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# Water vapour self-continuum in near-visible IR absorption bands: Measurements and semiempirical model of water dimer absorption

Anna A. Simonova<sup>a</sup>, Igor V. Ptashnik<sup>a</sup>, Jonathan Elsey<sup>b</sup>, Robert A. McPheat<sup>c</sup>, Keith P. Shine<sup>b</sup>,  
Kevin M. Smith<sup>c</sup>

<sup>a</sup> Atmospheric Spectroscopy Division, V.E. Zuev Institute of Atmospheric Optics, Siberian Branch of  
the Russian Academy of Sciences, Tomsk, 1 Academician Zuev square, 634055, Russia

<sup>b</sup> Department of Meteorology, University of Reading, Reading, RG66BB, UK

<sup>c</sup> Rutherford Appleton Laboratory, Didcot, Oxfordshire, OX11 0QX, UK

**Corresponding author:** Igor V. Ptashnik (piv@iao.ru)

## Abstract

The nature of the water vapour continuum has been of great scientific interest for more than 60 years. Here, water vapour self-continuum absorption spectra are retrieved at temperatures of 398 K and 431 K and at vapour pressures from 1000 to 4155 mbar in the 8800 and 10600  $\text{cm}^{-1}$  absorption bands using high-resolution FTS measurements. For the observed conditions, the MT\_CKD-3.2 model underestimates the observed continuum on average by 1.5–2 times. We use the hypothesis that water dimers contribute to the continuum absorption to simulate the experimentally-retrieved self-continuum absorption spectra, and to explain their characteristic temperature dependence and spectral behaviour. The values of the effective equilibrium constant are derived for the observed temperatures. We find that the dimer-based model fits well to the measured self-continuum from this and previous studies, but requires a higher effective equilibrium constant compared to the modern estimates within the temperature range (268–431 K) and spectral region studied. It is shown that water dimers are likely responsible for up to 50% of the observed continuum within these bands. Possible causes of the incomplete explanation of the continuum are discussed. Extrapolating these measurements to atmospheric temperatures using the dimer-based model, we find that the newly-derived self-continuum reduces calculated surface irradiances by  $0.016 \text{ W m}^{-2}$  more than the MT\_CKD-3.2 self-continuum in the 8800  $\text{cm}^{-1}$  band for overhead-Sun mid-latitude summer conditions, corresponding to a 12.5% enhancement of the self-continuum radiative effect. The change integrated across the 10600  $\text{cm}^{-1}$  band is about 1%, but with significant differences spectrally.

**Keywords:** continuum absorption, water vapor, absorption band, water dimer, line wings, semiempirical model

## 1. Introduction

As one of the main gaseous absorbers of solar radiation, water vapour plays an important role in radiative processes occurring in the Earth's atmosphere. Positive feedback between water vapour concentration and temperature of the Earth's surface significantly affects the weather and climate of the Earth. Part of the water vapour absorption, the so-called water vapour *continuum*, has been a special subject of study since it was first measured in the mid-infrared atmospheric window (8–14  $\mu\text{m}$ ) in 1918 [1]. Whilst we have a good understanding of the mechanisms responsible for water vapour absorption lines, the physics underlying the water vapour continuum is not yet as clear. The

45 intensity of the latter is characterized by a slowly varying spectral dependence that makes a small  
46 contribution to the total absorption of solar radiation by water vapour in the Earth's atmosphere (up  
47 to 3% in the global average) [2]. The spectrum of water vapour continuum absorption can be divided  
48 into so-called *self* and *foreign* components. The former is a result of interactions between water  
49 molecules, while the latter is caused by the interaction of water molecules with other gases, most  
50 notably nitrogen and oxygen in the Earth's atmosphere. This paper focuses on improved  
51 understanding of the water vapour *self-continuum*. Despite the much stronger intensity of water  
52 absorption lines compared to the underlying continuum, there are particular features of the latter that  
53 allow it to be spectrally discerned. A strong negative exponential temperature dependence and  
54 quadratic pressure dependence of the water vapour self-continuum absorption are among such  
55 features.

56 From an atmospheric radiative transfer perspective, the most relevant contributions of the self-  
57 continuum absorption to the water vapour absorption spectrum are located predominantly in the  
58 atmospheric window regions, where the spectral lines are relatively weak. In these atmospheric  
59 windows, there is significant interest in the continuum absorption for several applications. For  
60 example, the continuum strongly impacts the radiative balance of the atmosphere, affects the  
61 propagation of laser radiation through the atmosphere and can interfere with the retrieval of  
62 atmospheric gases, aerosols and clouds by optical methods [3].

63 Depending on the spectral region, the continuum within water absorption bands is between two  
64 and three orders of magnitude weaker than the overlying spectral lines. Nevertheless, even within  
65 these bands, the continuum absorption can be comparable with the local line absorption or even  
66 dominate it in many microwindows between spectral lines, which makes it distinguishable in  
67 measurements with sufficient spectral resolution. The first laboratory identification of water dimer  
68 spectral features in the in-band near-IR self-continuum was presented in [4,5] using the calculated  
69 dimer spectrum from [6]. Since then, distinct spectral peaks have been discovered in the  
70 measurements of the continuum absorption spectrum within other near-IR water vapour bands [4,7–  
71 9], which have allowed conclusions to be drawn about the nature of this component of the  
72 continuum. Therefore, the investigation of the continuum absorption within the bands has  
73 significance for our fundamental understanding of the underlying physics.

74 There are two physical mechanisms that are most often cited as being responsible for the  
75 continuum absorption in the IR and mm-wave spectral regions, both of which likely contribute to a  
76 certain extent in different spectral regions: (a) the cumulative absorption of the far wings of strong  
77 water monomer spectral lines [10–15], and (b) bound and quasibound water dimers<sup>1</sup> (b- and q-  
78 dimers, respectively) [7–9,16–21]. The first of these mechanisms, far-wing absorption, results from  
79 energetic collisions between water molecules, which perturb rovibrational energy levels. There are  
80 two main approaches to the far-wing hypothesis: asymptotic [12,15] and quasistatic [13,14]. Both  
81 approaches operate in terms of intermolecular potential and use a set of parameters derived by fitting  
82 models to experimental data. A satisfactory agreement of the far-wing model with the experimental  
83 continuum has been shown [22,23] in some atmospheric windows in the far and middle IR spectral  
84 regions. However, the existing far-wing models cannot provide sufficient accuracy in predicting the  
85 intensity or temperature dependence of the continuum absorption over a wide spectral region without

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<sup>1</sup>Bound (or stable) dimers require a third-body collision for their formation; quasibound (or metastable) dimers relate to multiple-approach pair collisions resulting in the temporary stabilization of a pair which has total internal energy in excess of the dissociation threshold.

86 a number of experimentally fitted *ad hoc* parameters that cannot be verified from independent  
87 sources.

88 The second mechanism, which is based on water dimer absorption, describes the main  
89 temperature and spectral dependences of the continuum absorption well (see, for instance, [24]) after  
90 adjusting just two physically-based parameters (the dimer equilibrium constants) to fit the  
91 experimental data. Bound and quasibound dimers exhibit different properties (e.g. dissociation  
92 energy and lifetime), and consequently they are expected to have different spectral features.  
93 Moreover, a statistical approach shows that absorption from either of these states can be the dominant  
94 contributor to continuum absorption depending on the thermodynamic conditions [19]; b-dimers  
95 dominate at lower temperatures and q-dimers are more prevalent at higher temperatures. The  
96 ‘transition’ temperature depends on the intermolecular potential and is different for different  
97 molecular pairs. For example, for water dimers the transition temperature is expected to be close to  
98 room temperature [19].

99 The absorption by water dimers is a dominant mechanism of so-called bimolecular absorption  
100 [by water vapour](#) (see, for instance, [19]) at near atmospheric conditions. With increasing temperature,  
101 the contribution of the third form of bimolecular absorption—free H<sub>2</sub>O pairs<sup>2</sup>—begins to increase: from  
102 negligible at room temperature to dominant at very high temperatures. Since this mechanism  
103 becomes noticeable only at temperatures much greater than the temperature range of 398–431 K  
104 investigated here, it is not considered further. Earlier considerations of the possible absorption of  
105 solar radiation by water dimers in the visible and near-IR regions were presented in [25,26] based on  
106 the first calculated water dimer vibrational spectra. To this day, quantum-chemical calculations of  
107 water dimer spectra are still challenging, especially at higher wavenumbers (in near-infrared and  
108 visible regions). Nevertheless, quantum-chemical and quantum-mechanical calculations [27–29] that  
109 are now available together with the experimental data in the microwave [30,31], mid-infrared [3,32]  
110 and near-infrared [4–8] spectral regions, demonstrate the explicit involvement of water dimers in the  
111 water vapour continuum spectrum.

112 For practical applications, the MT\_CKD continuum model is commonly used [33]. It is a  
113 semiempirical model, which modifies the Lorentzian profile in the line wings using a special  $\chi$ -  
114 function, assuming a so-called “weak interaction” between molecules, which is more important for  
115 the in-band continuum, and makes a number of other empirical adjustments to fit the model to  
116 experimental data. The model has therefore changed significantly since it was described in [33] as  
117 new observations have become available; however many of these changes are not yet described in the  
118 literature. In the spectral regions analysed here the MT\_CKD continuum has not been subjected to  
119 any experimental constraints and needs to be evaluated using observations. Although MT\_CKD is  
120 primarily intended for application at atmospheric temperatures, the form of its temperature  
121 dependence is based on extrapolation of laboratory measurements made between temperatures of 296  
122 and 338 K [33] in bands at lower wavenumbers and hence it may not be appropriate in other bands or  
123 at other temperatures.

124 This paper focuses on the investigation of the water vapour self-continuum absorption at  
125 elevated temperatures (398 and 431 K) and pressures (1000–4155 mbar) in the near-visible absorption  
126 bands centred at 8800 and 10600 cm<sup>-1</sup> (1.13 and 0.94  $\mu$ m) using laboratory observations. To our  
127 knowledge these are the first reported measurements of the self-continuum in these bands. These

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<sup>2</sup> Free pairs are two water monomers, which experience one-off collisions and influence each other weakly.

128 measurements are then interpreted in terms of the water dimer hypothesis. This work is an extension  
 129 of earlier investigations [24] on the origin of the continuum in the 1600 and 3600  $\text{cm}^{-1}$  (6.25 and 2.7  
 130  $\mu\text{m}$ ) absorption bands at close to room temperature. Finally, calculations of the atmospheric  
 131 absorption due to this continuum are presented, by using a dimer-based model to extrapolate the  
 132 measurements to atmospheric conditions.

133 The paper structure is the following. Section 2 contains the main details of the measurements.  
 134 In Section 3, the measurement errors are considered. The retrieval procedure of the water vapour  
 135 continuum is described in Section 4. The water dimer model of the continuum is presented in Section  
 136 5 and is discussed in Section 6. Section 7 contains the estimate of the effect of the newly-retrieved  
 137 water vapour continuum to the atmospheric absorption. Conclusions are summarized in Section 8.  
 138 The retrieved water vapour continuum data are given in the Appendix and in the Supplementary  
 139 Materials 1 and 2.

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## 2. Experiment

142 The pure water vapour absorption spectra were obtained at the Molecular Spectroscopy  
 143 Facility, Rutherford Appleton Laboratory (UK) in the near-visible spectral region 8500–13000  $\text{cm}^{-1}$ .  
 144 The experimental setup included a Bruker IFS 125HR Fourier Transform spectrometer (FTS),  
 145 multipass absorption cell with optical path lengths of 9.7 and 17.7 m, Si-diode detector, 50 W quartz  
 146 tungsten halogen bulb and vacuum system. In order to detect the weak continuum absorption in these  
 147 absorption bands, the measurements were carried out at elevated water vapour pressures up to 4155  
 148 mbar and temperatures of 398 and 431 K (see measurement details in Table 1). The relative humidity  
 149 did not exceed 75% to avoid water vapour condensation on the cell walls; the mirrors were also  
 150 checked visually for any evidence of condensation. The total optical path lengths in the multipass  
 151 absorption cell were 9.7 m for pressures above 3000 mbar and 17.7 m for lower pressures. The  
 152 spectral resolution varied from 0.1 to 0.4  $\text{cm}^{-1}$  depending on pressure and was about 0.2–0.25 of an  
 153 average halfwidth of a spectral line.

154 A set of absorption spectra of pure water vapour at various pressures and temperatures were  
 155 obtained. Each measurement was conducted in three stages to reduce the error in determining the  
 156 baseline: (1) a background absorption spectrum of pure argon at the same pressure as the water  
 157 vapour pressure in step 2; (2) a sample absorption spectrum of pure water vapour; (3) repeat of stage  
 158 1. The background measurements with argon were found to be more effective than measurements of  
 159 an empty cell. Argon does not absorb radiation in this spectral region and was therefore useful to  
 160 minimise possible effects of cell deformation on optical alignment caused by the elevated gas  
 161 pressures. The baseline spectrum was derived as an average of the two background spectra.

162

163

**Table 1** Thermodynamic conditions and configuration of pure water vapour absorption spectra measurements

Temperature, K	Spectral interval, $\text{cm}^{-1}$	Pressure, mbar	Optical length, m	Resolution, $\text{cm}^{-1}$
398	8505–9200, 10135–11110	1000 (6% ↓)	17.7	0.1
		1370 (8.7% ↓)		0.2
431	8530–9195, 10055–11110	1080 (3% ↑)	17.7	0.1
		1580 (3% ↑)		0.2
		2070 (1.5% ↑)	9.7	0.2
		2101 (1.3% ↑)		0.2
		3145 (2.4% ↑)		0.4
4155 (3% ↑)	0.4			

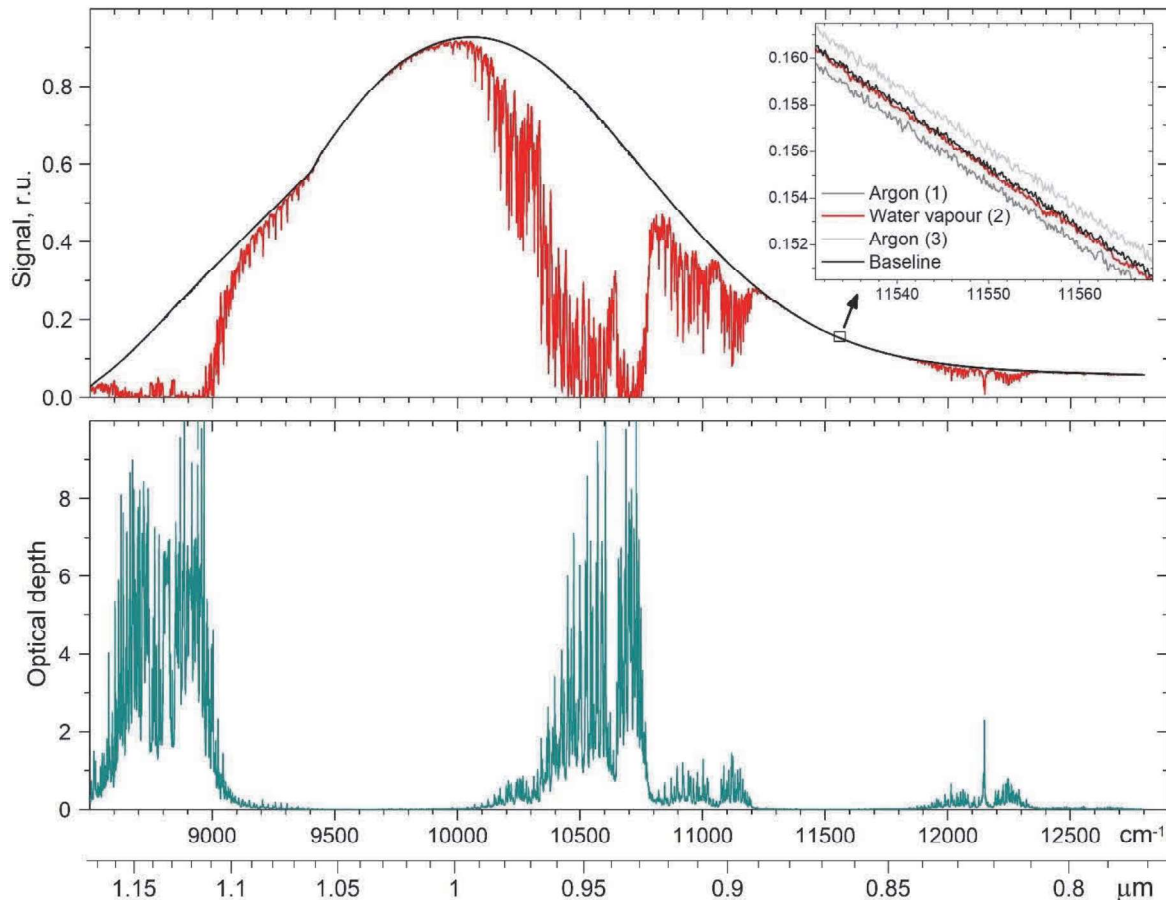
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\* The pressures given here are the spectroscopically-adjusted values using the method described in Section 3.2. The arrows indicate the reduction ( $\downarrow$ ) or increase ( $\uparrow$ ) due to this adjustment.

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168  
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The experimental optical depth of water vapour absorption  $\tau(\nu, T)$  at wavenumber  $\nu$  and temperature  $T$  was derived from the Beer–Lambert law. An example of an optical depth spectrum of water vapour in the spectral region investigated is shown in Fig.1.



171

172 **Fig. 1.** FTS signals from measurements in the cell with argon (black curve) and water vapour (red curve) at a pressure of  
173 3145 mbar and temperature of 431K (upper panel); the resulting spectrum of pure water vapour optical depth (dark cyan  
174 curve, bottom panel). To demonstrate the small baseline uncertainty, the inset in the upper panel shows the water vapour  
175 signal (red curve) and the baseline signal (black curve) obtained as an average of the signals from the cell with argon  
176 measured before (steps 1, light grey curve) and after (steps 3, dark grey curve) the sample measurements in a “window”  
177 spectral region where the continuum absorption is very weak compared to the in-band region. The kink in the baseline at  
178 about 9400  $\text{cm}^{-1}$  is due to the detector’s sensitivity function.

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Deriving the water vapour continuum absorption from high-resolution absorption spectra first requires the calculation and subtraction of the local contribution from water monomer lines. These calculations were made using the  $\text{LBL}_{\text{IAO}}$  line-by-line program [34]. The local line contributions were calculated within  $25 \text{ cm}^{-1}$  from the centre of each Lorentzian line without the CKD “plinth”. Water vapour line parameters were taken from HITRAN-2016 [35]. The continuum data beyond  $11150 \text{ cm}^{-1}$  demonstrate weak values compared to the noise level; therefore, only the 8800 and  $10600 \text{ cm}^{-1}$  absorption bands are investigated. The retrieval of the water vapour continuum at higher wavenumbers requires more sensitive measurements, for example, using the CRDS technique [36].

189

### 190 3. Error analysis

#### 191 3.1 Error types

192 Discussion of the main sources of uncertainties for FTS measurements of the weak continuum  
193 absorption can be found, for example, in [37]. Here, four main error sources of error were identified  
194 and taken into account.

##### 195 3.1.1 Random measurement error caused by the FTS system.

196 This error was evaluated by comparison of the noise within formation content at an optical  
197 depth of 1. To minimize this noise each measurement was averaged over hundreds of individual  
198 spectrometer scans. As a result, the information-to-noise ratio was not less than 500:1.  
199

##### 200 3.1.2 A quasi-random error due to uncertainties in spectral line parameters used for the 201 water vapour spectra calculations.

202 Although these errors do not depend on time, they are often not correlated with each other and  
203 have a random character over the spectrum. Error codes given in the HITRAN database for the line  
204 centres, intensities, temperature coefficients, and pressure broadening coefficients were used to  
205 estimate the upper limit of the absolute error of this type (see details in [38]).

##### 206 3.1.3 Systematic errors caused by uncertainty in the spectral baseline (the FTS signal 207 recorded when the cell contained argon).

208 The baseline was derived as an average of the signals obtained in measurements with argon  
209 before and after the water vapour absorption measurements. The inset in Figure 1 shows an example  
210 in a window spectral region around  $11550\text{ cm}^{-1}$  where the continuum absorption should be negligible  
211 under the experimental conditions. These errors may be caused by slow temporal drifts in the  
212 spectrometer system or gas cell, and for individual measurements were partially mitigated by equal  
213 separation in time of background spectra acquisitions in relation to that of the water sample.  
214 However, this type of error is usually negligible for the measurements of in-band continuum  
215 absorption and does not exceed 1% in our case (see upper panel in Fig. 1).

##### 216 3.1.4 Systematic errors caused by the inaccuracy in measured water vapour pressure and 217 temperature.

218 The main uncertainty here was from the pressure measurements. A description of how these  
219 errors were reduced using a spectroscopic technique is given in Section 3.2.

220

#### 221 3.2 Adjustment of the water vapour pressure

222 The measured intensities of water vapour absorption lines are proportional to the water vapour  
223 pressure, while the intensity of the continuum absorption is proportional to the square of the vapour  
224 pressure. Therefore, the precise value of the water vapour pressure plays an important role in retrieval  
225 of the water vapour continuum. To reduce the respective systematic error in this work, we performed  
226 a spectroscopic assessment of the measured water vapour pressures by comparing measured and  
227 calculated line intensities using the HITRAN database.

228 To exclude lines which are very weak or saturated, and lines with uncertain spectral  
229 parameters, we selected only spectral lines that have measured optical depths in the range 0.2 to 5 at  
230 line centre and an error-index for the line intensity and self-broadening of not less than 5 in  
231 HITRAN-2016. Then the measured intensities of the selected spectral lines were compared with



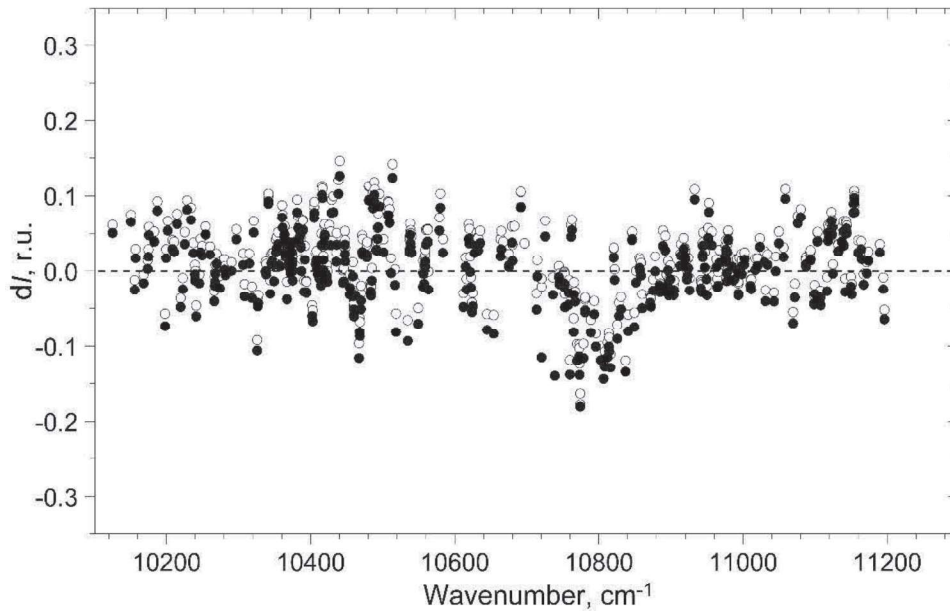
232 those calculated line-by-line using the HITRAN-2016 parameters within a distance of a few  
 233 halfwidths from the line centre. Figure 2 shows an example of a distribution of relative deviation for  
 234 each selected  $i$ -th line ( $\delta I(v_i)$ ) in the investigated spectral region calculated using the equation:

$$235 \quad \delta I(v_i) = \frac{I_{\text{RAL}}(v_i) - I_{\text{HIT16}}(v_i)}{I_{\text{RAL}}(v_i)}. \quad (1)$$

236 In Eq. (1),  $I_{\text{RAL}}(v_i)$  and  $I_{\text{HIT16}}(v_i)$  are line intensities obtained from the experiment and simulation,  
 237 respectively. The average relative deviation between measured and calculated intensities of all  
 238 selected lines was used as a criterion for the water vapour pressure adjustment factor. Systematic  
 239 divergence of the  $\delta I(v_i)$  distribution from zero indicates inaccuracy in the measured water vapour  
 240 pressure. At the same time, strong deviations of  $\delta I(v_i)$  were also observed for individual lines, which  
 241 may be caused by errors in the parameters of relatively weak water vapour lines in the spectral  
 242 database. Generally, the discrepancy was 4% on average in our measurements and we adjusted the  
 243 pressures to agree with the spectroscopically-derived values (see Table 1).

244 Measurements at  $T=471$  K were also performed in this work. However, at some pressures these  
 245 measurements had poor agreement between the measured and spectroscopically-derived pressure, as  
 246 well as poor agreement with the pressure-squared dependence expected for the self-continuum  
 247 absorption. Therefore, we excluded these measurements from analysis in this paper.

248



249

250 **Fig. 2.** Relative deviation of line intensities in the spectral region under investigation for measurements at 431K and 2070  
 251 mbar: empty circles – before pressure adjustment (2039 mbar), black points – after pressure adjustment (increased by  
 252 1.5%).

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#### 4. Retrieval of the water vapour continuum absorption

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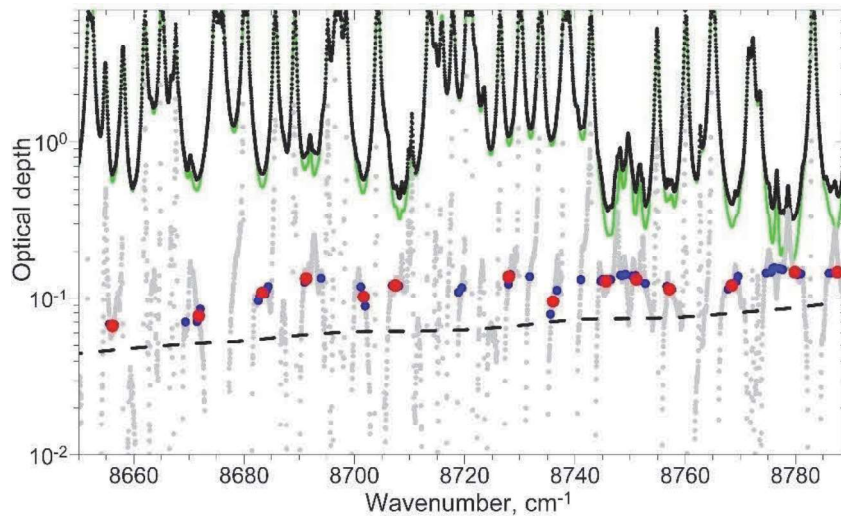
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At the first stage of the analysis, the water vapour continuum optical depth  $\tau_c(v)$  was derived as a difference between the experimental optical depth spectrum  $\tau(v)$  (see Section 2) and the cumulative local contribution of water monomer lines  $\tau_{\text{mon}}(v)$  calculated with the line-by-line technique [34]. An example of the preliminary retrieval of the continuum absorption is given in Fig.3 (grey points). Fluctuations of the continuum at frequencies corresponding to water monomer line centres are caused by uncertainties in spectral line parameters. Generally, the retrieval of the continuum is not possible at line centres within absorption bands, because the continuum component is much less (2 orders of

262 magnitude) than the line contribution. Even small relative errors in line parameters lead to large  
 263 errors in the retrieved continuum. Therefore, the continuum absorption can only be derived in the  
 264 microwindows between absorption lines (blue points in Fig. 3), where the impact of uncertainties in  
 265 line parameters on the retrieved continuum is often relatively small (less than 10–20%). The  
 266 exclusion of line centres from the continuum retrieval does not lead to significant information loss  
 267 since the continuum possesses a rather smooth spectral character within several halfwidths of a  
 268 spectral line. Moreover, spectral smoothing was applied to select the most reliable continuum  
 269 information within these microwindows – the continuum data points were obtained by averaging over  
 270 ten data points, corresponding to a derived continuum at a spectral resolution of between 1 to 4  $\text{cm}^{-1}$   
 271 depending on the measurement pressure. This procedure helps to exclude false minima in the  
 272 experimental spectrum within microwindows. An example of the retrieved continuum spectrum  
 273 including smoothing is shown by the red points in Fig. 3. In the remainder of this paper, this  
 274 smoothed continuum is used throughout. The semi-empirical MT\_CKD-3.2 continuum model [33] is  
 275 also shown (dashed line in Fig.3) for the measurement conditions.  
 276

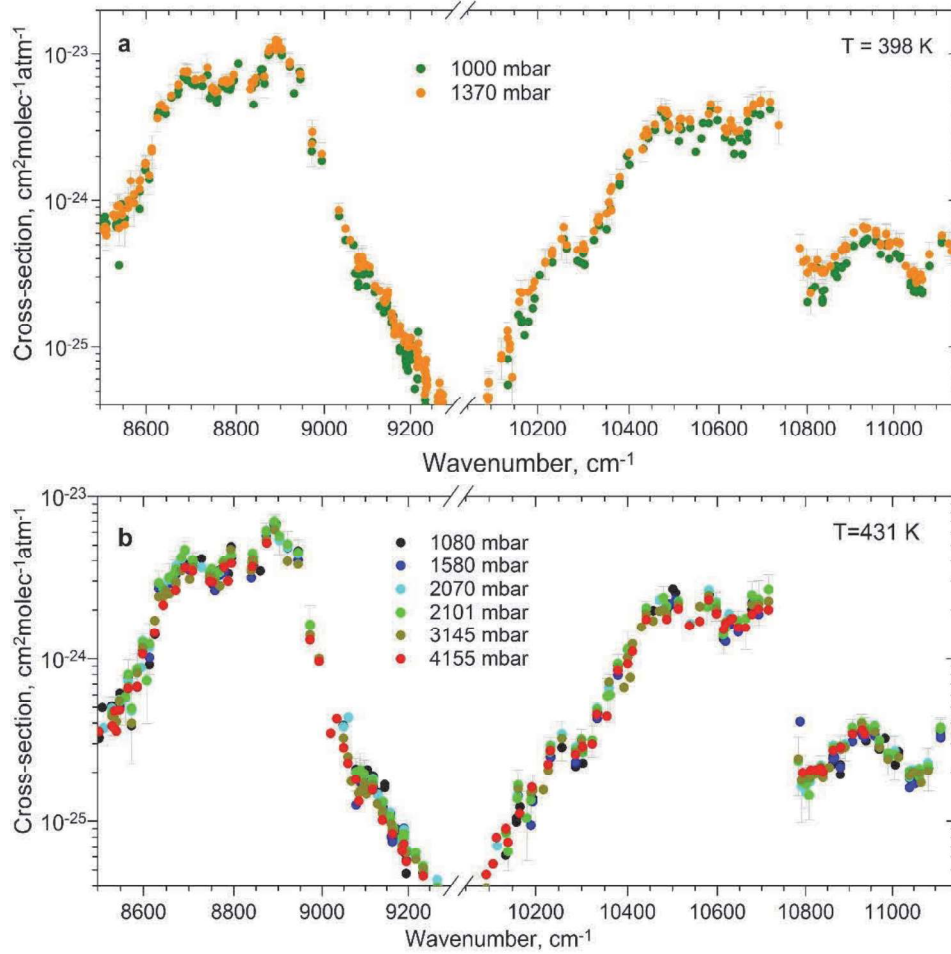


277  
 278 **Fig. 3.** Example of the continuum absorption spectrum retrieved from the experimental data (431K, 1080 mbar):  
 279 measured absorption spectrum of pure water vapour ( $\tau(\nu)$ , black points), MT\_CKD-3.2 model (dashed line), calculated  
 280 spectrum of the local line absorption  $\tau_{\text{mon}}(\nu)$  without the “CKD plinth” (green line), difference between the measured  
 281 water vapour absorption and calculated local lines monomer absorption ( $\tau(\nu) - \tau_{\text{mon}}(\nu)$ , grey points), the differential  
 282 spectrum  $\tau(\nu) - \tau_{\text{mon}}(\nu)$  after filtering (blue points), smoothed continuum spectrum  $\tau_c(\nu)$  (red points).  
 283

284 The self-continuum cross-section  $C_s(\nu, T)$  in units of  $\text{cm}^2 \text{molec}^{-1} \text{atm}^{-1}$  was derived using the  
 285 equation

$$286 \quad C_s(\nu, T) = \frac{\tau_c(\nu)}{\rho_s P_s L} = \tau_c(\nu) \frac{kT}{P_s^2 L} = \alpha(\nu) \frac{kT}{P_s^2} \quad (2)$$

287 where  $\rho_s$  and  $P_s$  are water vapour number density and pressure, respectively,  $k$  is the Boltzmann  
 288 constant,  $T$  is temperature and  $L$  is the optical path length,  $\alpha(\nu)$  is the absorption coefficient. Figures  
 289 4 (a,b) illustrate the close agreement of cross-sections obtained from a range of pressures at both  
 290 temperatures (398 and 431 K).  
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**Fig. 4.** Cross-section spectra of the water vapour continuum absorption obtained using eq. (2) for two pressure sets: 1000 and 1370 mbar at 398 K (a) and six pressures from 1080 to 4155 mbar at 431 K (b). The error bars are given for the continuum cross-section spectra corresponding to 1370 mbar, 398 K (a), and 2101 mbar, 431 K (b).

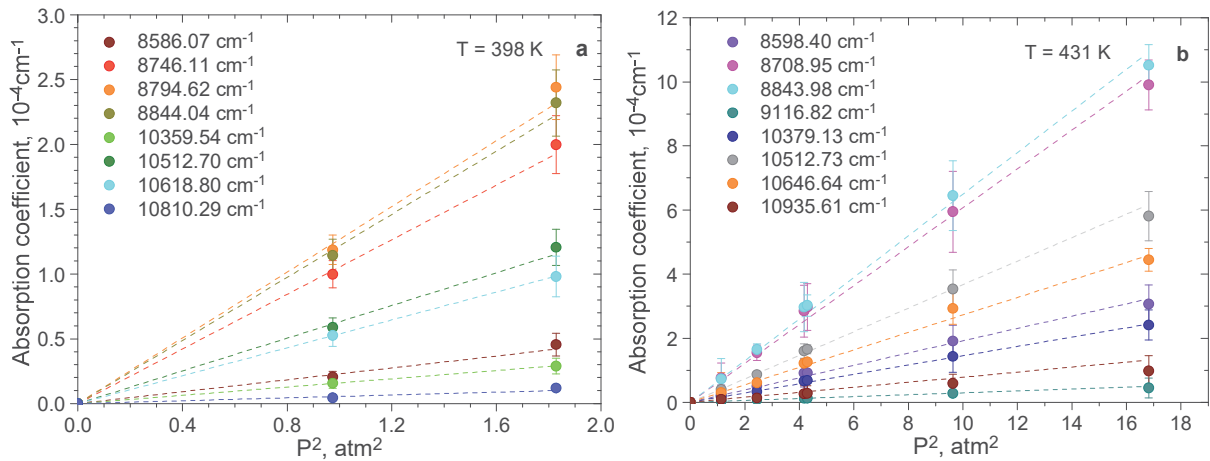
A linear fitting was performed to confirm the pressure-squared dependence of the measured water vapour continuum absorption. The continuum absorption coefficients  $a(\nu)$  versus  $P^2$  are presented in Fig. 5 for some microwindows. There is good agreement between the experimental points and the fitted linear function ( $y=kx+b$ ) and the intercept  $b$  is always close to zero. This helps confirm the quality of the observations. The slope of the straight line determines the cross-section value (Fig. 6). Figure 6 demonstrates the expected inverse temperature dependence of the retrieved continuum absorption.

The retrieved self-continua within the 8800 and 10600  $\text{cm}^{-1}$  absorption bands demonstrates the presence of several spectral peaks that are absent in the MT\_CKD-3.2 continuum model (dashed lines in Fig. 6), although the MT\_CKD-3.2 represents the overall shape of the continuum absorption quite satisfactorily. Similar peaks were previously reported within more intense near-IR water vapour absorption bands [9]. It is also apparent that the MT\_CKD-3.2 model underestimates the observed continuum by about 1.5–2 times on average at the investigated temperatures in the centre of the bands (see lower panel of Fig. 6). The data at 11084 and 11113  $\text{cm}^{-1}$  wavenumbers demonstrate the greatest deviation from MT\_CKD-3.2 and may reflect the beginning of the q-dimer subband in the continuum spectrum (see Fig. 9 and further discussion in Section 6). However, it was not possible to retrieve this spectral feature completely since the difference between the experimental data and the calculated contribution of water monomers turned out to be too noisy.

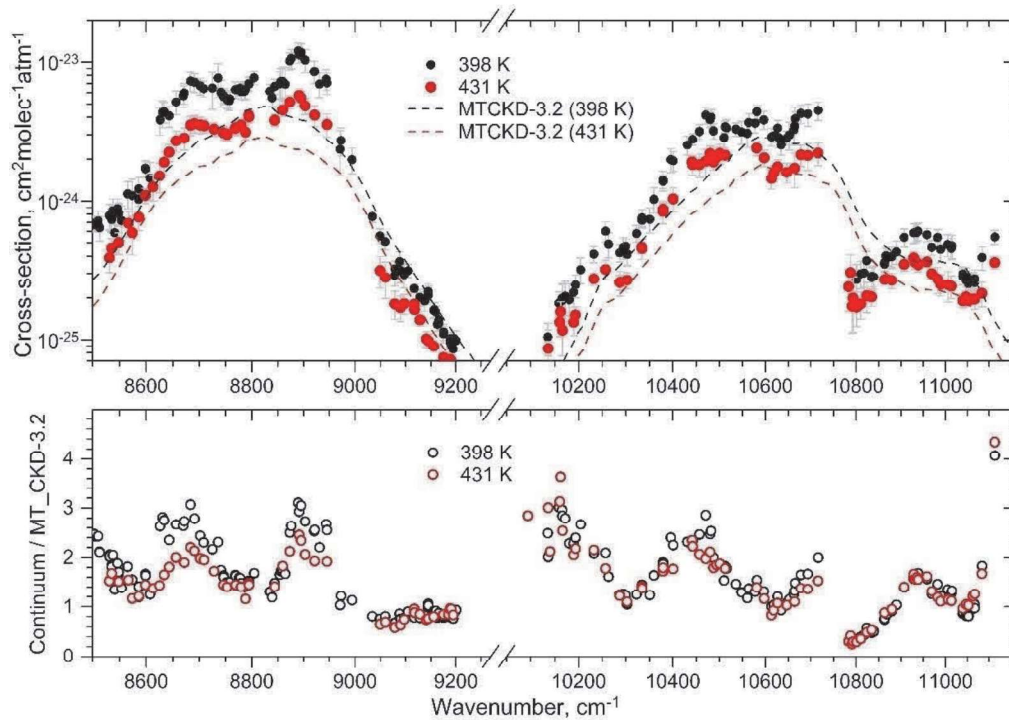
316 We acknowledge that MT\_CKD was not designed for application at such high temperatures, as  
 317 it was intended for use in atmospheric conditions, although as noted in Section 1, the temperature  
 318 dependence was defined using measurements at elevated temperatures at lower wavenumbers.

319 As a consequence of the above arguments, our measurements clearly indicate limitations in the  
 320 MT\_CKD model in this spectral region and at these temperatures. A more physically-based model of  
 321 the water vapour continuum is now required to address the limitations highlighted here. Such a model  
 322 should include significant advances in experimental and theoretical capabilities, and to have a quite  
 323 wide range of applicability beyond the conditions (both spectral and temperature) for which it was  
 324 derived.

325 The cross-sections of the water vapour self-continuum absorption, obtained here for the first  
 326 time from laboratory measurements at elevated temperatures, are given in Appendix 1.



327 **Fig. 5.** Examples of  $P^2$  dependence of the retrieved self-continuum absorption coefficients in some microwindows at 398  
 328 (a) and 431 (b) K.  
 329



331 **Fig. 6.** Cross-section spectra of the water vapour self-continuum absorption retrieved from the experiment (upper panel)  
 332 at 398 K (blue) and 431 K (red). The dashed lines show the corresponding MT\_CKD-3.2 model spectra. Respective ratios  
 333 of the derived continuum to the MT\_CKD-3.2 model are shown in the bottom panel.  
 334

### 335 5. Simulation of water dimer absorption spectra

336 It has been shown in [7–9,20] that the spectral features of the water vapour self-continuum  
 337 absorption within near-IR spectral bands are likely caused by a significant contribution from water  
 338 dimers. In our study, the parameterization of the dimer model proposed in [9] was used for the 8800  
 339 and 10600  $\text{cm}^{-1}$  absorption bands. The total water dimer absorption cross-section (b-dimers + q-  
 340 dimers)  $C_s$  (in [ $\text{cm}^2/\text{atm}/\text{molec}$ ], where 'atm' and 'molec' applies to the pressure and number of water  
 341 monomers, respectively) was simulated using the following equation:

$$342 \quad C_s(\nu) = K_{eq}^b \sum_i S_i^b f_i^b(\Delta\nu_i, \gamma^b) + K_{eq}^q \sum_j S_j^q f_j^q(\Delta\nu_j, \gamma^q), \quad (3)$$

343 where  $K_{eq}^b$  and  $K_{eq}^q$  are the equilibrium constants of b- and q-dimers (in [ $\text{atm}^{-1}$ ]  $\equiv$  [ $n_{\text{dimers}}/n_{\text{monomers}}$  per  
 344 1 atm of water monomers]);  $S_i^b$  is the intensity of i-th subband of b-dimers [ $\text{cm}/\text{dimer}$ ];  $S_j^q$  is the  
 345 intensity of j-th line of q-dimers [ $\text{cm}/\text{dimer}$ ];  $f_i^b(\Delta\nu_i, \gamma^b)$  and  $f_j^q(\Delta\nu_j, \gamma^q)$  are Voigt profiles [ $\text{cm}$ ] with  
 346 halfwidths at half-maximum intensity  $\gamma^b$  and  $\gamma^q$  [ $\text{cm}^{-1}$ ] of b- and q-dimers, respectively;  $\Delta\nu_i$  is the  
 347 distance from the centres of b-dimer subbands;  $\Delta\nu_j$  [ $\text{cm}^{-1}$ ] is a distance from q-dimer line centre. The  
 348 calculation was carried out using the LBL<sub>IAO</sub> line-by-line program [34]. It is important to note that all  
 349 parameters in Eq.(3) have a clear physical meaning as opposed to the semi-empirical parameters that  
 350 are often used in continuum models. The physical background of the model parameters – and so, the  
 351 possibility to verify them from other sources – will allow us (similar to that in [24,39]) to estimate the  
 352 contribution of water dimers to the continuum absorption in the investigated bands (see Section 6). In  
 353 Section 7 (devoted to the atmospheric calculations), we will use this relatively simple dimer model to  
 354 extrapolate the self-continuum from 400-430 K to the 260-296 K temperature range.

355 Some data on the frequencies and strengths of several main bending and stretching oscillations  
 356 in b-dimers can be obtained from theoretical calculations and low-temperature measurements [28,40–  
 357 42]. In this work, the b-dimer spectrum was simulated on the basis of quantum-chemical calculations  
 358 of the O-H stretching vibrational overtone spectrum of the water dimer presented as two individually  
 359 vibrating monomer units [29]. The used data for the intensities of b-dimer transitions is presented in  
 360 Table 2. The Voigt profile with 20  $\text{cm}^{-1}$  halfwidth was used to simulate the subbands shape of b-  
 361 dimers, as it fits best the respective experimental features. However, this parameter has a minor effect  
 362 on the total water dimer spectrum (absorption by b- and q-dimers), since b-dimers contribute weakly  
 363 to the water vapour self-continuum at high temperatures within the bands investigated here (see  
 364 details below). Recently interpreted measurements [43] of the self-continuum in the 3600  $\text{cm}^{-1}$  band  
 365 at 296 K used a more sophisticated, although still speculative, approach to modelling the b-dimer  
 366 band shape. This is based on estimates of the b-dimer rotational constants and distinguishing between  
 367 parallel and perpendicular bands; at this lower temperature, the contribution of b- and q-dimers is  
 368 expected to be more equal, so that assumptions on the b-dimer shape are more important than is the  
 369 case here.

370

371 **Table 2.** Positions and intensities of transitions in bound dimer [29] used for the water dimer model.  
 372

Local mode assignments*	Wavenumber, $\text{cm}^{-1}$	Intensity, $\text{cm}/\text{molec}$
$ 0\rangle_{\text{f}} 2\rangle_{\text{b}} 1\rangle$	8530.5	2.35E-21
$ 20\rangle_{\text{+}} 1\rangle_{\text{+}}(70\%) +  11\rangle_{\text{+}} 1\rangle_{\text{+}}(16\%)$	8754.9	6E-22
$ 2\rangle_{\text{+}} 0\rangle_{\text{b}} 1\rangle_{\text{+}}(63\%) +  1\rangle_{\text{+}} 1\rangle_{\text{b}} 1\rangle_{\text{+}}(22\%)$	8804.8	7E-21

$ 20\rangle_{-} 1\rangle_{+}$	8806.9	5.5E-20
$ 1\rangle_{f} 1\rangle_{b} 1\rangle_{+}(66\%)+ 2\rangle_{f} 0\rangle_{b} 1\rangle_{+}(25\%)$	8930.1	1.9E-21
$ 11\rangle_{+} 1\rangle_{+}(74\%)+ 20\rangle_{+} 1\rangle_{+}(18\%)$	9006.9	4.85E-24
$ 0\rangle_{f} 2\rangle_{b} 2\rangle_{+}(69\%)+ 0\rangle_{f} 3\rangle_{b} 0\rangle_{+}(13\%)$	10057.5	2.65E-22
$ 0\rangle_{f} 3\rangle_{b} 0\rangle_{+}(80\%)+ 0\rangle_{f} 2\rangle_{b} 2\rangle_{+}(12\%)$	10161.1	1.95E-21
$ 30\rangle_{+} 0\rangle_{+}(77\%)+ 21\rangle_{+} 0\rangle_{+}(9\%)$	10601	1.85E-21
$ 3\rangle_{f} 0\rangle_{b} 0\rangle_{+}(67\%)+ 2\rangle_{f} 1\rangle_{b} 0\rangle_{+}(12\%)$	10611	6.5E-21
$ 30\rangle_{-} 0\rangle_{+}$	10615.3	1.8E-20
$ 1\rangle_{f} 2\rangle_{b} 0\rangle_{+}(68\%)+ 3\rangle_{f} 0\rangle_{b} 0\rangle_{+}(15\%)$	10673.7	9.5E-21
$ 21\rangle_{+} 0\rangle_{+}(80\%)+ 30\rangle_{+} 0\rangle_{+}(10\%)$	10869.7	8E-22
$ 2\rangle_{f} 1\rangle_{b} 0\rangle_{+}(74\%)+ 1\rangle_{f} 2\rangle_{b} 0\rangle_{+}(15\%)$	10889.1	3.5E-21
$ 21\rangle_{-} 0\rangle_{+}$	11042	2.25E-21

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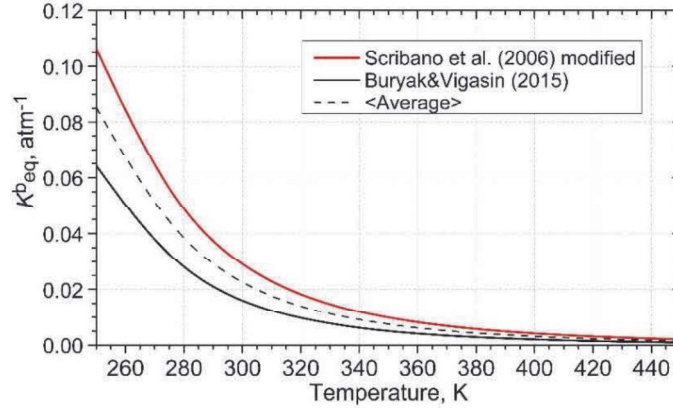
\* According to the notation [28],  $|x\rangle_{f}|y\rangle_{b}|z\rangle_{+}$  and  $|xy\rangle_{\pm}|z\rangle_{+}$  label the vibrational modes in the donor and acceptor water unit respectively. Here,  $x$  and  $y$  denote number of the vibrational quanta respectively in the free ('f') and bound ('b') OH-stretching mode in the donor unit,  $z$  is the quanta in the  $\text{H}_2\text{O}_b$  bending mode, while " $\pm$ " refers to the symmetry of the stretching vibrations in the acceptor unit.

Quasibound dimers, which can be considered as a transitional state between free-pairs and b-dimers, have not been studied as much as the bound states. Therefore, a very simple approximate model of q-dimer lines was used here. In a similar way to [9], the q-dimer absorption spectrum was simulated as a sum of strongly broadened water monomer lines with doubled intensity  $S_i$  (i.e.  $S_i^q = 2S_i$ ). Strong broadening occurs because the lifetime of q-dimers is rather short ( $\sim 10^{-12}$  s). The halfwidth of q-dimer lines was set to  $10 \text{ cm}^{-1}$ , which corresponds to estimates of their average lifetime (see [9]). Intensities of q-dimer lines were assumed to be equal to double the intensities of the corresponding water monomer lines, as an approximation for two slightly interacting water monomers in a short-lived metastable state. For simulation of the q-dimer spectrum, intensities and centres of monomer lines were taken from the HITRAN-2016 database [35]. It was shown that the total dimer spectrum agrees well with the measured continuum within  $1600$  and  $3600 \text{ cm}^{-1}$  absorption bands [9] despite using this quite simple model for the description of the q-dimer spectrum.

The main challenge in parameterization of the dimer model (Eq. (3)) is to determine the equilibrium constant of q-dimers. Direct quantum-chemical calculations of this value, especially for the high temperatures observed here, are not available at present. In this work, an attempt was made to derive both  $K_{\text{eq}}^b$  and  $K_{\text{eq}}^q$  values by fitting the model (Eq. (3)) to the retrieved continuum within  $8800$  and  $10600 \text{ cm}^{-1}$  absorption bands. As a result, a satisfactory spectral agreement between the dimer model and the continuum absorption spectrum was established. A significant difference in the expected contribution of b- and q-dimers at the measurement temperatures was also observed, with a strong prevalence of q-dimers. This result supports the conclusion made on the basis of the statistical approach [19,21] for the temperature dependence of  $K_{\text{eq}}^b$  and  $K_{\text{eq}}^q$ . However,  $K_{\text{eq}}^b$  values derived from this fitting were characterized by significant estimated errors that exceed 100% in some cases. This is due to the very small relative contribution of b-dimers to the total absorption at the investigated temperatures, so that a simultaneous fitting of b- and q-dimer spectra to the continuum leads to large estimated errors in the derived  $K_{\text{eq}}^b$  values and in the fitting itself.

Currently two relatively recent independent estimates of  $K_{\text{eq}}^b$  temperature dependence are available [40,41]. The first [40] requires recalculation adjusted for a more accurate value of the dissociation energy obtained from measurements [44] ( $D_0^{\text{new}} = 1105 \text{ cm}^{-1}$  instead of  $D_0 = 1234 \text{ cm}^{-1}$  used in [40]). In our work, the adjusting factor  $e^{(D_0^{\text{new}} - D_0)/kT}$  was applied to  $K_{\text{eq}}^b$  from [40]. The available calculated temperature dependences of  $K_{\text{eq}}^b$  (Fig.7, red [40] (modified) and black [41] (with  $D_0 = 1105 \text{ cm}^{-1}$ ) solid curves) noticeably differ from each other at low temperatures. Moreover, both estimates are partially confirmed by different experimental data at temperature up to  $350 \text{ K}$  (see, for example, Fig.6 (left panel) in [24]). Therefore, in the next step, the average value of these two

411 estimates (further denoted as  $K_{eq}^{b(aver)}$ ) was taken for simulation of b-dimer absorption spectra.  
 412 Table 3a contains the model parameters for b-dimer spectra calculation. Thus, the main fitting  
 413 parameter of the dimer model was the q-dimer equilibrium constant. Table 3b (column 5) presents  
 414 the obtained  $K_{eq}^q$  values as a result of fitting the dimer model (Eq. (3)) to the retrieved continuum  
 415 spectra with  $K_{eq}^{b(aver)}$  values from theoretical calculations (Table 3a, column 5) using the least square  
 416 method. The rms deviation of  $K_{eq}^q$  is 29% on average.  
 417



418  
 419 **Fig. 7.** Temperature dependence of b-dimer equilibrium constant obtained in *ab initio* calculations [40] and modified for  
 420  $D_0$  (see the text above) (red curve), and in [41] (black solid curve). The average values between [40] modified and [41]  
 421 are shown by dashed black curve.  
 422

423 **Table 3.** Result of the dimer model parameterization:

424 **a** – Parameters for simulating b-dimer absorption spectra using theoretical calculations for equilibrium constant  
 425  $K_{eq}^b$  (see details above).  
 426

Temperature, K	Absorption band, $\text{cm}^{-1}$	Intensities and centre positions	Subband HWHM, $\gamma$ , $\text{cm}^{-1}$	$K_{eq}^{b(aver)}$ , $\text{atm}^{-1}$
398	8800, 10600	Quantum-chemical calculations [29]	20	0.0031
431	8800, 10600			0.0019

427  
 428 **b**– Parameters for simulating q-dimer absorption spectra using fitted values (5th column) and theoretical  
 429 calculations for equilibrium constant  $K_{eq}^q$  (column 6, see Section 6).

Temperature, K	Absorption band, $\text{cm}^{-1}$	Intensities and centre positions	Line HWHM, $\gamma$ , $\text{cm}^{-1}$	$K_{eq}^{q(\text{fit})}$ , $\text{atm}^{-1}$	$K_{eq}^{q(\text{calc})}$ , $\text{atm}^{-1}$
398	8800 10600	Strongly broadened monomer lines from HITRAN-2016 [35]	10	0.0306	0.0090
				0.0284	
431	8800 10600	with doubled monomer intensities		0.0170	0.0069
				0.0168	

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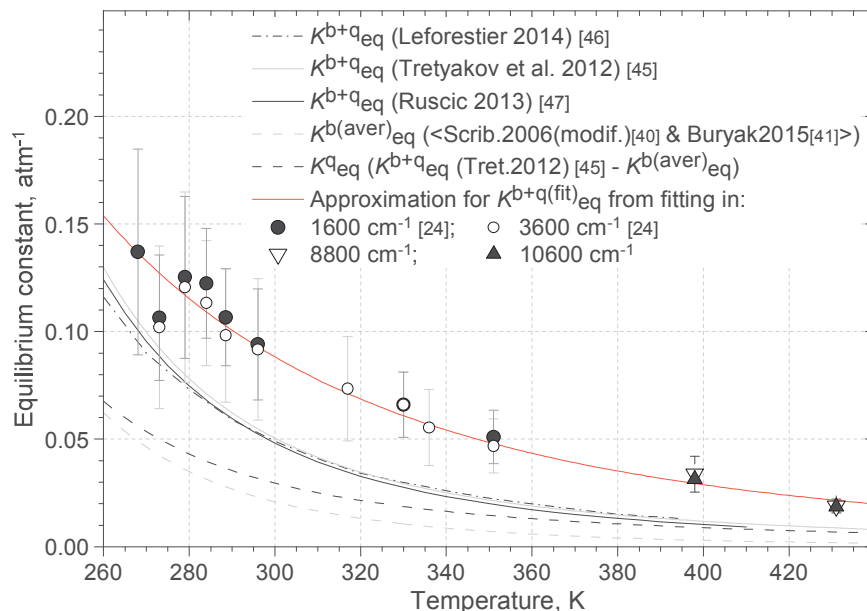
## 431 6. Discussion

432 As mentioned earlier, there is no direct information about the q-dimer equilibrium constant at  
 433 present, but it can be roughly estimated using information about the b-dimer and the total equilibrium  
 434 constants as defined by Eq. (4)

$$435 K_{eq}^{b+q} = K_{eq}^b + K_{eq}^q. \quad (4)$$

436 Currently, three estimates of the total equilibrium constant  $K_{eq}^{b+q}$  are known from different  
 437 approaches to determine the second virial coefficient [45,46] and from the thermodynamic properties  
 438 of water dimers [47]. These data can be considered reliable as they are in good agreement with each

439 other (see Fig.8, solid grey, solid black, and dash-dot black curves). In this work, we apply the  
 440 temperature dependence of  $K^{b+q}_{eq}$  derived from the virial equation of state for real gases, using highly  
 441 accurate measurements of water vapour thermodynamic properties [45]. The difference between  
 442  $K^{b+q}_{eq}$  [45] and  $K^{b(aver)}_{eq}$  was taken to get approximate temperature dependence of  $K^{q(calc)}_{eq}$  (see black  
 443 dashed curve in Fig.8 and values in column 6 of Tab.3b). Column 5 in Tab.3b contains the values of  
 444  $K^{q(fit)}_{eq}$  obtained as a result of the dimer model fitting to the retrieved water vapour self-continuum  
 445 spectra.



446  
 447 **Fig. 8.** Temperature dependences of equilibrium constants obtained from different approaches: total equilibrium constant  
 448  $K^{b+q}_{eq}$  obtained from quantum-chemical calculation [46] (dash-dot curve), from the second virial coefficient [45] (solid  
 449 grey curve), and thermodynamic properties of water dimers [47] (solid black curve); average values of b-dimer  
 450 equilibrium constant  $K^{b(aver)}_{eq}$  [40] (modified) and [41] (grey dashed curve); q-dimer equilibrium constant  $K^{q(calc)}_{eq}$   
 451 obtained in this work as a difference between  $K^{b+q}_{eq}$  [45] and  $K^{b(aver)}_{eq}$  (black dashed curve); total equilibrium constant  
 452  $K^{b+q}_{eq}$  obtained from the fitting of the dimer model to experimental water vapour continuum spectra within 1600 and 3600  
 453  $\text{cm}^{-1}$  bands (black and white circles) [24];  $K^{b+q}_{eq}$  obtained from the fitting within 8800 and 10600  $\text{cm}^{-1}$  bands (white and  
 454 black triangles) in the current work; approximation function of all experimental points for the total equilibrium constant  
 455 derived using the water dimer continuum model [9] within the near-IR absorption bands (solid red curve).

456  
 457 The values of  $K^{q(fit)}_{eq}$  obtained from fitting the dimer model (Eq. (3)) to the experimental  
 458 continuum in two different absorption bands at each temperature are close to each other (see triangle  
 459 symbols in Fig. 8). This seems a reliable result as the concentration of water dimers (characterized by  
 460 an equilibrium constant) in water vapour should not depend on the spectral region. The examples of  
 461 fitting the dimer model (3) to the experimental data are presented in Fig.9 (a,b,g,h). Given the very  
 462 approximate character of the q-dimer absorption model (the second term in Eq. (3)) and the dominant  
 463 contribution of q-dimers at the investigated temperatures, the dimer model provides a fairly detailed  
 464 spectral description of the retrieved self-continuum spectra.

465 Comparison of values in columns 5 and 6 in Tab. 3b shows evidence that the fitted values  
 466  $K^{q(fit)}_{eq}$  are significantly greater than  $K^{q(calc)}_{eq}$  derived from Eq. (4) using reliable values, by about a  
 467 factor of 3 on average. A more complete picture of the dimer model parameterisation can be seen in  
 468 Fig.8. The total equilibrium constant  $K^{b+q}_{eq}$  data obtained at relatively low temperatures within 1600  
 469 and 3600  $\text{cm}^{-1}$  bands [24] and at elevated temperatures within 8800 and 10600  $\text{cm}^{-1}$  absorption bands  
 470 was interpolated in this work using the empirical fit



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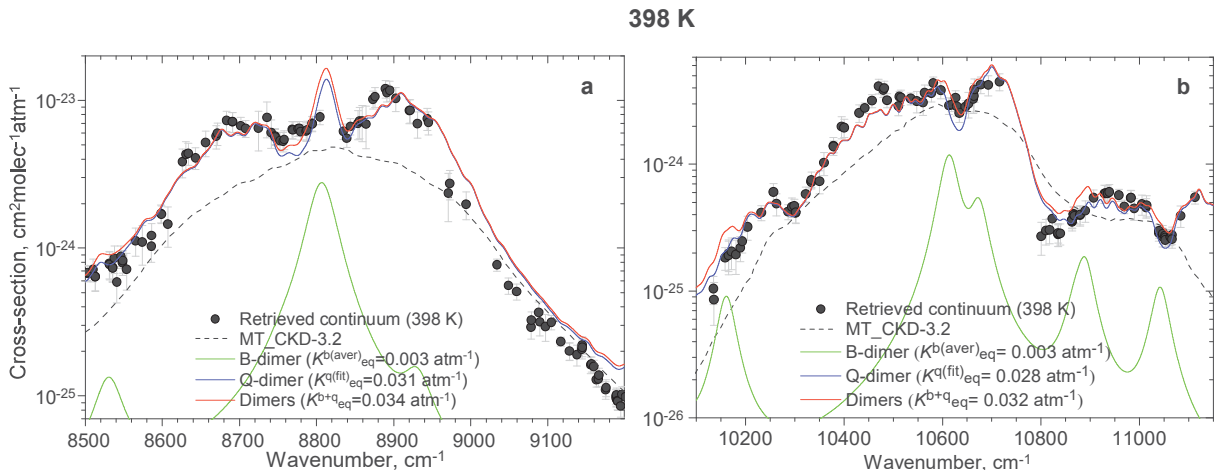
$$K_{eq}^{b+q}(T) = 3.717 \cdot 10^8 \cdot T^{-3.886}. \quad (5)$$

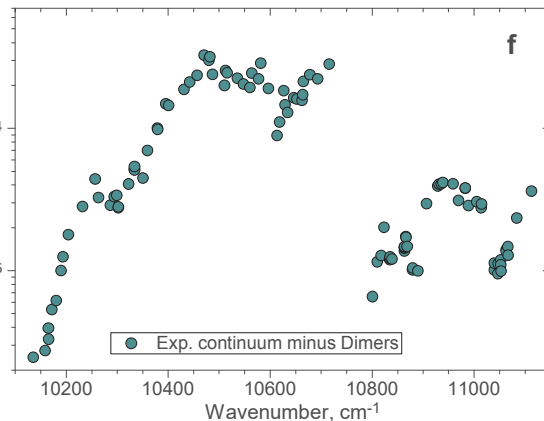
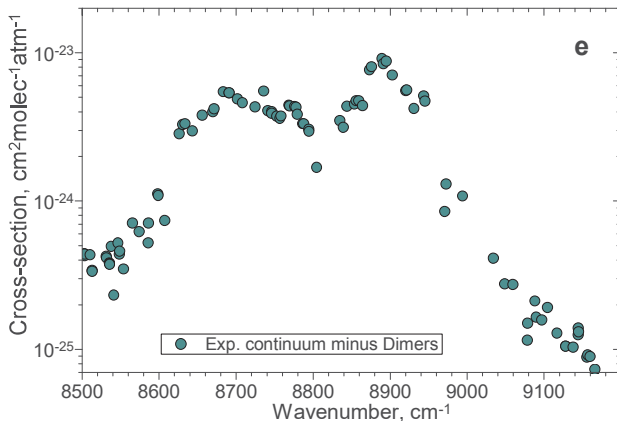
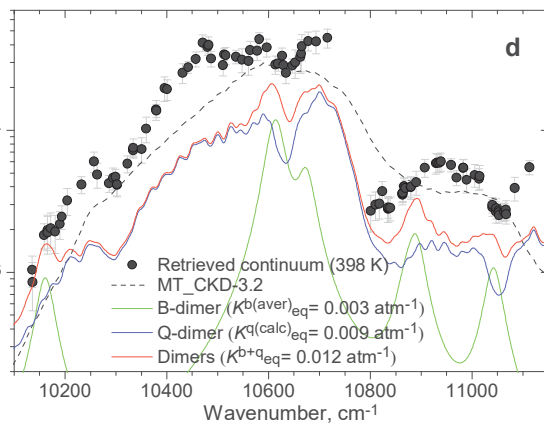
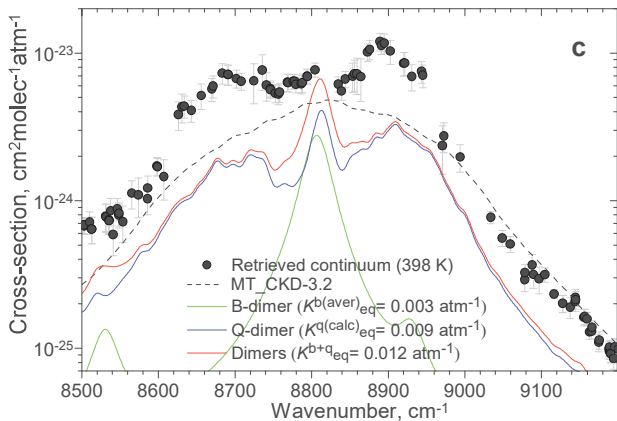
472 This can be considered as the temperature dependence of some *effective* total dimerization constant  
 473 (solid red curve in Fig. 8); i.e. it is the constant that gives a satisfactory description of spectral  
 474 behaviour and strength of the water vapour self-continuum in the investigated spectral regions,  
 475 irrespective of the physical origin of the continuum (see upper panels at each temperature (a,b,g,h) in  
 476 Fig.9) if the intensities of the b- and q-dimer used here are assumed to be correct and no other  
 477 mechanisms were responsible for the continuum. We refer to the dimer model using this empirical fit  
 478 as the “dimer-based model”.

479 The effective equilibrium constant  $K_{eq}^{b+q(\text{fit})}$  obtained in this work is a factor of 1.5-2.5 greater  
 480 than values of  $K_{eq}^{b+q}$  from prior estimates [45–47] across the entire temperature range. This means  
 481 the best fitting of the dimer model (Eq. (3)) requires a larger quantity of water dimers than can be  
 482 objectively explained at the considered thermodynamic conditions (according to the independent  
 483 estimates), and it is  $K_{eq}^q$  that is strongly overestimated in our model. One possible explanation of this  
 484 result can be a contribution from additional mechanisms for the water vapour self-continuum which  
 485 is not accounted for in our model. For example, it could be absorption by intermediate line wings as  
 486 suggested in [39]. The recent analysis [43] of measurements in the 3600 cm<sup>-1</sup> band at 296 K reached  
 487 a broadly similar conclusion, finding a factor of about 1.35 greater  $K_{eq}^{b+q(\text{fit})}$  (which is within the  
 488 uncertainty at 296 K shown in Fig. 8) than expected from the prior estimates; they also suggested that  
 489 enhanced absorption in the intermediate wings [39] may explain the difference. Another explanation  
 490 could be overestimation of the intensities of fundamental transitions of the b-dimers in [29] caused by  
 491 the neglect of intermolecular vibrations in the dimer model. Inclusion of the intermolecular modes  
 492 into quantum-chemical calculations may potentially decrease the intensity of fundamental transition  
 493 (the main spectral peaks) up to 30% [48,49], but strongly increase the calculated underlying part of b-  
 494 dimer absorption which is currently mostly attributed to the q-dimers by the fitting procedure. It  
 495 should be stressed that it is more likely that an overestimation of  $K_{eq}^{q(\text{fit})}$  in our current fitting that  
 496 leads to the overestimation of the total  $K_{eq}^{b+q(\text{fit})}$ .

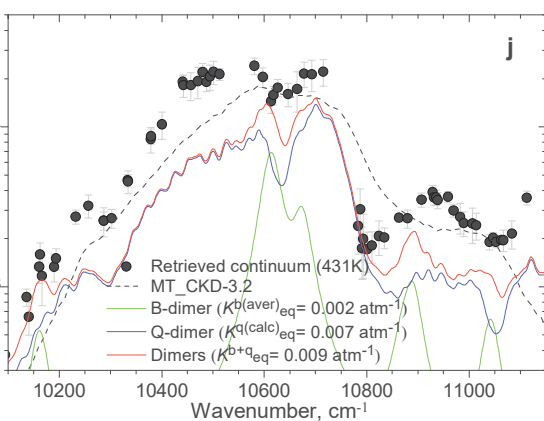
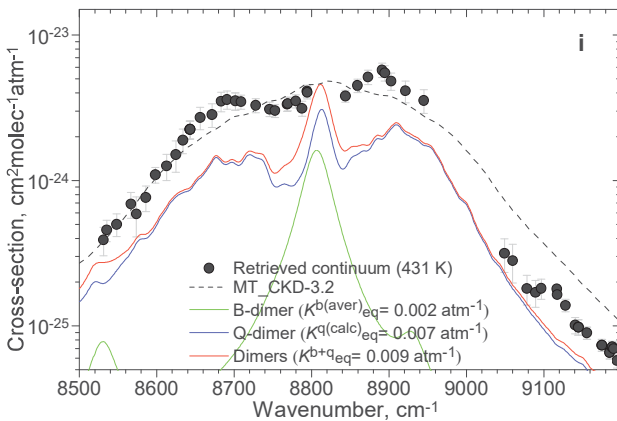
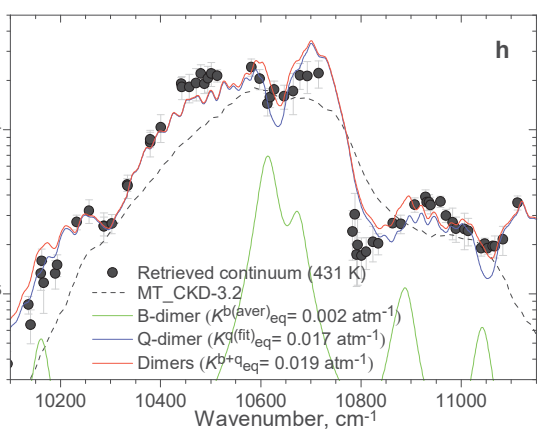
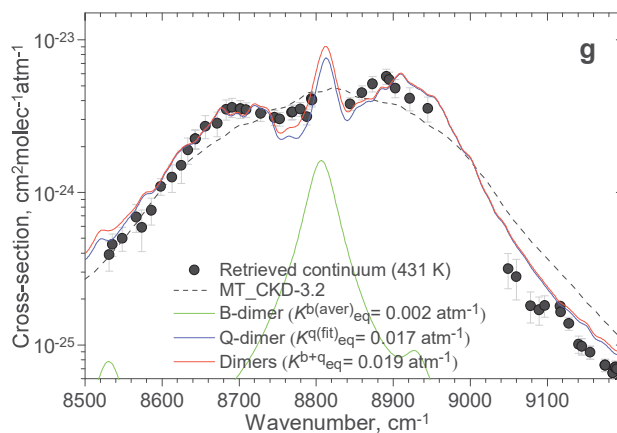
497 Fig. 9 (c,d,i,j) contains the simulated water dimer absorption spectra using the values of  
 498  $K_{eq}^{b(\text{aver})}$  (Table 3a, 5 column) and  $K_{eq}^{q(\text{calc})}$  (Table 3b, column 6) obtained from Eq. (4). The  
 499 integrated spectral contribution of the b-dimer and q-dimer absorption to the continuum is 36% at  
 500 398 K and 45% at 431 K in this case. The part of the retrieved continuum that is unexplained by  
 501 water dimers using the currently-available theory, and total equilibrium constant, is presented in  
 502 Fig. 9 (e,f,k,l).

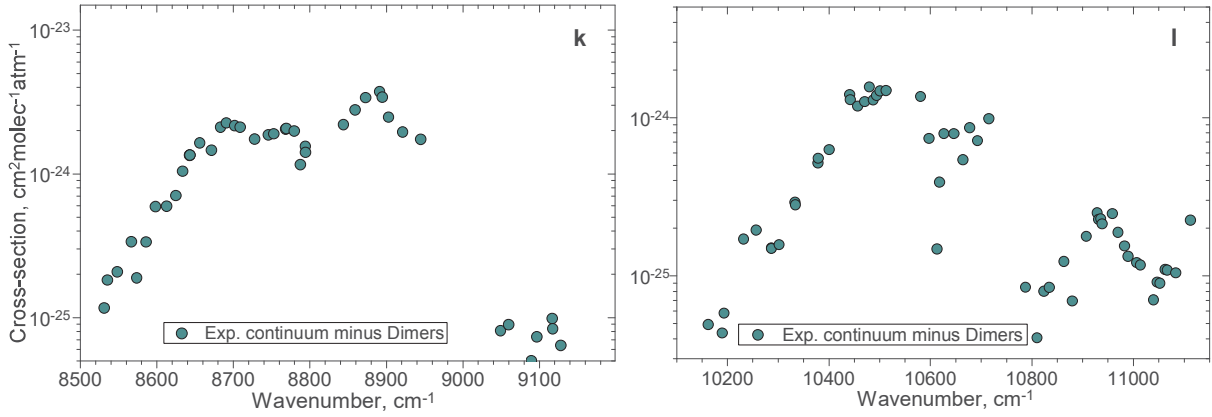
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## 431 K





504 **Fig. 9.** Result of the water dimer model (Eq. (3)) fitting within the 8800  $\text{cm}^{-1}$  (left panels) and 10600  $\text{cm}^{-1}$  (right panels)  
 505 absorption bands at 398 K (a-d) and 431 K (g-j). Upper panels at each temperature: the result of the water dimer model  
 506 fitting to the retrieved water vapour self-continuum cross-section spectra using the fitting parameter  $K^{q(\text{fit})}_{\text{eq}}$ . Middle  
 507 panels at each temperature: the result of the water dimer model simulation using theoretically-derived estimated values  
 508  $K^{b(\text{aver})}_{\text{eq}}$  and  $K^{q(\text{calc})}_{\text{eq}}$ . Lower panels (e,f at 398 K and k,l at 431 K): the unexplained part of the continuum absorption  
 509 obtained as a difference of the retrieved continuum and the dimer model from middle panels (c,d at 398 K and i,j  
 510 at 431 K). The water vapour self-continuum spectrum derived from measurements (black circles), model spectra of b- and  
 511 q-dimers (green and blue curves, respectively), total model spectrum of water dimers (red curve), MT\_CKD-3.2 model  
 512 (dashed curve), the unexplained absorption spectrum (dark green circles). The parameter values of the water dimer model  
 513 are given in Tab. 3 a,b.

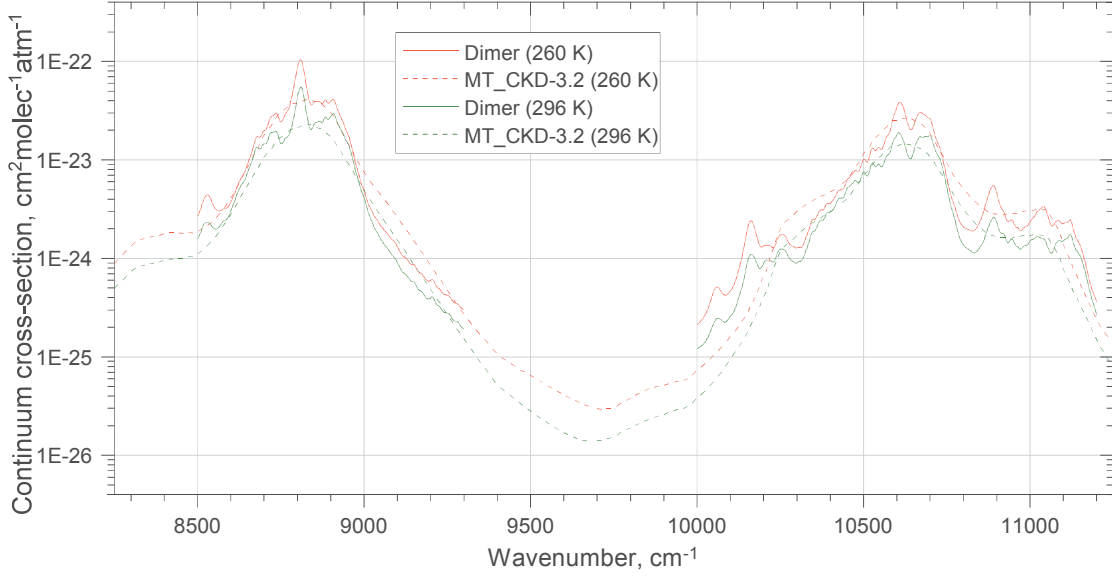
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## 515 7. Radiative impact of the new self-continuum

516 This section aims to determine how much of an effect the retrieved water vapour self-  
 517 continuum absorption has from the perspective of atmospheric radiative transfer. Within the  
 518 investigated 8800 and 10600  $\text{cm}^{-1}$  absorption bands, water vapour lines and the self-continuum are  
 519 weaker than in the bands at lower wavenumbers. The near-visible absorption bands, unlike the  
 520 stronger near-IR bands, do not completely attenuate solar radiation between the top-of-atmosphere  
 521 and the surface layer (i.e. their absorption is not saturated); therefore, uncertainty in absorption within  
 522 these bands has more impact on the calculated [shortwave surface](#) fluxes than near-IR bands at lower  
 523 wavenumbers.

524 Despite the fact that our observations are limited by the elevated temperatures (398 and 431 K),  
 525 the good agreement between the experimentally-retrieved water vapour continuum and the dimer-  
 526 based model (see Fig. 9, a,b,g,h) allows us to simulate  $\text{H}_2\text{O}$  self-continuum spectra at atmospheric  
 527 temperatures by extrapolating the dimer-based model. Here, for the temperatures of interest, we  
 528 calculated the water dimer cross-sections (Eq. (3)) with the effective values of  $K^{b+q}_{\text{eq}}$  obtained from  
 529 the best fit to the experimental data at different temperatures and approximated using the temperature  
 530 dependence from Eq. (5). Figure 10 shows the extrapolated coefficients from the dimer-based model  
 531 at 296 and 260 K (see Supplementary materials 3), compared to those from MT\_CKD-3.2 at the  
 532 same temperatures. Despite MT\_CKD-3.2 being a factor of  $\sim 1.5$ -2 weaker on average than the  
 533 observed continuum at elevated temperatures, at atmospheric temperatures there is reasonable  
 534 agreement between the dimer-based model (using the effective value of  $K^{b+q}_{\text{eq}}$ ) and MT\_CKD-3.2.  
 535 However, this agreement must be treated with caution, as the true temperature dependence in these  
 536 bands, strictly speaking, may be different to that obtained from the combination of these and near-IR  
 537 bands at different temperatures (Fig. 8 and Eq. (5)) – we do not have direct observational evidence  
 538 that this is the case. Also, the dimer model and MT\_CKD-3.2 demonstrate different spectral  
 539 behaviour; the dimer-based model has various peaks and troughs corresponding mainly to the

540 transitions of the q-dimer, and there are also some larger differences at the edges of the two  
 541 bands.



542

543 **Fig. 10** MT\_CKD-3.2 (dashed lines) and dimer-based model coefficients (solid lines) at 260 K (red) and 296 K (green).

544 We derived the dimer-based model spectrum at 296 and 260 K, which are the temperatures at  
 545 which the MT\_CKD continuum coefficients are specified. For ease of incorporation into our  
 546 radiative transfer model, we then use the MT\_CKD temperature dependence to interpolate the dimer  
 547 absorption between these temperatures. The MT\_CKD temperature dependence is of the form

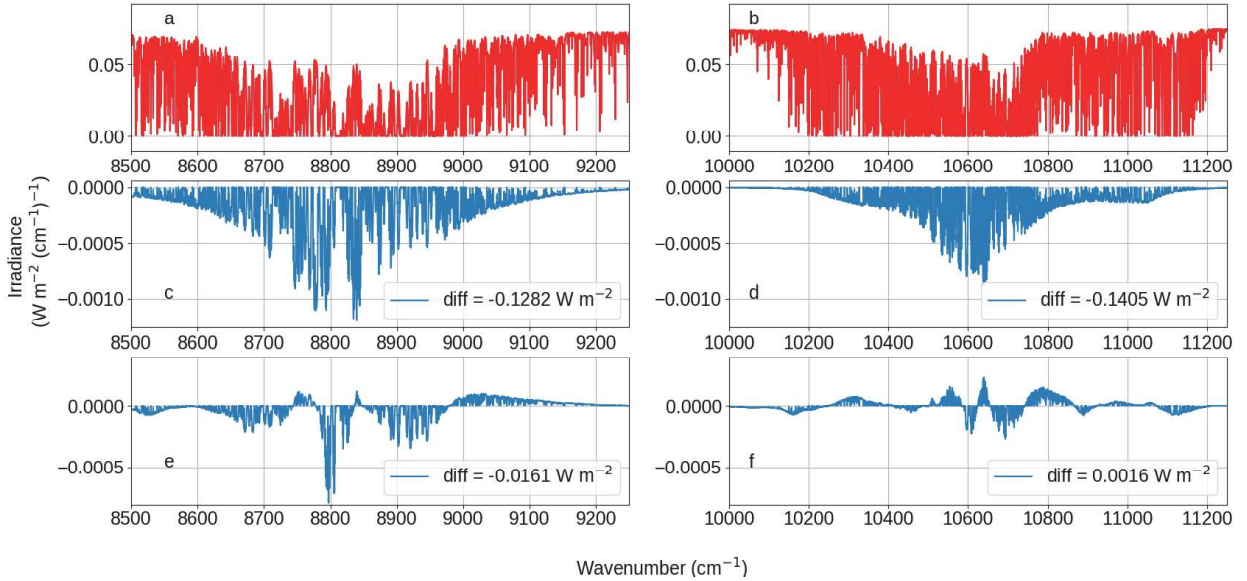
548

$$C_s(\nu, T) = C_s(\nu, T_0) \left( \frac{C_s(\nu, T_1)}{C_s(\nu, T_0)} \right)^{(T-T_0)/(T_1-T_0)}, \quad (6)$$

549 where  $T_0$  is 296 K and  $T_1$  is 260 K. Since this temperature dependence interpolates absorption cross-  
 550 sections between 296 and 260 K, and the dimer-based model shows a reasonable agreement with  
 551 MT\_CKD at these two temperatures (Fig. 10), one can expect that the temperature dependences of  
 552 these two models do not deviate significantly in this temperature region. The highest tropospheric  
 553 temperature used in our model atmospheres is 300 K, meaning that the MT\_CKD temperature  
 554 dependence is suitable for modelling the range of temperatures we explore here (260-300 K); at 280  
 555 K the difference is no more than 3% at any wavenumber, and averages out to 0.15%.

556 To estimate irradiances, we use an updated version of the RFMDISORT radiative transfer tool  
 557 (used, for example, in [50]). This is a combination of two established radiative transfer codes; the  
 558 Reference Forward Model [51] (a line-by-line code used to determine gas absorption) and DISORT  
 559 [52] (a multiple scattering code used to compute irradiances). A spectral resolution of  $0.1 \text{ cm}^{-1}$  is  
 560 used here. We use an offline version of MT\_CKD-3.2 to calculate continuum absorption, with  
 561 modifications using user-provided continuum absorption cross-sections. For this work, we used  
 562 tropical (TRO), mid-latitude summer (MLS) and sub-arctic winter (SAW) standard atmospheres,  
 563 with specified profiles of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  (at 380 ppmv),  $\text{CH}_4$  (1.7 ppmv),  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{O}_3$ . Spectral data is  
 564 obtained from the HITRAN2016 database. We used the Kurucz solar spectral irradiance [53]. These  
 565 calculations are for clear-sky conditions, and include the effects of Rayleigh scattering, with a  
 566 spectrally constant surface albedo of 0.3. For an overhead Sun, the original MT\_CKD-3.2 self-  
 567 continuum reduces the downwelling surface irradiance by  $\sim 0.26 \text{ W m}^{-2}$  in MLS conditions compared  
 568 to the no-continuum case across the  $8500\text{-}9250 \text{ cm}^{-1}$  and  $10000\text{-}112000 \text{ cm}^{-1}$  bands (see Fig.11 (c,  
 569 d)). This value is strongly dependent on the humidity; for SAW the absorbed irradiance is as low as

570  $\sim 0.014 \text{ W m}^{-2}$ , but as high as  $\sim 0.46 \text{ W m}^{-2}$  for TRO. This makes up  $\sim 15\%$  of the total (self + foreign)  
 571 continuum absorption and 0.5% of the total water vapour absorption in this spectral region in the  
 572 MLS case; this contribution will be greater for more humid atmospheres, and lesser for less humid  
 573 ones. In most radiation models, the continuum at these wavelengths is parameterised using versions  
 574 of MT\_CKD. The results in many studies were obtained on the basis of MT\_CKD-2.5 in the  
 575 shortwave (e.g. [54]). Here, we use MT\_CKD-3.2 as a benchmark, as this is the most recent version  
 576 in which the water vapour continuum was updated.



577

578 **Fig. 11** Downwelling surface irradiance in the 8000-9250  $\text{cm}^{-1}$  (panels a, c and e) and 10000-11200  $\text{cm}^{-1}$  (panels b, d and  
 579 f) bands for a mid-latitude summer atmosphere with overhead Sun (panels (a) and (b)), the modelled impact of the  
 580 MT\_CKD-3.2 self-continuum in these spectral regions (panels (c) and (d)), and the change in surface irradiance from  
 581 using the dimer-based model as opposed to MT\_CKD-3.2 (panels (e) and (f)). A negative value in panels (c), (d), (e) and  
 582 (f) indicates that the surface irradiance is being reduced, i.e. that additional absorption is occurring.

583

584 Figure 11 shows the calculated irradiances  $I$  at the surface for the model setup described above,  
 585 with the MT\_CKD-3.2 continuum shown in panels (a) and (b), the effect of the MT\_CKD-3.2 self-  
 586 continuum in this region (panels (c) and (d)), derived as  $I_{MT\_CKD} - I_{no\ self\_continuum}$  (where  $I_{MT\_CKD}$  and  
 587  $I_{no\ self\_continuum}$  are the irradiances including the MT\_CKD self-continuum and without it, respectively),  
 588 and the effect of the change between the continuum obtained by extrapolating the dimer-based model  
 589 in temperature and MT\_CKD-3.2 in panels (e) and (f), derived as  $I_{dimer\_model} - I_{MT\_CKD}$ . The data in  
 590 Fig. 11 was generated using MLS with an overhead Sun. The integrated difference (across the 8000-  
 591 12000  $\text{cm}^{-1}$  region) between the two in this case is relatively small (roughly  $0.021 \text{ W m}^{-2}$ ), due to the  
 592 broad similarity between the MT\_CKD-3.2 and the effective water dimer spectra at the relevant  
 593 temperatures. For the MLS case described in Fig. 11, the reduction in the surface irradiance across  
 594 the two bands due to the self-continuum is 7% greater using the dimer-based model rather than  
 595 MT\_CKD-3.2; however, this is dominated by a decrease in irradiance of  $\sim 12.5\%$  in the 8500-9250  
 596  $\text{cm}^{-1}$  region, with a much smaller decrease ( $\sim 1\%$ ) in irradiance in the 10000-11200  $\text{cm}^{-1}$  region. A  
 597 more detailed breakdown of the effect of the dimer-based model relative to MT\_CKD-3.2 is  
 598 presented in Table 4, for a range of atmospheric profiles and solar zenith angles. It is interesting to  
 599 note that the increase in atmospheric absorption for the 60-degree solar zenith angle case in Table 4a  
 600 using the dimer-based model is greater for the MLS atmosphere than the more humid TRO  
 601 atmosphere in the 8500-9250  $\text{cm}^{-1}$  band. This is an indication that the saturation of absorption lines in  
 602 the tropical atmosphere reduces the effect of the enhanced continuum absorption at these higher

603 zenith angles. A saturation effect may also explain why the sign of the contribution changes in the  
 604 10000-11200  $\text{cm}^{-1}$  band as the solar zenith angle increases in some cases.

605 The differences between MT\_CKD-3.2 and the dimer-based model from this work are largest  
 606 at the q-dimer band centres (according to blue curves in Fig. 9). These bands are included explicitly  
 607 within our model, whereas in MT\_CKD 3.2 they could be interpreted as being included indirectly in the “weak  
 608 interaction term”, which would spread their effect over a wider spectral range (see e.g. Fig. 10). It is clear  
 609 from Fig. 11(e) that the narrow q-dimer peaks at  $\sim 8800 \text{ cm}^{-1}$  have a significant impact on the total  
 610 self-continuum absorption. There is better agreement with MT\_CKD when integrating across the  
 611 band, due in part due to the peaks and troughs in the dimer-based model cancelling each other out.  
 612 The sign of the change relative to MT\_CKD is dependent on the atmospheric conditions and solar  
 613 zenith angle; it is likely that some of the spectral features are causing some bands to saturate sooner  
 614 than others, within certain monomer band centres (which correspond to the q-dimer peaks which give  
 615 the dimer-based model its more detailed spectral structure). Despite this, the presence of these peaks  
 616 means that there may therefore be some useful spectral information that could be used to validate the  
 617 dimer model. An atmospheric measurement with a high enough precision (e.g. those used as part of  
 618 the Total Carbon Column Observing Network [55]) could potentially observe the sharply-peaked  
 619 features especially noticeable, for example, at  $\sim 8530$  and  $10160 \text{ cm}^{-1}$  (see Fig. 11).

620 While a change in the continuum may have an effect on water vapour retrievals (e.g. MODIS  
 621 retrievals in the 915-965 nm band [56]), the significant cancellation of the peaks in this band (see e.g.  
 622 Fig.11 c) results in a minimal change in the optical depth averaged over this spectral region going  
 623 from MT\_CKD-3.2 to the dimer-based model.

624 **Table 4** Differences between the spectrally integrated surface irradiances (dimer-based model – MT\_CKD-3.2) for  
 625 different solar zenith angles and atmospheres, separated by spectral band.

626 a) 8500-9250  $\text{cm}^{-1}$

Solar zenith angle	TRO	MLS	SAW
0	-0.0218 (-11.7%)	-0.0161 (-12.5%)	-0.001 (-13.9%)
30	-0.0168 (-10.11%)	-0.0165 (-14.3%)	-0.0009 (-12.8%)
60	-0.0035 (-3.49%)	-0.0057 (-3.95%)	-0.0007 (-11.9%)

627

628

b) 10000-11200  $\text{cm}^{-1}$

Solar zenith angle	TRO	MLS	SAW
0	-0.0003 (-0.14%)	0.0016 (1.14%)	0.0002 (3.1%)
30	0.0002 (0.1%)	-0.0016 (-1.23%)	0.0002 (3.2%)
60	0.0011 (0.8%)	-0.0002 (-0.11%)	0.0002 (3.3%)

629

630 \* Values are in  $\text{W m}^{-2}$  integrated over each band. Values in brackets indicate the percentage change in the surface  
 631 irradiance due to self-continuum absorption within each band using the dimer-based model rather than MT\_CKD-3.2. A  
 632 negative number indicates that the surface irradiance has decreased (i.e. absorption has increased) when making this  
 633 change from MT\_CKD3.2 to the dimer-based model, and vice versa.

634

## 635 8 Conclusions

636 Measurements of IR radiation absorption in pure water vapour using Fourier transform  
 637 spectroscopy were used to retrieve the water vapour self-continuum absorption in the 8800 and  
 638  $10600 \text{ cm}^{-1}$  water vapour bands at 398 and 431 K, and at pressures between 1000 and 4155 mbar. To  
 639 our knowledge these are the first experimental derivations of the self-continuum in these bands. The  
 640 dimer-based model of the water vapour self-continuum absorption, proposed for other infrared  
 641 absorption bands in the earlier work [24], was parameterized and extended to higher wavenumbers

642 and higher temperatures by fitting the model to the experimental continuum spectra. A good  
643 quantitative description of the continuum absorption by this model was established, but required  
644 more water q-dimers than can be objectively explained by independent thermodynamic estimates.  
645 The MT\_CKD-3.2 model demonstrates an underestimation of the observed continuum by about a  
646 factor of 1.5-2 on average in the measured absorption bands at elevated temperatures. Moreover, the  
647 characteristic spectral peaks observed in the measured self-continuum spectra are absent in  
648 MT\_CKD-3.2. The temperature dependence of the total *effective* dimerization constant was derived  
649 in a broad temperature region from 268 to 430 K based on fitting of the dimer model to the measured  
650 continuum spectra with one fitted parameter (the equilibrium constant of quasibound dimers) in this  
651 work and the results of the lower temperature data in near-IR bands [24]. Using this temperature  
652 dependence, the dimer-based model for 8800 and 10600  $\text{cm}^{-1}$  water vapour bands was then  
653 extrapolated from 400-430 K to the temperatures 260-296 K, and was found to be in reasonable  
654 agreement with the MT\_CKD-3.2 continuum model at these temperatures (see Section 7), but with  
655 less agreement toward the band edges, and with some significant differences in narrow spectral  
656 regions (corresponding to absorption features of the quasibound dimer). The dimer-based model  
657 provides some support for the values produced by the MT\_CKD model at atmospheric temperatures  
658 but not for the physical assumptions underlying that model. We suggest that the dimer-based model  
659 could now be considered as a replacement to MT\_CKD for the in-band self-continuum as it is has  
660 now been shown to simulate, with reasonable accuracy, the observed self-continuum in several near-  
661 IR bands.

662 It is shown that without our empirical adjustment to the equilibrium constant of quasibound  
663 dimers, water dimers could account for not more than 50% of the detected water vapour self-  
664 continuum absorption within the 8800 and 10600  $\text{cm}^{-1}$  absorption bands at the investigated  
665 temperatures. Possible reasons for the difference between this and the observed absorption could be  
666 the presence of additional mechanisms that contribute to the in-band continuum (such as intermediate  
667 line wings) or so-far neglected contributions in theoretical models of the bound dimer spectrum. In  
668 addition, to minimize the uncertainty of the water dimer model, the spectrum of quasibound dimers  
669 also needs to be studied in more detail. Hence, to advance understanding, improvements in  
670 theoretical calculations are needed. Measurements of the continuum strength over a wider range of  
671 experimental conditions would also be very beneficial in constraining theoretical models. The  
672 extension of such work to include the foreign continuum would also be beneficial.

673

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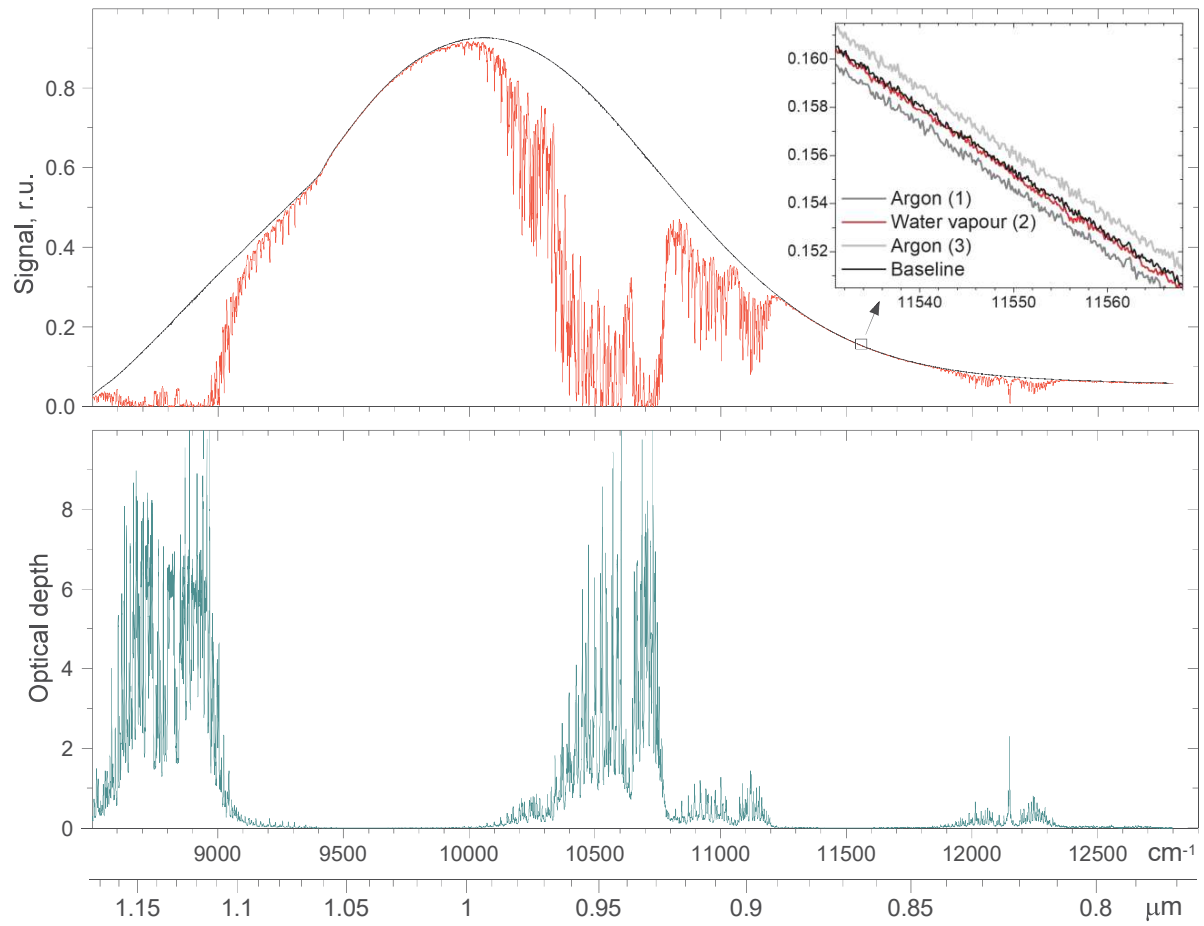
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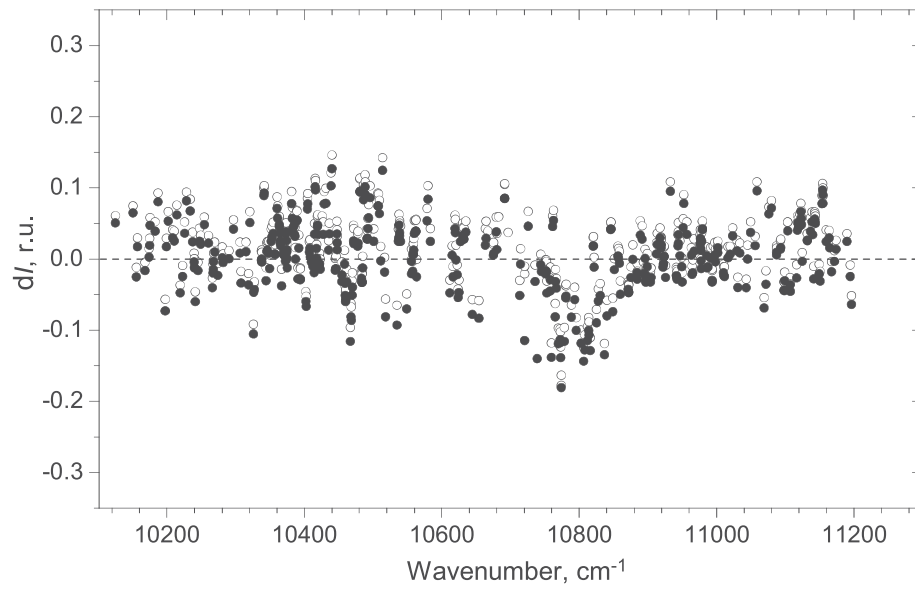
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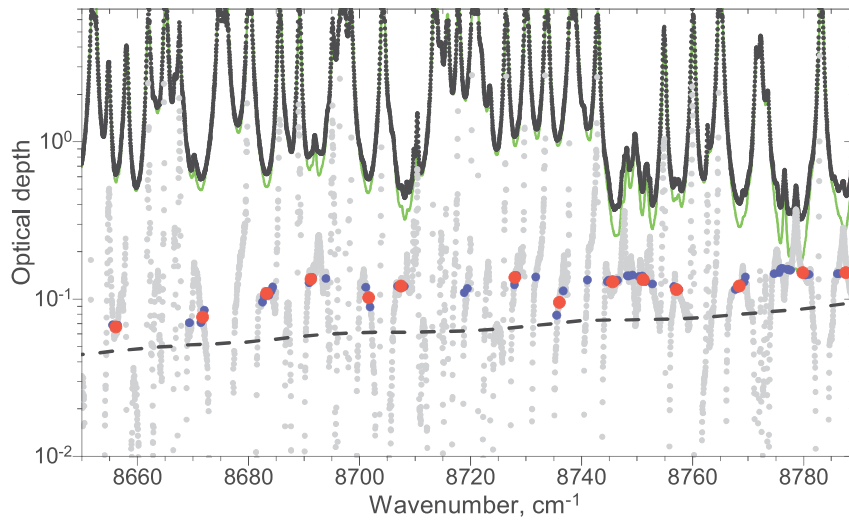
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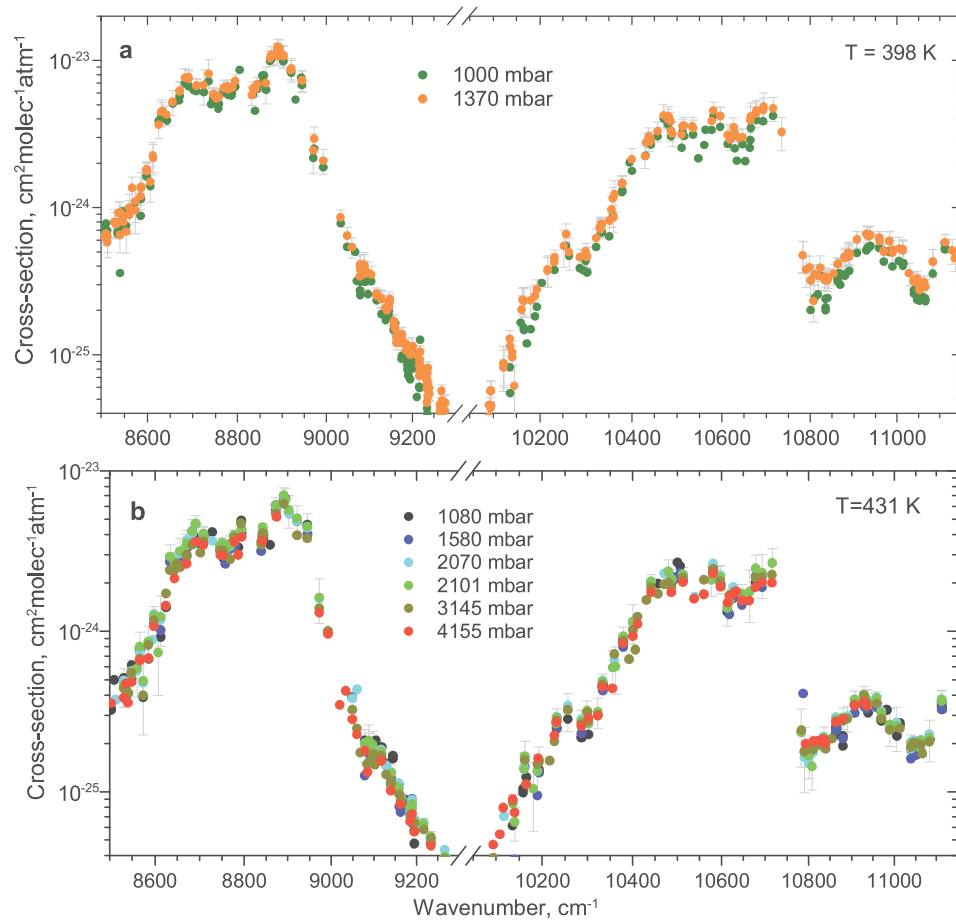


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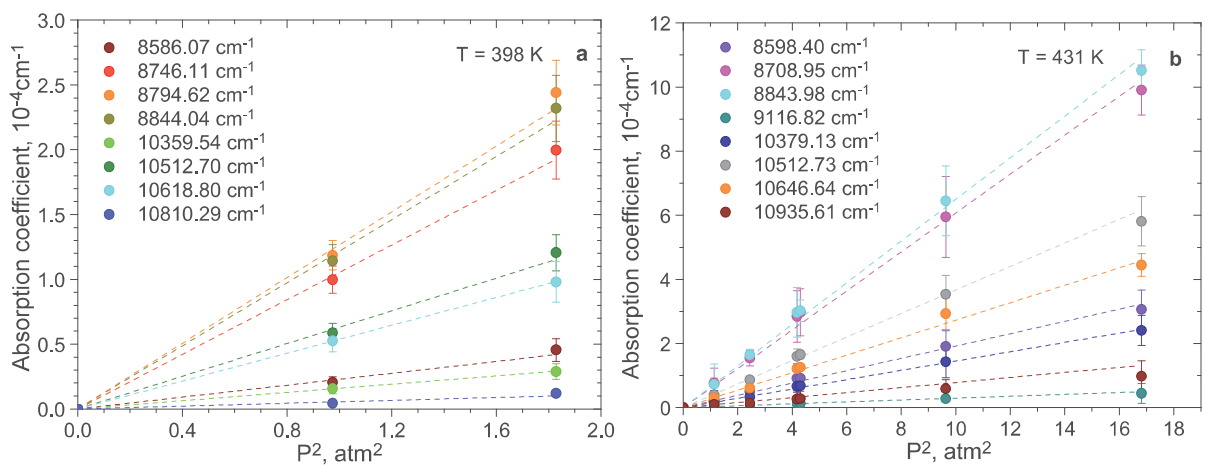


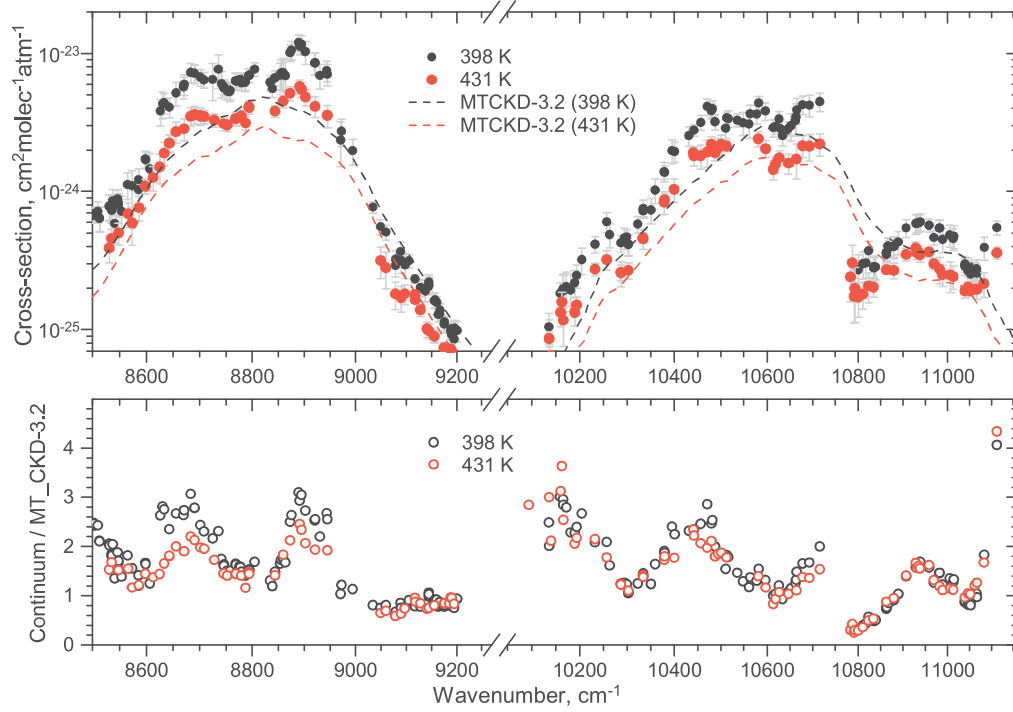


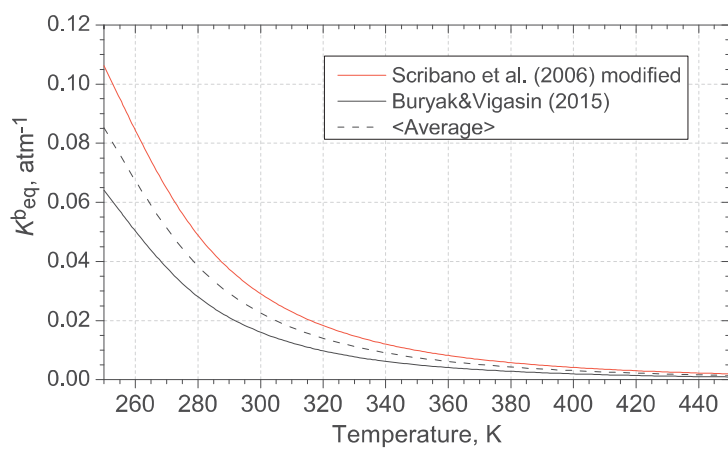


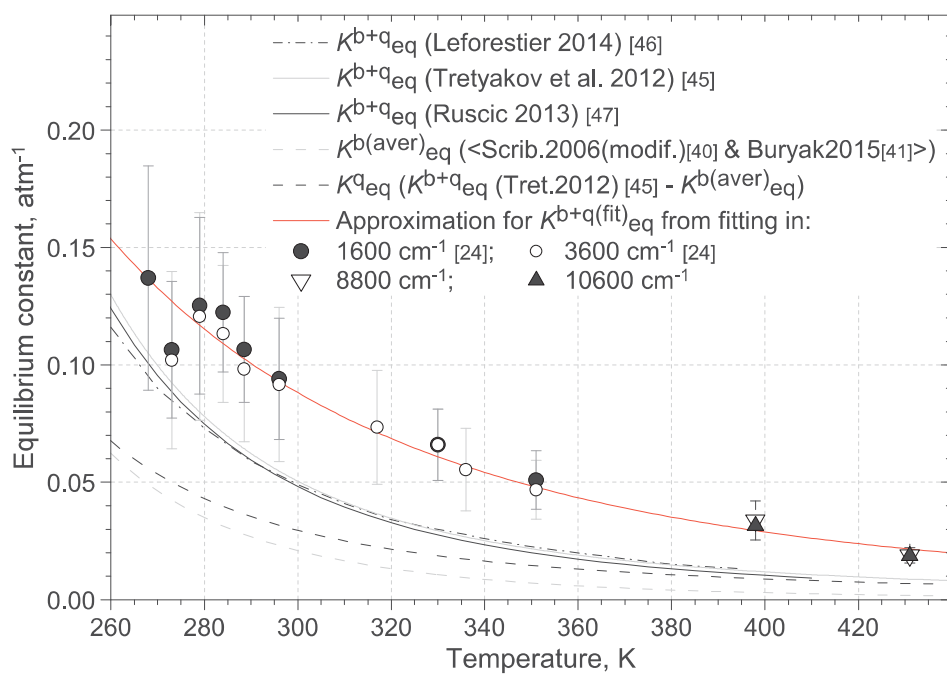




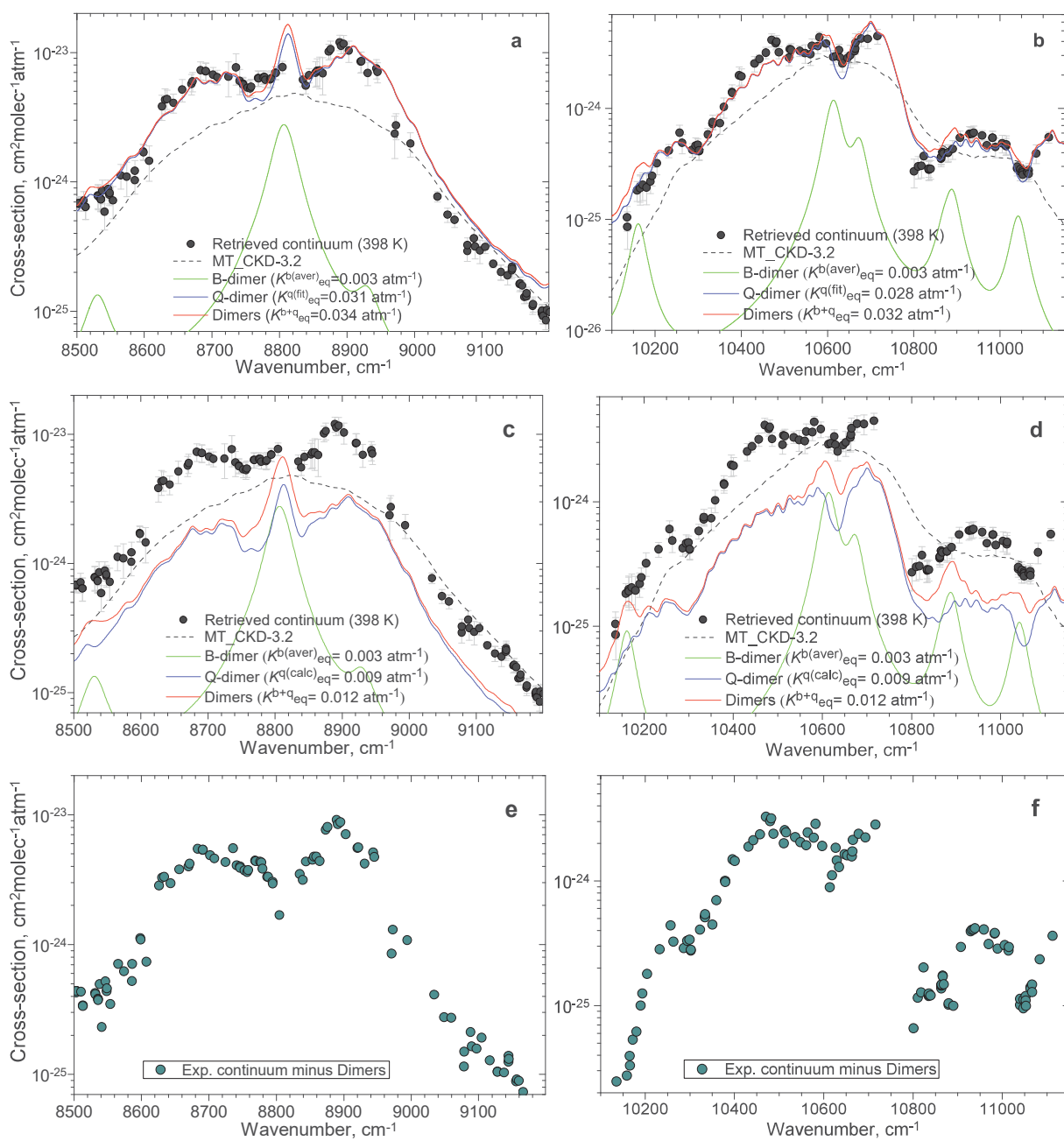








398 K



431 K

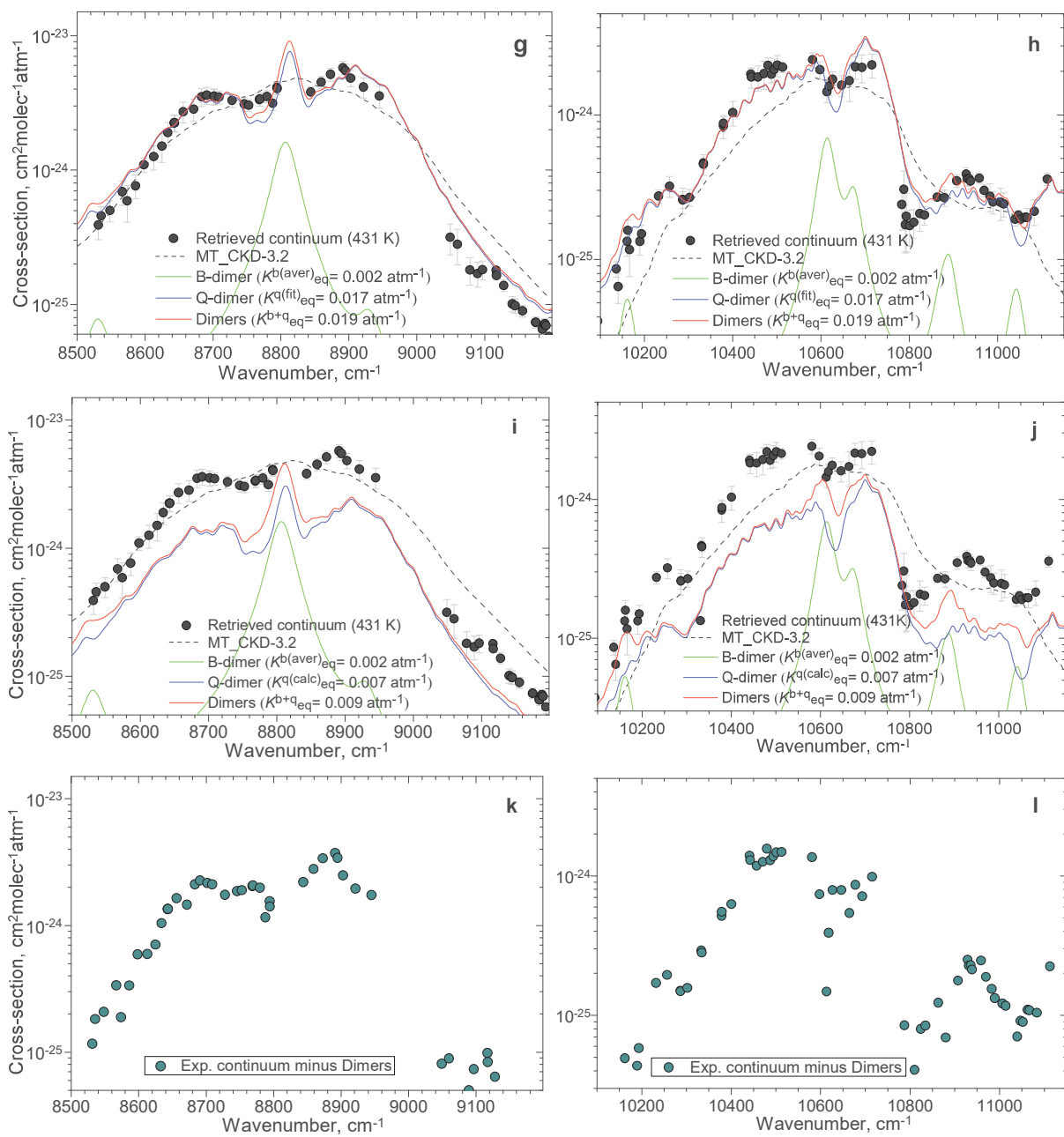


Figure 10

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