Fourier-transform intensity measurements with 0.1% accuracy

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DLR

Why 0.1% absolute intensity accuracy?

- Example: CO2M Mission global bias from spectroscopy <0.5%
  - Allowed error contribution from intensity <0.2%
  - Remark: Differential error more critical -> demanding requirements for temperature dependence parameters

- Validation of *ab initio* calculations

- Anyhow, the issue is of metrological interest, pushing the accuracy limits

Who claims ca. 0.1% absolute intensity accuracy?

- CRDS: NIST (Gaithersburg, USA), NCU (Torun, Poland), CO, CO_2
- FTS: PTB (Braunschweig, Germany), CO, 0.13%, based on single measurement!
- FTS: DLR (Oberpfaffenhofen, Germany), CO_2, 0.15%

Can we achieve 0.1% with an FTS? How?

Test case: CO 3-0 intensities in frame of TGAS (CCQM/GAWG Task Group on Advanced Spectroscopy), initiated by Joe Hodges

Uncertainty budget for CO_2 1.6 µm DLR measurements (M. Birk et al., JQSRT 272 (2021) 107791)

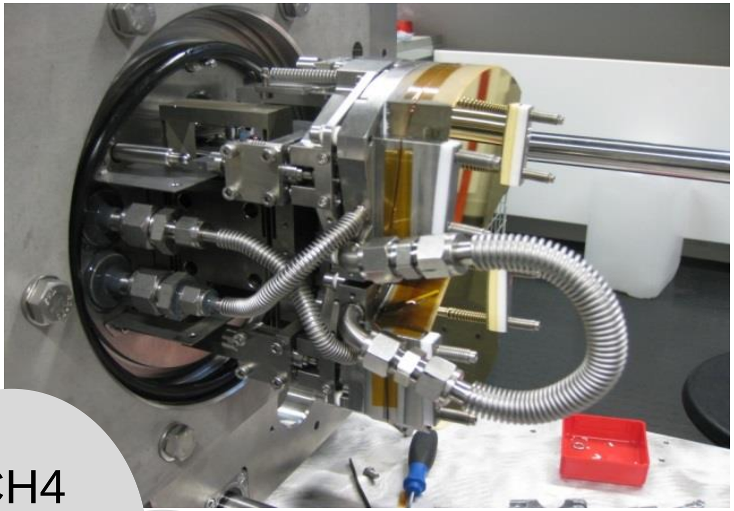
Physical Effect	Uncertainty/%	Relevant for relative band uncertainty
Systematic uncertainty in ILS	0.08	X
Pathlength	0.10	
Molecular lineshape	0.04	X
Pressure (drives density)	0.06	
Sample temperature (±0.1 K)/300 K (drives density)	0.03	
RSS	**0.15**	

Improvements:

- Path length: 0.02%
- Pressure: 0.008% >300 mbar, 0.02% @ 125 mbar, 0.06% @ 5 mbar
- Instrumental lineshape: negligible

Multireflection cell

- 14-165 m absorption path
- 190-350 K temperature range
- Mirrors actively thermalized
- 0.1 K temperature homogeneity
- Attached to Bruker IFS 125 HR
- Transfer optics in sample chamber
- Mirror coating selected for minimum reflection loss

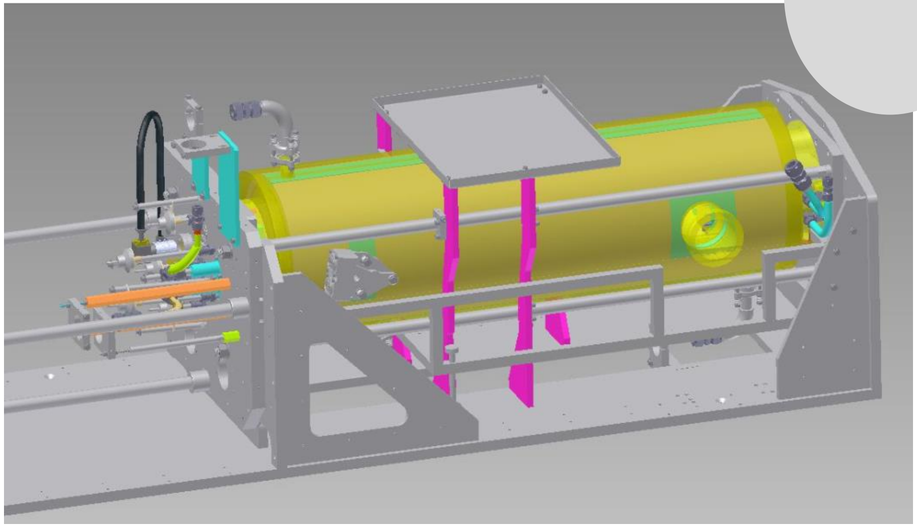


CH_4

H_2O

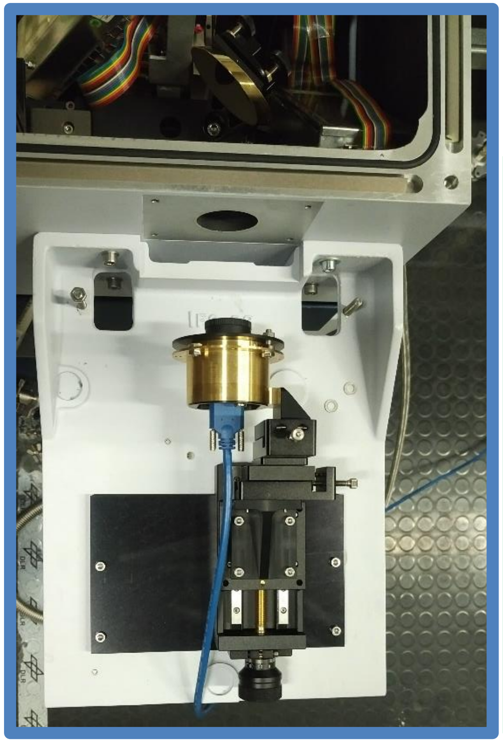
CO

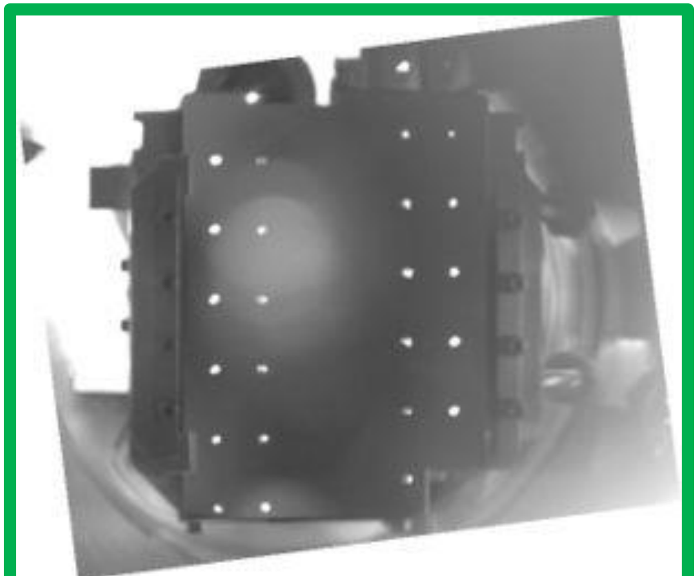
CO_2

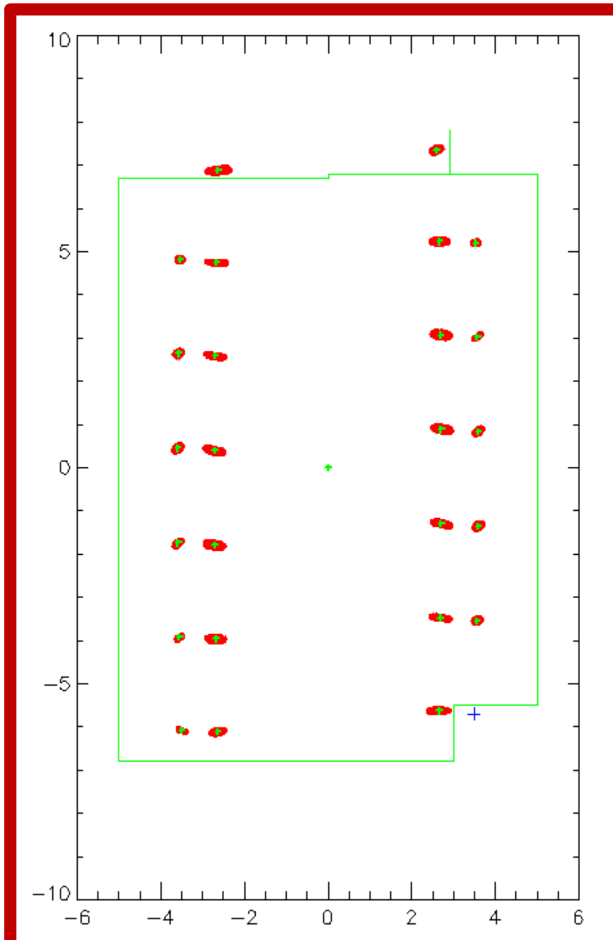


Multireflection cell: Alignment

- Dedicated raytracing tool for marginal rays: Source $\Rightarrow$ interferometer $\Rightarrow$ multireflection cell $\Rightarrow$ detector
- Adjustment multireflection cell: Camera for observation of spot pattern on T-mirror
- Camera at detector exit of spectrometer to visualise image on detector







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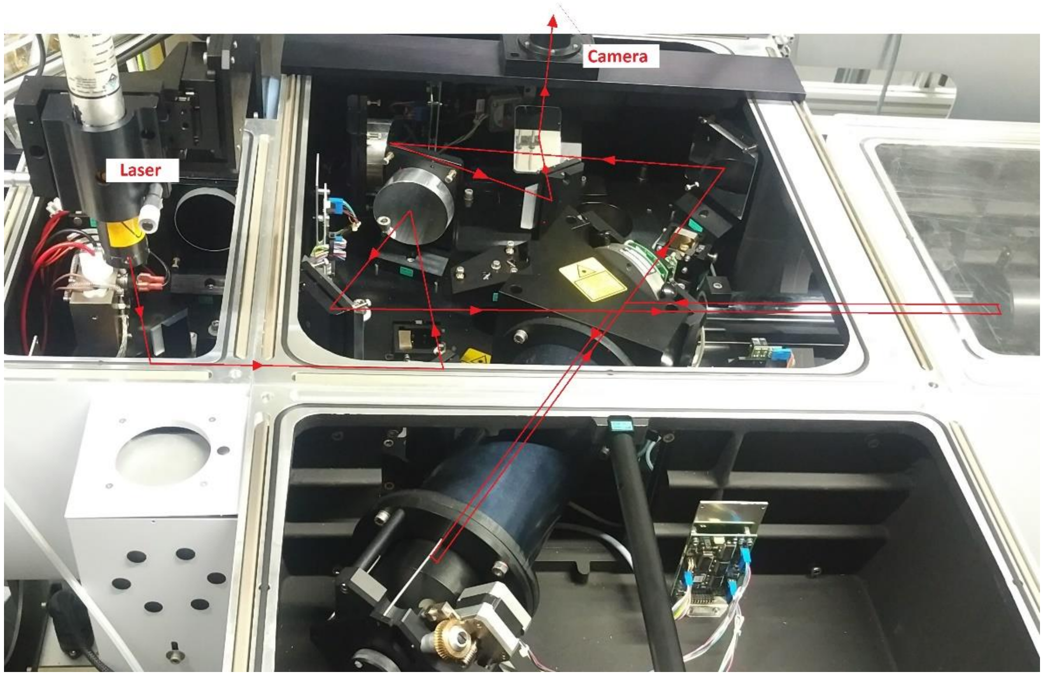
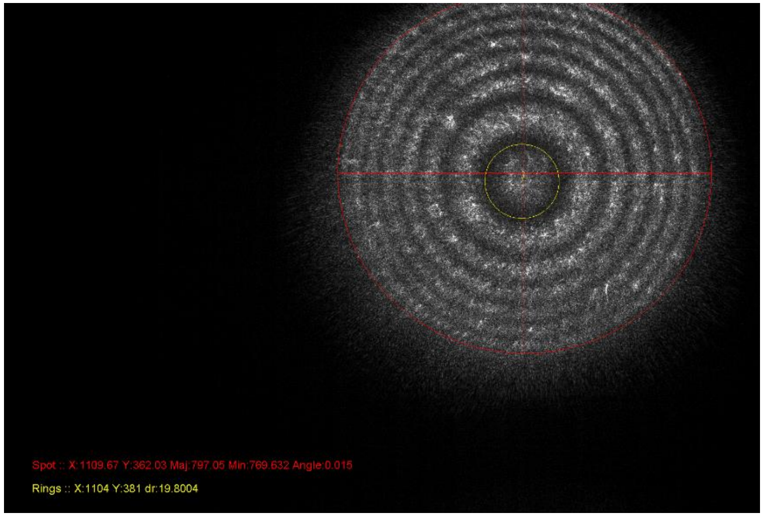
Interferometer alignment

- Dedicated Hardware for interferometer alignment for optimal instrumental line shape (ILS)
  - HeNe laser with two consecutive scattering surfaces for appropriate field-of-view illumination
  - CCD camera for Haidinger fringe recording
  - Haidinger fringes can be recorded with evacuated spectrometer





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DLR CO measurements in 1.6 µm region

- Bruker IFS 125 HR + DLR coolable multireflection cell.
- Instrument evacuated with cryo/turbomolecular pump to 0.002 mbar.
- Detector: RT-InGaAs, cut-on 5900 cm-1
- Optical filter: LP 7000 cm-1
- Source: Tungsten lamp
- Beamsplitter: Si on CaF2
- MOPD: 100 cm
- Input aperture diameter: 0.8 mm
- Sample: CO 4.7 Linde
- 2 measurement campaigns (hardware problems 1st campaign: non-reproducible offset approx. 0.2%, randomly varying antisymmetric ILS contribution)
- 2nd campaign after service by Bruker company

DLR CO measurements in 1.6 µm region

Measurement plan inputs

- Opaque lines for offset determination
- Pressure >100 mbar mostly -> high pressure accuracy
- Large column amounts for weak lines to compare with NIST/NCU
- Redundancy
- 5 mbar measurement, Doppler limited, optically thin -> intensity strong lines
- 10 mbar CO_2 measurements for instrumental line shape determination
- $\leq$10 mbar gas flow, >100 mbar static
- H_2O outgassing corrected/H_2O partial pressure determined spectroscopically
- Leak rate negligible

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DLR CO measurements in 1.6 µm region

- Measurement time 6-36 h

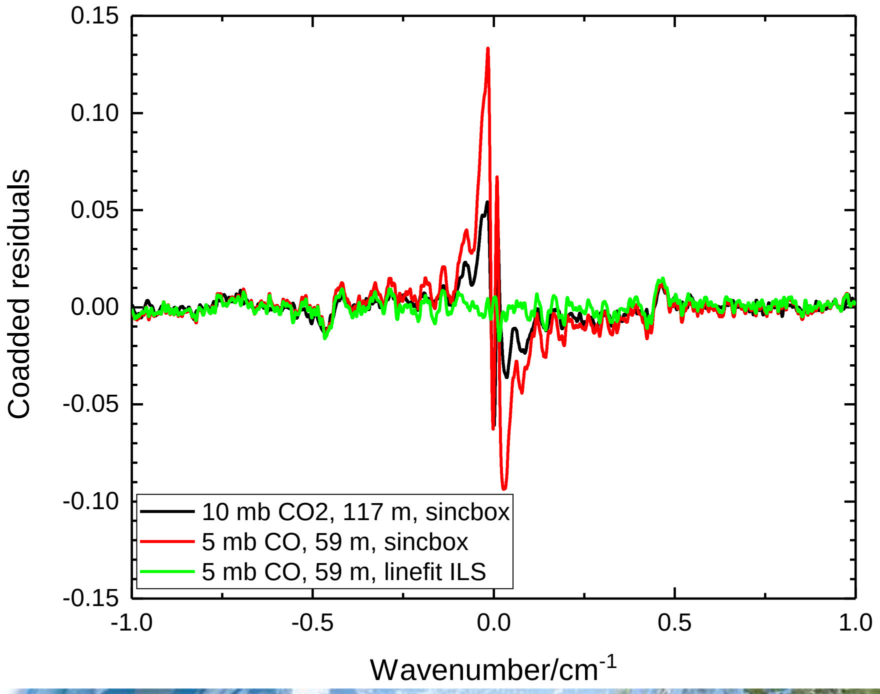
Molecule	Pressure/mbar	Abs.path/cm	RMS noise/% transmittance
CO	496	1456	0.010
CO	125	1456	0.009
CO	503	5936	0.020
CO	257	5936	0.012
CO	126	5936	0.021
CO	5	5936	0.013
CO	502	11696	0.022
CO	250	11696	0.034
CO	117	11696	0.016
CO2 (ILS)	10	1456	0.010
CO2 (ILS)	10	5936	0.023
CO2 (ILS)	10	11696	0.024

Multispectrum fitting

- Microwindows ca. 1 cm-1 wide
- For most lines fitted: S, γ_{0_self}, γ_{2_self}, ν_{VC_self}, δ_{2_self}, Rosenkranz line mixing
- For each microwindow in each spectrum fitted: quadratic baseline polynomial, frequency calibration
- Offset correction -0.0005 - +0.0005 determined from opaque lines, not available for 14 m and 5 mbar 59 m
- Absorption path correction for 117 m: 0.999
- Van der Waals correction for number density applied (max. 1.00043) – total pressure unchanged
- 14 m measurements omitted, discrepancy to 5 mbar measurement: residuals up to 0.1% - reason unclear (line model or ??)

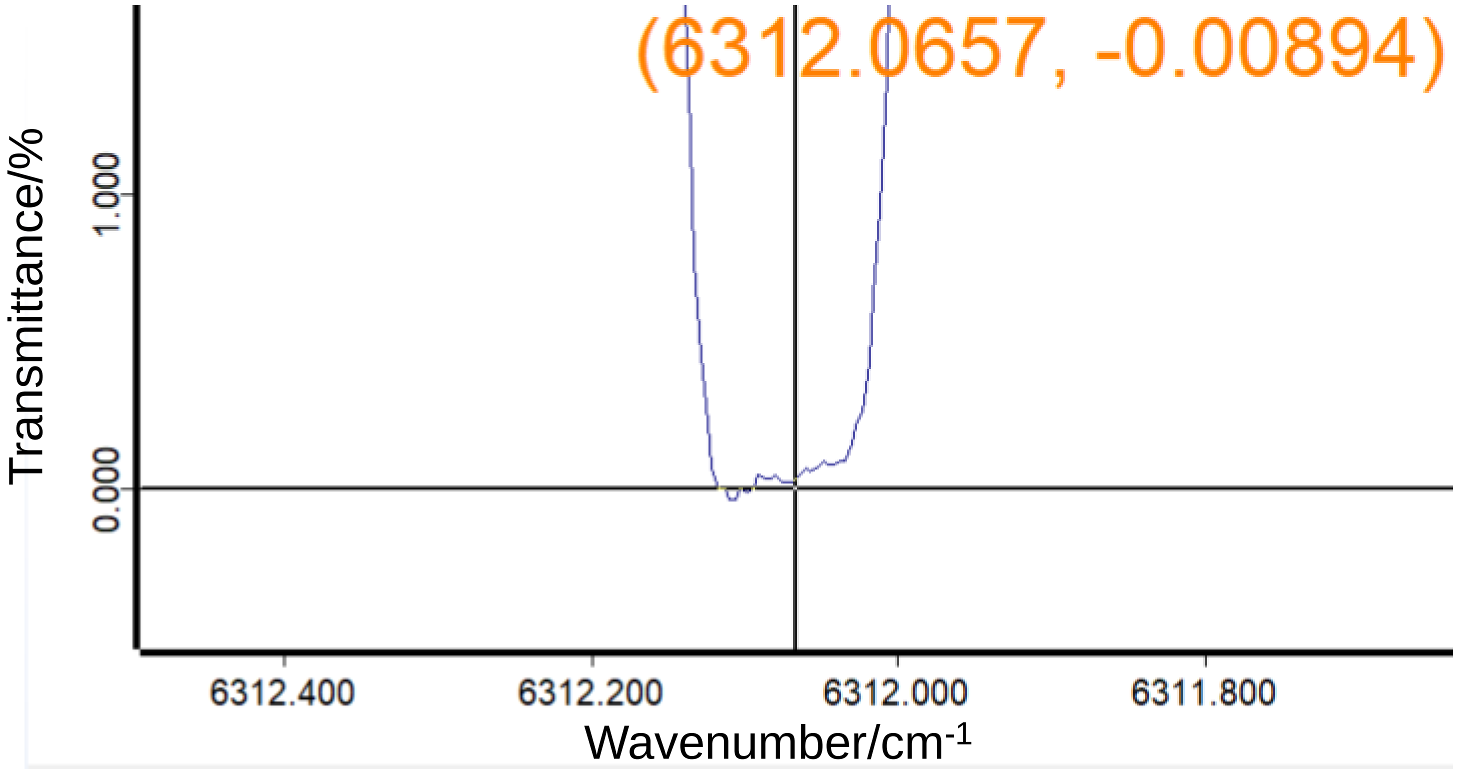
Instrumental line shape (ILS)

- ILS determined with linefit software, Frank Hase, IMK, from nearly Doppler-limited CO2, CO spectra
- Analysis of spectra with sincbox ILS shows difference to ideal ILS
- Residuals are normalized with area under absorption line and averaged
- Antisymmetric function detected, getting stronger with time, corresponding to an interferogram sampling error of a few nm decreasing from ZPD to zero in about 15 cm OPD. Reason unknown, to be fixed by Bruker service.
- Nicely taken into account by linefit ILS



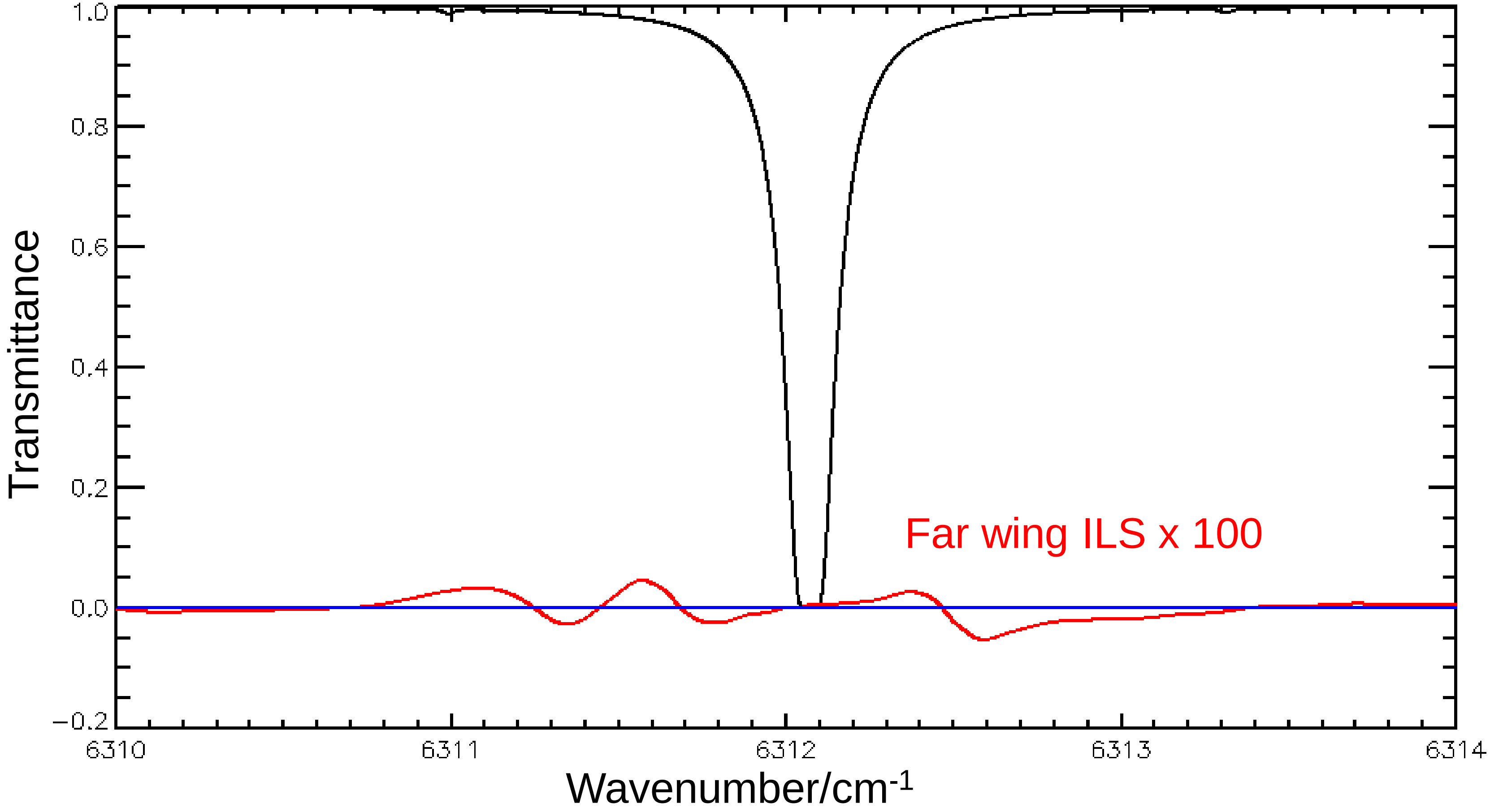
Instrumental line shape

- The antisymmetric ILS causes a slope on the 0% transmittance of an opaque line
- A small offset is visible

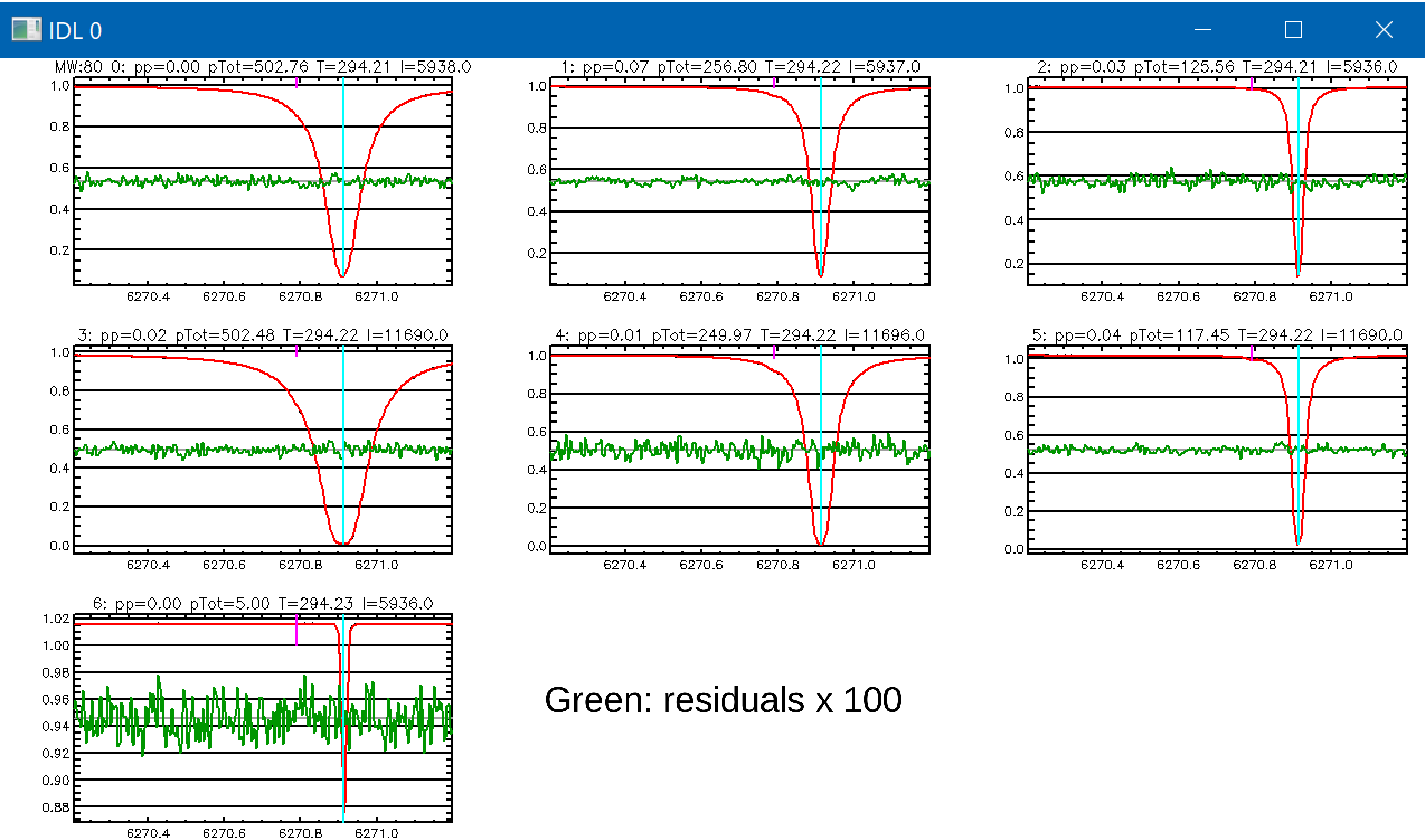


„Far wing“ instrumental line shape (<0.05%)

- Low resolution ILS detected, not changing in time, cannot be covered by linefit, negligible contribution to line area, origin unknown
- Implemented in multispectrum fit: Negligible impact on line intensities, but better residuals, impact on line mixing



Example of multispectrum fitting: P(17)



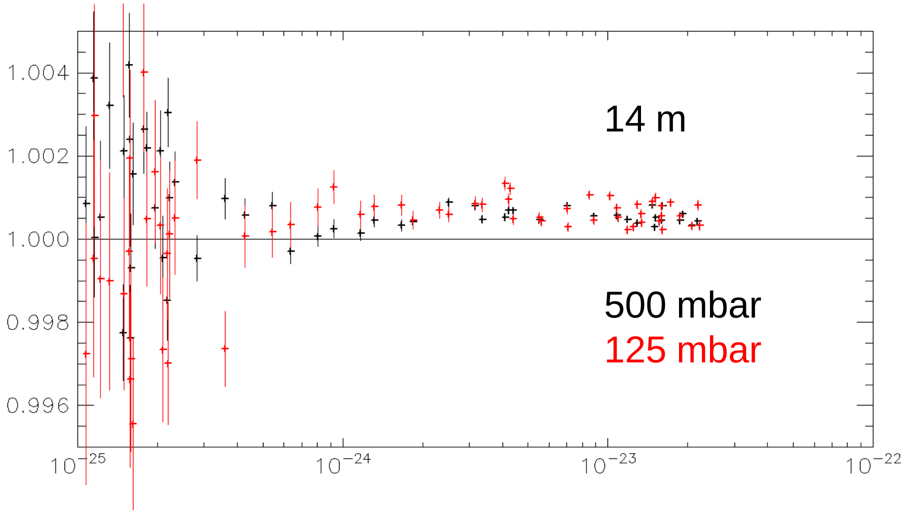
Green: residuals x 100

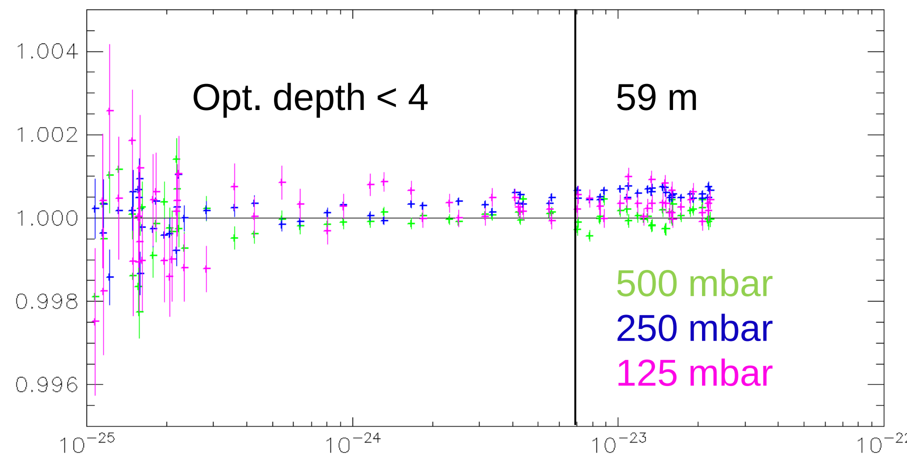
Systematic intensity error budget CO

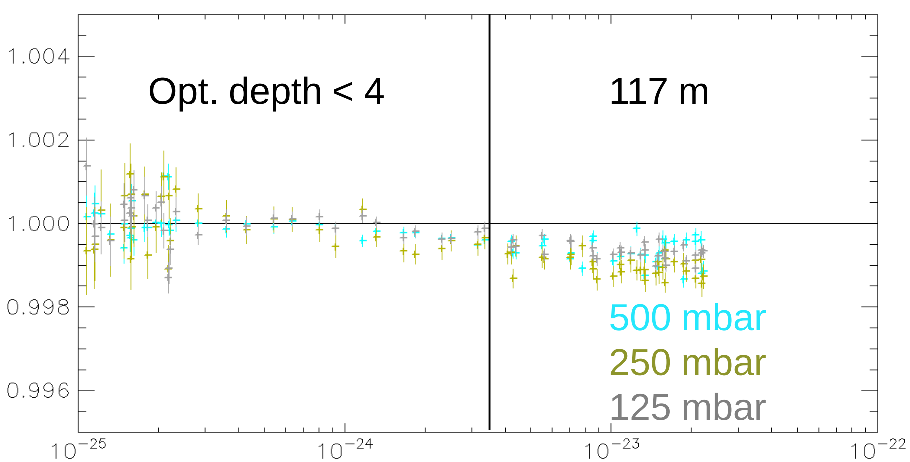
Physical Effect	Uncertainty/%
Systematic uncertainty in ILS	negligible
Offset error	0.05
Pathlength	0.02
Molecular lineshape	See ND-factor fits
Pressure (drives density)	0.008 >300 mbar 0.02 @ 125 mbar 0.06 @ 5 mbar
Temperature error 0.1 K	<0.07 S>1e-24 <0.2 S>1e-25
Sample purity uncertainty	negligible
Isotopic composition uncertainty (composition determined spectroscopically)	negligible

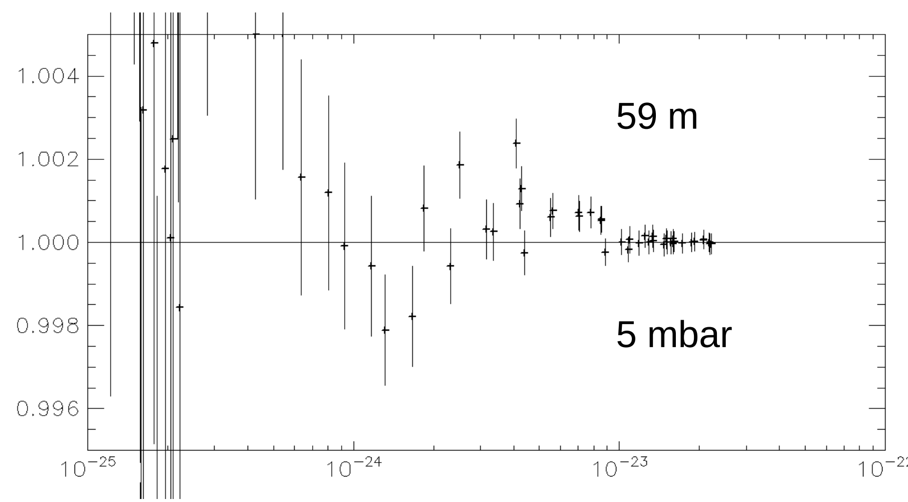
Quality check using redundancy:

Fitted number density factors vs. line intensity. Spectroscopic parameters taken from global fit and fixed. ND factors <0.05% for lines contributing to line intensities. Includes: ILS, line model, abs. path, pressure, temperature









DLR

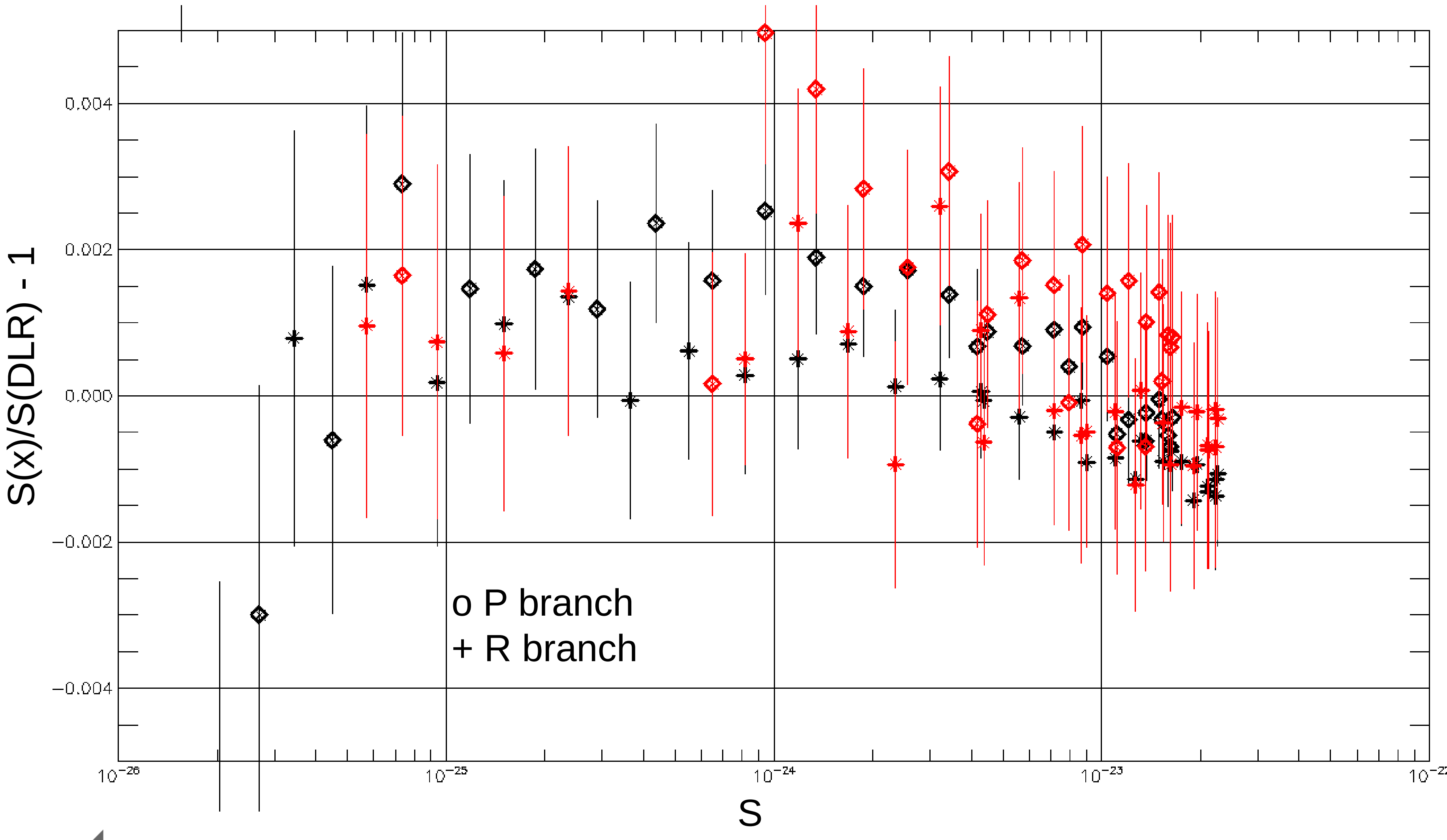
Comparison with *ab initio* and NIST/NCU/PTB

Bielska et al. PRL 129, 043002 (2022)

m	S(DLR)	(Abinitio-DLR) /%	(exp-DLR) /%	Unc. Exp /%	Unc. DLR /%
-30	1.560E-26	0.89	1.08	0.10	0.40
-27	7.352E-26	0.29	0.16	0.07	0.21
-22	6.496E-25	0.16	0.02	0.13	0.12
-21	9.440E-25	0.25	0.50	0.14	0.11
-20	1.346E-24	0.19	0.42	0.13	0.10
-19	1.878E-24	0.15	0.28	0.13	0.10
-18	2.565E-24	0.17	0.18	0.13	0.09
-17	3.429E-24	0.14	0.31	0.13	0.09
-16	4.485E-24	0.09	0.11	0.13	0.08
-15	5.735E-24	0.07	0.19	0.13	0.08
-14	7.164E-24	0.09	0.15	0.13	0.08
-13	8.741E-24	0.09	0.21	0.14	0.08
-12	1.041E-23	0.05	0.14	0.13	0.09
-11	1.209E-23	-0.03	0.16	0.13	0.09
-10	1.366E-23	-0.02	0.10	0.13	0.09
-9	1.500E-23	0.00	0.14	0.13	0.09
-8	1.597E-23	-0.05	0.08	0.13	0.10
-7	1.642E-23	-0.03	0.08	0.13	0.10
-6	1.624E-23	-0.07	0.07	0.14	0.10
-5	1.532E-23	-0.03	0.02	0.13	0.10
-4	1.362E-23	-0.06	-0.07	0.13	0.11
-3	1.115E-23	-0.05	-0.07	0.13	0.11
-2	7.949E-24	0.04	-0.01	0.14	0.11
-1	4.176E-24	0.07	-0.04	0.13	0.10

m	S(DLR)	(Abinitio-DLR) /%	(exp-DLR) /%	Unc. Exp /%	Unc. DLR /%
1	4.364E-24	-0.01	-0.06	0.13	0.10
2	8.675E-24	-0.01	-0.05	0.14	0.11
3	1.271E-23	-0.11	-0.12	0.13	0.11
4	1.621E-23	-0.08	-0.09	0.14	0.11
5	1.906E-23	-0.14	-0.10	0.13	0.11
6	2.109E-23	-0.12	-0.07	0.13	0.10
7	2.228E-23	-0.14	-0.07	0.13	0.10
8	2.262E-23	-0.11	-0.03	0.13	0.10
9	2.219E-23	-0.11	-0.02	0.13	0.10
10	2.111E-23	-0.13	-0.07	0.13	0.09
11	1.951E-23	-0.09	-0.02	0.13	0.09
12	1.755E-23	-0.09	-0.02	0.13	0.09
13	1.540E-23	-0.09	-0.04	0.14	0.09
14	1.317E-23	-0.06	0.01	0.14	0.09
15	1.101E-23	-0.09	-0.02	0.14	0.08
16	8.993E-24	-0.09	-0.05	0.13	0.08
17	7.179E-24	-0.05	-0.02	0.13	0.08
18	5.607E-24	-0.03	0.13	0.13	0.09
19	4.284E-24	0.01	0.09	0.13	0.09
20	3.206E-24	0.02	0.26	0.13	0.10
21	2.349E-24	0.01	-0.09	0.13	0.10
22	1.685E-24	0.07	0.09	0.13	0.11
23	1.185E-24	0.05	0.24	0.13	0.12
24	8.164E-25	0.03	0.05	0.05	0.13
27	2.363E-25	0.14	0.14	0.08	0.18
28	1.503E-25	0.10	0.06	0.09	0.20
29	9.382E-26	0.02	0.07	0.10	0.22
30	5.729E-26	0.15	0.10	0.09	0.25

Comparison with ab initio and NIST/NCU/PTB



Conclusion

- Investigation whether FT measurements can deliver line intensities with accuracy better than 0.1%
- Test case: 3-0 band of CO
- High accuracy intensity measurements from NIST, UNC, PTB, and *ab initio* calculations available
- Absorption path, pressure, and ILS accuracy improved
- Overall accuracy for several lines 0.08%, most $\leq$0.1%, including statistical, systematic, and temperature uncertainty induced uncertainties
- Comparison to averaged NIST/UNC: 6 of 7 lines <1σ(DLR), 0.13% < σ(DLR) < 0.25%
- Comparison to PTB: >60% of lines agree within 0.1%
- Comparison to *ab initio*: ca 70% of lines agree within 0.1%

DLR