FLAIR 2009 - Field Laser Applications in Industry and Research, September 6-11, 2009, Garmisch, Germany

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Simultaneous, Absolute In Situ Water-Vapor and Extractive Total-Water Detection in Cold Ice Clouds Using a Dual 1.37 µm TDL-Spectrometer

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Motivation

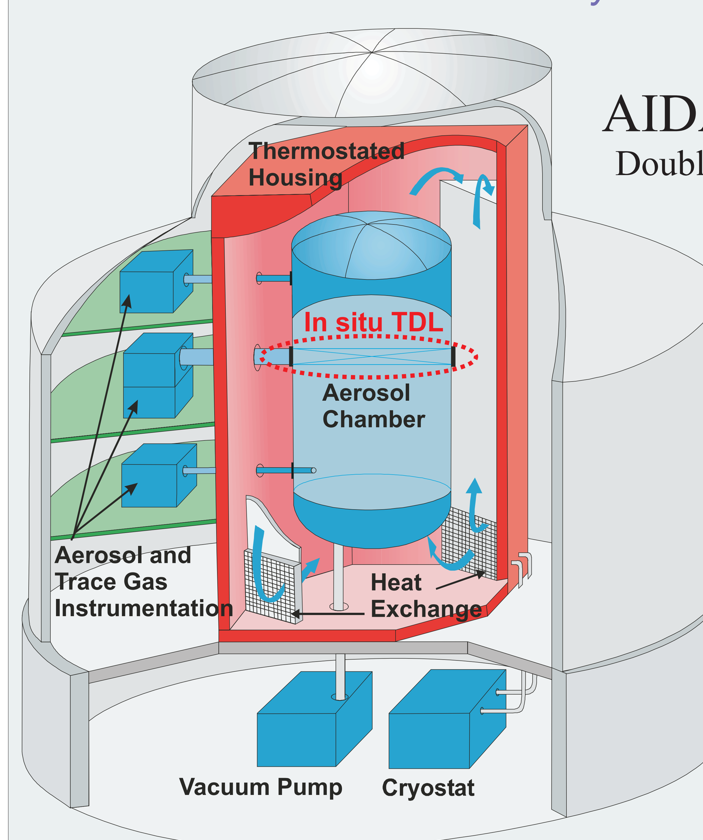
Clouds and their formation dynamics play an important role in the climatic system of our planet. In order to better understand the different cloud formation processes, it is necessary to study the controlling parameters, e.g. in **cloud simulation chambers like AIDA** in Karlsruhe. Here, clouds can be generated in a wide pressure/temperature range by adiabatic expansion experiments, i.e. controlled dynamic pressure and temperature variations, thereby simulating the ascent of an atmospheric air parcel.

To better characterize the cloud formation and achieve the microscopic process parameterization needed for improved global climate models, it is highly desirable to quantitatively monitor **the dynamics of the distribution of water into its three phases** (vapor, droplets, ice crystals).

Due to the fragility of the H_2O phase equilibrium and the problems associated with the water vapor sensor calibration, we developed a highly sensitive, **calibration-free dual laser hygrometer based on direct TDLAS** which is capable of selectively measuring **vapor phase water in situ**, i.e. directly in the cloud without any gas sampling, while simultaneously permitting absolute, **extractive total water** measurement. Furthermore, from the difference of the results of both instruments a simultaneous precision measurement of the **ice water content** could be obtained for the first time.

Cryogenic Test Chamber AIDA

AIDA: Aerosol Interactions and Dynamics in the Atmosphere



AIDA Physical Data:

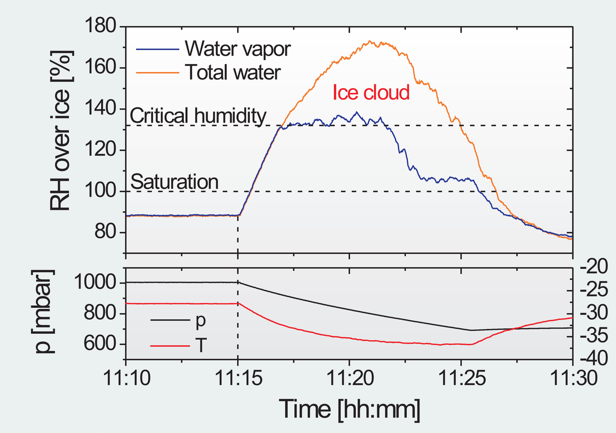
Double walled containment

Diameter	4 m
Height	7 m
Volume	83 m^3
P:	10^{-2}mbar to 1 bar
T:	-90 °C to 60 °C
ΔT_{wand}	±0,3 K
ΔT_{gas}	±0,1 K
dp/dt	100 mbar/min
dT/dt	4 K/min
dRHi/dt	>100 %/min
Rhi_{max}	>160 %

Temperature stabilized and ice covered inner reactor wall
⇨ Well defined water vapor pressure
Ice cloud formation ⇨rapid pressure drop ⇨adiabatic cooling
⇨ Super saturation of atmosphere with H_2O vapor
⇨ Condensation of vapor
⇨ Freezing of particles / rapid particle growth / cloud formation

Cloud Formation

Dynamic Ice Cloud Formation in Adiabatic Expansion Experiments inside AIDA



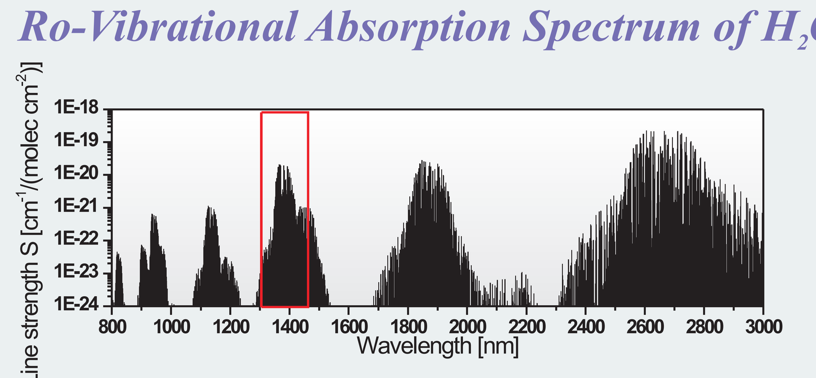
Adiabatic expansions:
During the adiabatic expansion (pressure reduction) the temperature is reduced and therefore the relative humidity rises above 100 % (saturation). At a certain critical humidity ice crystals start to form around aerosol particles from condensed water vapor.

Investigate:
- Growth processes of ice particles
- Influence of primary-particle type (aerosol) → heterogenous nucleation
- Phase transitions (droplet formation, droplet freezing)
- Water phase equilibrium

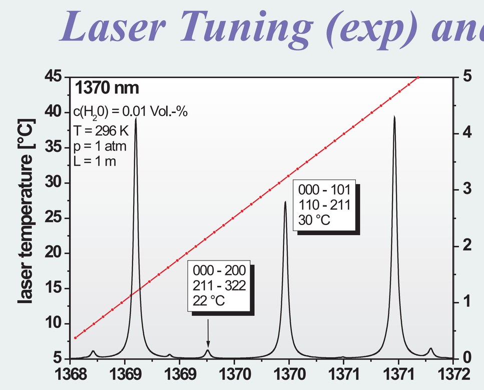
Critical parameters:
- Threshold for ice particle formation and growth
- Particle growth rates

Spectroscopy

Ro-Vibrational Absorption Spectrum of H_2O



Laser Tuning (exp) and Modelled H_2O Spectrum



Used absorption lines:
- For $[H_2O]$ < 1000 ppm
  30 °C, (110>211)(000>101)
- For $[H_2O]$ > 1000 ppm
  22 °C, (211>322)(000>200)

Direct Absorption Spectroscopy

Lambert-Beer-Law

$$I(\lambda,t)= I_0(\lambda,t)\cdot Tr(t)\cdot \exp[-S(T)\cdot\phi_{line}\cdot N\cdot L]+ E(t)$$

$$N = \frac{-1}{S(T)\cdot L}\int \ln\left(\frac{I(\lambda,t)-E(t)}{I_0(\lambda)\cdot Tr(t)}\right)\frac{\delta\lambda}{\delta t}\,dt \Rightarrow$$

Absolute number densities
Self calibrating

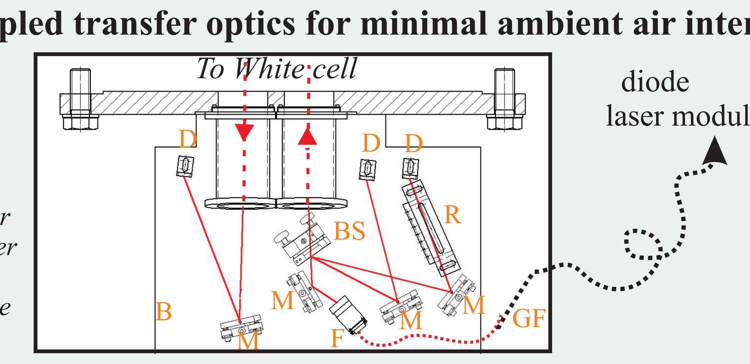
In Situ and Extractive TDL

In situ TDL for Measurement of H_2O Vapor in AIDA

White-type multi-path absorption cell inside AIDA vessel
- Base length 3.73 m
- Path length range 15 - 254 m

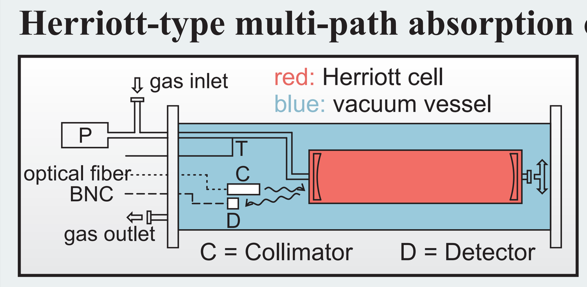
Fiber-coupled transfer optics for minimal ambient air interference

D = Detector
M = Mirror
BS = Beam Splitter
FC = Fiber collimator
GF = Glass fiber
R = Ref.-cell
B = Base plate



Extractive TDL for Measurement of Total H_2O in AIDA

Herriott-type multi-path absorption cell in external vacuum vessel

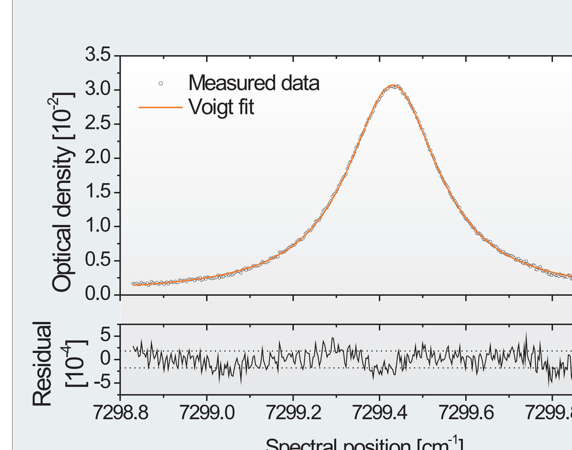


- Base length: 0.40 m
- Path inside Herriott cell: 29.9 m
- Total path length: 30.3 m

- Gas sampling from AIDA via heated stainless steel tubes
- Fiber coupled transfer optics
- Entire optical path inside purged vacuum vessel
⇨ Minimal parasitic absorption from ambient air contamination

Typical Fit Results

In situ TDL

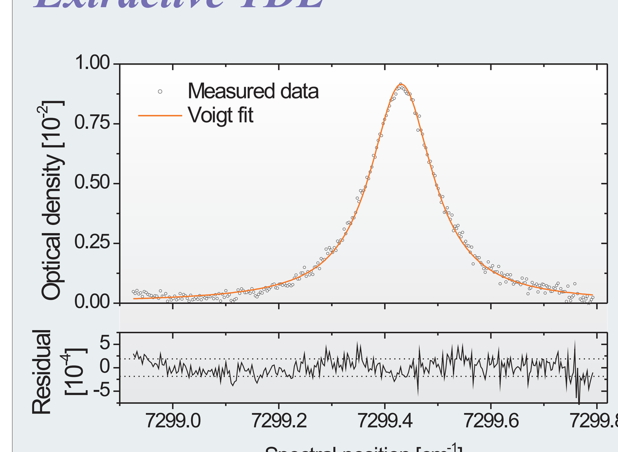


$[H_2O$ vapor$]$ = 3.16 ppm
- p = 997.84 mbar
- T = 203.92 K
- (110>211)(000>101)
- 68.9 m absorption path
- Voigt fit

Optical resolution
- $1.8\cdot10^{-4}$ OD (1σ)
- S/N = 169 → Δc = 18.7 ppb
- average of 250 single scans

Time resolution ~ 1 s

Extractive TDL



$[$Total $H_2O]$ = 3.75 ppm
- p = 720.09 mbar
- T = 293.90 K
- (110>211)(000>101)
- 30.3 m absorption path
- Voigt fit

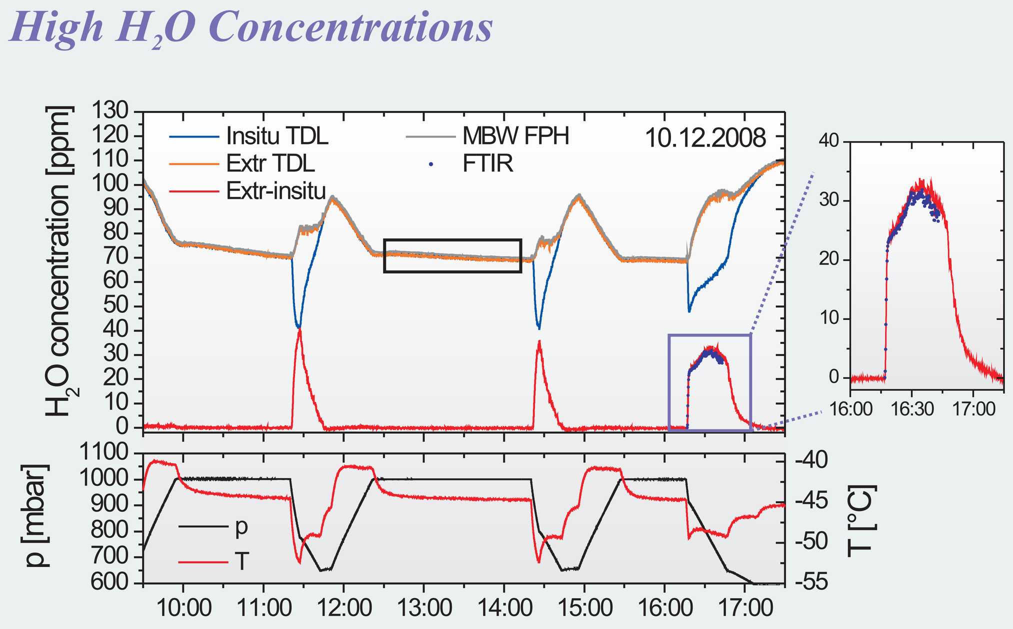
Optical resolution
- $1.9\cdot10^{-4}$ OD (1σ)
- S/N = 49 → Δc = 76.5 ppb
- average of 350 single scans

Time resolution ~ 1 s

Simultaneous Multiphase Water Detection in AIDA

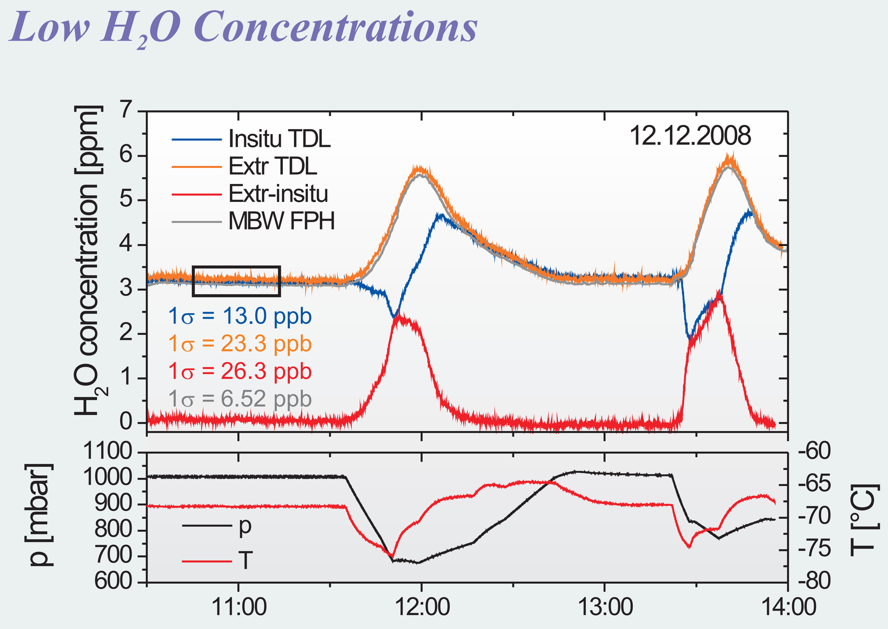
Determination of Ice water concentration from the difference Total water (extractive TDL) - Water vapor (in situ TDL)

High H_2O Concentrations



Absolute Accuracy at cloudfree conditions
Deviation between
- Insitu and extractive TDL: 0.1 ppm/0.1 % (black box)
⇨ highly accurate measurement of Ice Water from the difference of both TDLs
- TDLs and MBW Frost Point Mirror: 1.3 ppm/1.9 % (black box)
- TDL Ice Water and FTIR Ice Water: 1.2 ppm/4.2 % (purple box)

Low H_2O Concentrations



$[H_2O]$ Resolution
from $[H_2O]$-noise (1σ over 30 min, black box)
- Insitu TDL: 13.0 ppb
- Extractive TDL: 23.3 ppb
- TDL Ice Water: 26.3 ppb

Conclusion

A **dual laser hygrometer** has been developed with the following characteristics, fulfilling the **demanding needs of cloud dynamics research**:
- **Simultaneous measurement** of water vapor, total water and condensed water concentration
- **High sensitivity:** $[H_2O]$ resolution better than 30 ppb
- **High accuracy:** very low deviation (0.1 %) between both TDLs wihout calibration, validation of TDL results by other instruments (FPH, FTIR)

Outlook

In order to extend the dynamic range of the in situ TDL, a **new single-path in situ TDL** with an optical path length of around 4 m is developed at the moment.

For the extractive TDL, the **validation** of the instrument at the **primary humidity standard** of the German national labratory of standards (PTB) is planned in near future.

The incorporation of absorption lines in the band around **2.6 µm** can increase the sensitivity of the present instruments by a factor of 20. The realization of these TDL hygrometers is currently under development.

LITERATURE: Environ. Res. Lett. 3, 025007 (2008) // Atmos. Chem. Phys. 6, 4775-4880 (2006) // Springer Handbook of Experimental Fluid Dynamics, 1241-1316 (2007)