

Jonas S. Wilzewski^{1,2}, Joep Loos^{1,*}, Manfred Birk¹, Georg Wagner¹

¹ German Aerospace Center (DLR), Remote Sensing Technology Institute, Weßling, Germany ² Ludwig-Maximilians-Universität München, Faculty of Physics, Munich, Germany
* joep.loos@dlr.de

Introduction

CO is a key constituent of the terrestrial atmosphere. Its role as a relatively long-lived tracer for atmospheric transport processes (see e.g. [1]) and its significance for tropospheric ozone chemistry [2,3] have led to numerous remote sensing studies of carbon monoxide (e.g. [4,5]), many of which study the overtone band near 4260 cm⁻¹. This CO band (2←0 band) will be used by the TROPOMI Atmospheric Monitoring Instrument (TROPOMI) aboard the European Space Agency's Copernicus Sentinel-5 Precursor satellite to study global air quality in the troposphere [6]. Since strong water vapor absorption signals interfere with the CO 2←0 band in atmospheric measurements, the TROPOMI mission mandates high-accuracy spectral reference data for both CO and H₂O in the 2.3 μm region. To this end, we have carried out measurements of absorption line parameters for H₂O and CO to be used in TROPOMI atmospheric retrievals. The experiments were carried out on a Bruker IFS 125HR Fourier transform spectrometer and a multispectrum fitting software developed at DLR was used for parameter retrieval [7] using the Hartmann-Tran-Profile (HTP) [8,9] with Rosenkranz line mixing [10].

TROPOMI Spectroscopy Requirements

The TROPOMI instrument will be launched aboard ESA's Sentinel-5 Precursor satellite this year with an expected operational time of seven years. We summarize the general features and spectroscopic requirements:

Instrument

- UV-VIS-NIR-SWIR push broom grating spectrometer on Sentinel-5P
- Spectral ranges 270-495 nm, 710-775 nm, 2305-2385 nm
- Measurement of backscattered light in the 2.3 μm spectral range

Data Products in 2.3μm Region

- CO (and CH₄) columns with 15% (and 2%) accuracy
- Retrieve H₂O, because it interferes with other signals

User Requirements/Retrieval Simulations

- Spectroscopic uncertainties should only contribute about 30% to total errors for column amounts → 5% for CO
- Uncertainties in H₂O spectroscopy lead to uncertainties in CO and CH₄ results
- Retrieval of TROPOMI data products from simulated measurements using distorted spectroscopy yield sensitivity of retrieval products to specific spectroscopy parameter changes
- Retrieval simulations using AFGL data for number density, mixing ratio and temperature profiles
- Calculations were done for 'tropical' (most cases, worst-case for H₂O) and 'subarctic winter' (few cases)
- Determination of sensitivities to correlated and uncorrelated errors

Derivation of spectroscopy requirements

- Spectroscopy requirements were derived based on the retrieval simulation results
- Non-Voigt line shape has to be used
- Narrowing effects have to be taken into account for H₂O
- Accuracy and precision defined for all parameters to be measured



Fig. 1: The Sentinel-5 P satellite

Measurements and Parameter Retrieval

Fourier Transform Spectroscopy (FTS)

- Bruker IFS 125HR Fourier transform spectrometer
- White-type multireflection cell attached to the interferometer
- Absorption path 14.4-206.4 m
- Temperature range 198-360 K
- Flow experiments for H₂O



Fig. 2: The lab at DLR

Spectroscopic parameter retrieval

- Parameter retrieval using an interactive, microwindow-based multispectrum least-squares fitting software [7]
- Data were used for a fit to a quadratic speed dependent hard collision (qSDHC) model in the HTP implementation [8,9] with Rosenkranz line mixing [10].

Parameter	Symbol	H ₂ O	CO
Position	σ	X	X
Intensity	S	X	X
Air broadening	γ_{air}	X	X
Air shift	δ_{air}	X	X
Self Broadening	γ_{self}	X	
Self Shift	δ_{self}	X	
Speed dependent narrowing (air)	γ_2	X	X
Dicke narrowing (air)	v_{vc}	X	X
Rosenkranz line mixing	γ_0	X	X

Table 1: Overview of spectroscopic line parameters investigated in this study

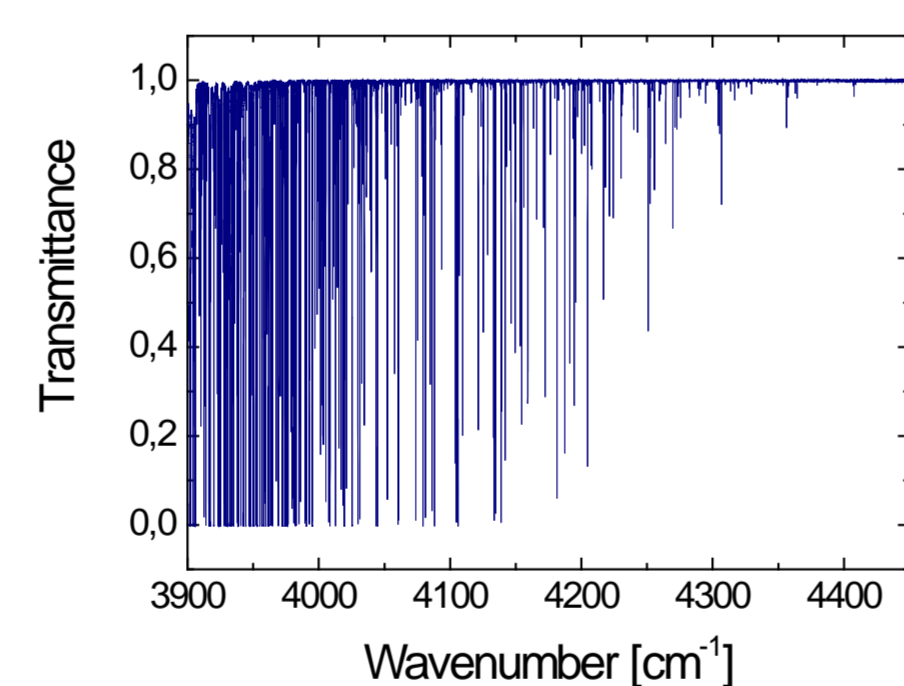


Fig. 3: An example of a pure H₂O transmittance spectrum (abs. path=14.4 m, p=10 mb) In this wavenumber region one finds mostly v₁ and v₃ transitions

CO Results

- Multispectrum fit of pure CO and CO/air spectra
- Voigt profile leads to w-shaped and asymmetric residuals
- Speed-dependent Voigt + Rosenkranz line mixing needed for fit to noise level
- Line intensities in excellent agreement with HITRAN2012 [11] values (by Devi et al. [12,13]): 0.05% difference on average (see Fig. 4)
- Broadening coefficients show systematic differences to HITRAN values, which can be attributed to the different lineshape model used, HITRAN values can be seen as effective since non-Voigt effects are not accounted for (see Fig. 5)
- Air-shift parameters agree with HITRAN2012 (Devi et al.) within 3%
- The retrieved narrowing parameters have an average value of about 0.1 γ_{air}
- Measured Dicke narrowing is $v_{\text{vc}} = 0.005 \text{ cm}^{-1}\text{atm}^{-1}$ on average
- Line mixing parameters compare well with data by Devi et al. (see Fig. 6)

CO Results (continued)

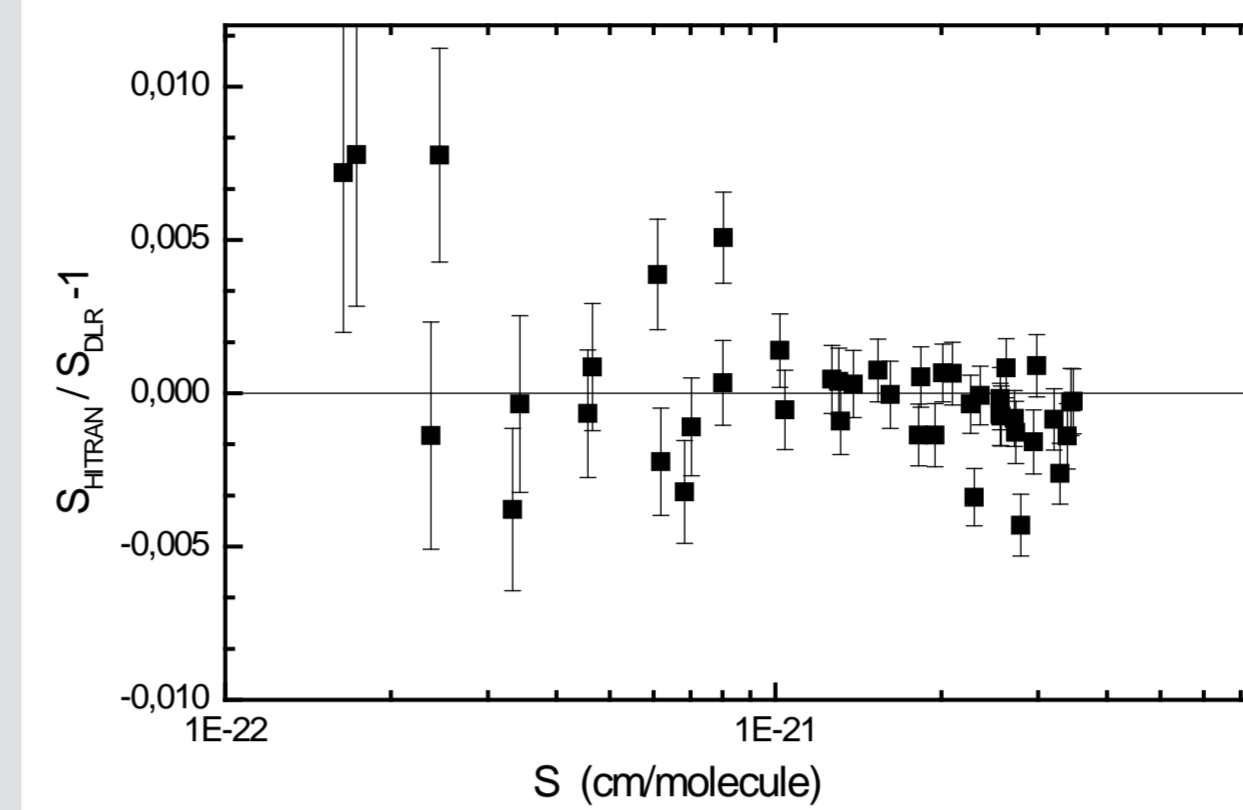


Fig. 4: (top) Comparison of measured line intensities with HITRAN12 values: 0.05% difference on average

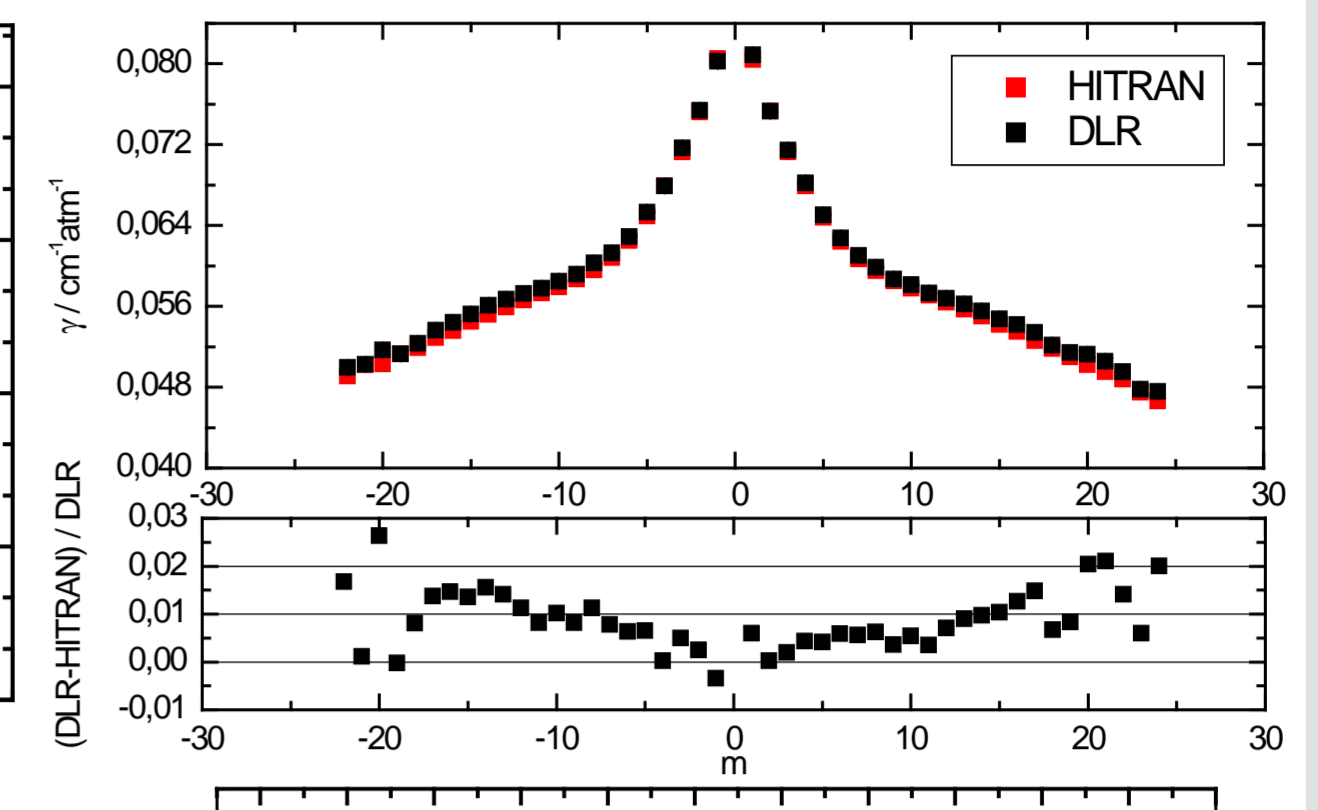


Fig. 5: (top right) Comparison of measured air-broadening parameters with HITRAN12 values

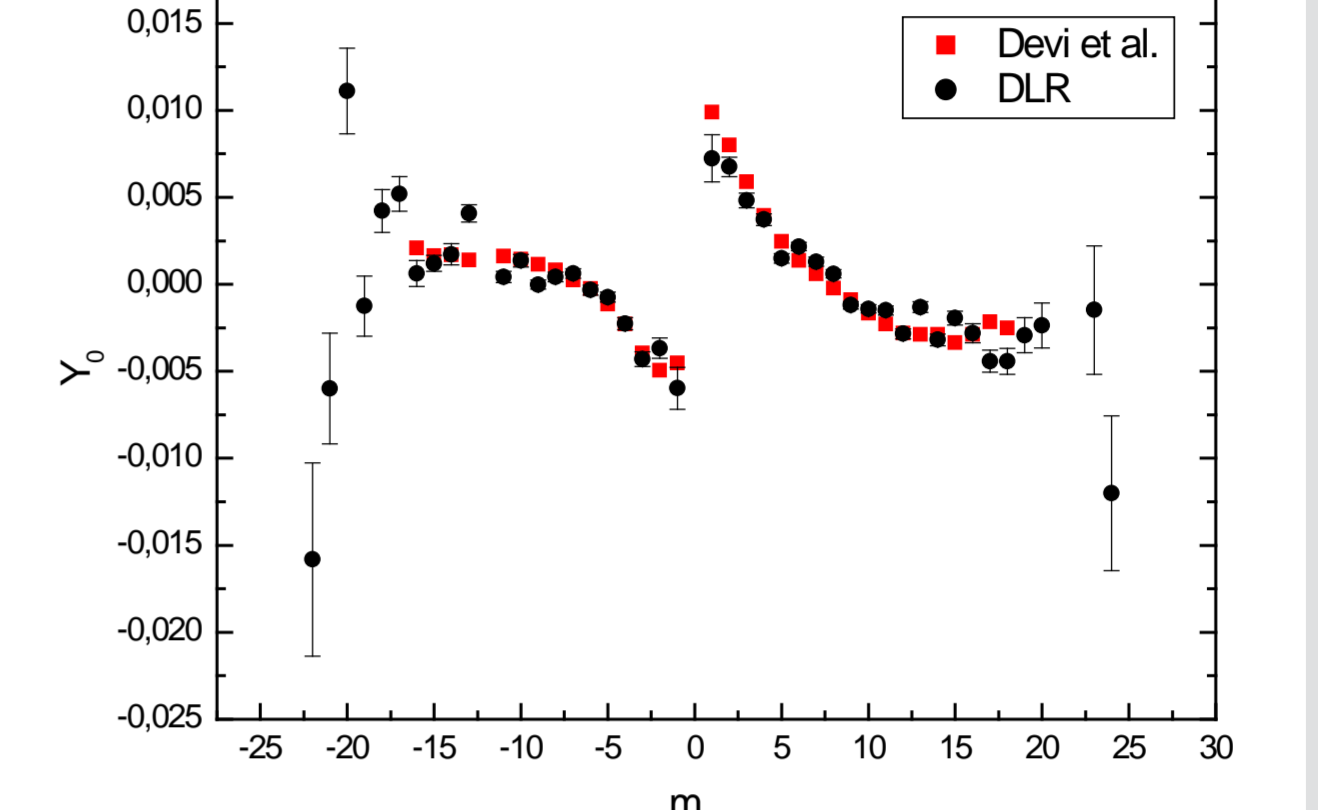


Fig. 6: (right) Comparison of measured line mixing parameters with Devi et al. [12,13] values

H₂O Results

- Multispectrum fit of pure H₂O and H₂O/air spectra
- Voigt profile leads to w-shaped and asymmetric residuals
- HTP + line mixing needed to fit data to noise level:

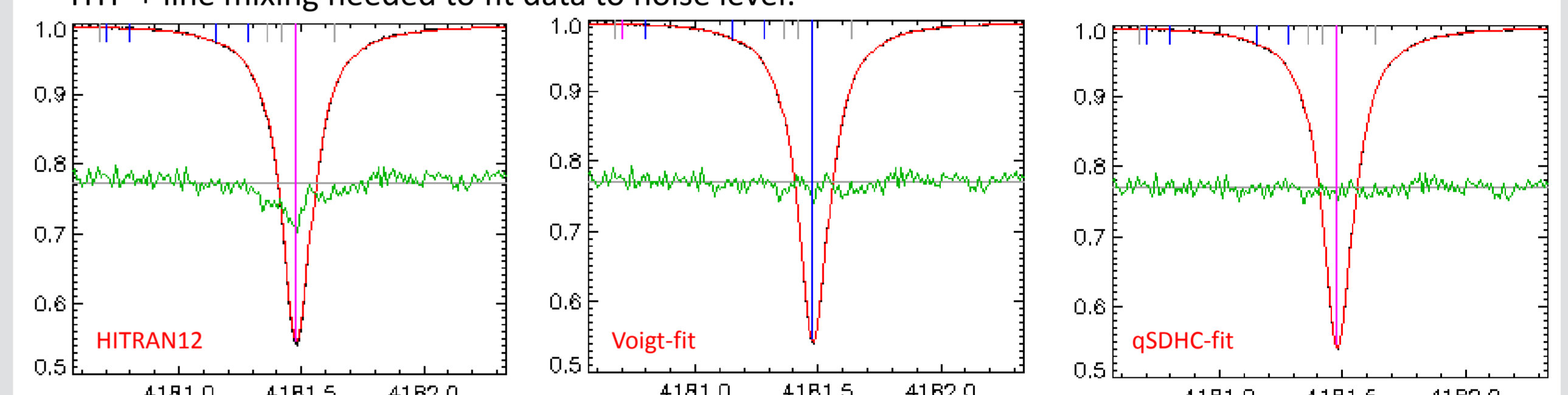


Fig. 7: The 9_{4,6} ← 8_{2,7} transition of the v₃ band in different fit configurations (black=obs., red=calc., green=residuals). Left: forward calculation using HITRAN12 values; Center: Voigt fit; Right: qSDHC fit

Intensities:

- HITRAN12 values show deviations up to 80% (see Fig. 8)
- Comparison with Scheepmaker et al. [14] shows offset of about -4%
- Agreement with ab initio data [15,16] < 1.5% on average!

Air-broadened halfwidths:

- Systematic deviation between measurements and HITRAN12 ≈ ±1.5%
- Local deviations up to 20% (see Fig. 9)

Air-shift:

- HITRAN12 and present measurements are within 6% of each other on average

HTP-parameters:

- The retrieved narrowing parameters have an average value of about 0.12 γ_{air}
- Measured Dicke narrowing is $v_{\text{vc}} = 0.012 \text{ cm}^{-1}\text{atm}^{-1}$ on average

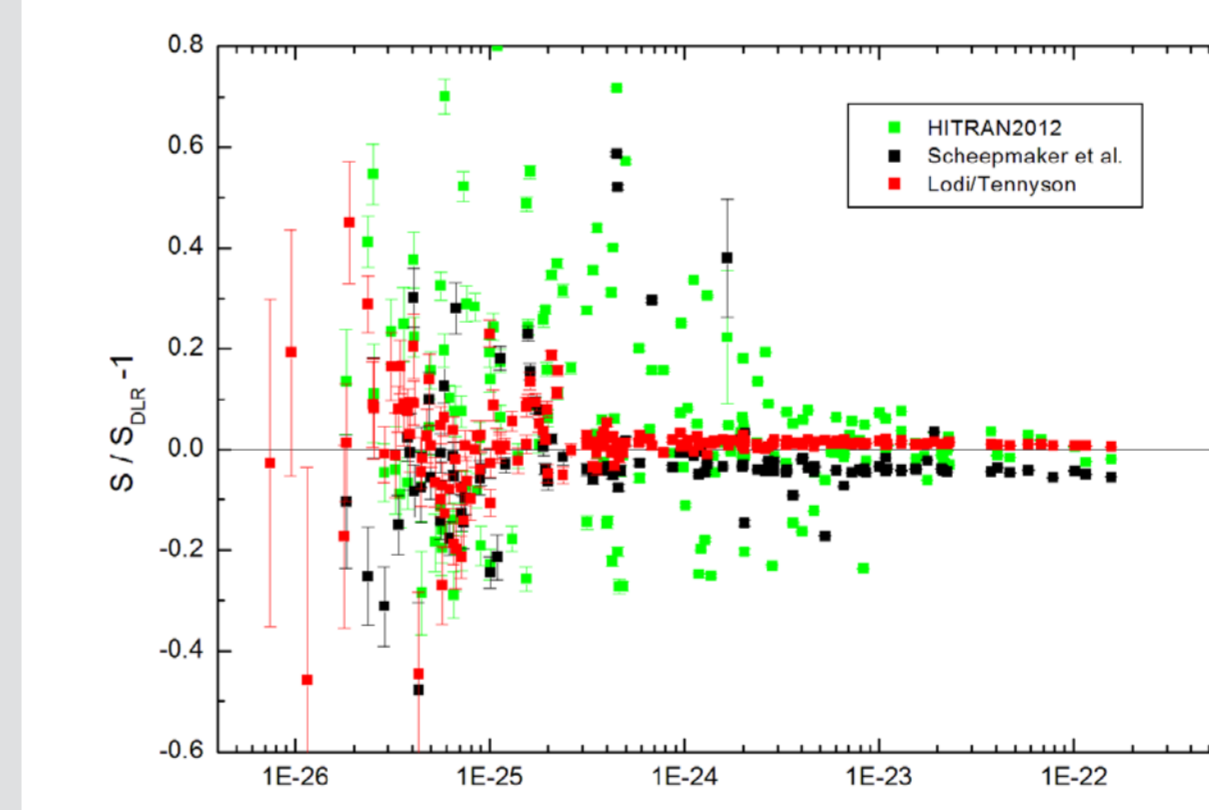


Fig. 8: Comparison of retrieved H₂O line intensities with HITRAN2012, Scheepmaker et al., and Lodi/Tennyson values.

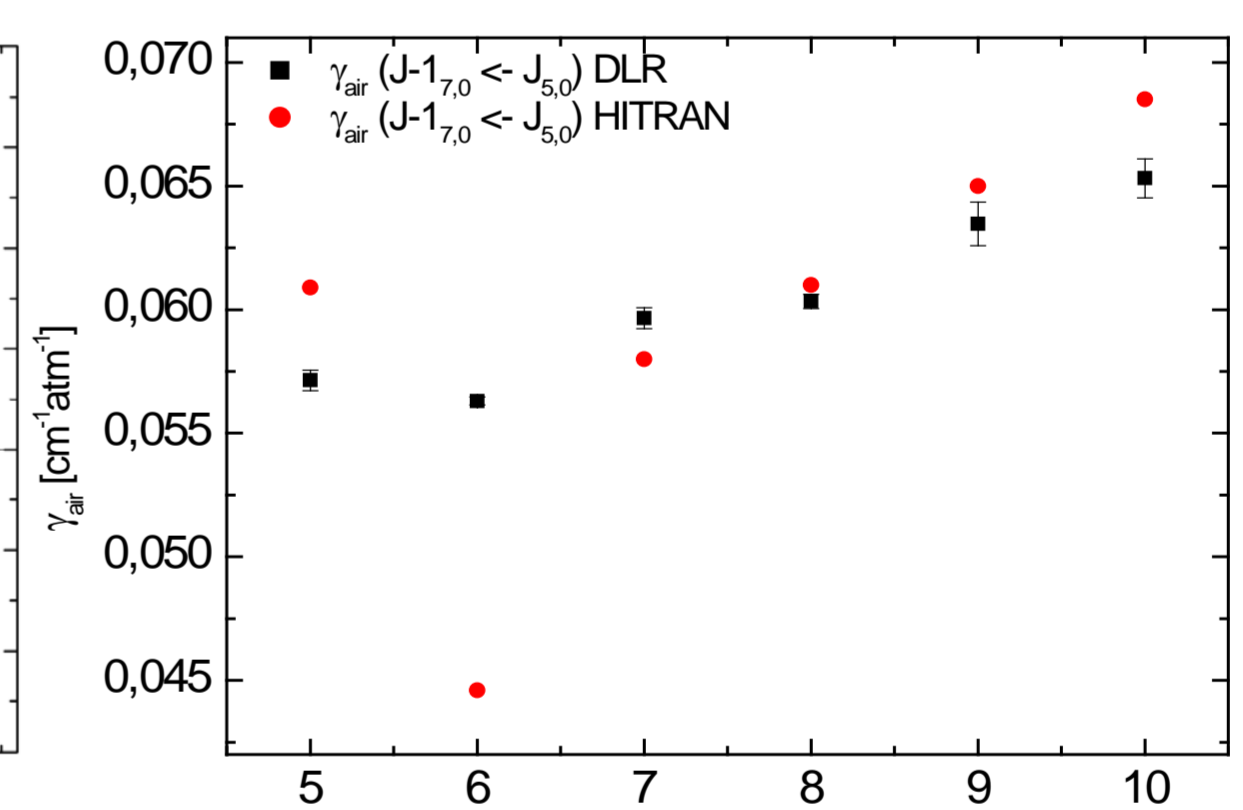


Fig. 9: Measured γ_{air} compared to HITRAN12 in the J-1,7,0 ← J_{5,0} v₃ subband (J_{ka,j}-K_a-K_c). For |m|=6, the HITRAN data from [17] deviate strongly from the measured value.

Summary and Perspectives

The reported CO line intensities, air-broadening and -shift parameters can serve as useful validation of the HITRAN2012 spectral database while the analysis of Dicke narrowing, speed dependence and Rosenkranz line mixing parameters emphasizes the importance of modern line shape functions.

In the case of water vapor, the new line list reduces residuals in atmospheric retrievals by 50% on average [18]. The agreement between fitted line intensities and theoretical values [15,16] (<1.5%) is unprecedented.

Water spectra at higher and lower temperatures have already been recorded and we will analyze these for temperature dependences as a next step.

References

- [1] J. Lelieveld et al., SCIENCE, 291,1031 (2001)
- [2] J. A. Logan et al., J Geophys Research: Oceans, 86, 7210 (1981)
- [3] D. T. Shindell et al., Journal of Geophysical Research: Atmospheres, 111, D19306 (2006)
- [4] C. Liu et al., Atmos. Chem. Phys., 14, 1717 (2014)
- [5] C. Clerbaux et al., Atmos. Chem. Phys., 8, 2569 (2008)
- [6] J.P. Veeckind et al., Remote Sensing of Environment 120, 70 (2012)
- [7] J. Loos et al., 13th HITRAN conference, 2014 (doi: 10.5281/zenodo.11156)
- [8] N.H. Ngo et al., JQSRT 129, 89 (2013)
- [9] N.H. Ngo et al., JQSRT 134, 105 (2014)
- [10] P. W. Rosenkranz, IEEE Trans Antennas Propag. AP-23, 498 (1975)
- [11] L. Rothman et al., JQSRT 130, 4 (2013)
- [12] M. Devi et al., JQSRT 113, 1013 (2012)
- [13] M. Devi et al., JQSRT 116, 199 (2013)
- [14] R. A. Scheepmaker et al., Atmos Meas Tech, 6, 879 (2013)
- [15] L. Lodi et al., J Chem Phys, 135, 034113 (2011)
- [16] J. Tennyson, University College London, Private communication
- [17] D. Jacquemart et al., JQSRT, 96, 205 (2005)
- [18] F. Hase, Karlsruhe Institute of Technology, Private communication

Acknowledgements

This work has been performed within the framework of ESA project „SEOM-Improved Atmospheric Spectroscopy Databases (IAS)“, ESA/AO/1-7566/13/I-BG