Multispectrum fit of non-Voigt lineshape in the H_2O ν_2 band

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Abstract

A new fitting tool for analysis of multiple molecular absorption spectra utilizing a microwindow-based line-by-line-approach has been developed. Its capabilities include the choice of numerous different line shape models, from a simple Voigt to more sophisticated models like a speed-dependent Galatry including line-mixing. A comfortable manual mode as well as a fully automatic mode have been implemented including various quality assessment procedures like the monitoring of correlation coefficients or the supply of useful information e.g. needed for file cuts (single spectrum residuals) [1].

As a first application the new tool is used to re-analyze water vapor absorption spectra in the 1250-1750 cm^{-1} range [1,2]. The measurements include pure water as well as water/air-mixture measurements and cover a wide range of column densities. The total air pressure and partial pressure ranges were 50-1000 mb and 0.001-5 mb, respectively.

Whereas the original analysis was based on single spectrum fits applying the Voigt procedure, in the present multispectrum fit the speed-dependent Voigt lineshape was used. The advantages of a multispectral analyis approach as well as the need for consideration of narrowing effects is illustrated by the presentation of differences in residuals as well as resulting line parameters for selected transitions. As indicated in [3] opaque as well as non opaque lines could be fitted with the speed-dependent Voigt while the pure Voigt yields to narrow opaque lines.

New multispectrum fitting tool

The software - written in IDL - has been developed for fitting of multiple absorption spectra recorded with a Fourier-transform spectrometer. Great effort was taken to make it as generic and comfortable as possible. Although it is tailored to the needs of high resolution FT-spectroscopy, it might be easily customized to be applied to spectra recorded with other instrument types. The results of the tool were validated vs. a single-spectrum IDL DLR fitting tool [4] and FITMAS [5].

Line models
- Voigt
- Speed-dependent Voigt [6]
- Speed-dependent Galatry + Rosenkranz line mixing (based on PROFFWD-routine [7,8])

Spectrum/microwindow-specific fitting capabilities
- polynomial baseline
- channelling
- wavenumber-calibration factor
- offset
- ILS (delta, sincbox, modulation + phase as a function of path difference as provided by LINEFIT [9])

Multispectrum fitting capabilities
- line parameters (position, intensity, self-/foreign-broadening + T-dependency, self-/foreign-shift + T-dependency, self-/foreign-narrowing parameters, line-mixing Y-paramerters)
- entrance aperture

Automatic mode
- automatic microwindow-, spectra- and line-fit parameter selection
- automatic fit
- automatic iteration of fit parameters (e.g. parameter error above threshhold)

Quality assessment
- goodness-of-fit (reduced χ^2, residua analysis planned)
- identification/prevention of parameter correlations

$$C_{ij} = \frac{(J^T WJ)^{-1}_{ij}}{\sqrt{(J^T WJ)^{-1}_{ii}(J^T WJ)^{-1}_{jj}}} \qquad |C_{ij}| \overset{!}{\leq} C_{\max}$$

i,j = fitted parameter number

- single-spectrum-fits with line-specific parameters (position, intensity, width, narrowing)
- differences of calculated parameters from multispectrum fit results
- measurement-specific differences can be investigated (as a function of position, intensity, ...) -> file cut [1], e.g. Fig. 1
- helps to identify systematic spectrum-specific errors
- calculation of contribution matrix B
  percentage information contribution of single spectrum to parameter

$$B^1_{sp} = \frac{\sum_{k\in s} \left|((J^T WJ)^{-1} J^T W)_{kp}\right|}{\max_k \left|((J^T WJ)^{-1} J^T W)_{kp}\right|} \qquad B_{sp} = \frac{B^1_{sp}}{\sum_s B^1_{sp}}$$

W = weight matrix, s = spectrum number,
p = parameter number, k = data point number

- redundancies
  virtual number of statistically independent data points with equal information content

$$R_p = \sum_s B^1_{sp}$$

s = spectrum number, p = parameter number

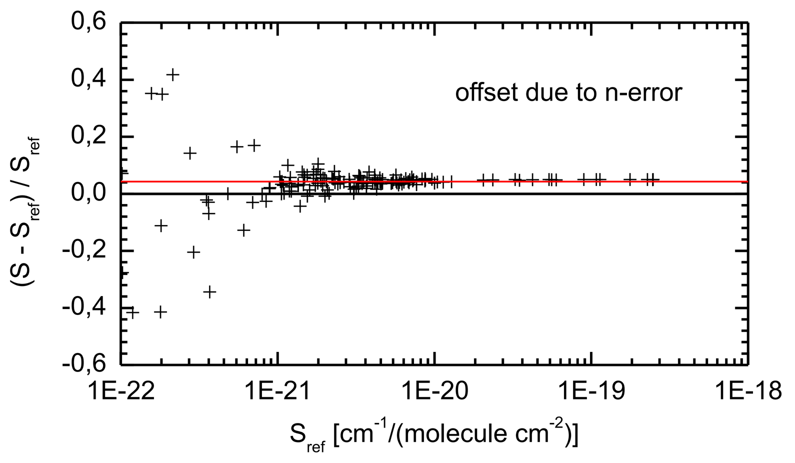

Fig. 1: File cut example of measurement with number density error

Experiment

Experimental conditions
- Mar ´03 - Jun ´05
- Bruker IFS 120 HR
- improved MCT-detector [10]
- p_{total} = 50 - 1000 mb
- p_{H2O} = 0.001 - 5 mb
- l = 16 - 8500 cm
- T = 240 -316 K

Setup
- 26 cm double-jacket short cell
- double-jacket White-type multireflection cell with absorption path up to 85 m
- 800 l vessel for H_2O/air-mixture preparation
- Pt100 temperature sensors, mks baratron pressure gauges, mks constant pressure valve
- short cell: sealed off pure H_2O @ room temperature
- multireflection cell: pure H_2O flow @ room temperature
- multireflection cell: pressure broadened H_2O flow @ 240 - 316 K

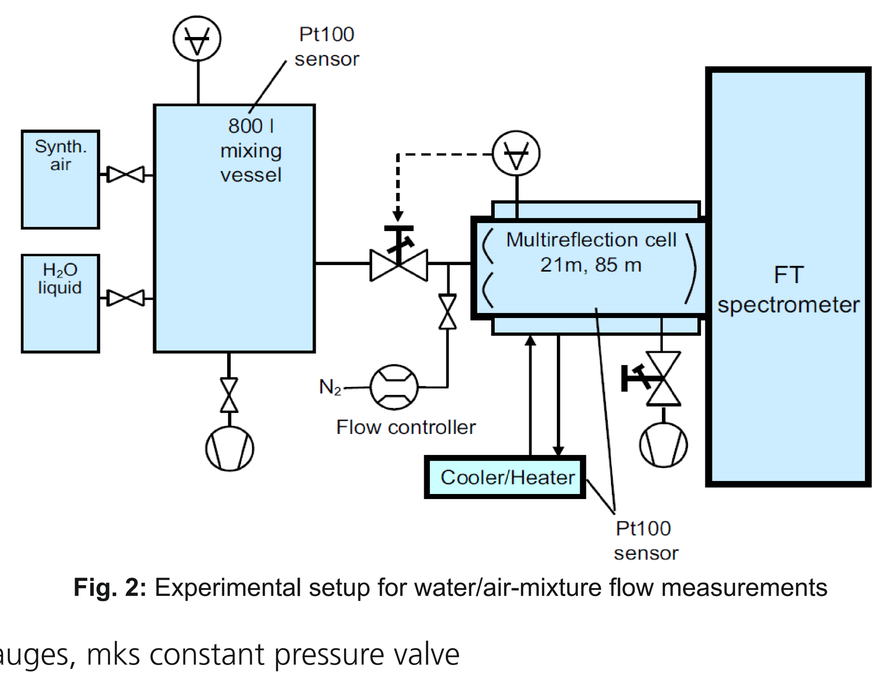

Fig. 2: Experimental setup for water/air-mixture flow measurements

A more detailed description can be found in [1].

Analysis procedure and results

As a first application previously done measurements are re-analyzed with special focus on non-Voigt effects. The following analysis is based on a speed-dependent Voigt lineshape and does not account for temperature dependencies. A complete analysis is to be done in the near future.

1. Generation of a linestrength reference
- multispectrum fit of 9 room temperature pure water spectra
- Voigt-fit of position, linestrength, width parameter

2. Fit of column density and temperature for water/air-mixture room-temperature spectra
- single spectrum fit of mixture-spectra
- Voigt fit of position, effective linestrength, width
- fit of number density and temperature -> effective linestrengths match linestrength reference on average

3. Fit of all room-temperature spectra
- multispectrum fit of 9 pure an 16 mixture spectra (corrected column density and temperature)
- speed-dependent Voigt (SDV) lineshape for lines with a wide range of opacities - including opaque lines

Results
- opaque and non-opaque lines fitted simultaneously
- case 1: Voigt, case 2: speed-dependent Voigt (SDV)
- Voigt shows W-shaped residuals for non-opaque lines and line wing residuals for opaque lines
- speed-dependent Voigt improves residuals significantly

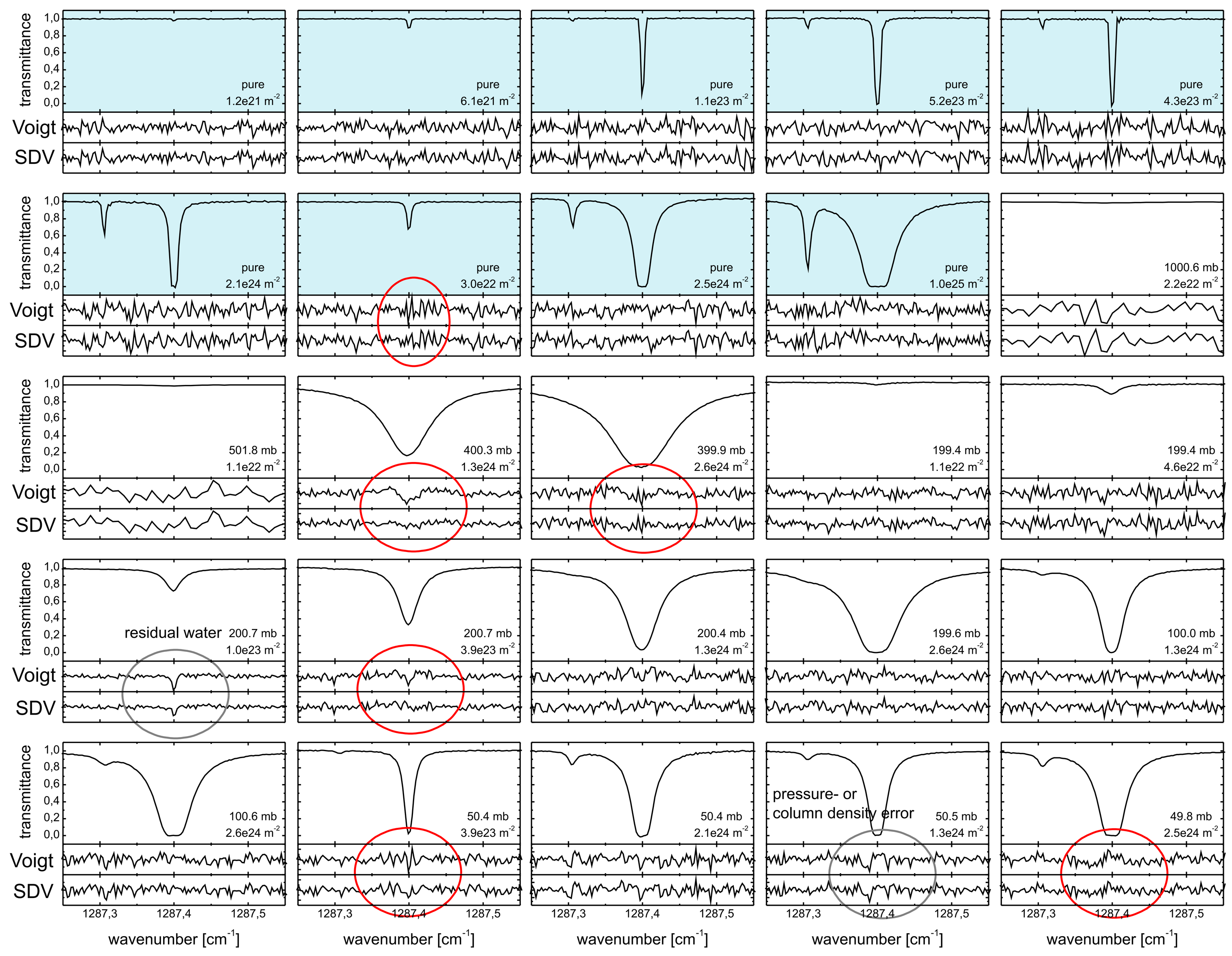

Fig. 3: Comparison between Voigt and SDV fitting residuals (residua are scaled for easier comparison)

- fitted broadening parameters systematically greater when fitting with SDV in comparison to a Voigt fit of lines with opacities < 4 [1] -> opaque lines are modeled too narrow with Voigt [3]
- influence of narrowing is greater when the broadening parameter is lower, i.e. when the J-quantum number is higher

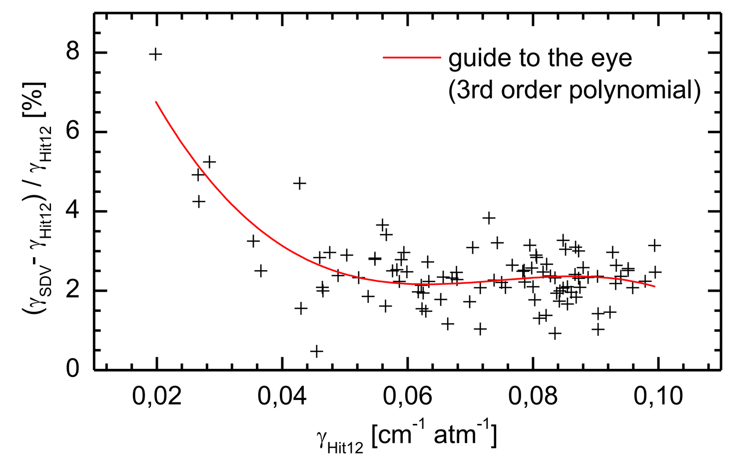

Fig. 4: Relative differences of broadening parameters from SDV-analysis and HITRAN 2012

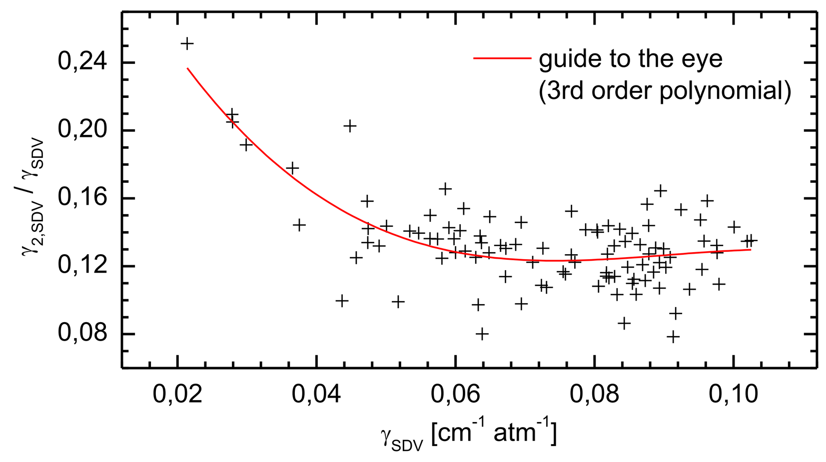

Fig. 5: Comparison of narrowing and bradening parameters

Conclusion

- a new multispectrum tool has been developed and testet against two independent tools
- innovations like an automatic mode and quality control mechanisms have been implemented
- widely used line profile models are implemented
- sophisticated ils-modelling included
- as a first test water absorption spectra were re-analyzed
- Voigt lineshape not sufficient
- opaque and non-opaque lines have to be fitted simultaneously to prevent too narrow broadening parameters
- the narrowing parameter shows a clear trend with the broadening parameter
- complete analysis (T-dependencies, shifts, etc.) to be done

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