Water Pressure Broadening: A Never-ending Story

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Requirements

- Database for limb sounding with MIPAS/ENVISAT down to 6 km

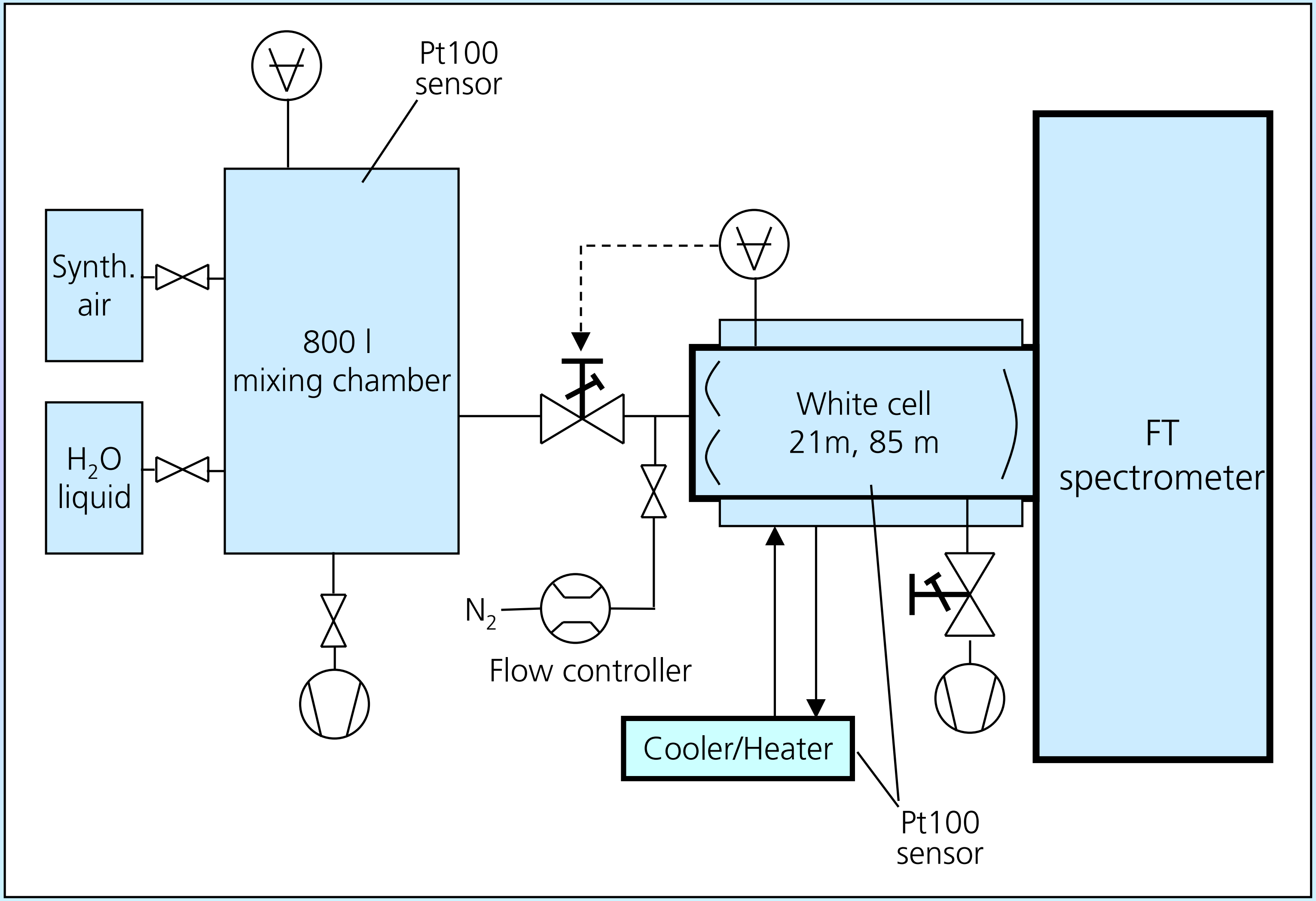
  ⇒ Linestrength range: 10^{-19} - $2x10^{-25}$ $cm^{-1}cm^{2}molecule^{-1}$, >6 orders of magnitude

- Line positions, linestrengths, air broadening parameters + temperature dependence, lineshifts + temperature dependence
- Total pressure range: 0 - 200 hPa
- Temperature range: as large as possible
- Spectral range: 600 - 1800 cm^{-1}
- Linestrength accuracy <2%
- **Broadening parameter accuracy <2%**
- Lineshift accuracy tbd

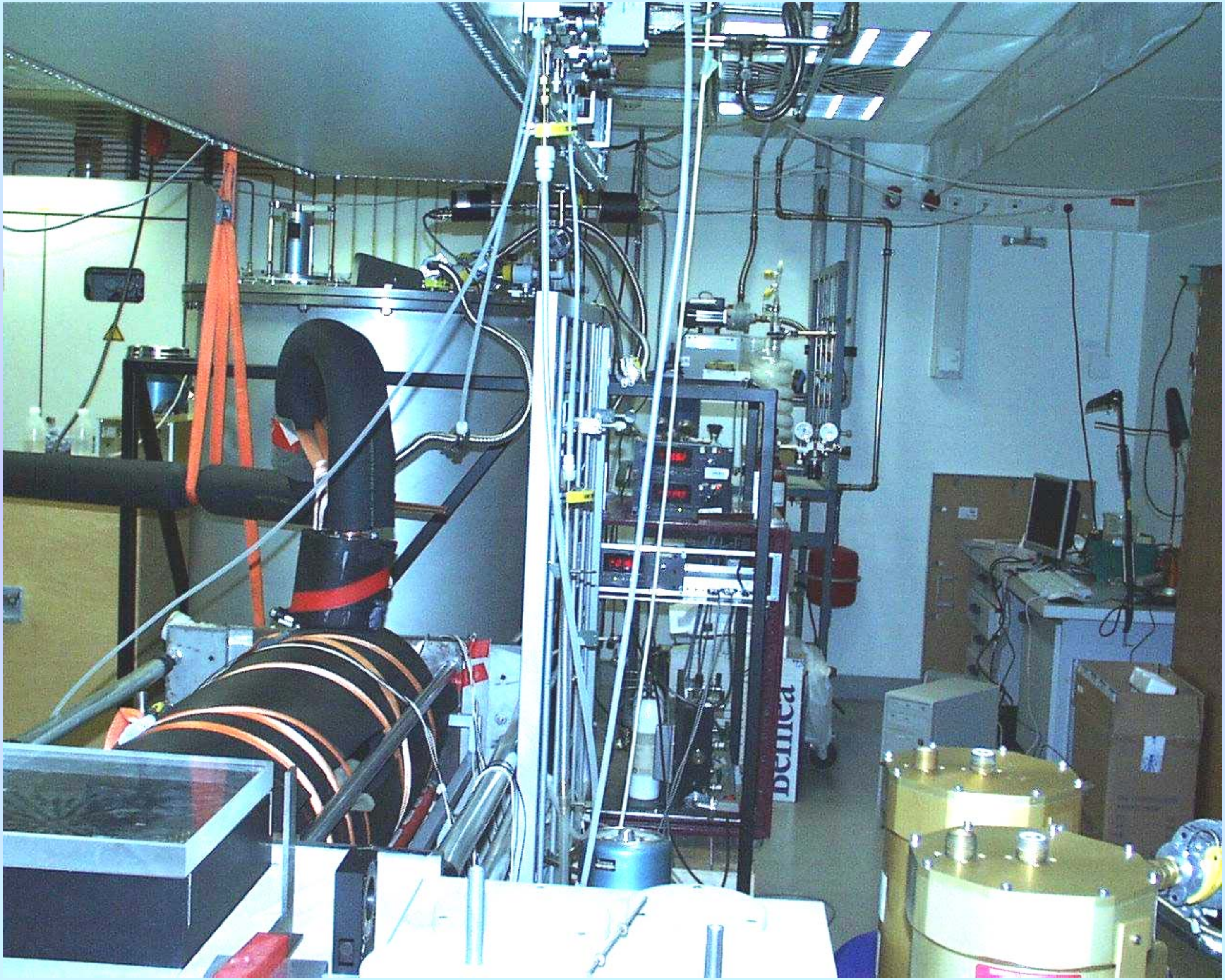
Measurement strategy

- Pure water measurements for line positions, linestrengths, self broadening
  - Ambient temperature only
  - Short cell (0.25 m) without flow + White cell (20, 80 m) with flow
- Air-broadened measurements for air broadening parameters + temperature dependence, lineshifts + temperature dependence
  - Maximum accessible temperature range (vapour pressure limit)
  - White cell (20, 80 m) with flow
  - Water/air mixture generated in mixing chamber. Reason: Absolute linestrength assessment

Experimental setup - White cell - water+air



Laboratory setup for H_2O/air measurements



Measurement strategy

- Measurements at 50, 200 mb + few at 100, 400 mb
  - Reasons: Relevant pressure region, redundancy
- Temperature range: 208-316K
- Decreasing number of steps of factor 2-4 column amount from high to low T
- Most transitions covered by several measurements with differnet optical depth and line width - required for quality assurance
- Column amounts ranging from 0.03 - 400 mb·m
- Due to discrepancies in initial analysis ambient temperature measurements added
- Pure water measurements at 272-316K added for self broadening
- Total number of measurements 47: High redundancy available

Generation of transmittance spectra

Problems

- Residual water in reference spectra
- Strong channeling from ZnSe windows, especially at low temperature due to high temperature drift sensitivity of White cell
- For last measurements these problems are reduced by windows with lower refractive index and turbo + cryo pumping of FT spectrometer
- Future measurements with wedged windows

Processing

- Detector non-linearity correction (new method)
- Channel removal by linear combination of several reference measurements
- Modelling of residual water spectra
- Few spectra had to be rejected

Line parameter retrieval

- FitMAS software: Non-linear least squares fitting with ILS⊗monochromatic transmittance (Voigt profile used)
- Automatic microwindow and fit parameter selection tool
- ILS parameters from Doppler-limited H_2O and N_2O measurements
- Line position, linestrength, Lorentzian linewidth, polynomial for baseline fitted
- Fully blended lines rejected in further data reduction
- After first run temperature/number density fit. Reference: Ambient temperature linestrengths of pure water -- **ADVANTAGE: Average gas temperature retrieved**
- **Quality indicator: fitted number density of gas mixtures at non-ambient temperature in agreement with pressure measurements better than 1%.**
- Second run with iterated experimental parameters resulting in Lorentzian widths at correct temperature

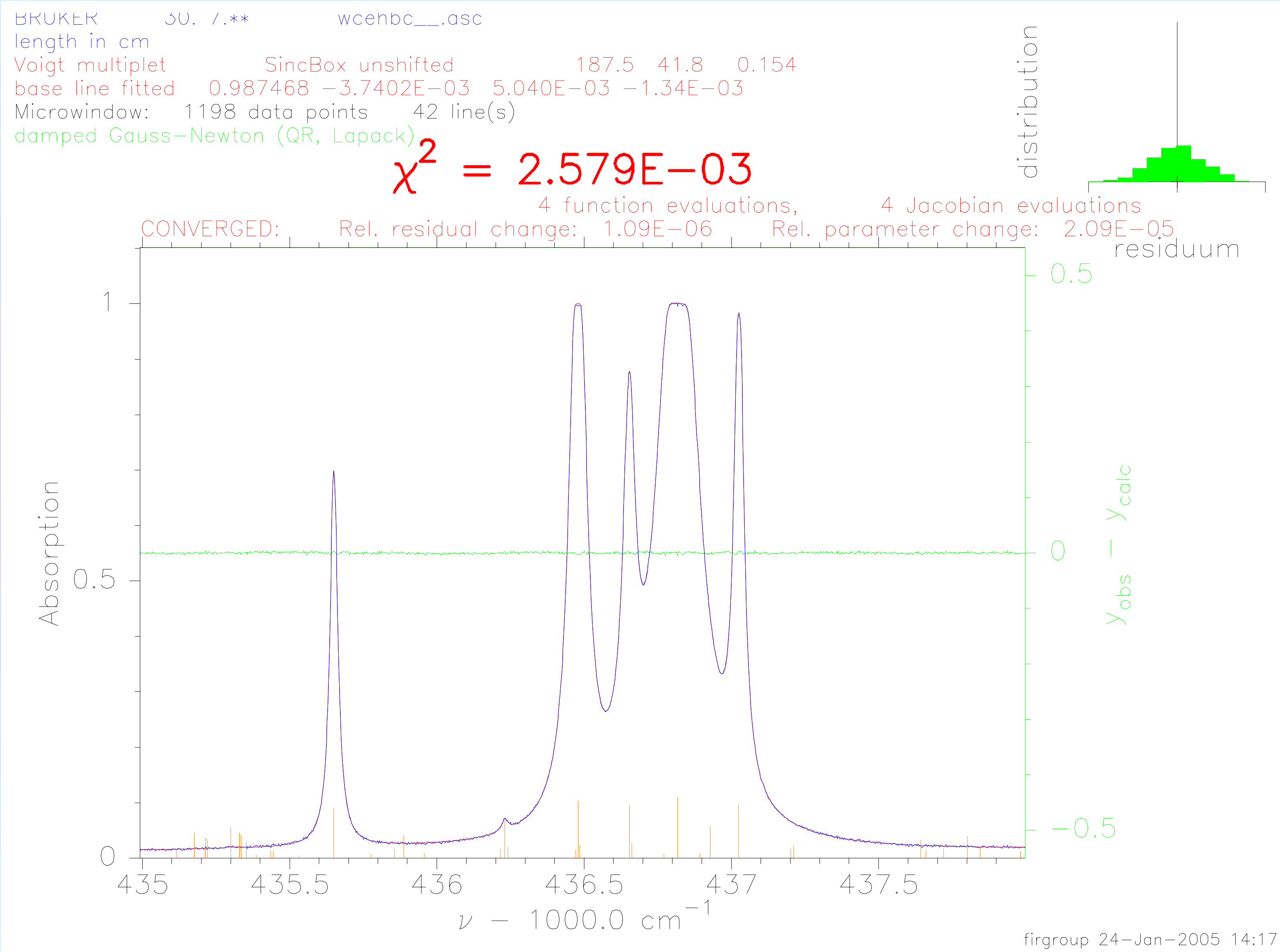
Measurements for γ: Number density/temperature fit

Test of method for defined water air mixtures

T_{bath}/°C	T_{bath}/K	T_{mirror}/K	P_{tot}/mb	P_{H2O}/mb	VMR	Absorpt. path/m	T_{fit}/K	$P_{H2O-fit}/P_{H2O}$
44.15	317.29	313.43	50.51	0.04947	9.8e-4	20	316.256(83)	**1.00535(72)**
44.15	317.29	313.40	201.1	0.04936	2.5e-4	20	316.484(57)	**0.99252(29)**
44.15	317.29	313.48	50.51	0.2016	4.0e-3	20	316.085(59)	**0.99802(68)**
44.15	317.29	308.3-311.5	50.37	1.0050	2.0e-2	85	315.645(75)	**0.99611(132)**
44.15	317.29	312.58	50.44	2.534	5.0e-2	78	315.348(100)	**0.99776(209)**
44.15	317.29	313.11	200.7	0.2043	1.0e-3	78	316.131(45)	**1.00739(55)**
44.15	317.29	313.18	200.7	1.1597	5.8e-3	78	315.779(42)	**0.99305(66)**
44.15	317.29	313.27	200.7	2.505	1.2e-2	78	315.655(50)	**0.99309(85)**
21.45	294.59	295.36	50.37	0.2020	4.0e-3	78	293.756(88)	**1.00400(146)**
24.15	297.29	297.35	200.7	0.2017	1.0e-3	20	297.185(34)	**0.99310(33)**
24.15	297.29	297.50	200.7	0.2022	1.0e-3	78	297.307(41)	**1.00344(56)**
0.1	273.24	279.35	199.7	2.500	1.3e-2	85	274.595(46)	**1.00047(111)**

Example of line parameter fit microwindow

T = 297 K, P_{tot} = 200 mb, P_{H2O} = 0.2 mb, l = 2000 cm



Pressure broadening parameter/temperature exponent determination

Inputs

- Lorentzian widths for different air/water pressures and temperatures

Model

$$b_L = p_{air} \cdot \gamma_{air} \cdot \left(\frac{296K}{T} \right)^{n_{air}} + p_{self} \cdot \gamma_{self} \cdot \left(\frac{296K}{T} \right)^{n_{self}}$$

Method

- Non-linear least squares fit

Outputs

- $\gamma_{\mathbf{air}}$, n_{air}, $\gamma_{\mathbf{self}}$, n_{self} with uncertainties

Pressure broadening parameter/temperature exponent determination

Software development

- IDL tool
- Data structures containing relevant measured and fitted data
- Reference/initial guess/default: HITRAN2004 database
- Complex process of selection of fit parameters as function of input data for a given transition
  Example: *n* fitted only if sufficient temperature range. If not, *n*(HITRAN) used
- Linestrength assessment:
  Linestrengths for all data in fit for a given transition averaged, outlier treatment
  Statistical uncertainty of b_L is scaled with (deviation from mean)/σ if deviation outside 4σ
  If less than 2 transitions with linestrength fitted $\Rightarrow$ transition excluded
- High and low opacity limits discrimination
- Generic: only b_L used with **uncertainty <20%**
- Non-linear least squares fit of γ_{air}, n_{air}, γ_{self}, n_{self} with outlier treatment

Pressure broadening parameter/temperature exponent determination

Software development

- Measurements with temperature/pressure ranges can be excluded by flagging
- Output flags: Exclude_flag, bad_gamma_fit, gamma_air_perturbed

show_fit_data - linestrength assessment

370 11 1348.7567 2 1 13 1 13 13 2 12

S Fit results:

	s_index	S_exp_a	S_exp_err_a	S_exp_b	S_exp_err_b	omc/sigma	err_fact	opacity
WCEIAG_aisov3	0	2.0844e-023	4.1327e-025	2.0844e-023	4.1327e-025	-0.7	1.0	0.09
WDEIAA_aisov3	0	2.1186e-023	2.5673e-025	0.0000e+000	0.0000e+000	0.2	1.0	0.49
WEEIAA_aisov3	0	2.1361e-023	4.7025e-025	2.1355e-023	6.4660e-026	0.5	1.0	1.02
WCEIBG_aisov3	0	2.0817e-023	6.7737e-025	2.0817e-023	6.7737e-025	-0.5	1.0	0.05
wedhba_a	0	2.0185e-023	2.4018e-025	2.0185e-023	2.4018e-025	-3.9	1.0	0.26
weehba_a	0	2.0443e-023	2.4942e-025	2.0443e-023	2.4942e-025	-2.8	1.0	0.16
wefhba_a	0	2.1759e-023	3.2236e-025	2.1759e-023	3.2236e-025	2.0	1.0	0.09
wfdhba_a	0	2.0793e-023	1.3109e-025	2.0783e-023	1.2100e-025	-2.6	1.0	0.46
wfehba_a	1	2.1281e-023	2.0057e-025	2.1251e-023	1.4040e-025	0.9	1.0	0.30
wffhba_a	1	2.1271e-023	2.1070e-025	2.1372e-023	1.7057e-025	1.4	1.0	0.17
WEEJCA_aisov3	0	2.1189e-023	1.4890e-024	2.1208e-023	1.1835e-025	0.0	1.0	0.37
WDEJDA_aisov3	0	2.0450e-023	5.7829e-025	2.0450e-023	5.7829e-025	-1.2	1.0	0.10
WFAHAA_aisov3	0	2.1220e-023	8.0183e-026	2.1226e-023	6.8729e-026	1.1	1.0	1.16
WFAIAA_aisov3	-1	0.0000e+000	0.0000e+000	2.0418e-023	1.4862e-025	-4.8	1.0	4.07
WFAHCA_aisov3	0	2.1354e-023	1.4051e-025	2.1354e-023	1.4051e-025	1.6	1.0	0.42
WFAJCA_aisov3	1	0.0000e+000	0.0000e+000	2.1239e-023	7.3308e-026	1.5	1.0	1.64
H2OLHHLaisov3	0	2.1210e-023	1.4254e-025	2.1201e-023	1.3304e-025	0.6	1.0	0.77

s_mean 2.1130e-023 s_mean_proz_err: 0.22 delta_coudert_proz: -0.66 SYES

Pressure broadening parameter/temperature exponent determination

Software development - show_fit_data

```
Gamma Fit results:
fit_index  370  nu 1348.756660  g_air  0.0185  g_self  0.1760  n 0.37
sqrt(chisq) 1.940e+000
pars       0.02015  0.61762  0.17253  0.28660
par errs   0.00013  0.21273  0.00124  0.11029
%par errs      0.7     34.4      0.7     38.5
fit flag   1  1  1  1
npar eq nlines 0  gammas perturbed 0   n self fit canceled 0   bad_gamma_fit 0
   id  filename   T_fit   P_tot     P_h2o   abs_path  w_exp   w_err% w_calc omc/err  opac  op excl rej
    2WCEIAG_aisov 316.121 200.70000 0.2077   78.620  0.003862 3.3  0.003863 -0.01   0.088  0  0   0
    3WDEIAA_aisov 316.144 200.70000 1.1598   78.620  0.003981 2.1  0.004004 -0.27   0.490  0  0   0
    4WEEIAA_aisov 315.738 200.70000 2.5095   78.620  0.004179 4.0  0.004207 -0.16   1.019  0  0   0
    6WCEIBG_aisov 297.290 200.70000 0.2050   78.620  0.004120 5.3  0.004012  0.50   0.054  0  0   0
    7wedhba_a     295.700  99.95000 2.5185   20.990  0.002111 2.5  0.002368 -4.91   0.261  0  0   0
    8weehba_a     295.700 200.40000 2.5197   20.990  0.004292 1.9  0.004367 -0.91   0.162  0  0   0
    9wefhba_a     295.700 400.30000 2.5120   20.990  0.008573 2.1  0.008344  1.26   0.092  0  0   0
   10wfdhba_a     295.700 100.57000 5.0295   20.990  0.002710 1.2  0.002758 -1.47   0.463  0  0   0
   11wfehba_a     295.700 199.60000 5.0134   20.990  0.004807 1.1  0.004726  1.57   0.304  0  0   0
   12wffhba_a     295.700 399.90000 5.0250   20.990  0.008920 1.2  0.008714  2.00   0.174  0  0   0
   15WEEJCA_aisov 274.890 199.70000 2.5140   85.020  0.00455311.3  0.004542  0.02   0.366  0  0   0
   16WDEJDA_aisov 261.581 199.80000 1.0584   85.020  0.004378 4.4  0.004453 -0.39   0.102  0  0   0
   26WFAHAA_aisov 316.481   5.04200 5.0420   20.990  0.000848 1.3  0.000842  0.50   1.165  0  0   0
   28WFAHCA_aisov 273.483   5.02800 5.0280   20.990  0.000828 2.4  0.000876 -2.41   0.418  0  0   0
   29WFAJCA_aisov 272.990   5.02400 5.0240   85.020  0.000890 1.1  0.000876  1.46   1.640  0  0   0
   31H2OLHHLaisov 297.350   5.02500 5.0250   20.990  0.000813 2.5  0.000855 -2.00   0.772  0  0   0
   32H2OLHMHaisov 296.200   5.02200 5.0220   85.020  0.000870 1.7  0.000855  1.02   3.032  0  0   0
```

Software development quantum number cut

$K_a'' = 1$

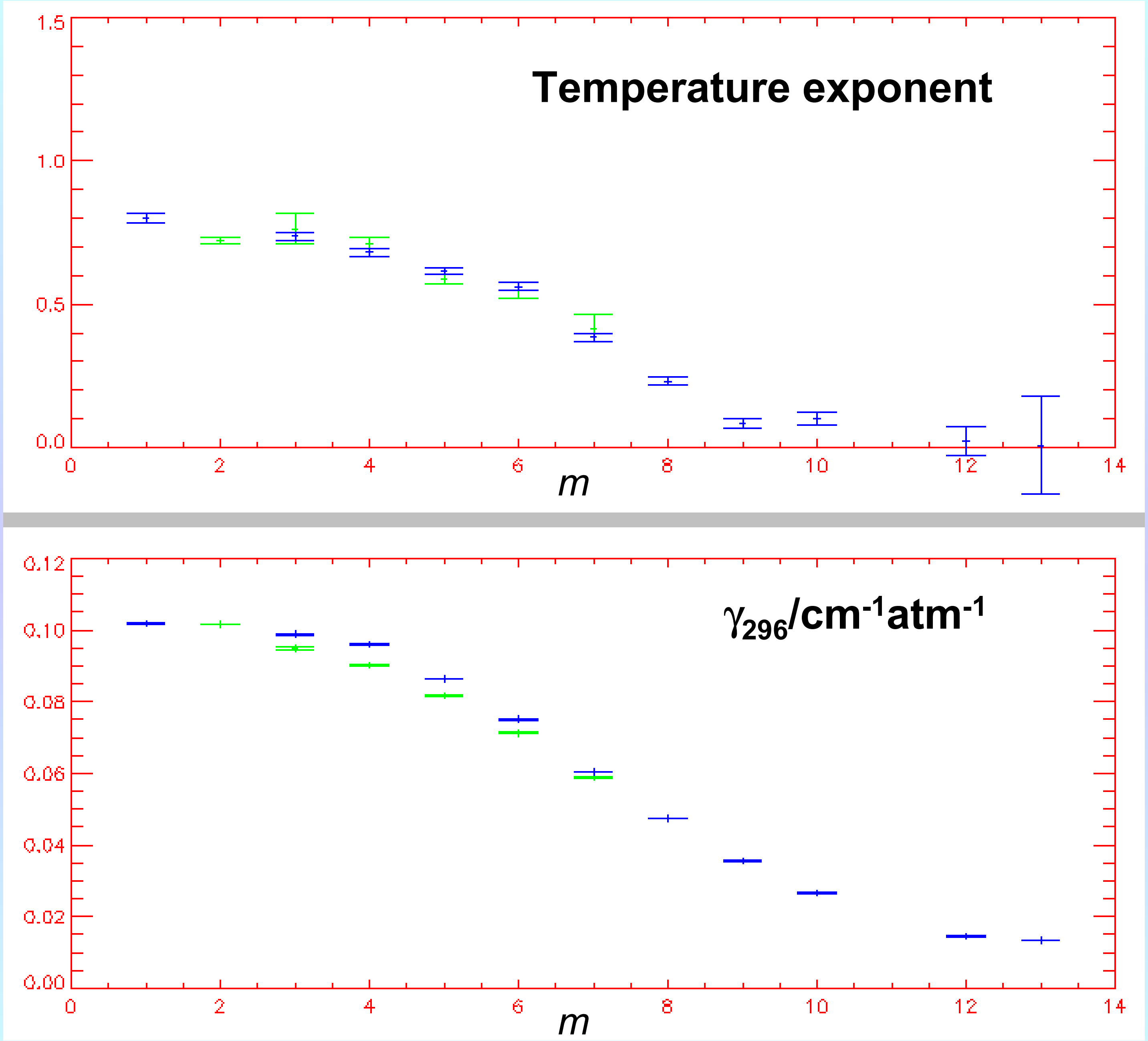
$\Delta K_a = -1$

$J''-K_a''-K_c'' = -1$

P-branch

Q-branch

R-branch



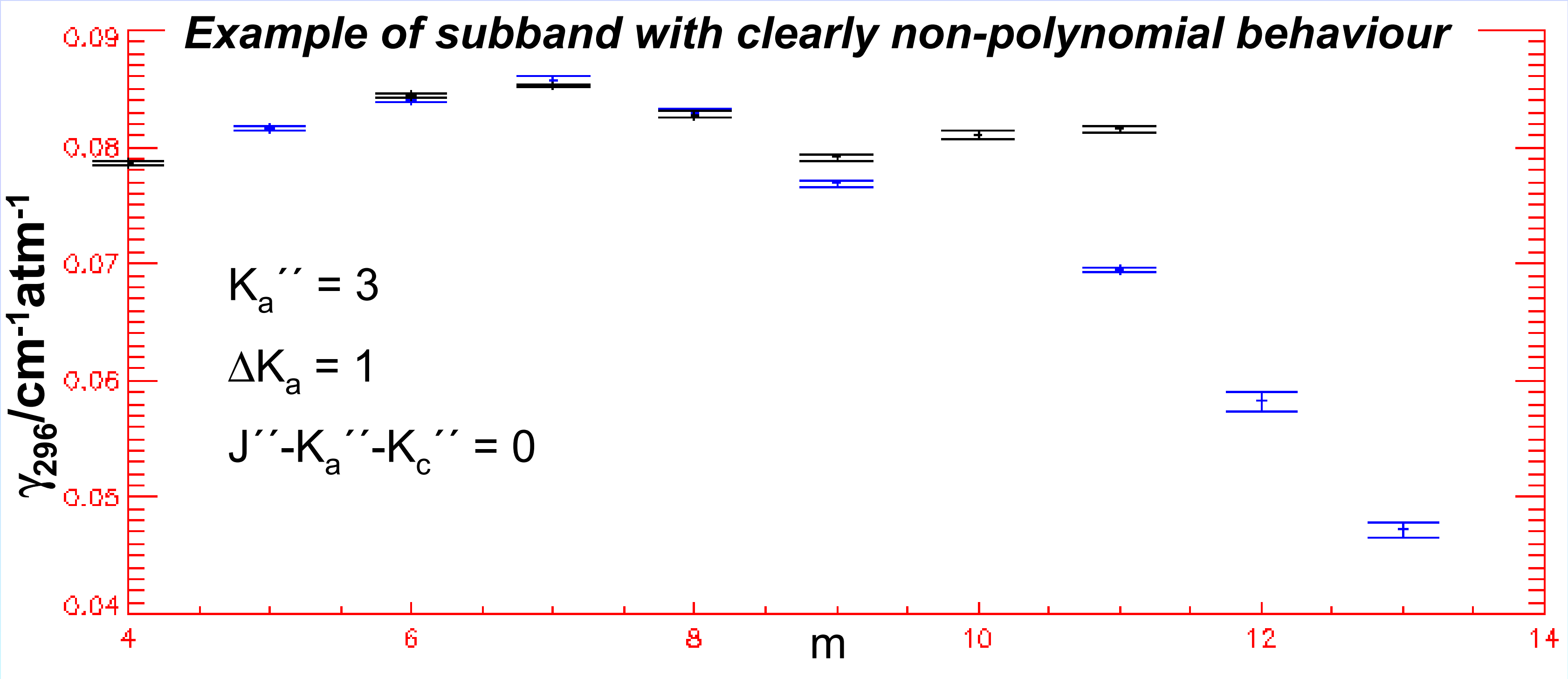
Software development - quantum number dependence

- Smooth *m*-dependence only on first glance
- Polynomial approach was tried but failed
- P/R-branch transition with exchanged upper/lower vibrational state: differ outside uncertainty (especially at higher K_a)

Conclusion: In contrast to ozone water must be treated on single line basis

Reason: H_2O γ variation > factor 10, O_3 factor 1.3

If water variations were reduced to a factor 1.3, quantum number dependence might look smooth within experimental uncertainty



Quality assessment

OMC file cuts

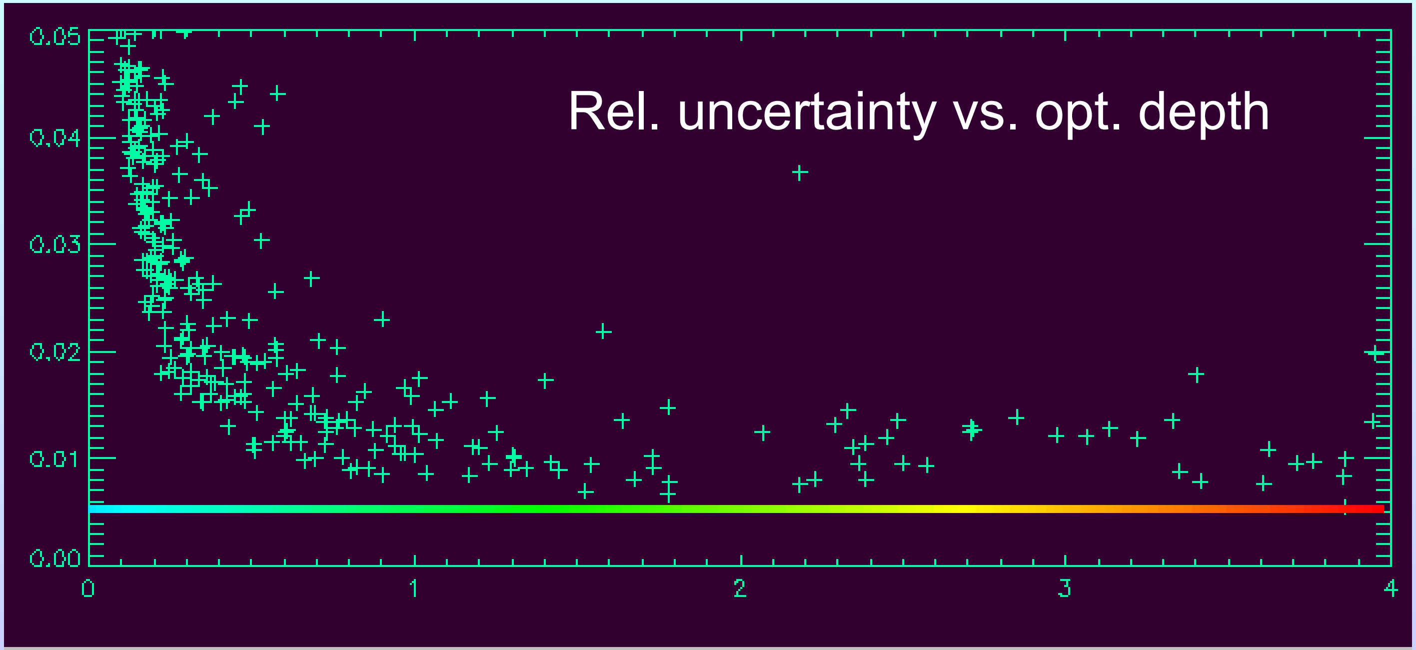
Example:

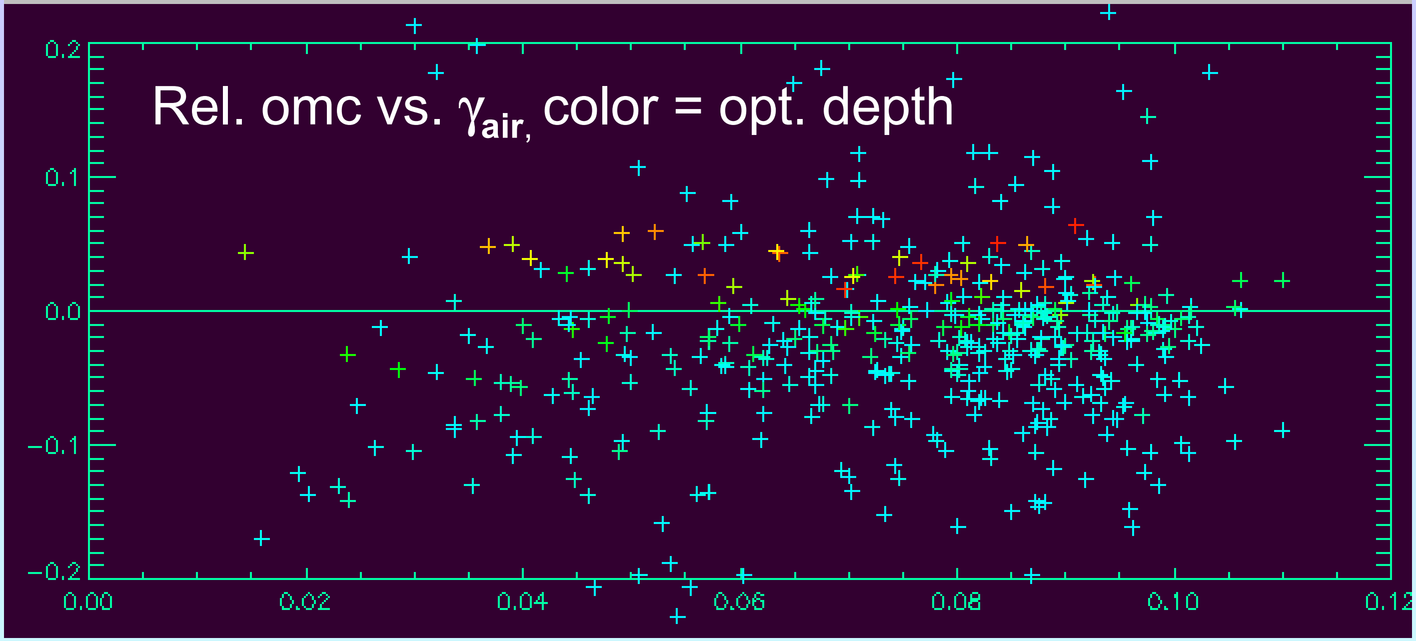
T = 316 K

P_{H2O} = 0.22 mb

P_{tot} = 50.42 mb

Abs. path = 78.6 m





Systematically positive OMC for high opt. depth

Systematically negative OMC for small γ_{air}

Binned OMC file cuts

Example:

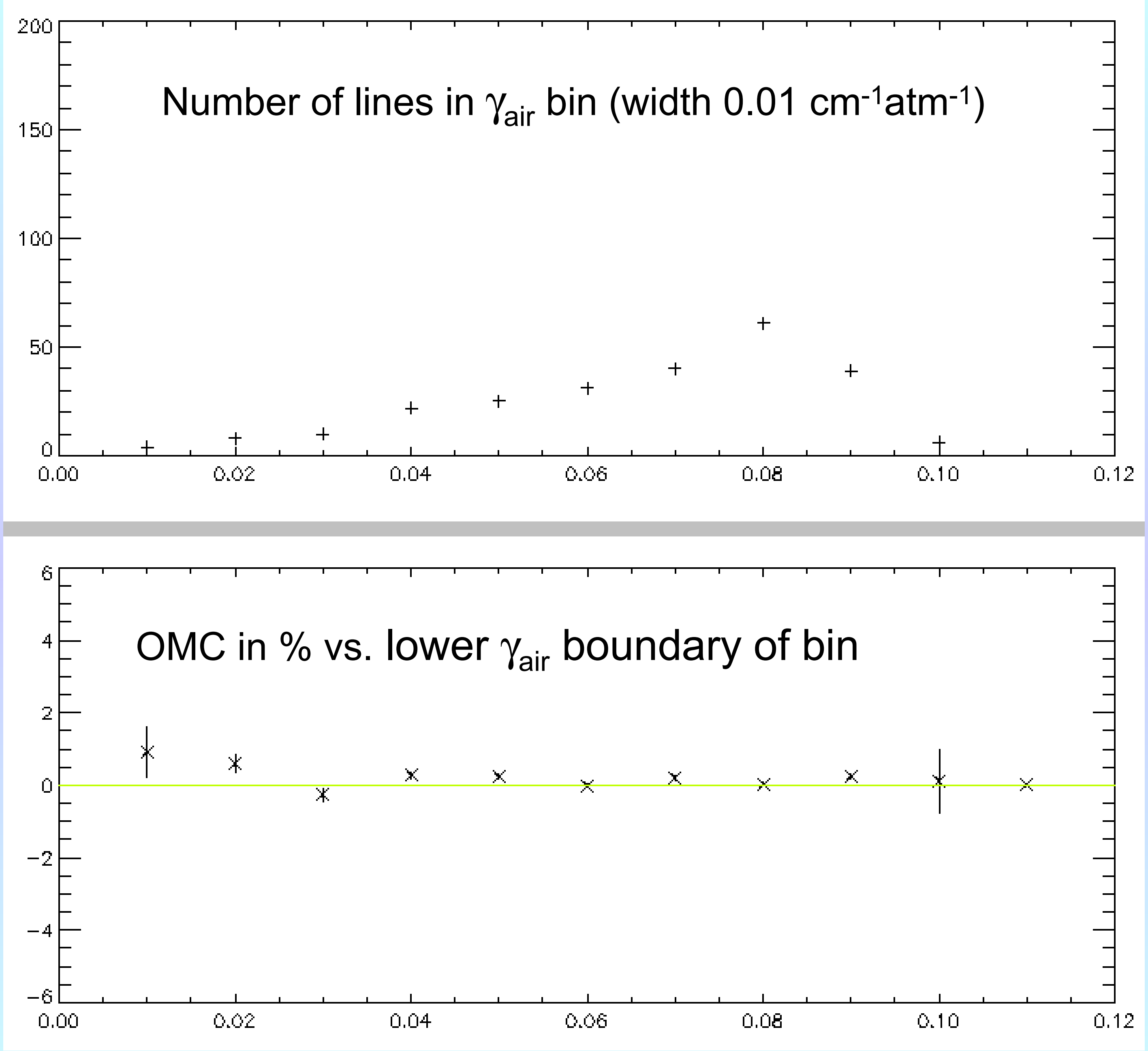
T = 316 K

P_{H2O} = 0.20 mb

P_{tot} = 201.00 mb

Abs. path = 21.0 m

⇒ no systematic error for all measurements with p≥200 mb



DLR

Binned OMC file cuts

Example:

T = 295.7 K

P_{H2O} = 2.52 mb

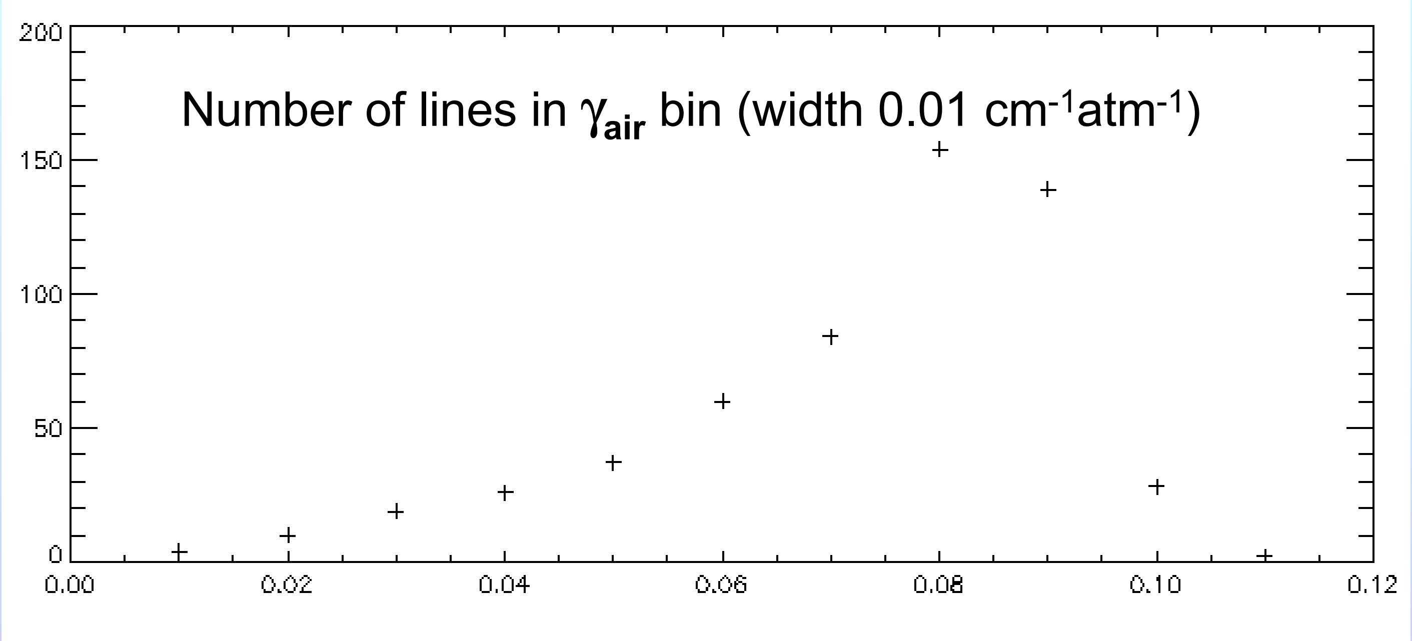
P_{tot} = 50.49 mb

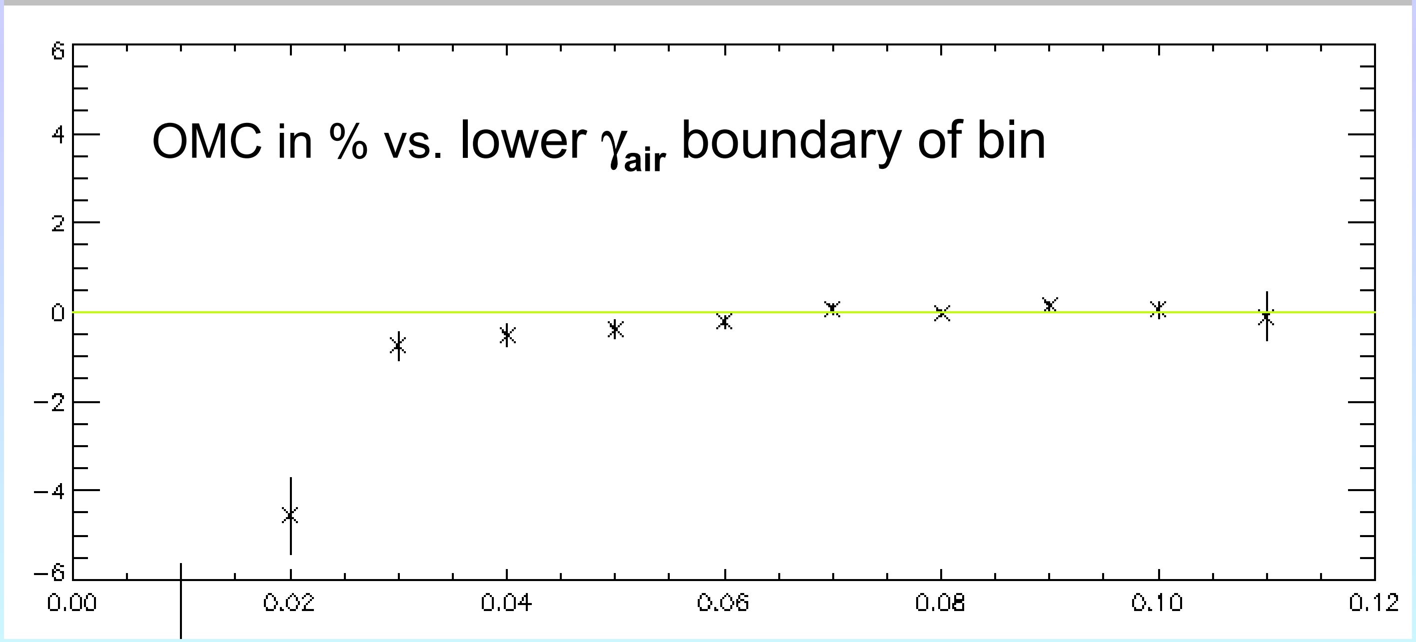
Abs. path = 21.0 m

⇒ systematic error at low width for all 50 mb measurements

⇒ 50 mb measurements rejected from fit

60000 ⇒ 40000 measured lines

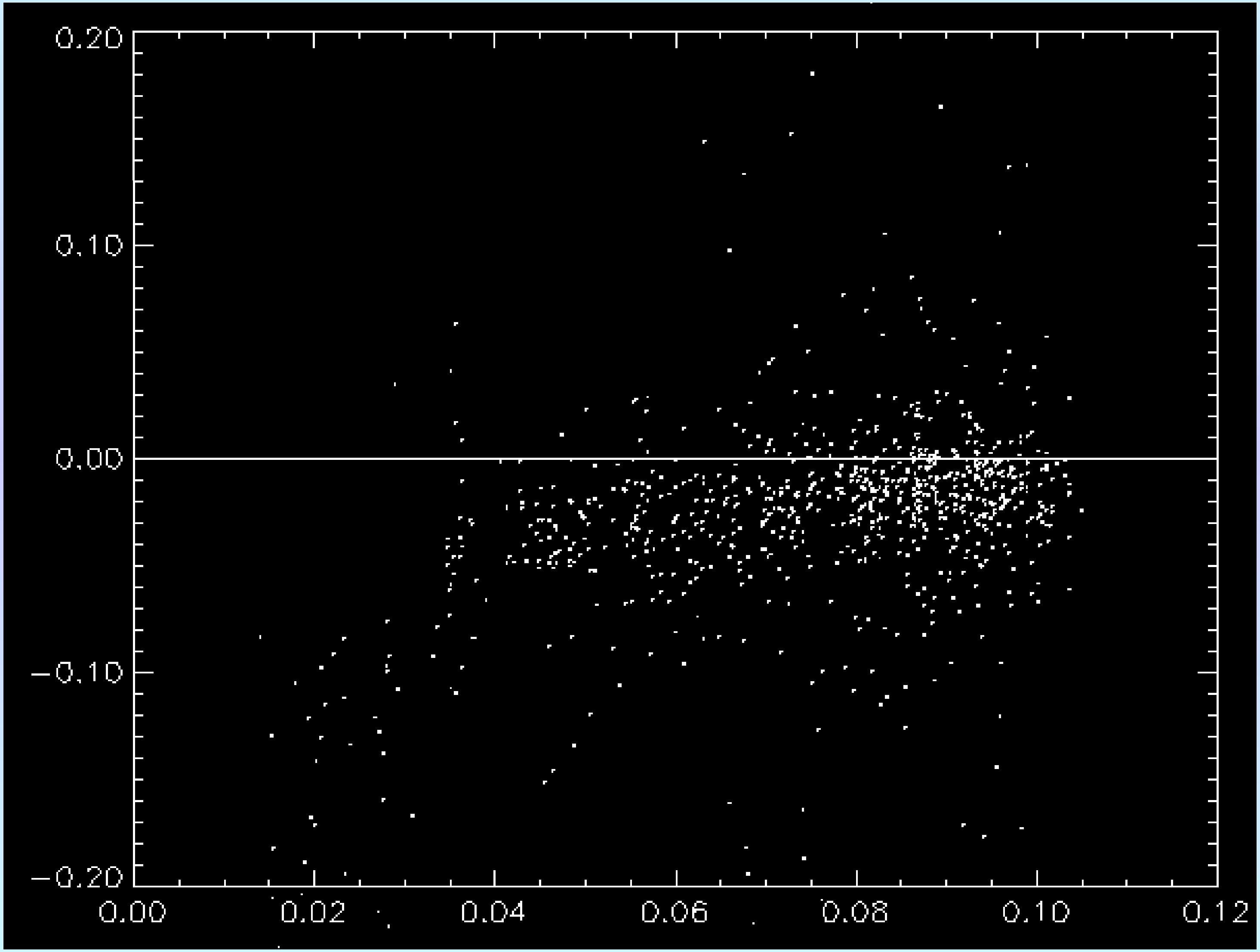




Quality assessment

DLR

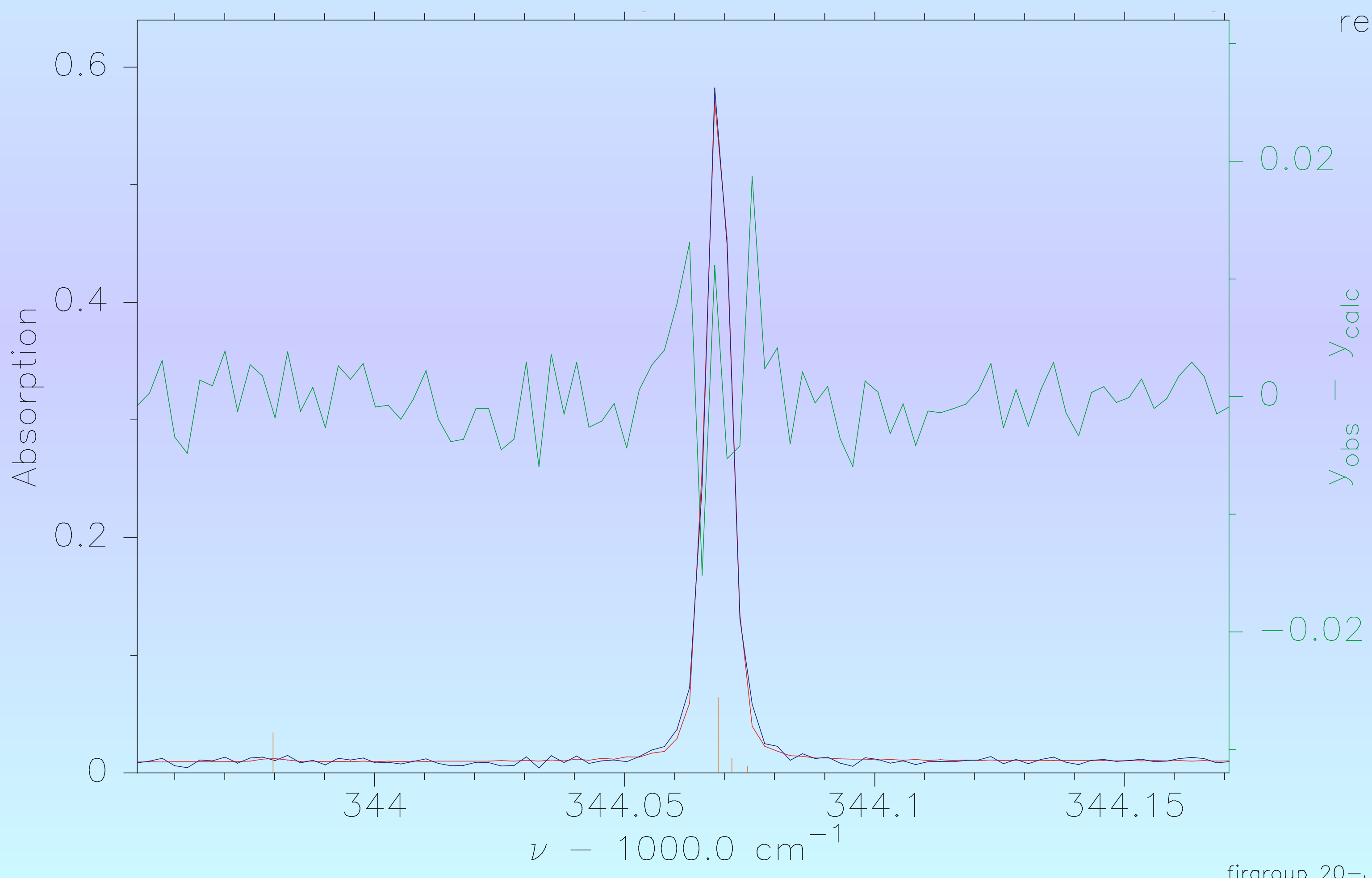
$[\gamma_{296}\ (p \leq 50mb) - \gamma_{296}\ (p > 50mb)] / [\gamma_{296}\ (p > 50mb)]$ **Average -0.0180(4)**



$\gamma_{296}/cm^{-1}atm^{-1}$

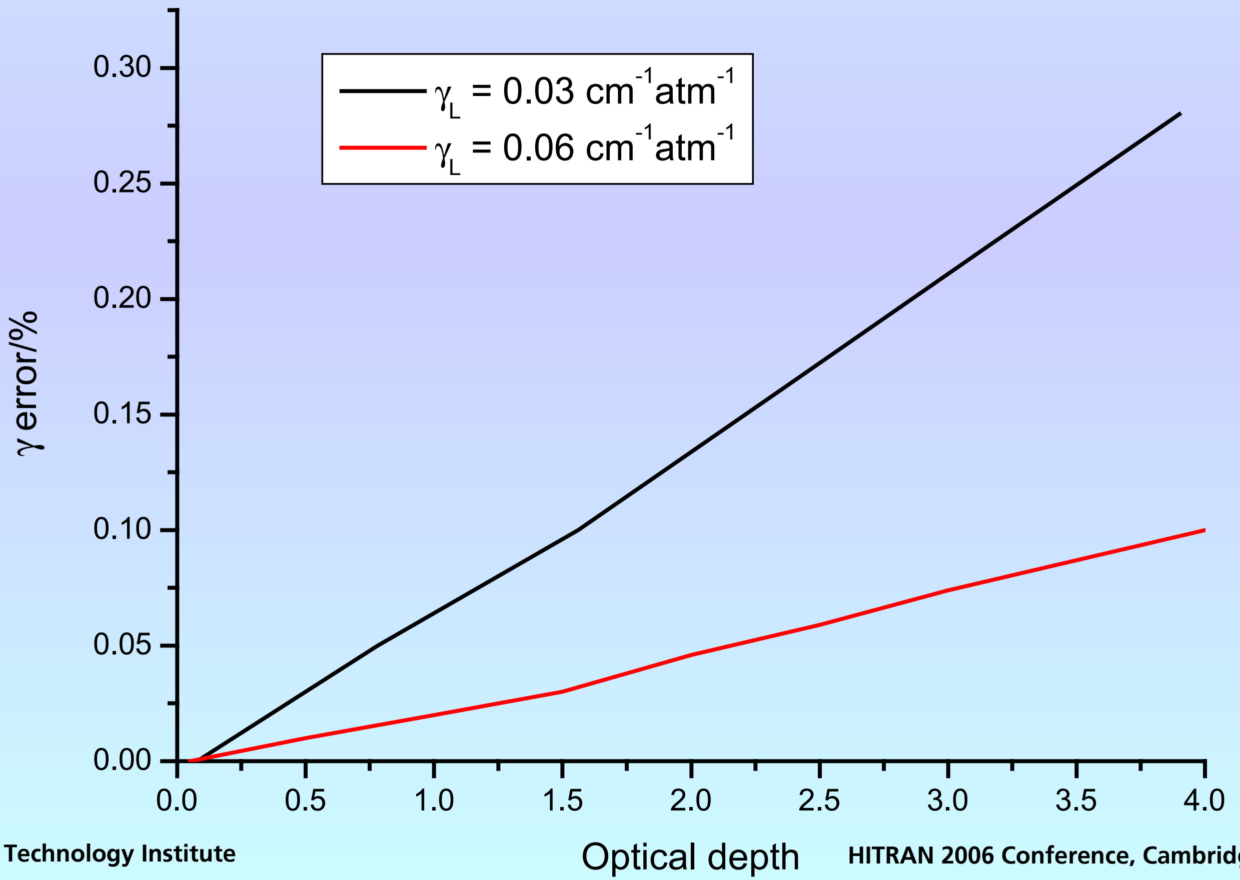
Deviations from Voigt: Example 50 mbar air-broadened measurement

Linefit shows strong residuals: Dicke narrowing



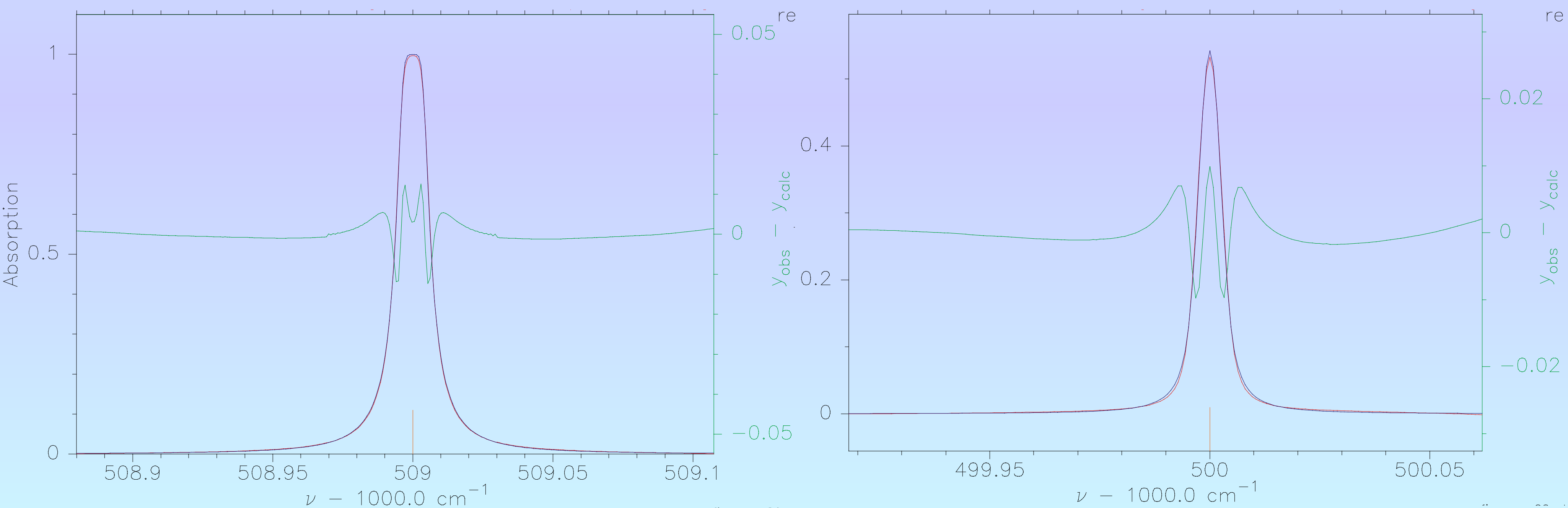
Deviations from Voigt: Line fit error

- Synthetic spectra of 50 mb measurements modelled
- Dicke narrowing simulated by lowering Doppler Temperature from 300 to 200 K
- Fit: Voigt with Doppler width @ 300 K used
- % differences of fitted γ with respect to small optical depth



Deviations from Voigt: Line fit error

- Optical depth of opaque lines weights information in line center and wings differently
- Reason: Strongly non-linear behaviour of exp(-optical depth) for optical depth>1
- Clearly different shape of residuals for opaque and non-opaque lines
- Explains dependence of fitted γ on optical depth

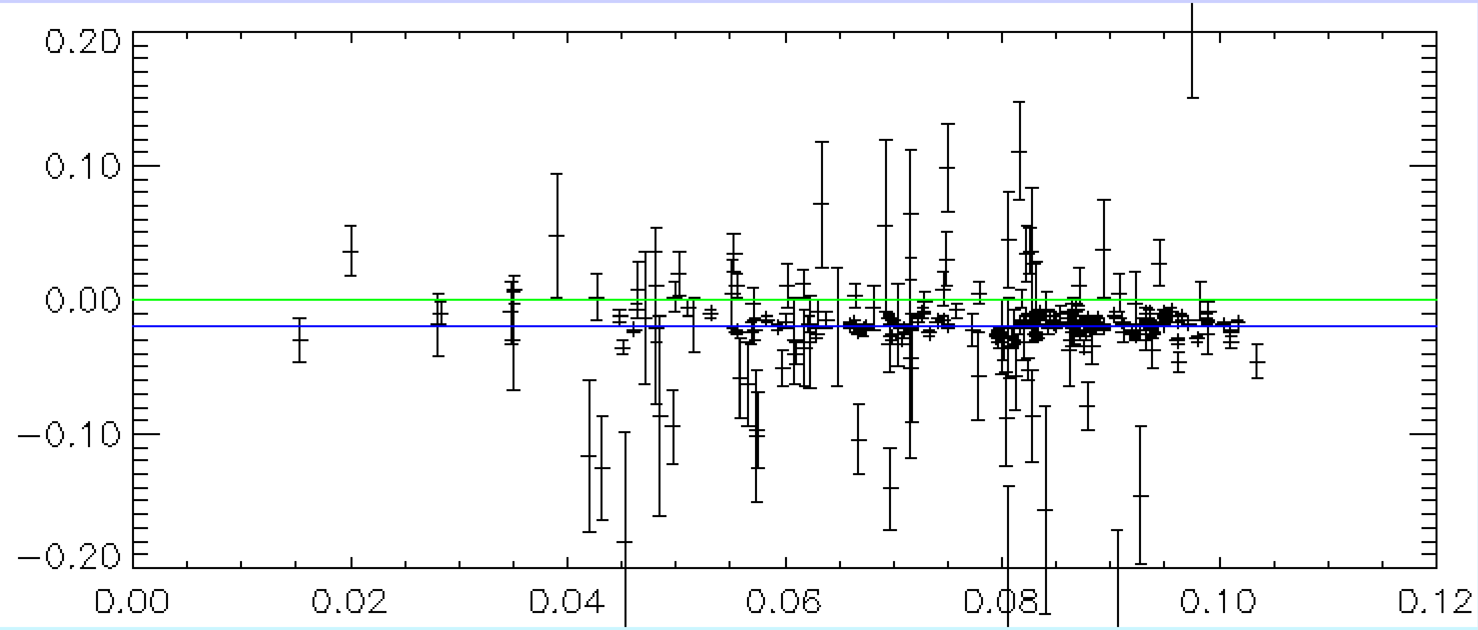


Quality assessment

- Intercomparison between hot cell measurements @296K and new data
- Different cell (16 cm), detector, beamsplitter, spectral resolution, pressure (500, 1000 mb), mixing chamber, pressure gauges
- Scalar difference **$(\gamma_{hot} - \gamma_{calc}) / \gamma_{calc}$** on average **-0.0172(3)**
- Since only White cell measurement available in new data, strong lines covered better by hot cell

⇒ Hot cell measurements @296K included in analysis

- When included in fit scalar difference drops to -0.67%



$(\gamma_{hot} - \gamma_{calc}) / \gamma_{calc}$

$\gamma_{296}/cm^{-1}atm^{-1}$

Quality assessment

Fit of self broadening parameter from airbroadened measurements only and compare to results from pure water measurements

averaged γ self difference $(\gamma_{self-air} - \gamma_{self-pure}) / \gamma_{self-pure}$:

average:	0.0245(29)
chi:	1.6
lines:	355

Self broadening contribution to airbroadened lines is only small fraction!!

Fit of air broadening parameter from data with line center optical depth 0-0.5 and compare to results from 0.5-4

average:	0.00374(30)
chi:	1.9
lines:	390

Error bars

Error sources refer to $\gamma_{296K}/\gamma_{220K}$

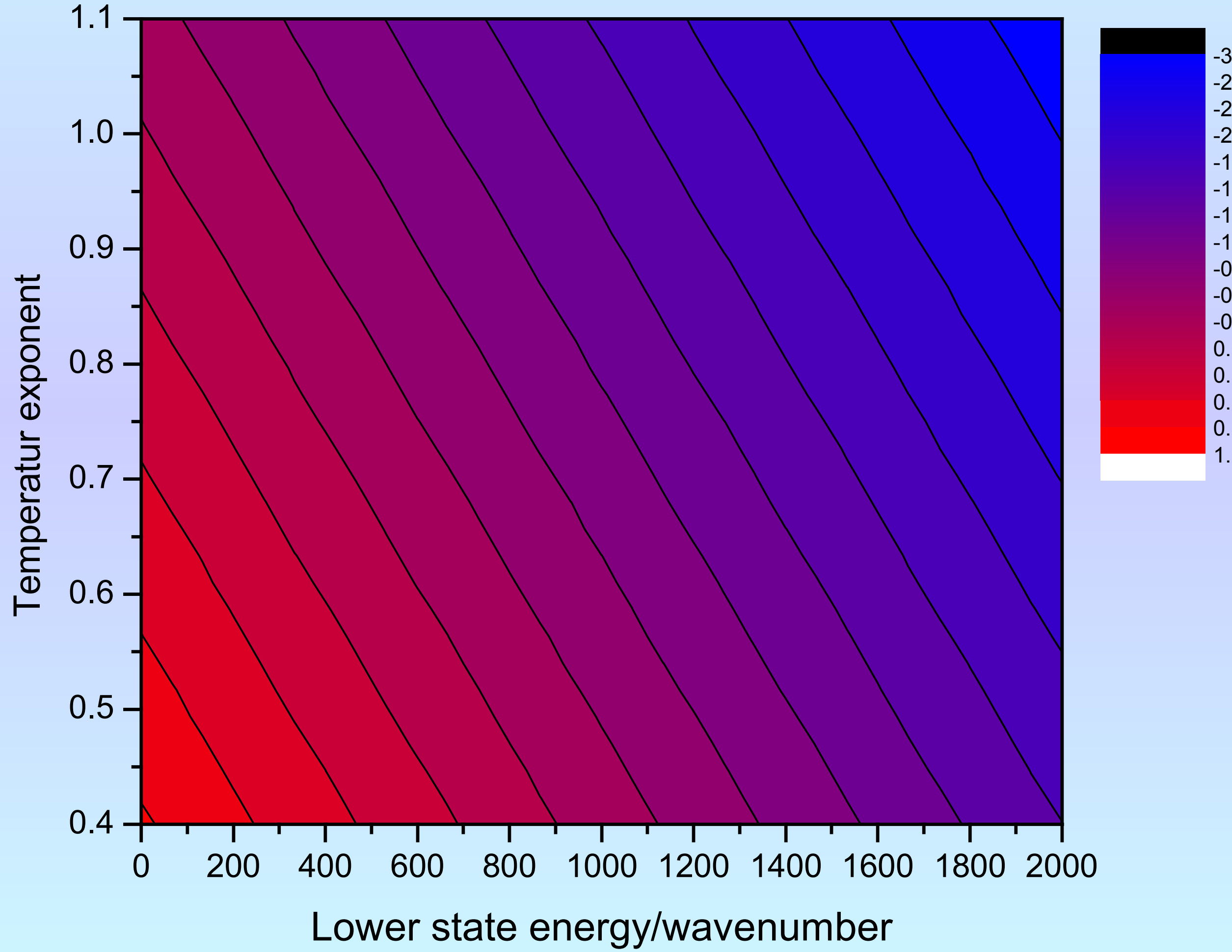
- **Statistical uncertainty** - from γ /n fit, scaled by χ
- **Pressure** - Thermostated pressure gauges, 0.35%
- **Temperature** - 0.5 K gives worst case 0.25%
- **Temperature inhomogeneity** - see next viewgraph
- **ILS** -
  - ILS error: uncertainty in retrieved field stop diameter
  - Width error expressed as function of width and optical depth
  - γ for all lines fitted with and without width error
  - Error is difference
- **(n_{HITRAN} use)** -
  - From comparison of temperature exponents from this work and HITRAN maximum *n* error = 0.2
  - γ_{220K} calculated for n_{HITRAN} and n_{HITRAN}+0.2
  - Error is difference

Sample errors - Temperature inhomogeneity

DLR

Impact on pressure-broadened line width

- Water spectra modelled: 0.65x233K + 0.35x253K
- Linefit, differences to model input data
- Parameterisation of differences wrt **E_{lower}** and **temperature exponent**
- Plot of percentage line width error for 0.65xT + 0.35x(T+40K)
- Errors 1% to -3%



Generation of database

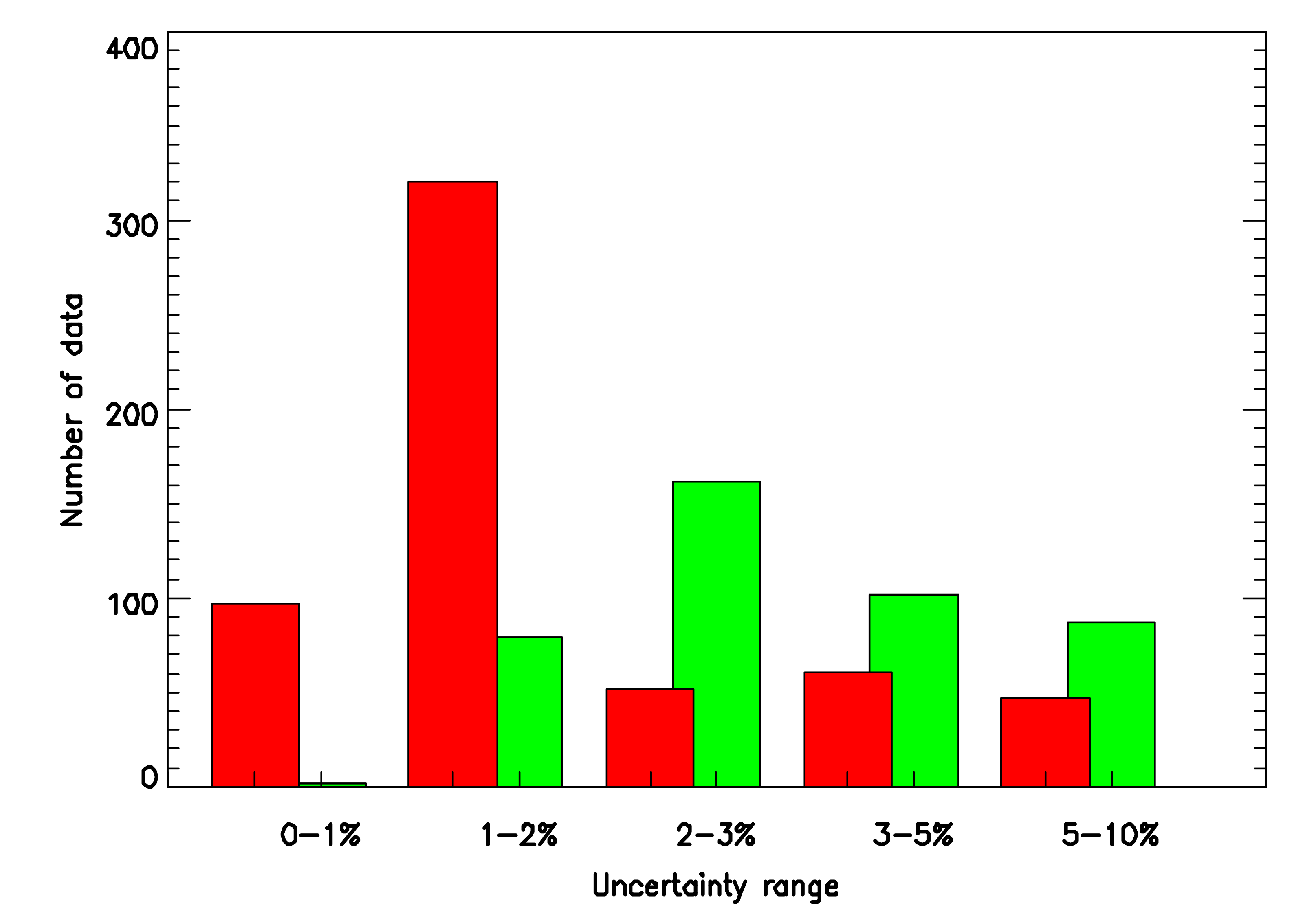
- HITRAN-type database with γ_{air}, γ_{self}, n_{air}, n_{self} (new column), combined errors for γ given at 296 and 220 K
- Best-of flag: overall error < 5%, chi <2, ≥4 measured airbroadened data in fit
- Additional updated parameters: line positions, line shift (+temperature dependence - new), linestrengths
- Beta version released: outliers: low quality lines (2 measurements in gamma-fit) with large systematic errors (blending, etc.) may be present but will be removed in next version

Number of updated line parameters, linestrength range 10^{-23} - 10^{-19}

	γ_{air}	n_{air}	γ_{self}	n_{self}
H_2O	431	372	352	107
H_2O (020)-(010)	161	87	237	128
$H_2{}^{18}O$	169	116	253	152
$H_2{}^{17}O$	101	53	189	129
HDO	123	44	399	247
Total	**985**	**672**	**1430**	**763**

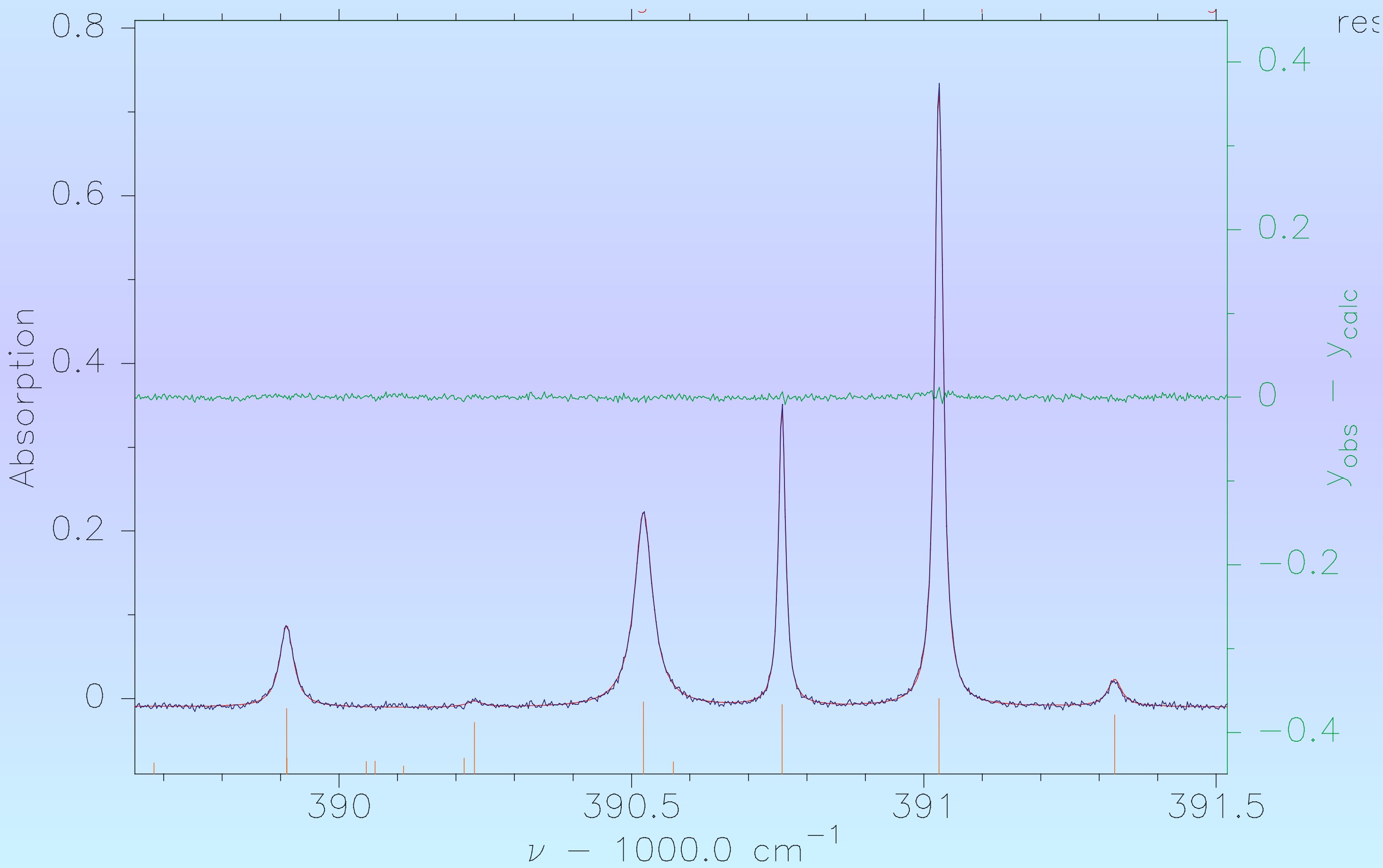
Generation of database

Overall uncertainty, main isotopomer, γ_{296}, γ_{220}



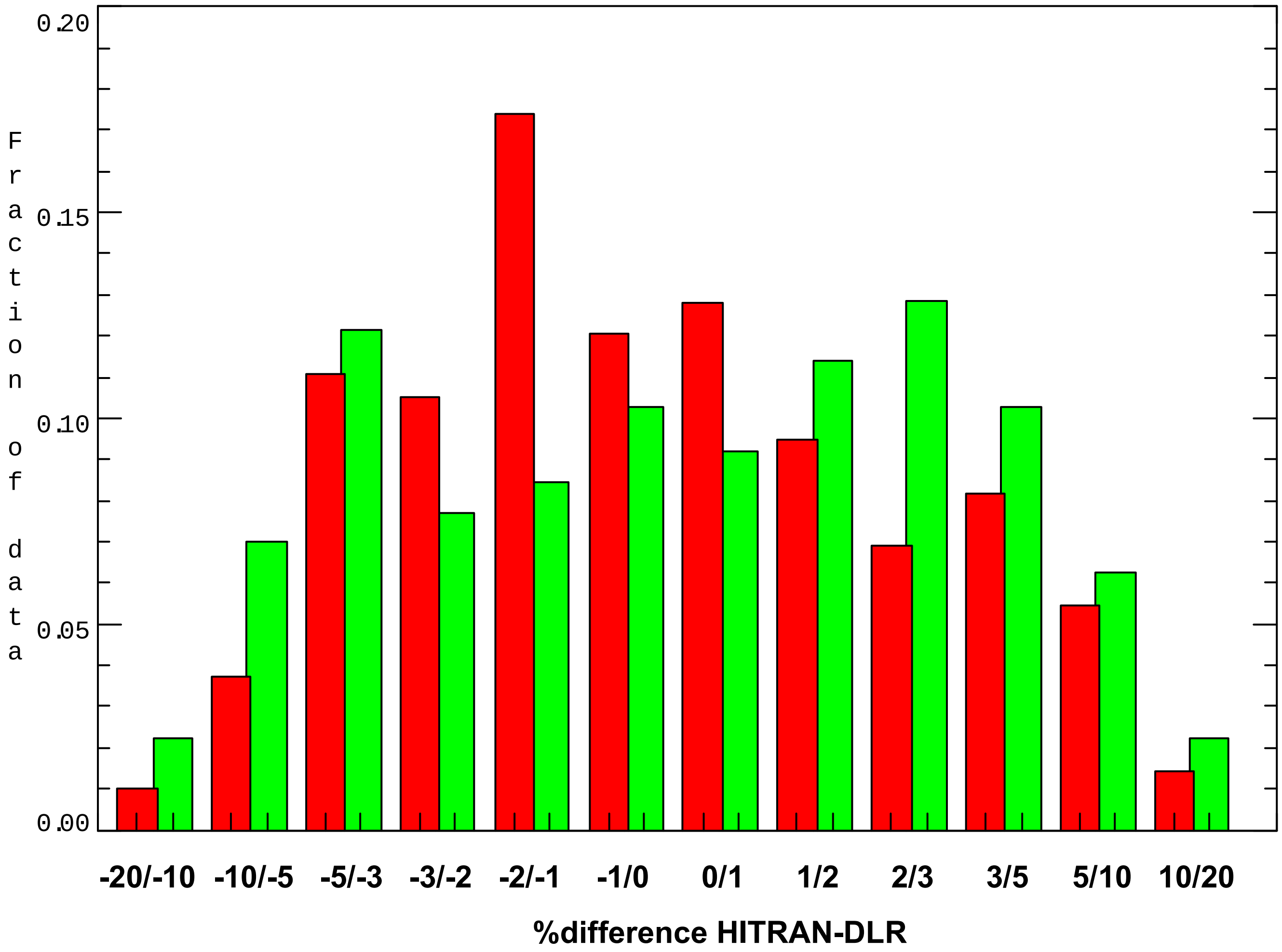
Quality assessment - new database

Model measured spectra with new database (lineopositions, shifts, linestrenghts and broadening updated)



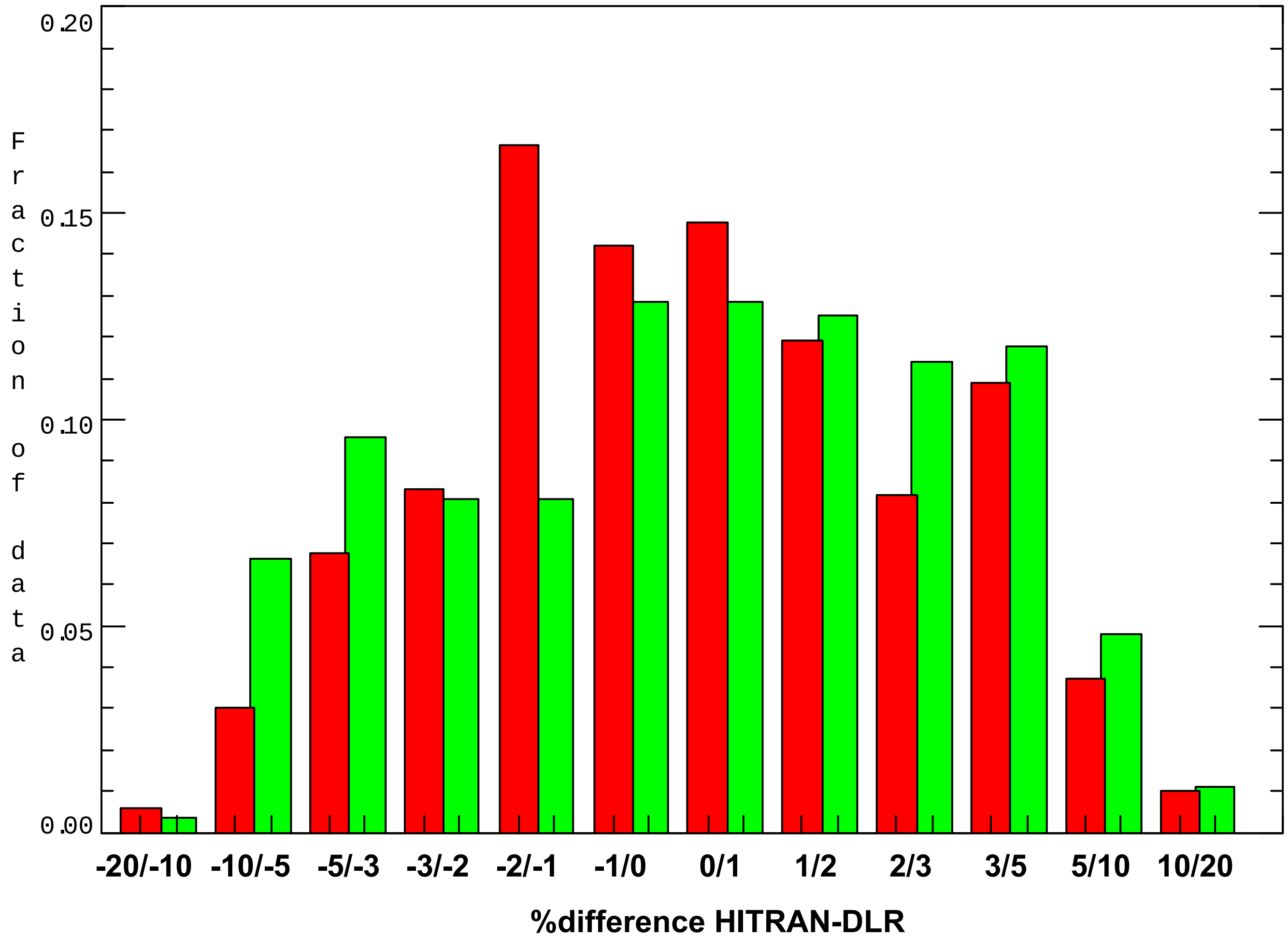
Comparison with HITRAN2004

DLR uncertainty <3%, γ_{296}(696 lines), γ_{220}(272 lines)



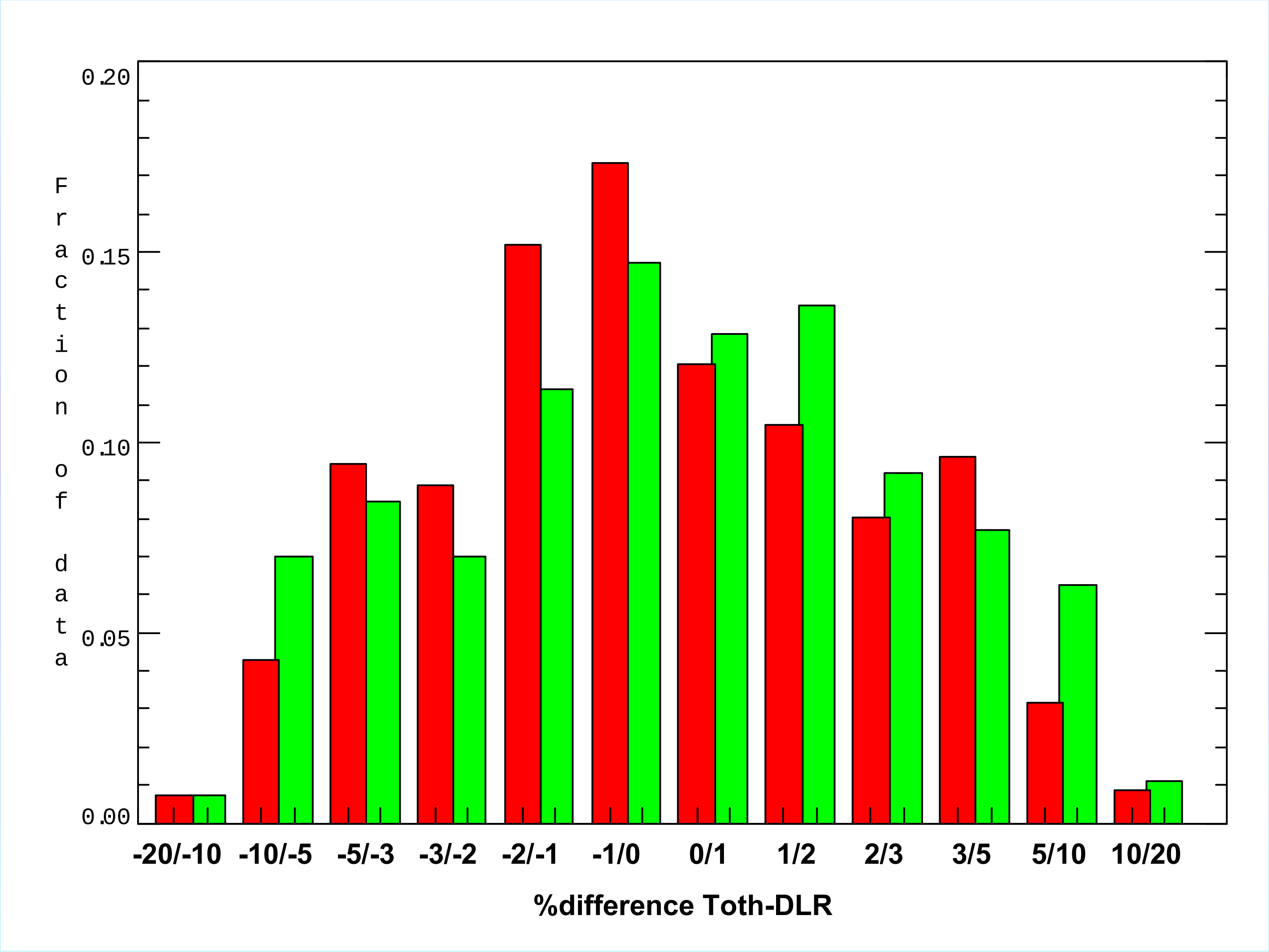
Comparison with HITRAN06_v7

DLR uncertainty <3%, γ_{296}**(696 lines)**, γ_{220}**(272 lines)**



Comparison with Toth (n for γ_{220} from HITRAN2004)

DLR uncertainty <3%, γ_{296}(698 lines), γ_{220}(272 lines)



Conclusion

- Extensive measurement program conducted (1250-1750 cm^{-1})
- New method for generating H_2O/air mixtures successfully tested
- Software tool developed for fitting of broadening parameters and temperature dependence from measured Lorentzian widths including linestrength assessment and filecuts for quality improvement/assessment
- Analysis had to be done on single line basis
- 50 mb measurements were excluded due to Dicke narrowing
- Further quality assessment performed
- Extensive error analysis performed including temperature inhomogeneities and instrumental lineshape errors
- New extended HITRAN type database including line positions, linestrengths, line shifts and broadening
- 12% of γ_{296} differ from HITRAN2004 by more than 5% (18% for γ_{220})
- 8% of γ_{296} differ from HITRAN06_v7 by more than 5% (13% for γ_{220})
- 9% of γ_{296} differ from Toth by more than 5%

Comparison $H_2^{16}O$ with Toth (n for γ_{220} from HITRAN2004)

DLR uncertainty <3%, γ_{296}(469 lines), γ_{220}(242 lines)