

Remote sensing in the FIR

	<i>Troposphere</i>	<i>Lower Stratosphere</i>	<i>Upper Stratosphere</i>	<i>Mesosphere</i>	<i>Radiation Budget</i>
H_2O / HDO / $H_2^{18}O$	nadir	nadir/lim b	nadir/lim b/up boking	nadir/lim b	nadir
OH	–	lim b	lim b/up boking	lim b/up boking	–
HO_2	–	lim b	lim b/up boking	lim b	–
H_2O_2	–	lim b	lim b	–	–
O_3 , P , $T(?)$	nadir?	lim b/up boking	lim b/up boking	lim b	nadir
O_2 , P , T	–	lim b	lim b	lim b	–
$O(^3P)$	–	–	lim b	–	–
CO	–	lim b/up boking	lim b	–	–
N_2O	>8 km lim b	lim b/up boking	lim b	–	–
NO	–	lim b/up boking	lim b	–	–
NO_2	–	lim b/up boking	lim b	–	–
N_2O_5	>8 km lim b	lim b/up boking	lim b	–	–
HNO_3	>8 km lim b	lim b/up boking	lim b	–	–
HCl	–	lim b/up boking	lim b	–	–
$HOCl$	–	lim b/up boking	lim b	–	–
$ClOCl$	–	lim b	lim b	–	–
$ClONO_2$	>8 km lim b	lim b/up boking	lim b	–	–
HF	–	lim b/up boking	lim b	–	–
HBr	–	lim b	lim b	–	–
<i>Continuum</i>	–	lim b/up boking	–	–	nadir
<i>Clouds</i>	–	–	–	–	nadir
<i>Cirrus</i>	slant	slant/up boking	–	–	nadir

Up boking : observer above tropopause

FIR (50 – 500 cm⁻¹) lab spectroscopy groups

<i>Contact</i>	<i>Location</i>	<i>Technique</i>	<i>Remarks</i>
<i>Chance, Evenson</i>	Time and Frequency Division, NIST, U.S.A.	TuFR/IMR	
<i>DiDonardo, Inguscio</i>	LENS, Italy	TuFR/FTS	
<i>Nicolaisen</i>	Institute of Chemistry, University of Copenhagen, Denmark	FTS	
<i>Steyert, Sirota</i>	Joint Center for Earth Systems Technology, NASA Goddard Space Flight Center, U.S.A. Department of Physics, University of Maryland, U.S.A.	FTS/TDL	>400 cm ⁻¹
<i>Birk, Wagner</i>	Institute for Remote Sensing, DLR, Germany	FTS	
<i>Winnewisser, Klee</i>	Molecular Spectroscopy, Justus-Liebig-University Gießen, Germany	FTS	Future?
<i>Johns, McKellar</i>	Steacie Institute for Molecular Sciences, NRC, Canada	FTS	Future?

Any laboratory operating a commercial high resolution vacuum FTS could do work in the FIR with moderate extensions.

Requirements for generation of accurate database

- ◆ Well-characterized sensitive high-resolution (Doppler limited) spectrometer
- ◆ Detailed knowledge of instrumental error source prevention or correction
- ◆ Coolable absorption cells with high temperature homogeneity and precision gas temperature measurement capabilities
- ◆ Infrastructure for gas handling with accurate pressure measurement
- ◆ Infrastructure for sample synthesis and purification
- ◆ Infrastructure for generation of unstable species
- ◆ Validated software for data reduction
- ◆ Sophisticated quality assurance procedures

Problem : No standardized QA/QC procedures for new entries/updates of spectroscopic databases

⇒ Questionnaire for quality assessment of FT measurements

Characterization of measurements and data reduction

<i>Category</i>	σ	$\delta(T)$	S	$\gamma(T)$	$\alpha(p, T)$
<i>Table of measurements</i>	+	+	+	+	+
<i>Cell specification</i>		+	+	+	+
<i>Pressure measurements</i>		+	+	+	+
<i>Number density determination</i>			++		++
<i>Spectrum generation</i>	+	+	+	+	+
<i>Line parameter retrieval</i>	+	+	+	+	
<i>Instrumental lineshape specification</i>	+	+	+	++	++
<i>Line specification</i>		+	+	+	+
<i>Further data reduction</i>	+	+	+	+	+

Table of measurements

- Measurement number
- Target molecule
- Partial pressures $\pm \sigma$
- Total pressure $\pm \sigma$
- Temperature $\pm \sigma$
- Absorption path $\pm \sigma$
- Sample handling (sealed off, flow)
- Measurement time
- Spectrum type (transmittance, absorption, ...)
- Spectral range
- rms noise level (min, max)
- MOPD
- α_{div}
- MOPD_{ref}

Cell specification

- Type (White, single pass, ...)
- Material
- Cell dimensions
- Window material
- Window thickness
- Window wedge
- Window inclination
- f/number of beam
- Absorption path
- Temperature measurement (method, location of sensor, validated/calibrated with gas temperature?)
- Temperature range
- Temperature homogeneity (Comparison of retrieved gas temperature and cell temperature?)
- Cell mounting (inside spectrometer?, evacuated housing?)
- Filling without moving the cell?

Pressure measurements

- Pressure gauge type
- Accuracy stated by manufacturer
- Date of last calibration

Number density determination

- From pressure/temperature measurements?
- Decomposition, adsorption, leak, outgassing?
- From UV measurements?
- From FR measurements?

Spectrum generation

- Non-linearity correction? If yes, method?
- Thermal radiation correction? If yes, method?
- Reference measurements? (timing)
- Generation of transmittance, ... spectra
(Which reference spectra?)
- Baseline correction? If yes, method?
- Channeling correction? If yes, method?

Line parameter retrieval

- Which code was used?
- Which LS model?
- Which baseline model?
- Treatment of blended lines? How?
- Cross check with other codes?
- Checked with synthetic spectra?
- Which parameters were fitted, which fixed?
- Were the residuals noise only?

Instrumental lineshape specification

- Where are field stops located and where is the cell located (after or before interferometer)?
- Dedicated LS measurement with Voigt width $<$ LS width?
- Were LS parameters fitted? Were residuals of line fits noise only?
- Were LS parameters fitted at different wavenumbers? Did the results agree within their error bars?
- Was LS uncertainty propagated into spectroscopic parameters, especially $\gamma(T)$?

Line specification

- Monochromatic optical depths of line m axis a (m in μ axis)?
- Monochromatic line widths (m in μ axis)?
- LS widths (m in μ axis)?
- Observed line widths (m in μ axis)?

Further data reduction

- Quantum mechanical calculations?
- Empirical calculations?

Pressure broadening QA

- Redundant measurements: total pressure, temperature, opacity?
- Least squares fitting to obtain γ (296 K) and n ?
- After further data reduction (eg. polynomial fits): propagated uncertainties of input data equal to standard deviation from residuals?
- Model input spectra from new database. Residuals noise?
- Model test spectra from new database. Residuals noise?
- Fit atmospheric spectra with new database (several microwindows/lines simultaneously). Residuals noise?

Line position QA

- Calibration molecule line positions accuracy?
- Calibration lines distributed over spectral range?
- After calibration fit: propagated uncertainties of input data equal to standard deviation from residuals?
- Deviation from proportionality of σ_{ref} and σ_{obs} ?

Lineshift QA

- Redundant measurements: total pressure, temperature?
- After further data reduction (eg. polynomial fits): propagated uncertainties of input data equal to standard deviation from residuals?
- Model input spectra from new database. Residuals noise?
- Model test spectra from new database. Residuals noise?
- Fit atmospheric spectra with new database (several microwindows/lines simultaneously). Residuals noise?

Linestrength QA

- Redundant measurements: target gas pressure, absorption path?
- Temperature/number density fit of individual measurements?
- After further data reduction: propagated uncertainties of input data equal to standard deviation from residuals?
- Check if sum of linestrengths over entire band system in new database for different temperatures is constant?

Absorption cross section QA

- Redundant measurements: target gas pressure?
- Area under absorption cross section for entire band system invariant w.r.t p, T ?
- Data reduction performed? If yes, are residuals noise?
- Model input spectra from reduced data. Residuals noise?
- Model test spectra from reduced data. Residuals noise?
- Fit atmospheric spectra with reduced data. Residuals noise?

Generation of new database

Detailed error analysis

- Propagate **statistical error** of molecular constants, polynomial expansion, ... into spectroscopic database
- Propagate **systematic errors** (instrumental, particle density, temperature, ...) into spectroscopic database

Validated accuracies established at DLR by fulfilling requirements

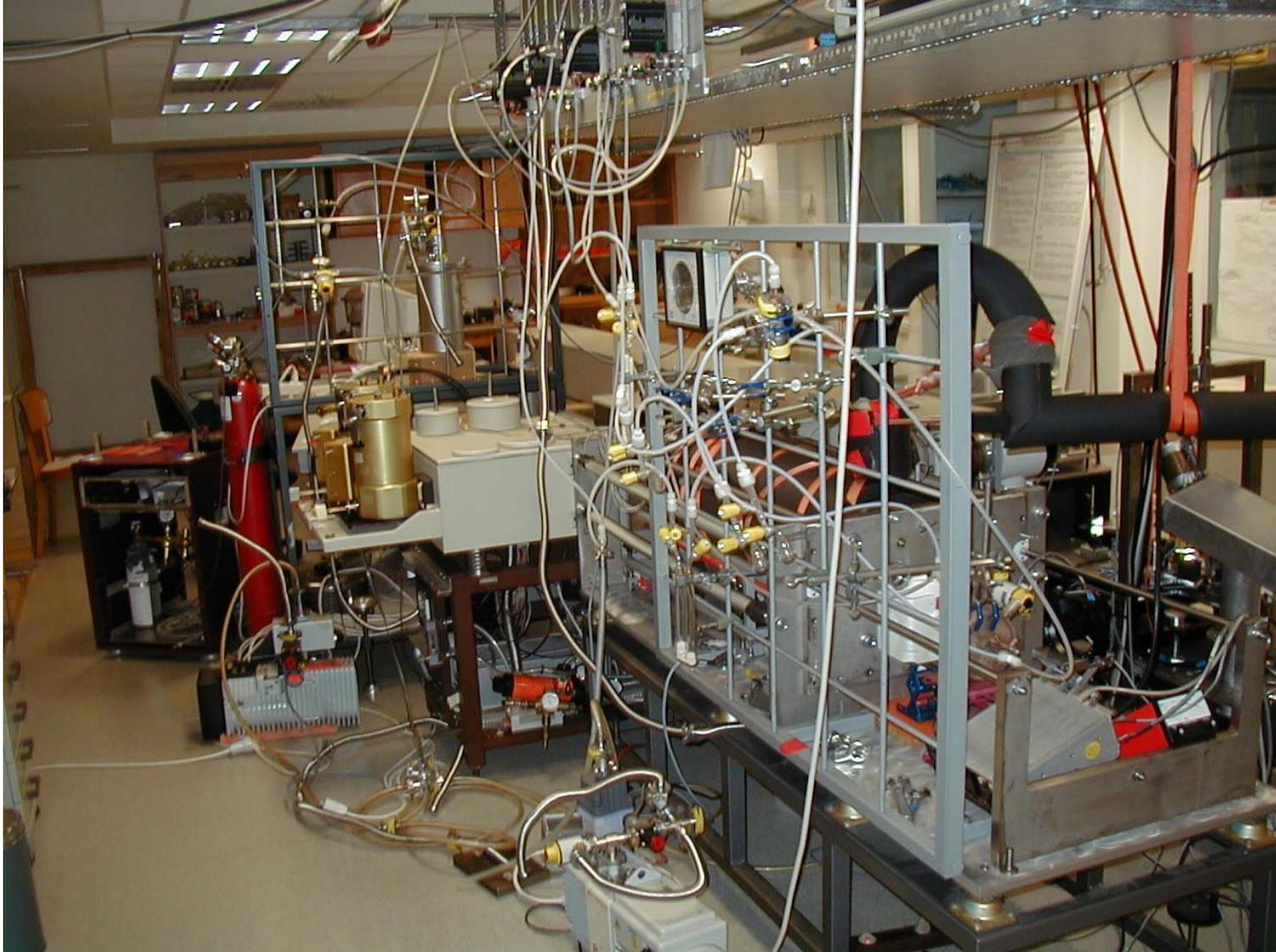
- ◆ **FIR CO : <1%** deviation for linestrengths by comparison with calculated linestrengths
- ◆ **FIR O₃ : <1%** deviation for linestrengths by comparison with calculated linestrengths
- ◆ **MMW CO / O₃ : <2%** deviation for linewidths by comparison with tunable MMW spectrometer (Bauer (Bauer et al., Lille))

Deviations always inside error margins!

Spectroscopic database work at DLR

Species	FTR	M IR	Purpose/Application	Remark
O_3	$S, \gamma(\Gamma)$	$\sigma, S, \gamma(\Gamma), \alpha(\Gamma_P)$	database improvement	
$CDNO_2$	$\alpha(\Gamma_P)$	$\alpha(\Gamma_P)$	database improvement, M PAS	difficult synthesis
N_2O_5	$\alpha(\Gamma_P)$	$\alpha(\Gamma_P)$	database improvement, M PAS	
OH/HO_2	σ		new methodology	extremely unstable
BrO	$\sigma, \gamma(\Gamma)$		database improvement, M ASTER/SOPRANO	extremely unstable
CD	$\sigma, \gamma(\Gamma)$	σ, S	database improvement, M ASTER/SOPRANO	unstable
$CDCl$	$\alpha(\Gamma_P)$	$\alpha(\Gamma_P)$	detectability with remote sensing	sample preparation difficult
$HOCl$	σ		FTR database	
CO	$S, \gamma(\Gamma)$	$S, \gamma(\Gamma)$	error characterisation, high temperature database, Q/A	<1% radiometric accuracy
CO_2		$\alpha(\Gamma_P)$	high temperature database	
H_2O		$\sigma, S, \gamma(\Gamma)$	high temperature database improvement, climate, M PAS, ASI	sample preparation difficult
NO		$\sigma, S, \gamma(\Gamma)$	high temperature database, engine emissions	
NO_2		$\alpha(\Gamma_P)$	high temperature database, engine emissions	

Laboratory view



Absorption cells

White-type cell

Temperature 190 – 300 K

Base length 80 cm

Diameter 20 cm

Material: Duran glass

Four-row design

Windows: Polypropylene, KBr

Max. absorption path ca. 100 m

Optimized for FR

Gold-coated mirrors, cooled

Roots blower (250 m³/h)

Coolable cell

Temperature 190 – 300 K

Absorption path 25 cm

Diameter 4 cm

Material: Duran glass

Windows: Polyethylene, AgCl

Mounted inside evacuable spectrometer

Gas and cell temperature agree within 0.5 K at 190 K

Heatable cell

Temperature 300 – 1000 K

Absorption path 16 cm

Diameter 4 cm

Material: Quartz glass

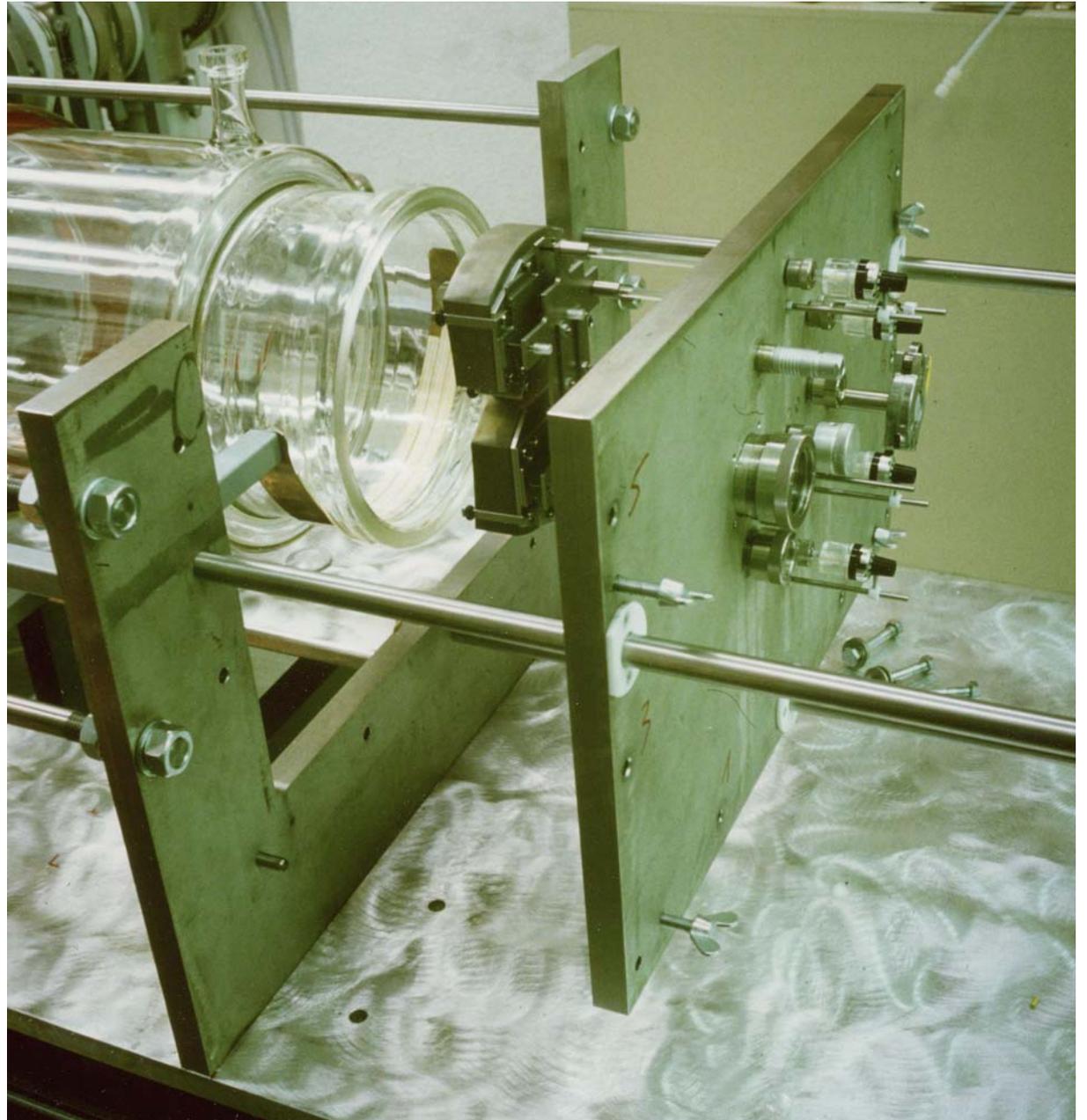
Windows: CaF₂

Mounted inside evacuable housing

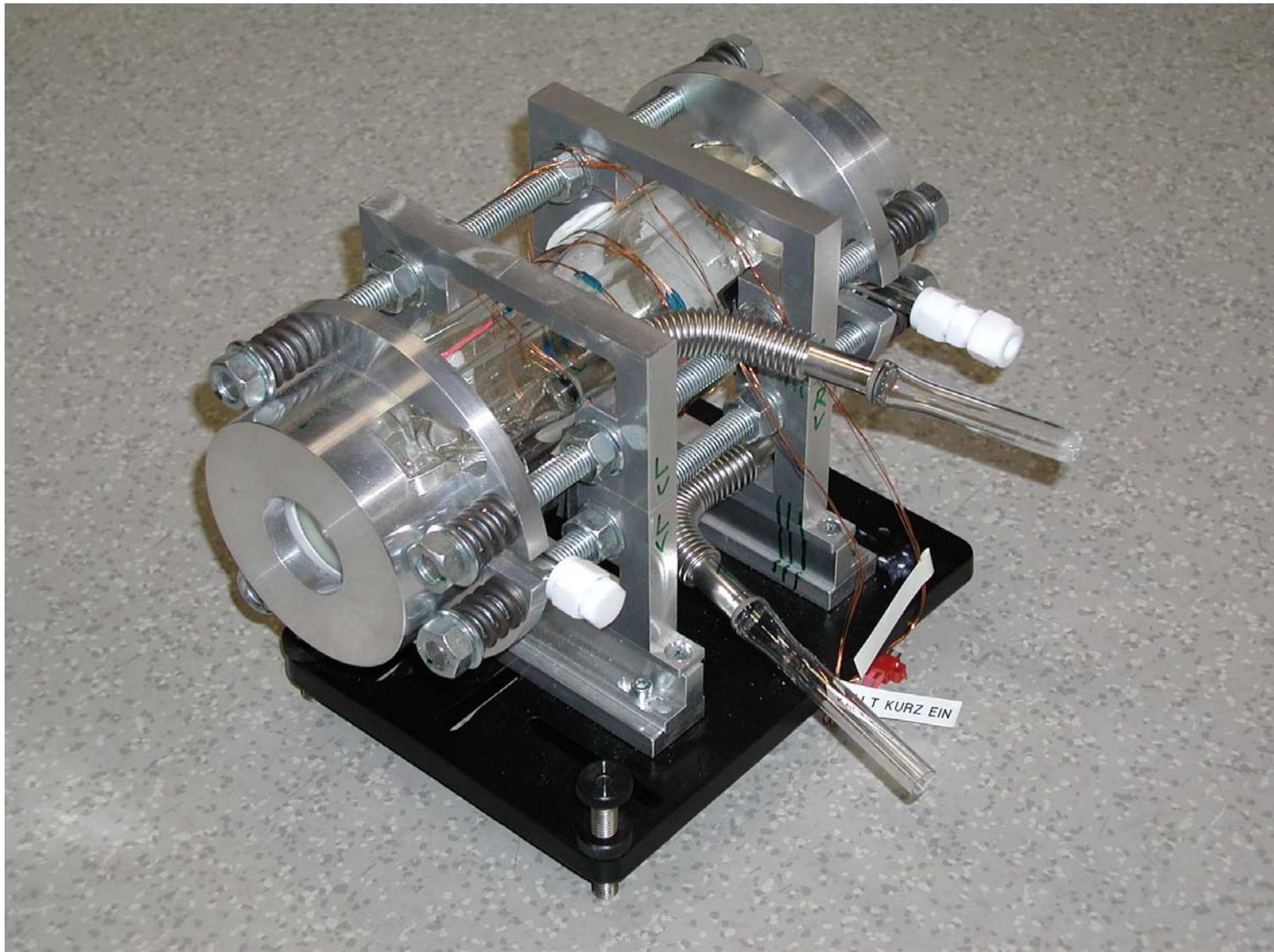
Heated gas inlet for steady flow

Multireflection cell

D-Mirror assembly



Coolable Cell



Status of FIR Database (1)

Rotational transitions

Line positions:

Source: accurate MW and submm measurements, MR combination differences

Quality: good, except very weak O_3 , H_2O lines observable in limb sounding geometry?

Linestrengths:

Source: can be calculated from permanent electric dipole moment

Quality: ok, except non-rigid molecules, large vibrational-rotational interactions (e.g. H_2O ?), low lying fundamentals (partition function, e.g. $CDCl$)

Status of FIR Database (2)

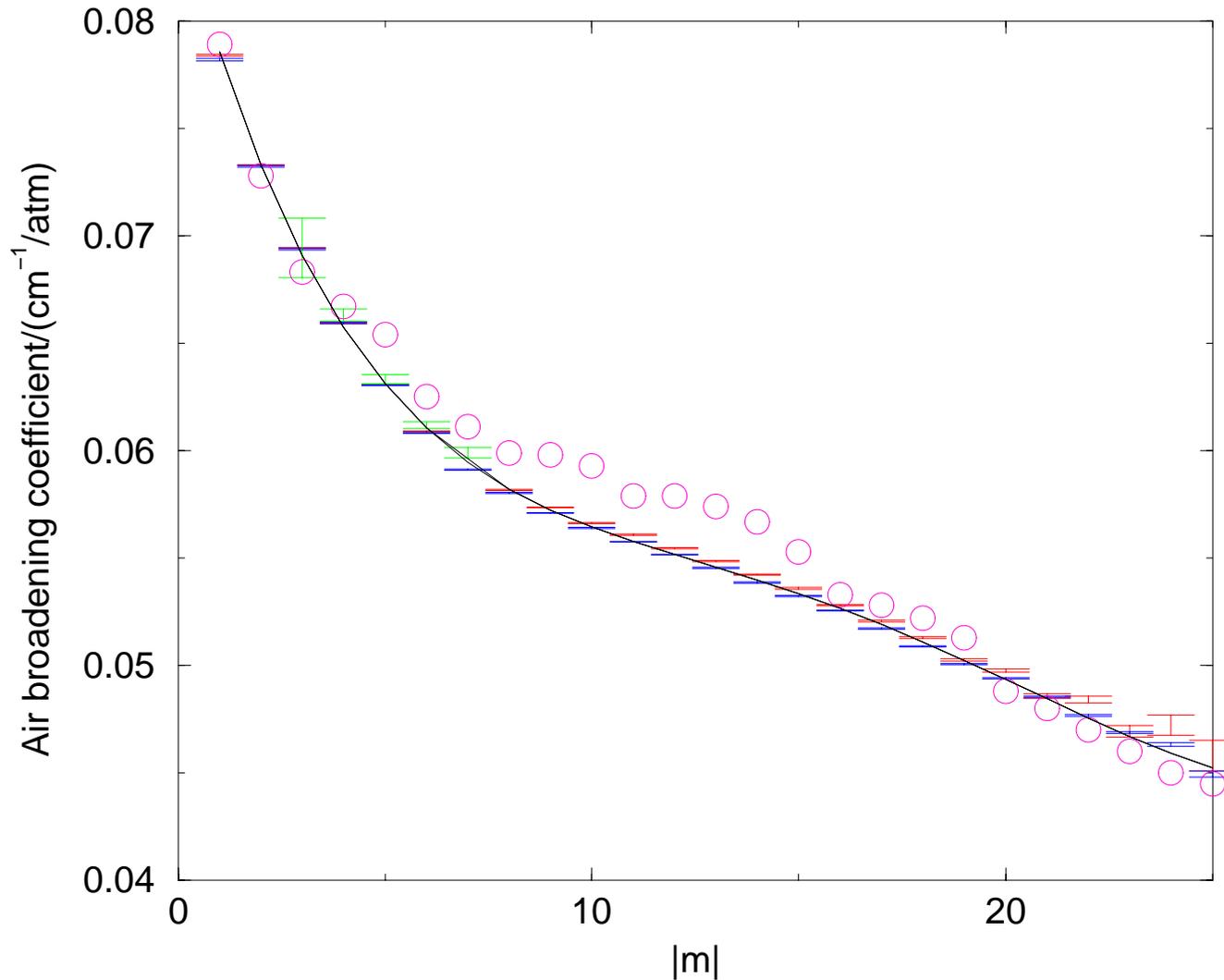
Pressure broadening/temperature dependence:

Source: FIR measurements, MIR measurements (in case vibrational dependence small)

Quality: sometimes inadequate since

- No experimental data available
- Data taken from MIR, error of vibrational dependence not assessed
- Temperature dependence not covered
- Accuracy insufficient
- Knowledge of accuracy insufficient due to unaccounted systematic errors (inhomogeneity, instrumental lineshape, channeling)

Air broadening parameters from high temperature ($T < 700$ K) measurements of the CO fundamental, **P branch**, **R branch** and **pure rot** ($190 \text{ K} < T < 300 \text{ K}$), **HITRAN 96**



Status of FIR Database (3)

Vibrational transitions: mainly absorption cross sections

Source: FIR measurements

Quality: sometimes inadequate since

- No experimental data available
- Temperature/pressure grid insufficient
- Spectral resolution insufficient
- Knowledge of accuracy insufficient due to unaccounted systematic errors (inhomogeneity, baseline errors)

Line-by-line vs. absorption cross sections

FTS resolution	$\leq \gamma_{\text{min}}$	$\leq 0.25 \gamma_{\text{min}}$
Baseline	no problem	critical
Temperatures	≥ 2	several
Pressures	≥ 2	several
Line density	bw	-
Analysis effort	depends on line density	bw
Molecules	e.g. CO, NO, H ₂ O	e.g. CDNO ₂ ,
Interpolation	-	Polynomial in T, p
Results	$\gamma, n, S, \text{shift}$	$\alpha(T, p)$

Status of FIR Database (4)

FIR continuum

Source: few remote sensing measurements (Carli, Jucks, Birk), C bugh continuum

Quality: insufficient

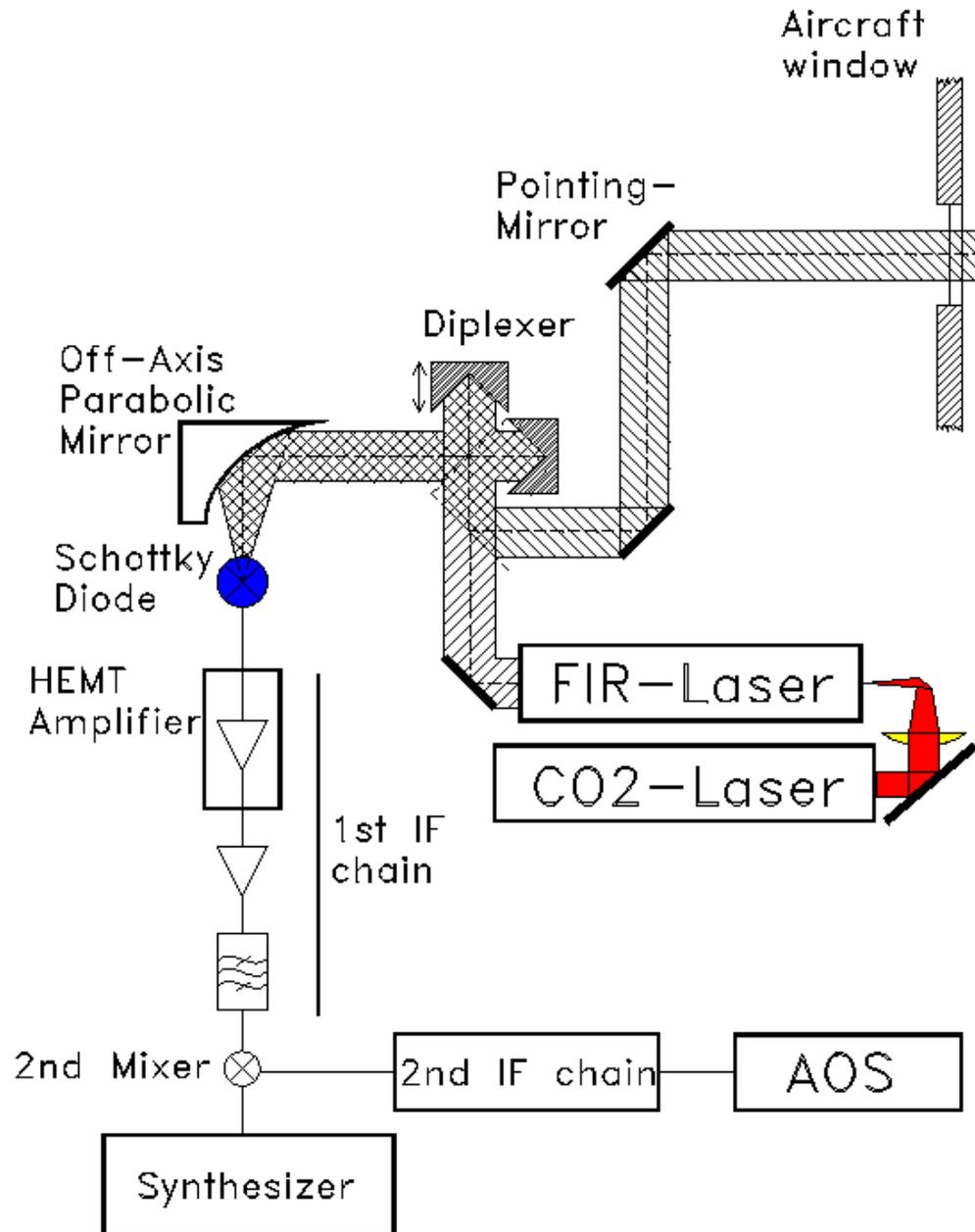
- Lim b sounding: problems caused by FOV and pointing knowledge due to steep continuum gradient
- Not enough laboratory measurements

Ice clouds, water clouds

Source: theoretical calculations

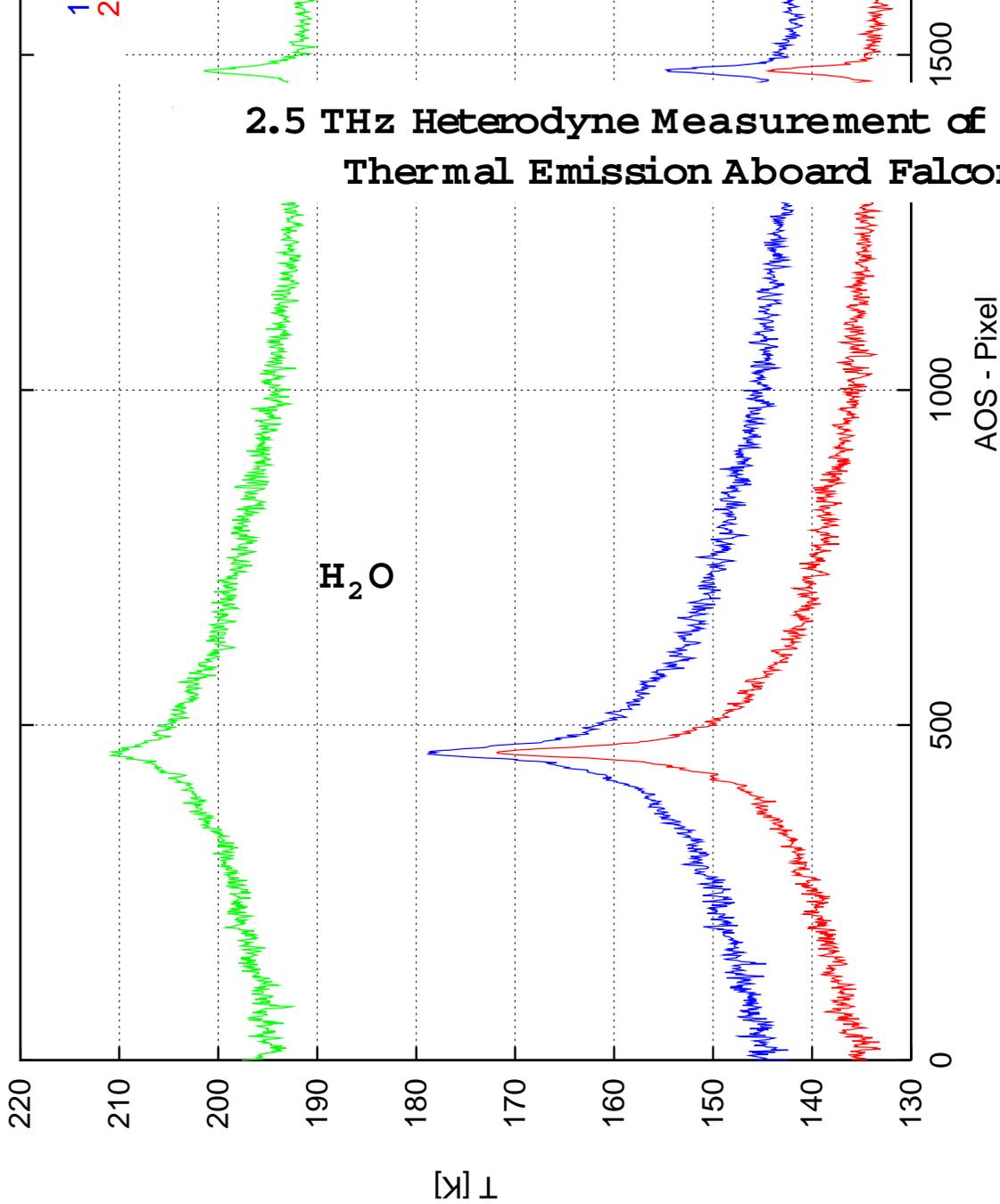
THOMAS

TeraHertz OH Measurement
Atmospheric Sounder



19.11.1999 H₂O, OH

2.5 THz Heterodyne Measurement of Hydroxyl/Water Thermal Emission Aboard Falcon 19.11.99



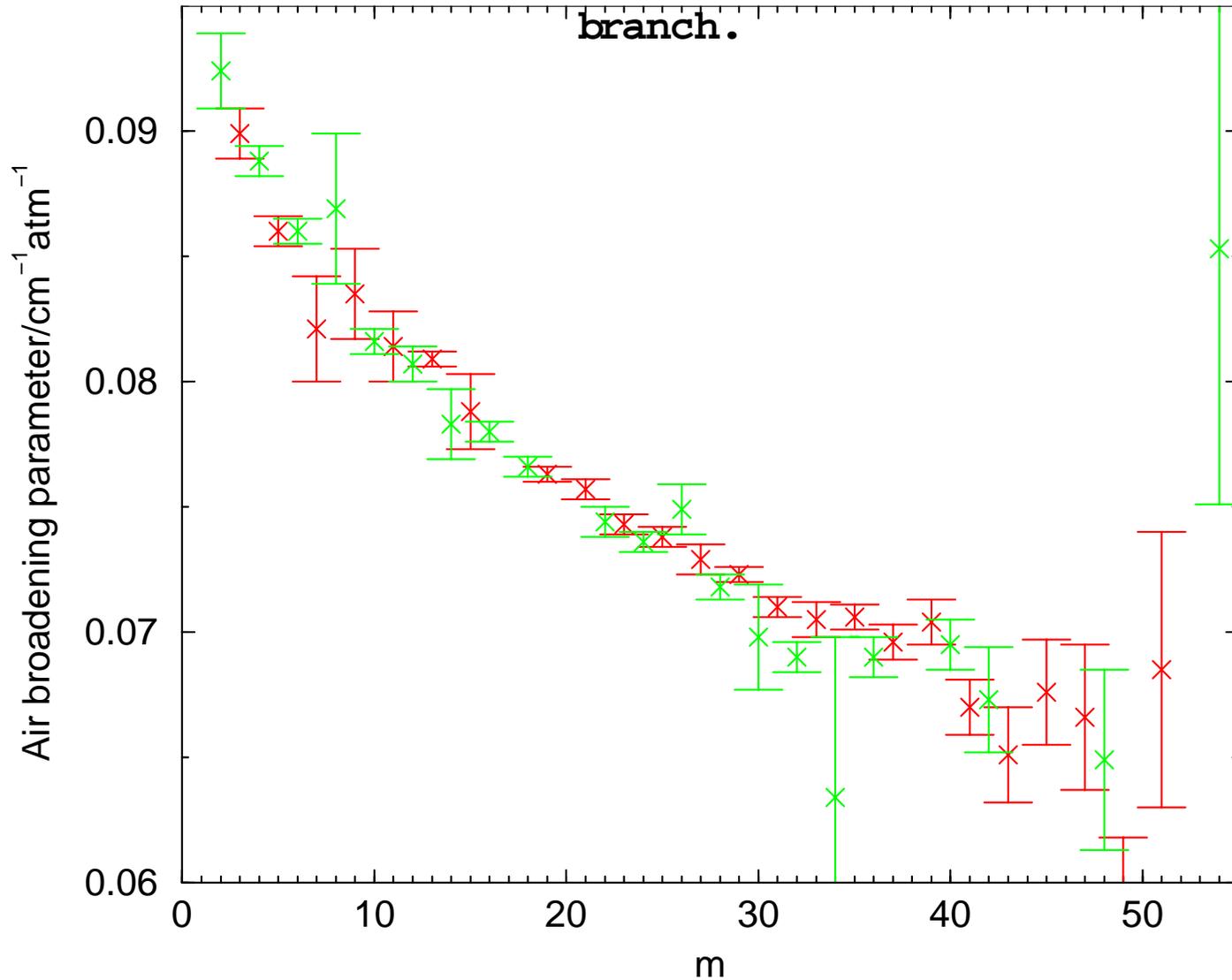
Specific needs for new data

Species	Quantity	Range/cm ⁻¹	Remark
$H_2O, HDO, H_2^{18}O$	S (?), $\gamma(T)$	50-600	Strong and weak lines
Water vapour continuum	$\alpha(T, P_{Air}, P_{H2O})$	50-600	
O_3 (?)	$\sigma, S, \gamma(T)$	50-200	Very weak lines
O_3	$\gamma(T)$	50-200	From MR measurements
O_2	$\gamma(T)$	60-100	Forp, T retrieval
HO_2	$\gamma(T)$	60-100	
OH	$\gamma(T)$	60-210	
HOCl	$\gamma(T)$	60-100	
HF, HCl	$\gamma(T)$	50-300	
NO	$\gamma(T)$	60-100	
NO_2	$\gamma(T)$	60-100	
N_2O_5	$\alpha(T)$	300-400	
$CDNO_2$	$\alpha(T, P)$	350-600	
HNO_3	S, $\gamma(T)$	380-500	
$(CH_3)_2CO$	$\alpha(T, P)?$	500-560	

High priority

Nitrogen broadening parameters for V_3 ,

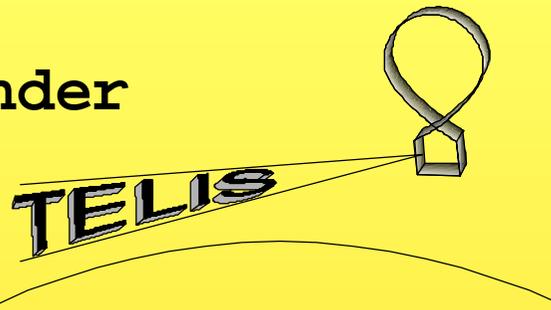
$K_A'' = 1, J'' - K_A'' - K_C'' = -1$. Red: *P* branch, green: *R*





TErahertz Limb Sounder

Forschungszentrum Karlsruhe
Technik und Umwelt



Baseline Concept

Thz generation Oscillator

Diplexer
HEB mixer

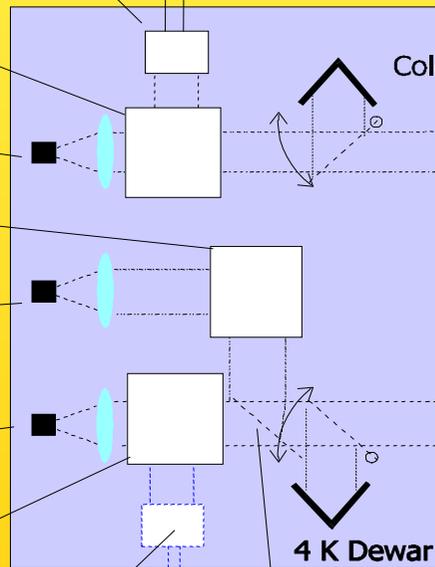
SSB filter

Integrated receiver

SIS mixer

Beamsplitter, SSB filter

Submm generation Oscillator



Cold Warm

Blackbody

Dichroic

Polarizer

Flat mirror

Telescope secondary

Pointing mirror
Telescope primary

1.8 Thz

600-654 Ghz

500 Ghz

DLR

SRON

RAL

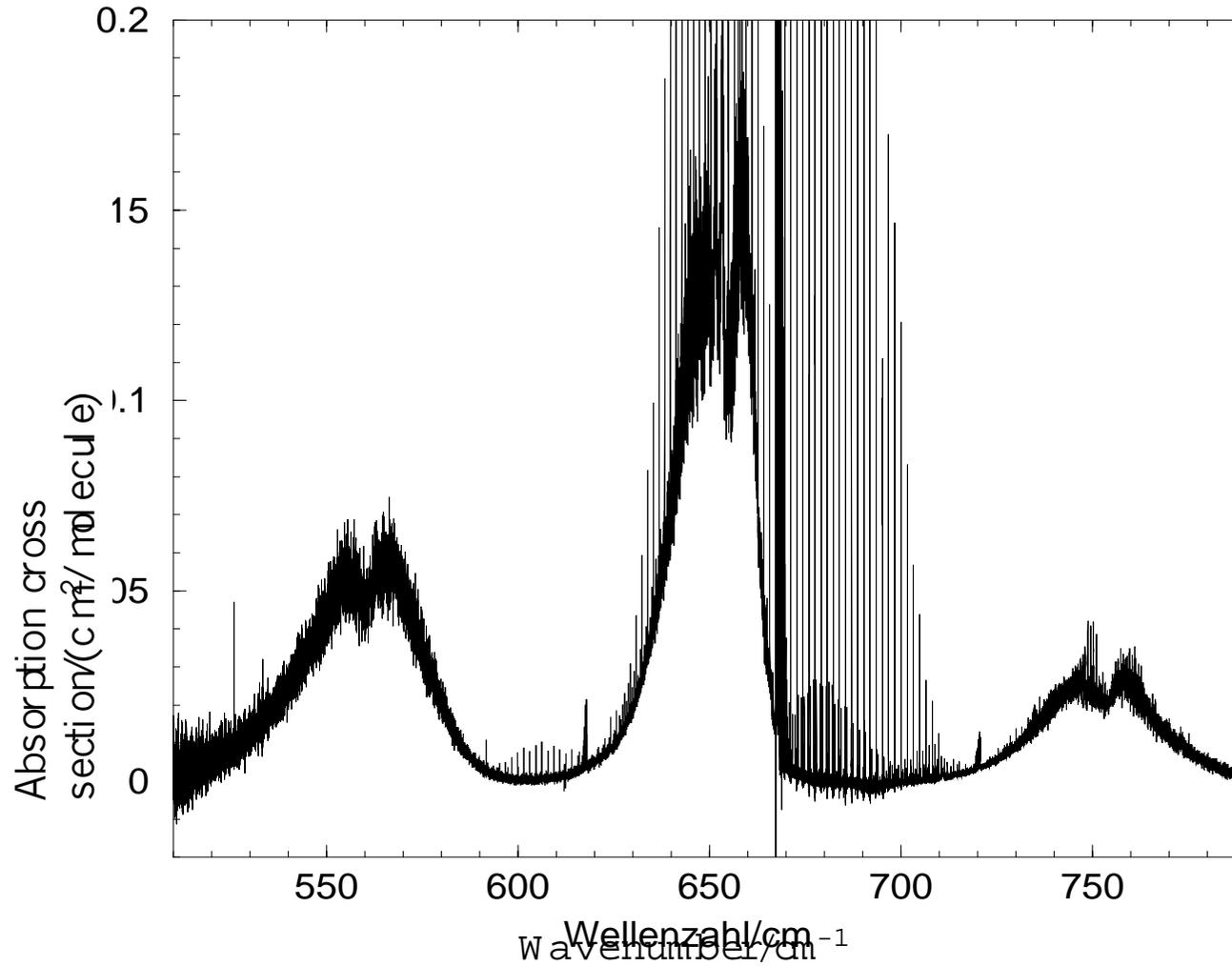
Future new FIR applications

- Water profiling from limb sounding of FIR continuum
- Water profiling with nadir geometry
- Limb sounding in region $200-600 \text{ cm}^{-1} : \text{H}_2\text{O}$
- Measurement of CO₂ under polar perturbed chemistry

ClOCl

- ◆ Involved in perturbed ozone depletion chemistry
- ◆ Lack of M IR spectroscopic database
⇒ No direct atmospheric measurements so far
- ◆ Flow synthesis from Cl + Cl₂O below 250 K
- ◆ Number density: $1 \times 10^{15} \text{ cm}^{-3}$
- ◆ M IR and FR measurements utilizing White-type cell
- ◆ Number densities deduced from pure rotational lines
- ◆ From relative intensities torsional fundamental wavenumber improved: $111.5(8.5) \text{ cm}^{-1}$
- ◆ M IR absorption cross sections at 20, 40 mbar pressure and 225, 250 K temperature
- ◆ High resolution measurements at 0.0028 cm^{-1} for line by line analysis

Spectrum of COCl at 250 K and 40 m bar N₂+He



Simulation of atmospheric and COCl18 km limb radiance spectrum

