cm-1)	lambdaR (1) (nm)	lambdaR (2) (nm)
Air	0	→ 354,7	532,1
O2	1556	375,4	580,1
N2	2331	→ 386,7	607,4
H2O	3654	→ 407,5	660,5
Excitation wavelength (lambda0)			
(1)	354,7	nm (Nd:YAG, THG)	
(2)	532,1	nm (Nd:YAG, SHG)	

Cross sections are computed assuming a λ^{-4} dependency

i.e. higher in the UV than in the NIR

Water-Vapor Mixing Ratio Error

$$\frac{\sigma_w^2}{w^2} = \frac{\sigma_{k^*}^2}{k^{*2}} + \frac{\sigma_{R_w}^2}{R_w^2} + \frac{\sigma_{\Delta\tau}^2}{\Delta\tau^2} \approx \frac{\sigma_{R_w}^2}{R_w^2}; \quad R_w = \frac{P_H(R)}{P_N(R)}$$



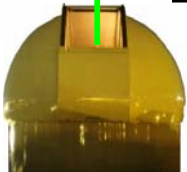
ERROR SOURCES AND UNCERTAINTIES

- *Water-Vapor Mixing Ratio Error*

$$\frac{\sigma_w^2}{w^2} = \frac{\sigma_{k^*}^2}{k^{*2}} + \frac{\sigma_{R_w}^2}{R_w^2} + \frac{\sigma_{\Delta\tau}^2}{\Delta\tau^2} \approx \frac{\sigma_{R_w}^2}{R_w^2}; \quad R_w = \frac{P_H(R)}{P_N(R)}$$

- k^* : *Calibration factor* → *Can be considered to be small*
 - Calibrated using a **radiosonde** (e.g. VAISALA RS80-A) or a MW radiometer
 - R_w : *Signal-induced statistical error dominates the error budget*
 - $\Delta\tau(\lambda_N, \lambda_H, R)$ = *Differential Transmission (DT)*.
 - λ_N and λ_H experience different amounts of attenuation on their return trips, caused **mainly by Rayleigh scattering**. The DT can be calibrated by using
 - 1) A **radiosonde** estimate the molecular number density (i.e, T(z), P(z))
 - 2) For hazy atmospheres (DT < 0.9 for $\tau_{PBL} > 2$), the *N₂-Raman channel* is used to estimate the aerosol extinction (typ., λ^{-1} dependence)
- See Sec. Inversion of Optical Parameters / Extinction inversion, $\alpha_{\lambda_H}^{aer}$, $\alpha_{\lambda_N}^{aer}$
- Note: WV absorbs weakly at $\lambda_H=660$ nm \Rightarrow $\lambda_L=355$ nm preferred to 532 nm

Fig. SOURCE: Inaba, H. Detection of Atoms and Molecules by Raman Scattering and Resonance Fluorescence. In *Laser Monitoring of the Atmosphere*, Hinkley, E. D., Ed.; Springer-Verlag: New York, 1976; Chap. 5, p.162.





LIDAR (LASER RADAR)

DEP. OF SIGNAL THEORY AND COMMUNICATIONS

WATER-VAPOR MEASUREMENT (V)

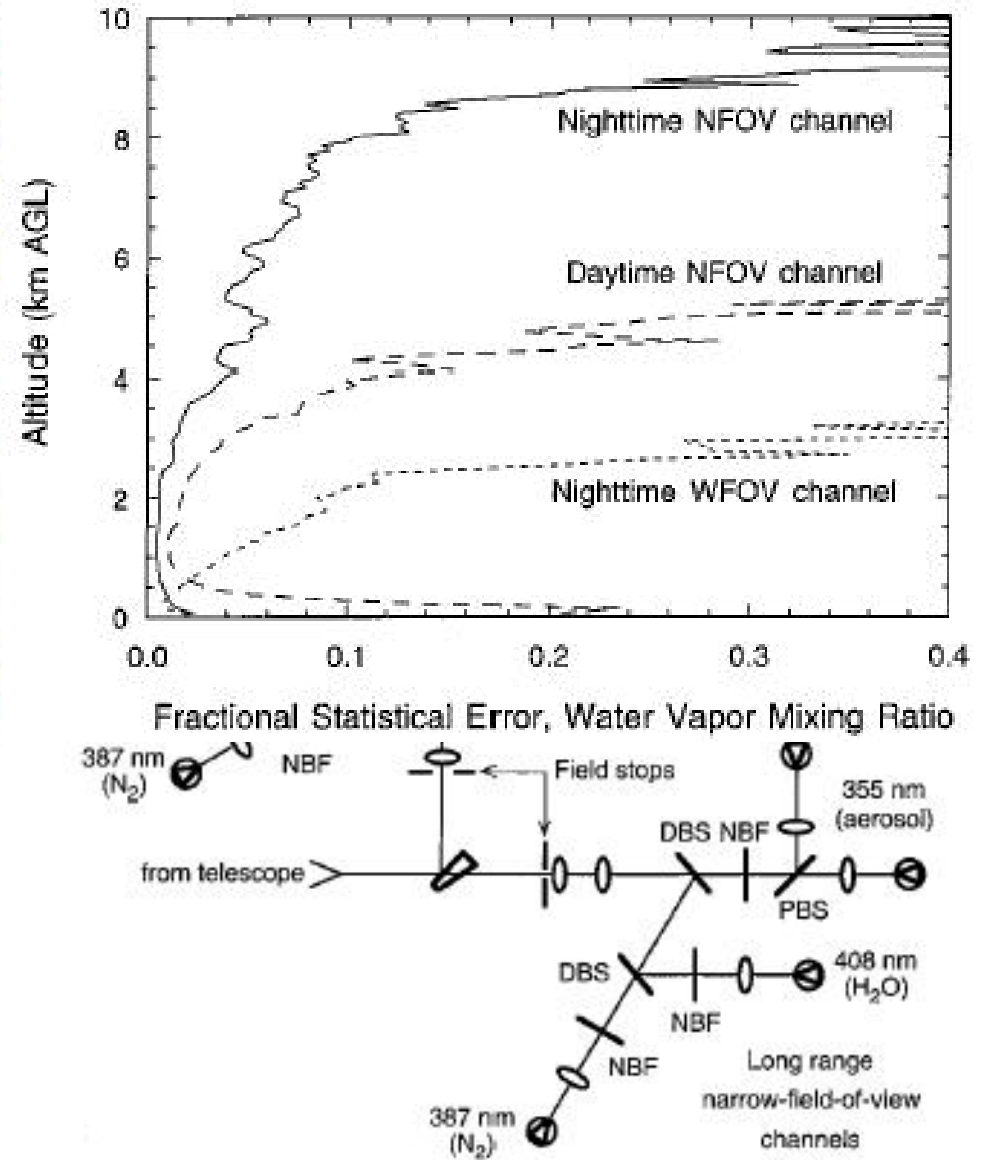
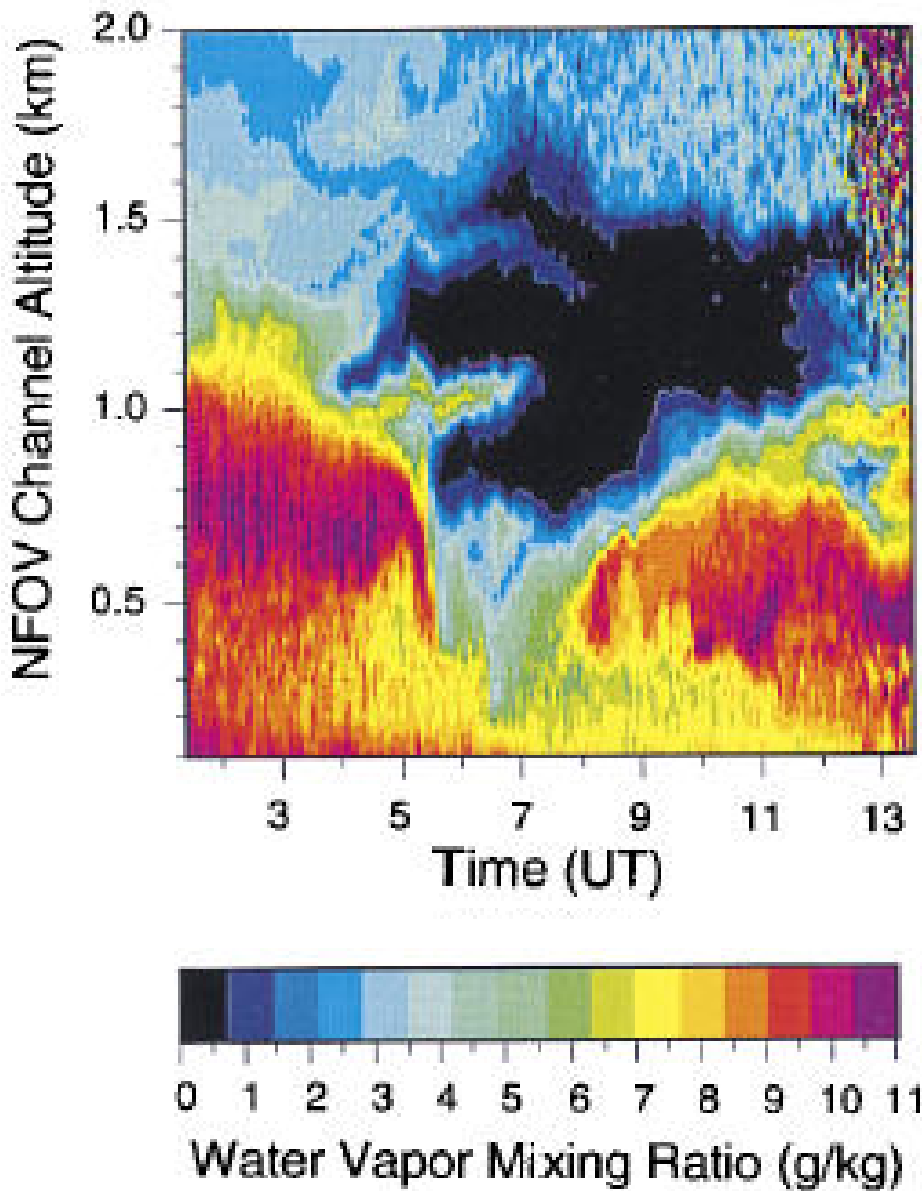


Fig. SOURCE: Goldsmith, J.E.M., et al., "Turn-key Raman lidar for profiling atmospheric water vapor, clouds, and aerosols", *Appl. Opt.* 27 (21), 4979-4990, (1998).

RELATIVE HUMIDITY MEASUREMENT

KEY

- *Water-vapor mixing ratio (w_{H_2O}) + Temperature profile \Rightarrow RH*
- *Derivation of the RH profile emerges from specific physical refs. 1,2*

$$RH(z) = \frac{e(z)}{e_w(z)}$$

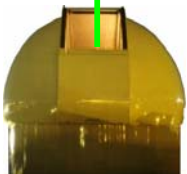
where $e(z)$ is the WV pressure, and $e_w(z)$ is the saturation pressure,

$$e(z) = \frac{P(z)w_{H_2O}(z)}{0.622 + w_{H_2O}(z)}, \quad e_w(z) = 6.107 \exp\left\{ \frac{M_A [T(z) - 273]}{M_B + [T(z) - 273]} \right\}$$

– $M_A=17.84, 17.08$ and $M_B=245.4, 234.2$ for $T <$ and > 273 K, respectively.

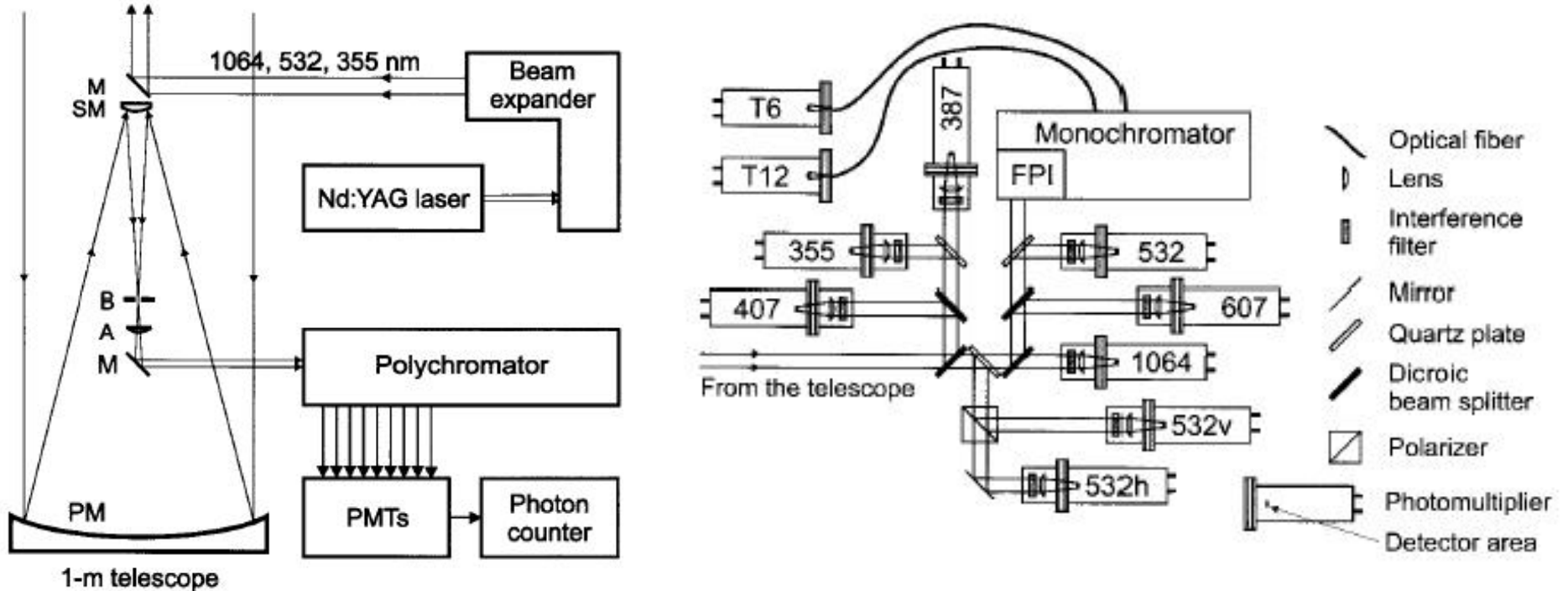
REFERENCES:

- 1) R.R. Rogers and M.K. Yau, *A Short Course in Cloud Physics* (Pergamon, New York, 1988).
- 2) R.J. List, ed., *Smithsonian Meteorological Tables* (Smithsonian Institution, Washington, D.C., 1951).



A COMPLETE RAMAN SYSTEM

LAYOUT



- 3 unshifted returns (1064, 532, 355 nm), NO polarization
- 4 returns (Stokes and anti-Stokes portions) of the N_2 RR spectrum
- 3 vibrational Raman returns (N_2 at 387, 607 nm and H_2O at 407 nm)
- 2 returns from the parallel and cross-polarized unshifted 532 nm

Fig. SOURCE: Matthis, I, Ansmann, A et al., "Relative-humidity profiling in the troposphere with a Raman lidar", *Appl. Opt.* **41** (30), 6451-6462, (2002).

A COMPLETE RAMAN SYSTEM

COMPOSITE OUTPUTS

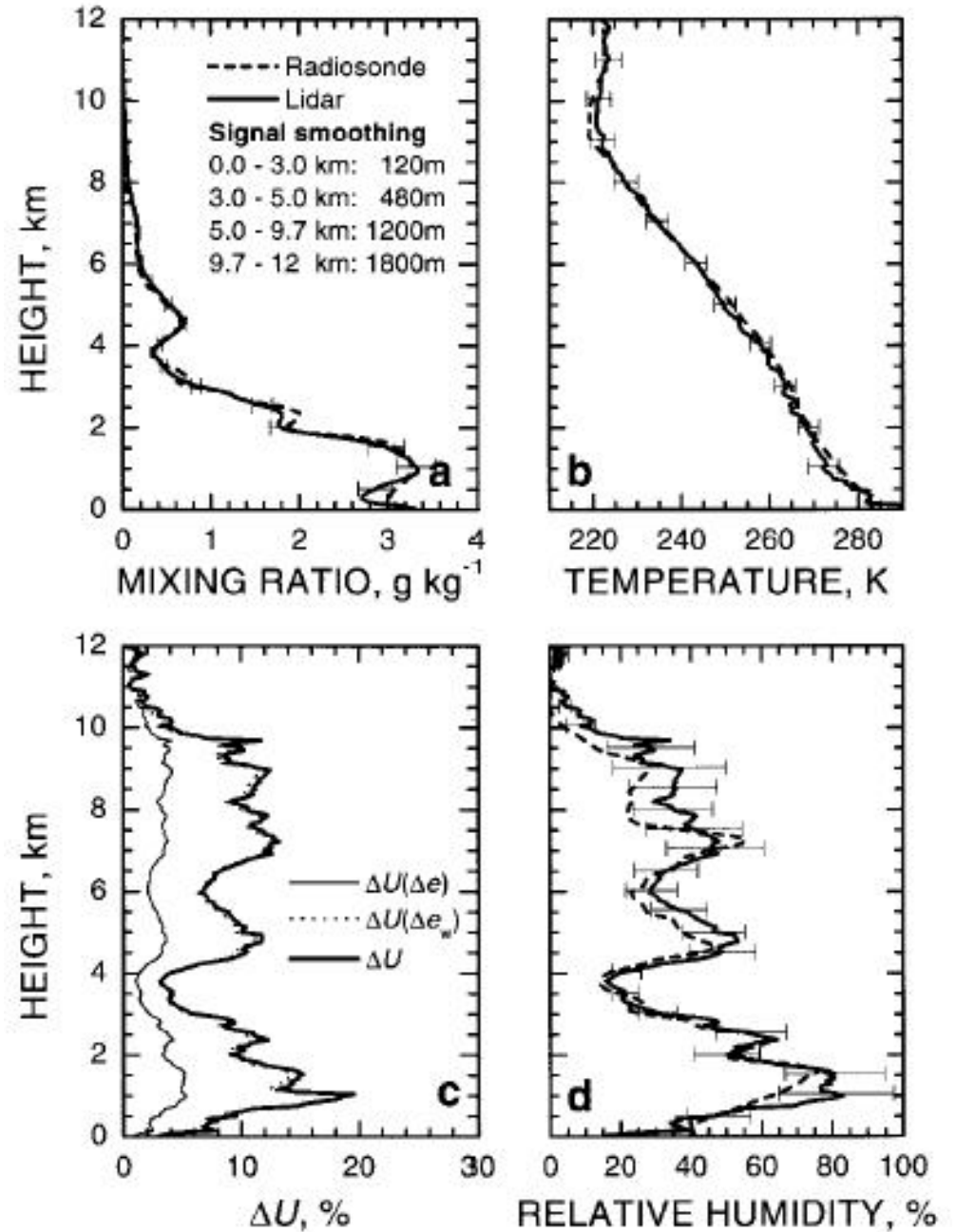
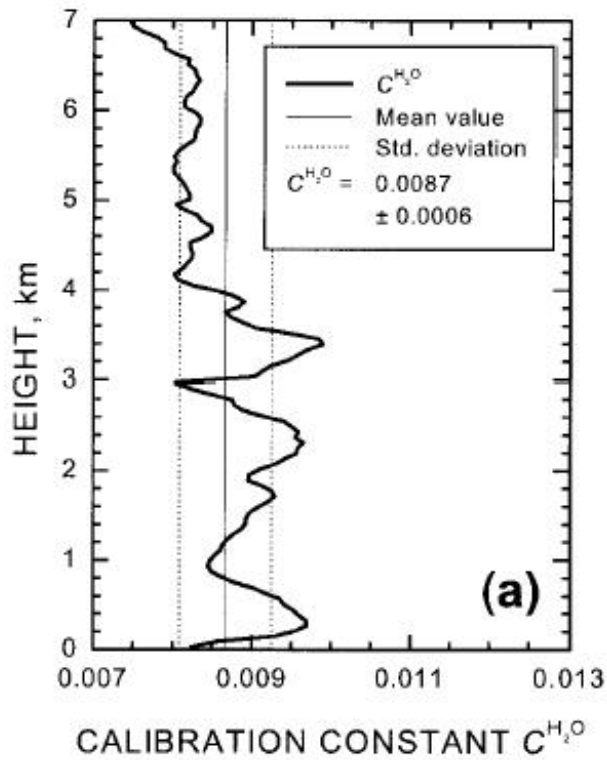


Fig. SOURCE: Matthis, I, Ansmann, A et al., "Relative-humidity profiling in the troposphere with a Raman lidar", *Appl. Opt.* **41** (30), 6451-6462, (2002).

PRINCIPLE

1) **Two receiving channels:** Besides the **ELASTIC receiver**, which is only sensitive to the elastic return, another receiver -i.e., the **RAMAN receiver**- is spectrally tuned to the Raman-shifted wavelength (Q-branch) of any abundant species of known relative concentration (usually N_2).

2) From:

- *radiosoundings or*
- *ground-level measurements of pressure and temperature + assumption of a standard atmosphere,*

the N_2 concentration -as a function of the range to the lidar- is inferred.

INVERSION OF OPTICAL PARAMETERS (II)

Raman-backscattered signal:

$$P_{\lambda_R}(z) = K_{\lambda_R} \frac{O(z)}{z^2} \left[N_R(z) \frac{d\sigma_{\lambda_R}(\pi)}{d\Omega} \right] \times \exp \left\{ - \int_0^z \left[\alpha_{\lambda_0}^{mol}(\xi) + \alpha_{\lambda_0}^{aer}(\xi) + \alpha_{\lambda_R}^{mol}(\xi) + \alpha_{\lambda_R}^{aer}(\xi) \right] d\xi \right\}$$

Scattering wavelength dependency: λ^{-k}

$$\frac{\alpha_{\lambda_0}^{aer}}{\alpha_{\lambda_R}^{aer}} = \left(\frac{\lambda_0}{\lambda_R} \right)^{-k}$$

Raman-channel *inverted extinction*:

$$\alpha_{\lambda_0}^{aer}(z) = \frac{\frac{d}{dz} \left[\ln \frac{N_R(z)}{P_{\lambda_R}(z) z^2} \right] - \alpha_{\lambda_0}^{mol}(z) - \alpha_{\lambda_R}^{mol}(z)}{1 + \left(\frac{\lambda_0}{\lambda_R} \right)^k}$$

INVERTED ATMOSPHERIC
OPTICAL PARAMETERS

Backscatter inversion requires:

- combination of lidar returns from *both elastic and Raman channels*

$$\beta_{\lambda_0}^{aer}(z) = -\beta_{\lambda_0}^{mol}(z) + \left[\beta_{\lambda_0}^{aer}(z_0) + \beta_{\lambda_0}^{mol}(z_0) \right] \times \frac{P_{\lambda_R}(z_0)P_{\lambda_0}(z)N_R(z)}{P_{\lambda_0}(z_0)P_{\lambda_R}(z)N_R(z_0)} \times \frac{\exp\left\{-\int_{z_0}^z [\alpha_{\lambda_R}^{aer}(\xi) + \alpha_{\lambda_R}^{mol}(\xi)] d\xi\right\}}{\exp\left\{-\int_{z_0}^z [\alpha_{\lambda_0}^{aer}(\xi) + \alpha_{\lambda_0}^{mol}(\xi)] d\xi\right\}}; \quad z \geq z_0$$

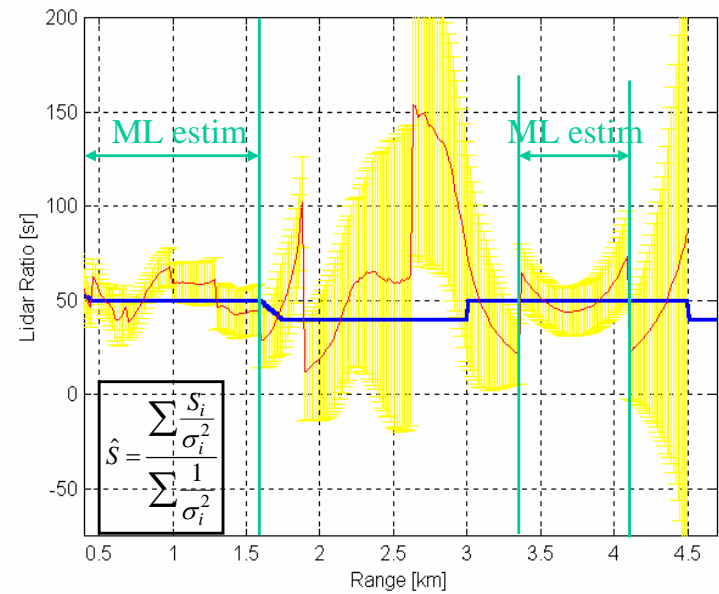
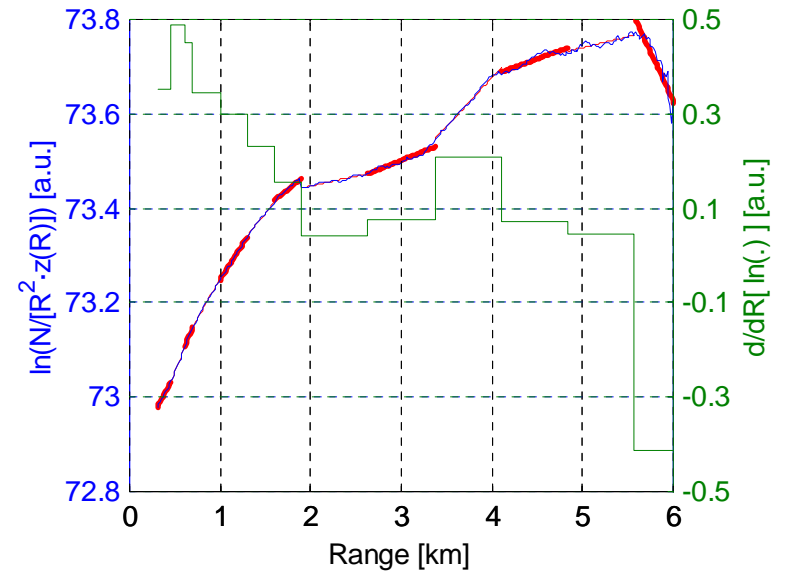
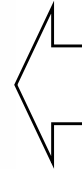
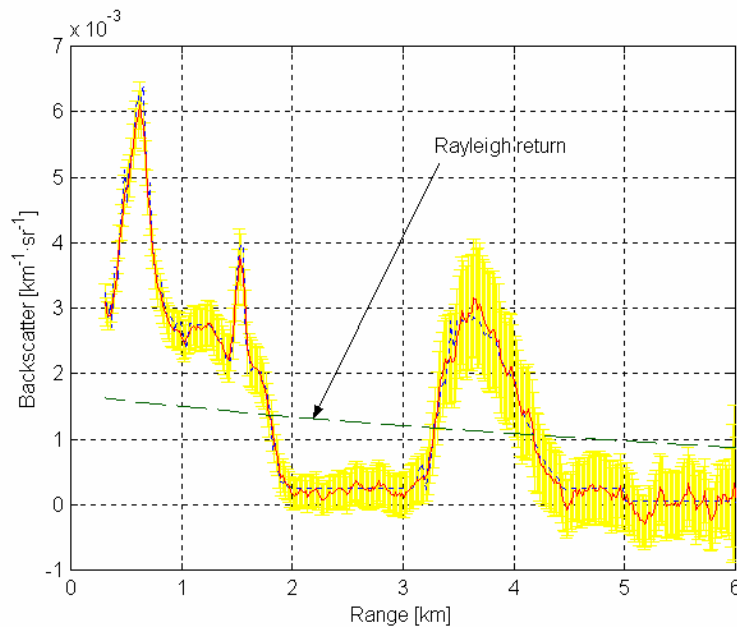
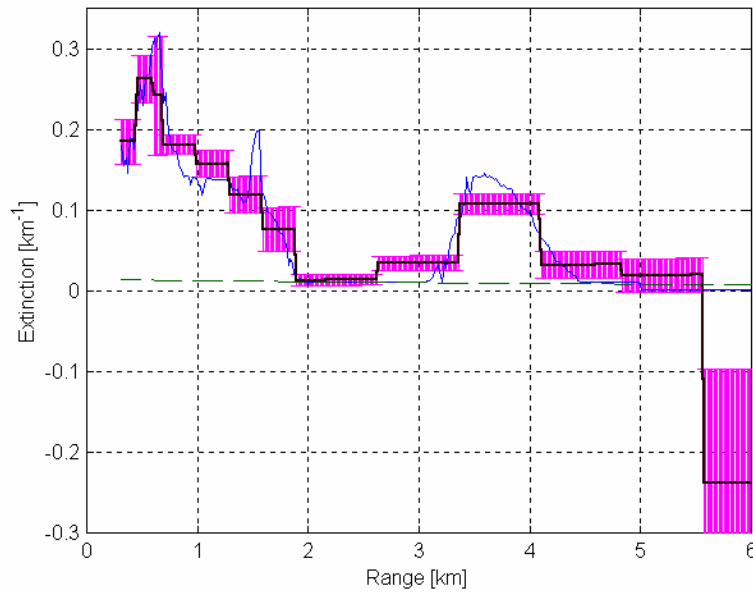
- a backscatter *calibration* at some height R_0 so that

$$\beta_{\lambda_0}^{mol}(R_0) \gg \beta_{\lambda_0}^{aer}(R_0) \rightarrow \left[\cancel{\beta_{\lambda_0}^{aer}(R_0)} + \beta_{\lambda_0}^{mol}(R_0) \right] \Rightarrow \beta_{\lambda_0}^{aer}(R) = f \left[\underbrace{P_{\lambda_0}, P_{\lambda_R}}_{\text{channel returns}}, \alpha_{\lambda_0}^{aer}, N_R, \underbrace{P, T}_{\text{Rayleigh comp.}} \right]$$

The lidar ratio is found as

$$S_{\lambda_0}^{aer}(z) = \frac{\alpha_{\lambda_0}^{aer}(z)}{\beta_{\lambda_0}^{aer}(z)}$$

4. INVERTED OPTICAL PARAMETERS



$$\hat{S} = \frac{\sum \frac{S_i}{\sigma_i^2}}{\sum \frac{1}{\sigma_i^2}}$$