



## Abstract

In recent updates of the HITRAN water vapour H<sub>2</sub>O spectroscopic compilation covering the blue spectral region (here: 394–480 nm) significant changes for the absorption bands at 416 and 426 nm were reported. In order to investigate the consistency of the different cross-sections calculated from these compilations, H<sub>2</sub>O vapour column density ratios for different spectral intervals were retrieved from Long-path and Multi-Axis – Differential Optical Absorption Spectroscopy (DOAS) measurements. We observed a significant improvement of the DOAS evaluation when using the updated HITRAN water vapour absorption cross-sections for the calculation of the reference spectra. In particular the magnitudes of the residual spectra as well as the fit errors were reduced.

However we also found that the best match between measurement and model is reached when the absorption cross-section of groups of lines are scaled by factors ranging from 0.5 and 1.9, suggesting that the HITRAN water vapour absorption compilation still needs significant corrections. For this spectral region we present correction factors for HITRAN 2009, HITRAN 2012, HITEMP and BT2 derived from field measurements. Additionally, upper limits for water vapour absorption in the UV-A range from 330–390 nm are given.

## 1 Introduction

Precise knowledge of the atmospheric water vapour absorption is not only crucial to calculate Earth's radiation budget since water vapour is the largest contributor to the natural greenhouse effect (Myhre et al., 2013), but water vapour absorptions also needs to be known at high precision when retrieving other atmospheric absorbers from spectroscopic measurements in the UV/VIS wavelength range. If their absorptions overlap, this can lead to errors in measurements of several trace-gases. Due to technical limitations and since the absorption cross-sections are small in the region below 500 nm (above 20 000 cm<sup>-1</sup>), in this spectral interval the body of available experimen-

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and/or increasing the measurement error. At the spectral region of maximum absorption of glyoxal the difference between the water vapour absorption cross-sections found in HITRAN 2000 and HITEMP for a typical  $S_{\text{H}_2\text{O}} = 4 \times 10^{23} \text{ molec cm}^{-2}$  is about  $4 \times 10^{-4}$  and amounts to one half of the reported glyoxal absorption.

Water vapour absorption can also have an impact on the spectral retrieval of the oxygen dimer  $\text{O}_4$  (also called  $\text{O}_2\text{--O}_2$ ) around 477 nm. Its column densities can be used to constrain radiative transfer simulations in remote sensing application and to obtain height profile information of aerosol extinction and trace gas concentrations (e.g. Frieß et al., 2006).

Water vapour column densities have been measured in the blue wavelength range from satellite (Wagner et al., 2013b; Wang et al., 2014) as well as from ground-based instruments (Wagner et al., 2013a). Here the  $7\nu$  absorption at 442 nm from HITRAN 2004 has been used for retrieving the atmospheric water vapour column density. These measurements require precise water vapour absorption cross-sections as well to minimize retrieval errors.

If significant absorptions of water vapour are present below 370 nm, these could have an effect on the spectral evaluation of measurements of e.g. BrO, Formaldehyde, HONO,  $\text{SO}_2$  and  $\text{O}_4$ . Based on currently available cross-section data no atmospheric water vapour absorptions in this spectral range have been reported for DOAS measurements so far.

## 2 Measurement campaigns

The data which was analysed here were collected during two field campaigns, where different instruments were used.

1. During the SOPRAN cruise M91 with the research vessel “Meteor” Multi-Axis (MAX-)DOAS data was collected in the Peruvian upwelling region in December 2012 (Bange, 2013).



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absorption cross-section as it would be determined by the instrument. In an analogous fashion to the optical density, also cross-sections can be subdivided into a broadband and narrow-band (differential) contribution:  $\sigma_j = \sigma_{B,j} + \sigma_{d,j}$ . The instrument function  $H$  is usually measured by observing individual atomic emission lines of mercury, which have a width which is two orders of magnitude smaller than the resolution of the instrument (Sansonetti et al., 1996). Corrections to this simple convolution procedure are discussed in Sect. 4.3.

### 3.1 MAX-DOAS measurements

The method of Multi-Axis DOAS (MAX-DOAS) measurements was first described by Hönninger and Platt (2002) and uses scattered sunlight collected by a telescope pointing towards the sky at different elevation angles. Each elevation has a different sensitivity for absorptions in different heights of the atmosphere. Low elevation angles have a higher sensitivity to absorbers close to the surface, because the additional lightpath compared to a zenith spectrum is mostly located within the lowermost layers of the atmosphere (Hönninger et al., 2004).

The SCD is defined as the integral over the concentration  $\rho$  along the lightpath  $L$  and is hence given in units of molecules  $\text{cm}^{-2}$ .

$$S = \int_L \rho(s) ds \quad (2)$$

From the MAX-DOAS measurements differential slant column densities (dSCDs)  $\Delta S$  can be calculated for each fitted trace gas: a Fraunhofer reference spectrum  $I_0(\lambda)$  is chosen from one of the measurement spectra and the dSCD  $\Delta S(\alpha) = S(\alpha) - S_{\text{ref}}$  is obtained from the DOAS fit for each elevation angle  $\alpha$  relative to the Fraunhofer reference. Typically, a zenith spectrum is taken as reference and thus  $S_{\text{ref}} = S(90^\circ)$ . In the measurements reported here, the DOAS fit includes the convoluted cross-sections listed in

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Table 3. In addition Ring Spectra are fitted (see Table 3), which serve to compensate for the effect of rotational Raman scattering. The influence of vibrational Raman scattering of  $N_2$  and  $O_2$  as described in Lampel et al. (2015) on the obtained results listed in Table 5 was not found to be significant. By choosing references recorded shortly before or after the measurement spectrum the influence of the instrumental instabilities on the result was minimized as well as the influence of stratospheric absorbers largely cancel out (see e.g. Hönninger and Platt, 2002).

A description of the instrument operated during the SOPRAN cruise M91 can be found in Großmann et al. (2013). The optical resolution of the instrument during this campaign was 0.45 nm and it covered a spectral range from 324 to 467 nm.

### 3.2 LP-DOAS Measurements

Longpath(LP)-DOAS instruments are based on an artificial light source, typically a xenon lamp or a light-emitting diode (LED), retro reflectors, a telescope and a spectrometer. The light is sent with a telescope across the measurement distance to a retro reflector, which reflects the light back onto the same telescope. It collects the received light and transfers it to a spectrograph. A sequence of background measurements, light-source spectrum measurements without absorption and actual measurement spectra is used to ensure independence of the measured spectra from external sunlight and instrumental instabilities. The LP-DOAS setup has the advantage that the actual light path is well-defined and thus concentrations of molecules can be directly derived, also measurements at night are possible.

The optical density  $\tau(\lambda)$  is calculated from a background corrected light source spectrum and a background corrected atmospheric spectrum and filtered by a binomial high-pass with 1000 iterations. The convoluted and high-pass filtered literature cross-sections listed in Table 3 are then fitted to the corrected OD.

A description of the LP-DOAS instrument can be found in Pöhler et al. (2010). The lightpath used for the measurements reported was 12.64 km long, similar to the one in Read et al. (2008). The spectral resolution was 0.5 nm.



To exclude the possibility of interferences with daylight, only spectra at a solar zenith angle of more than 90° (night-time) are reported here.

### 3.3 Spectral retrieval

The H<sub>2</sub>O cross-sections were calculated using modeled line widths according to Kuntz (1997) from the respective compilation or line list using an extraction program by Christian Frankenberg (Frankenberg, 2005) with a spectral resolution of 1 pm for an ambient temperature of 298 K and 1013 hPa.<sup>1</sup> For the BT2 dataset, a cross-section file from the exomol project (Tennyson and Yurchenko, 2012)<sup>2</sup> was downloaded, here only Doppler line broadening effects were considered (Hill et al., 2013). Variations of temperature and pressure within the range of atmospheric measurements were found not to have a significant effect on our measurements in the blue wavelength region and the bulk of the absorption by water vapour molecules takes place within the boundary layer.

The choice of cross-section to compensate for absorption of the oxygen dimer O<sub>4</sub> did not significantly affect the overall result. We tested cross-sections from Hermans et al. (1999), Thalman and Volkamer (2013) and Greenblatt et al. (1990).

The spectral window of this study for MAX-DOAS measurements was limited at the lower end to 398 nm to avoid a strong influence of the Ring effect caused by rotational Raman scattering (Shefov, 1959; Grainger and Ring, 1962). The upper bound (at 461.5 nm) was chosen due to instrumental limitations.

The water vapour absorption cross-section was divided into six spectral regions W0–W5 before convolution, as listed in Table 1. All other absorbers (Table 3) were fitted normally. An example fit can be seen in Fig. 2.

<sup>1</sup>The HITRAN 2009, HITEMP and HITRAN 2012 data used here was downloaded from the HITRAN website (<http://www.cfa.harvard.edu/hitran/>) with the file name “01 hit09.par”, HITEMP “01 hitemp.par” and HITRAN 2012 “01 hit12.par”

<sup>2</sup><http://www.exomol.com/xsecs/1H2-16O>

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To avoid problems in situations with low light intensity, we used only data where the signal was sufficiently high to provide a RMS noise of the residual spectrum below  $4 \times 10^{-4}$ .

### 3.3.1 Radiative Transfer effects (MAX-DOAS)

The lightpath of the LP-DOAS measurement is well defined and constant. Thus measurements of the different W0–W5 column densities can be directly used. However, the effective lightpath of MAX-DOAS measurements is not known and depends on several factors: wavelength, aerosol and trace gas profiles, viewing direction, position of the Sun etc.

The radiative transfer for the measurements was simulated using McArtim (Deutschmann et al., 2011). Water vapour dSCDs in the atmosphere were simulated at different wavelengths to estimate the effect of radiative transfer on the relative observed absorption band strengths for MAX-DOAS measurements. Since the data was taken from a measurement period of a whole month, a representative water vapour profile (surface mixing ratio of 2.3%, linearly decreasing to 0% at a height of 6 km, similarly as in Bleisch and Kampfer, 2012) and an exponentially decreasing aerosol profile with an AOT of 0.22 at 360 nm were used for the simulations. The results were averaged over a range of solar zenith angles (SZA) of 10–80° representing the used MAX-DOAS data and over all encountered relative solar azimuth angles.

The magnitude of the resulting water vapour dSCD obtained from the model agreed with the MAX-DOAS observations. McArtim allows calculating the wavelength dependence of the simulated water vapour dSCDs. The scatter in the correlations for the water absorption bands (Fig. 3) will then already include the scatter caused by different measuring geometries, which means that the observed differences in relative strengths of the absorptions especially for W1 and W2 are significant. However, the correction obtained from radiative transfer calculations (shown in Table 4) needs to be applied to MAX-DOAS observations to match the LP-DOAS results. The correction of the wavelength dependence reduces the discrepancy of MAX-DOAS and LP-DOAS

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measurements e.g. for W0 when using HITEMP and BT2. The wavelength corrected results are listed in Table 5.

It is a well known effect (see e.g. Platt et al., 1997) that strong absorbers influence the light path length in the atmosphere and thus the airmass factor. The change of the air mass factor within a water vapour absorption band due to the highly resolved water vapour optical density in the region  $< 480$  nm was found to be insignificant. Deviations of less than 2 % on the values listed in Table 5 were observed. The effect may, nevertheless, play a role for stronger absorbers.

However, if the focus is on weak absorbers being overlaid by strong water vapour absorptions, a correction for the change of airmass factors by strong absorption is necessary to avoid water vapour OD correlated structures in the residual spectra and effects on the retrieval of other absorbers.

## 4 Results

The water vapour dSCDs derived in different spectral regions of the same measured spectra were compared to each other. In principle the same water vapour dSCD values are expected, but significant differences were found.

Values of the retrieved water vapour SCDs in different spectral intervals were compared to each other. Relative to the SCD of W3  $S_{W3}$ , an error weighted linear regression was done to obtain  $a_x$  in  $f(S_x) = a_x \times S_{W3}$ .  $a_x$  is the relative absorption strength of the interval  $x$  relative to W3. The results are shown in Table 5. Typical DOAS fit errors for each cross-section in W0–W5 for individual measurements are summarized in Table 6. In order to illustrate the differences one of the data comparison plots with the relative absorption of W1 and W3 for HITEMP is shown in Fig. 3.

The weights for the linear regression were iteratively calculated according to Neri et al. (1989). A comparison with other methods for error-weighted linear regressions can be found in Cantrell (2008).

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The water vapour absorption of the 7ν polyad (W3) at  $\approx 444$  nm was used as a reference for the other polyads, because it is the strongest absorption in this spectral region (see Table 1).

The mathematical error from the regression is small compared to possible systematic errors, which might arise from the DOAS fit itself: Its relative size is estimated by using twice the fit error given in Table 6 following the argumentation of Stutz and Platt (1996). These errors are then used to calculate the weighted mean deduced from MAX-DOAS and LP-DOAS observations for each of the absorption bands given in Table 5, if their respective relative fit error is smaller than 25 %.

In the literature significant absorption structures due to glyoxal in the eastern Pacific region were reported by Sinreich et al. (2010). However during our cruise, no absorption due to glyoxal was found to exceed our detection limit of  $2\sigma = 5 \times 10^{14}$  molec cm<sup>-2</sup> glyoxal at low elevation angles of 1–3°. Nevertheless, in order to exclude an impact of glyoxal absorption on the evaluation of water vapour absorptions, the analysis procedure was repeated also including glyoxal. The result is comparable to the result without glyoxal absorption, only the amplitude of the weak water absorption around 426 nm was slightly reduced by the additional degree of freedom introduced to the spectral retrieval. For the LP-DOAS measurements an upper limit of 30 ppt glyoxal (Mahajan et al., 2014) was determined and its cross-section was also not included in the final analysis.

#### 4.1 Comparison of LP-DOAS data with data from meteorological stations

In order determine whether the assumed water vapour absorption cross-sections actually give the correct water vapour concentration, the main absorption W3 found in LP-DOAS data was compared to water vapour mixing ratios derived from meteorological parameters measured on CVAO.

The meteorological station provides temperature, pressure and humidity data (Carpenter et al., 2010). This information was used to calculate the water vapour mixing ratio using the Magnus formula and to compare the result with LP-DOAS data. Tak-

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in middle-latitudes on the radiation flux at the ground level is be comparable to ozone between 330–350 nm cannot be supported.

At a spectral resolution of 0.5 nm, the OD attributed to water vapour between 350 and 370 nm is according to HITEMP  $5.5 \times 10^{-4}$  (BT2:  $9.5 \times 10^{-4}$ ) for a typical  $\text{H}_2\text{O}$ -dSCD of  $4 \times 10^{23} \text{ molec cm}^{-2}$ . Under similar measurement conditions (dSCD<sub>O<sub>4</sub></sub> =  $4 \times 10^{43} \text{ molec}^2 \text{ cm}^{-5}$ ) the OD due to O<sub>4</sub> is  $2 \times 10^{-2}$ , i.e. by a factor of 20–40 larger. The OD according to HITEMP/BT2 from 330–350 nm is comparable to the optical density of 1 ppt BrO along a lightpath of 10 km and could thus be crucial for DOAS measurements of BrO in the remote marine boundary layer (compare e.g. Volkamer et al., 2015). Furthermore these absorptions could contribute to the observed problems during the retrieval of tropospheric HCHO as described by Pinardi et al. (2013).

To estimate the overall influence of water vapour on the retrieval of O<sub>4</sub>, BrO, HCHO and HONO further dedicated laboratory measurements of water vapour in this spectral region are needed.

### 4.3 Error sources

The residual spectra obtained from the DOAS evaluation procedure of the measurements were usually not dominated by photon shot noise, but showed recurrent residual structures as show in Fig. 2. Since the influence of other absorbers than H<sub>2</sub>O is probably negligible, these residual structures from instrumental instabilities, saturation and *I*<sub>0</sub>-effect (for MAX-DOAS) should be the dominating sources of interference. Their influence on the absolute magnitude of the absorption bands in discussed in the following subsections, the influence of radiative transfer effects is discussed in Sect. 3.3.1.

#### 4.3.1 Other absorbers

For MAX-DOAS measurements the OD of other absorbers than water vapour was kept low by using a Fraunhofer reference *I*<sub>0</sub>(λ) recorded within the same sequence of elevation angles. Using this approach the solar zenith angle only changed slightly between

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the measurements and most of the stratospheric absorption by ozone and NO<sub>2</sub> cancel out and do not affect the evaluation. Furthermore, the measurement campaigns selected took place in remote areas with background ozone concentrations around 30–40 ppb ozone and NO<sub>2</sub> typically well below 1 ppb. The OD associated with NO<sub>2</sub> was  $(2 \pm 9) \times 10^{-4}$ , ozone below  $1.5 \times 10^{-4}$  and iodine monoxide  $(2.2 \pm 2.2) \times 10^{-4}$ . In comparison, the typical OD of water vapour for the wavelength intervals W0–W5 ranged up to  $1.65 \times 10^{-2}$ , see Fig. 1. Since the measurements were performed on the ocean, the influence of possible vibrational Raman scattering in liquid water (Vountas et al., 2003; Peters et al., 2014) on the MAX-DOAS results was tested for and was not found to be significant. Changes in water vapour dSCDs were about 1 % when including liquid water Raman scattering in the fit.

For the LP-DOAS measurements the same upper limits for the absorption of NO<sub>2</sub> were found. The detection limits for O<sub>3</sub>, glyoxal and IO were 191 ppb, 30 and 0.36 ppt, which were not exceeded during our nightly measurements. Therefore these trace-gases were not included in the final analysis.

### 4.3.2 Saturation effects

The saturation effect originates from the fact that the convolution of literature cross-sections with the instrument function does not commute with the exponential function in the Lambert-Beer Law (Wenig et al., 2005). This effect can be corrected for by replacing the absorption cross-section  $\sigma(\lambda)$  by  $\sigma_{\text{Sat}}^*(\lambda)$  given by 3 for a given column density  $S$ .

$$\sigma_{\text{Sat}}^*(\lambda) = \frac{1}{S} \ln(\exp(-S \times \sigma(\lambda)) \otimes H) \quad (3)$$

The saturation effect for dSCD of  $6 \times 10^{23}$  molec cm<sup>-2</sup> would reduce the apparent OD for the strongest absorption discussed here at 442 nm by about 2 %. A significant influence of the saturation effect on the results presented here can therefore be ruled out. This consideration is supported by the observed linear relationship between the

retrieved water vapour SCDs retrieved for weaker (W1) and stronger (W3) absorption bands shown in Fig. 3.

### 4.3.3 The solar $I_0$ effect

The solar  $I_0$  effect (Platt et al., 1997) describes the effective weighting of the absorption cross-section, if the spectrum of the light source is highly structured itself, such as that of the Sun.

This needs to be corrected for MAX-DOAS measurements only, since the light source of LP-DOAS systems have usually broader structures than the absorbers itself. The zeroth order  $I_0$  correction does therefore not rely on the OD of the absorber, but can be corrected together with the saturation effect as described by (Aliwell et al., 2002; Vogel et al., 2013) for a fixed dSCD. For our measurements corrections were made by calculating a modified  $\sigma_{I_0}^*(\lambda)$  using the Kitt Peak solar flux atlas (Chance and Kurucz, 2010):

$$\sigma_{I_0}^*(\lambda) = \frac{1}{S} \ln \left( \frac{(I_0 \exp(-S \times \sigma(\lambda))) \otimes H}{I_0 \otimes H} \right) \quad (4)$$

The  $I_0$  effect can result in changes of apparent cross-section in MAX-DOAS measurements of up to 10%. Because these changes can reduce as well as enhance the apparent OD, the data were evaluated with and without solar  $I_0$  correction to estimate its effect on the relative absorption strength of different water vapour absorption bands. The data shown in Table 5 is  $I_0$ -corrected and the  $I_0$ -effect accounts here for changes of at most 2%. Including the  $I_0$  effect resulted in a significant reduction of the residual and therefore the fit errors. For the MAX-DOAS evaluation, a SCD for the  $I_0$  correction of  $1 \times 10^{15}$  molec cm<sup>-2</sup> for NO<sub>2</sub>,  $1 \times 10^{18}$  molec cm<sup>-2</sup> for O<sub>3</sub> and  $3 \times 10^{23}$  molec cm<sup>-2</sup> for H<sub>2</sub>O was applied.

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## 5 Discussion

From the fit errors listed in Table 6 especially for the weak absorption features of water vapour, it can be seen that the development of water vapour absorption compilations from HITRAN 2009 to HITEMP/HITRAN 2012 results in a better fit of the measurement data. The fit errors for the intervals (W0 to W5) of the water vapour absorption cross-section are reduced. Changing from HITRAN 2009 to HITEMP or BT2, reduces nearly all fit errors somewhat, the reduction is dramatic (20–75 %) for the weaker bands (W1, W2 and W4). The smallest relative fit errors are observed for most absorption bands for HITEMP.

The magnitude of the main absorption W3 at 442 nm agrees with data from a meteorological station as shown in Table 7.

Nevertheless, the relative absorptions of different groups of absorption lines are inconsistent and do not fit our measurements, they are listed relative to W3 in Table 5. In the BT2 line list and in HITEMP the absorptions from 410–434 nm overestimate the observed absorptions approximately by a factor of two.

Tennyson (2014) noted that the absorption line intensities for transitions involving highly excited vibrational states can depend strongly on the representation of the dipole moment surfaces in the *ab initio* models, particularly for transitions involving bending modes. This could be in agreement with our observations, since the largest discrepancy between modelled and measured absorptions was observed for the  $7\nu + \delta$ -polyad.

- For W0 (394–410 nm) the results from MAX-DOAS and LP-DOAS agree, that the magnitude of the absorption at W0 is found to be about  $5 \pm 6\%$  smaller in measurements than what is reported in HITEMP.
- For W1 (410–423.5 nm) the agreement of MAX-DOAS and LP-DOAS measurements is not as good, since the overall absorption is about half as large as W0. The absorption of this group of absorption lines is by  $60 \pm 10\%$  too high in HITEMP. For W1 in BT2 a better agreement is found, together with smaller fit errors. Even

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when considering the overestimation of the absorption W1 in HITEMP, the fit error was reduced from HITRAN 2009 to HITEMP. This shows that the shape of the absorption is reproduced more accurately in HITEMP.

- The absorption W2 (423.5–434 nm) was not regularly identified in LP-DOAS measurements, but is also close to the magnitude of the residuals for MAX-DOAS data. Therefore the result for W2 should be viewed with caution. The shape of the water cross-section is reproduced correctly within  $1 \times 10^{-27} \text{ cm}^2$  at 0.45 nm resolution. HITEMP overestimates this absorption compared to observations by  $30 \pm 25\%$ , BT2 even by  $82 \pm 33\%$ , but its shape is reproduced better in HITEMP than in HITRAN 2009, as seen from the smaller fit errors.
- The absorption W3 (434–451.5 nm) is relatively strong and therefore requires application of saturation and  $I_0$  corrections. Furthermore neglecting the changes in radiative transfer for MAX-DOAS measurements for individual absorption lines leads to significant structures in the residual spectra (up to  $5 \times 10^{-4}$ ), while the overall water vapour dSCD is only slightly changed by  $< 3\%$  for a dSCD  $S < 5 \times 10^{23} \text{ molec cm}^{-2}$ . The simple approximation of having a constant light path for the MAX-DOAS observation within this wavelength interval does not hold here for larger OD, therefore the fit errors also do not decrease as seen for the BT2 list for LP-DOAS measurements in Table 6.
- The absorption W4 (451.5–461.5 nm) is small, however absorptions in this wavelength range could interfere with measurements of glyoxal. In fact the optical density due to  $\text{H}_2\text{O}$  is comparable to previous observations of glyoxal on the open ocean which also absorbs in this spectral region. A water vapour dSCD correlated structure in the residuals is found at the absorption at 453.0 nm (HITEMP) which can be also seen in Fig. 2. This absorption seems to be better reproduced in BT2, the absorption is rather at 452.5 nm. The same error estimate for the convoluted cross-section as for W2 applies for W4.

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calculations and dedicated validation measurements of the water vapour absorption cross-section below 395 nm.

Another aspect which needs to be considered is the wavelength dependence of the air mass factor in MAX-DOAS measurements covering several significant absorption bands, which implies that low residuals can only be obtained when accounting for these effects. For example, for a water vapour dSCD of  $5 \times 10^{23}$  molec cm<sup>-2</sup> these effects will lead to residual structures of  $\approx 2.5 \times 10^{-4}$  when including W1–W3 or already  $\approx 1 \times 10^{-4}$  within W3 itself (compare also Table 4).

## 6 Conclusions

The revised line compilations HITEMP and BT2 lead to considerable improvements in DOAS measurements of water vapour and other trace gases. In particular lowering the threshold above which absorption lines are included in the HITRAN database as well as theoretical and experimental progress led to improved water vapour absorption cross-sections in the blue wavelength range.

We showed that the water vapour absorption fit errors of the DOAS retrieval can be reduced by up to 20–75 % by using current water vapour absorption cross-sections (e.g. HITEMP: Rothman et al., 2010) compared to older versions of HITRAN. This shows, that the shape of the water vapour absorption is better reproduced by the HITEMP, reducing the amplitude of residual spectra. When the error in the relative magnitude of several absorption bands are corrected (e.g. by scaling the water vapour absorption cross-sections in the different spectral intervals), the amplitude of residual spectra for larger fit intervals can be reduced significantly (compare e.g. Fig. 2), which then allows more reliable retrieval of weak absorbers.

Each of the water vapour absorption cross-sections evaluated here (HITRAN 2009, HITRAN 2012, HITEMP and BT2) was found to have certain limitations for the use in DOAS retrievals in the blue wavelength range. Even after water absorption cross-sections have improved they are still not sufficiently accurate for modern high precision

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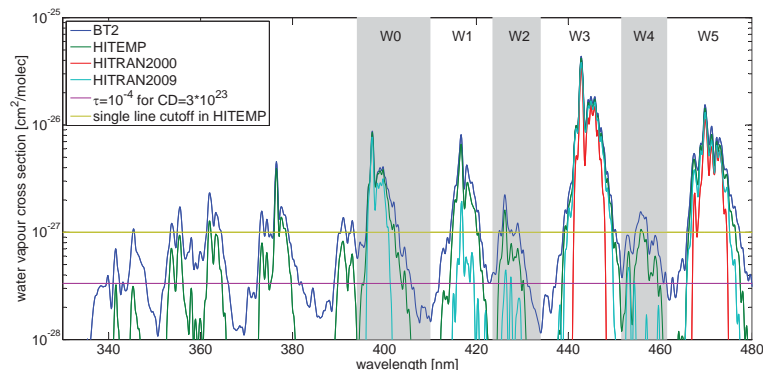






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**Figure 1.** Overview of a subset of published water vapour absorption cross-sections convoluted to a spectral resolution of 0.5 nm. Also indicated is a typical line detection limit for a differential OD of  $10^{-4}$  at a water vapour column density of  $3 \times 10^{23}$  molec  $\text{cm}^{-2}$  (purple line) at a spectral resolution of 0.5 nm. Note that the single absorption line cutoff in HITEMP (yellow) is set at about three times this value. The wavelength intervals W0–W5 are described in the text, integrated absorptions in these intervals are given in Table 1.

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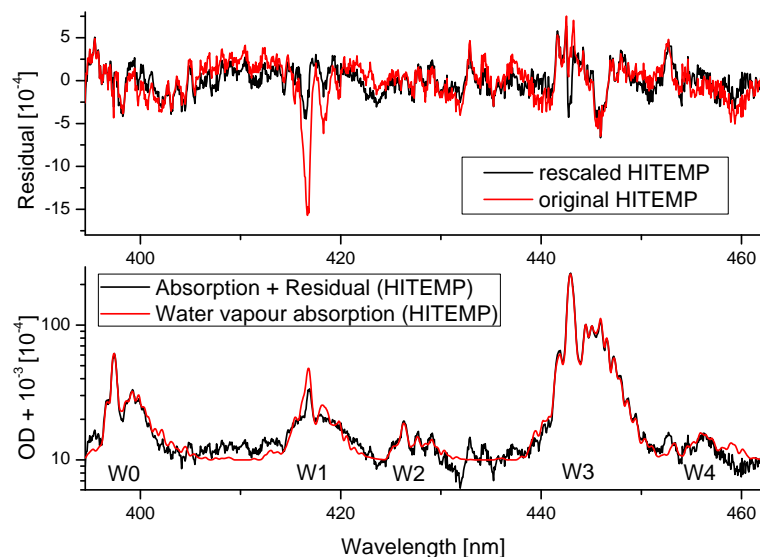
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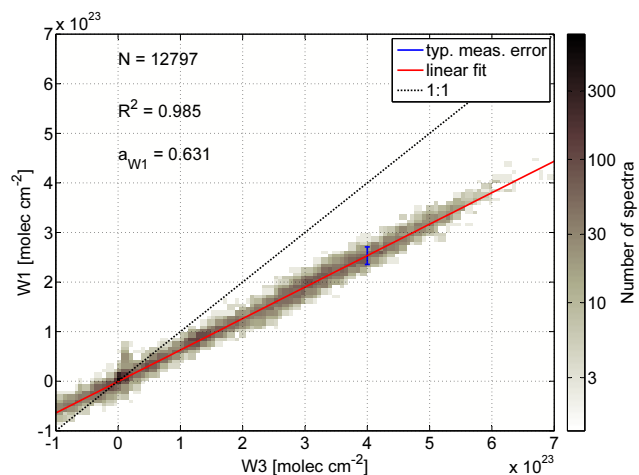


**Figure 2.** Fit residuals (top panel) and water vapour OD (bottom) for a MAX-DOAS observation using the HITEMP cross-section. A residual from an individual fit using the original HITEMP cross-section and a fit using separate column densities for each of the absorption structures in the windows W0–W4 from HITEMP is shown in the top panel. From all fits with separate column densities for the absorption bands, correlation plots with respect to W3 were performed as shown exemplary in Fig. 3. The results are listed in Table 5. The overall water vapour column density calculated from the data shown above is  $dSCD = 5.31 \times 10^{23} \text{ molec cm}^{-2}$ .

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**Figure 3.** Correlation of dSCD in  $\text{molec cm}^{-2}$  calculated for W1 ( $7\nu + \delta$  polyad) and W3 ( $7\nu$  polyad) from MAX-DOAS (M91) data using the HITEMP cross-section. The blue error bar (at  $\text{dSCD}_{W3} = 4 \times 10^{23} \text{ molec cm}^{-2}$ ) indicates a typical measurement error. The convoluted cross-section derived from the HITEMP compilation shows a maximum absorption cross-section of an individual absorption line in  $5.9 \times 10^{26} \text{ cm}^{-2}$  and  $4.0 \times 10^{25} \text{ cm}^{-2}$  for W1 and W3, respectively. The linear relationship of W1 and W3 dominates.

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