

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

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1 Water vapour self-continuum in near-visible IR absorption bands: 2 Measurements and semiempirical model of water dimer absorption

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13 14 Abstract

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

33
34 **Keywords:** continuum absorption, water vapor, absorption band, water dimer, line wings, semiempirical
35 model

36 37 1. Introduction

38 As one of the main gaseous absorbers of solar radiation, water vapour plays an important role
39 in radiative processes occurring in the Earth's atmosphere. Positive feedback between water vapour
40 concentration and temperature of the Earth's surface significantly affects the weather and climate of
41 the Earth. Part of the water vapour absorption, the so-called water vapour *continuum*, has been a
42 special subject of study since it was first measured in the mid-infrared atmospheric window (8–14
43 μm) in 1918 [1]. Whilst we have a good understanding of the mechanisms responsible for water
44 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 dimers¹ (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

¹Bound (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 H₂O pairs²—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 χ -
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^{−1} (1.13 and 0.94 μ m) using laboratory observations. To our
127 knowledge these are the first reported measurements of the self-continuum in these bands. These

² 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 cm^{-1} (6.25 and 2.7
 130 μm) 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.

140

141 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 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 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

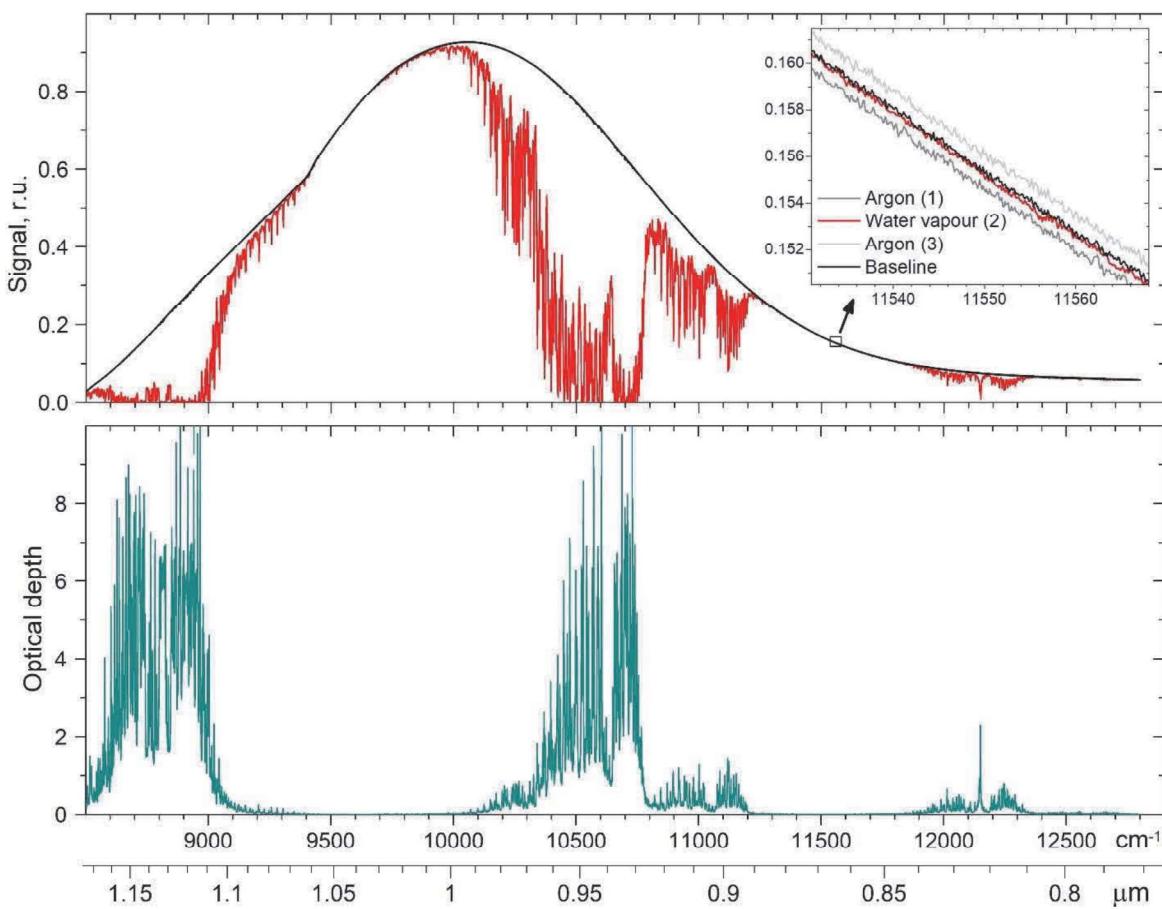
163 **Table 1** Thermodynamic conditions and configuration of pure water vapour absorption spectra measurements

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

164

165 * The pressures given here are the spectroscopically-adjusted values using the method described in Section 3.2.
 166 The arrows indicate the reduction (↓) or increase (↑) due to this adjustment.

167 The experimental optical depth of water vapour absorption $\tau(v, T)$ at wavenumber v and
 168 temperature T was derived from the Beer–Lambert law. An example of an optical depth spectrum of
 169 water vapour in the spectral region investigated is shown in Fig.1.
 170



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

179 Deriving the water vapour continuum absorption from high-resolution absorption spectra first
 180 requires the calculation and subtraction of the local contribution from water monomer lines. These
 181 calculations were made using the LBL_{IAO} line-by-line program [34]. The local line contributions were
 182 calculated within 25 cm⁻¹ from the centre of each Lorentzian line without the CKD “plinth”. Water
 183 vapour line parameters were taken from HITRAN-2016 [35]. The continuum data beyond 11150 cm⁻¹
 184 demonstrate weak values compared to the noise level; therefore, only the 8800 and 10600 cm⁻¹
 185 absorption bands are investigated. The retrieval of the water vapour continuum at higher
 186 wavenumbers requires more sensitive measurements, for example, using the CRDS technique [36].
 187

188

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 *3.1.2 A quasi-random error due to uncertainties in spectral line parameters used for the
 200 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 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

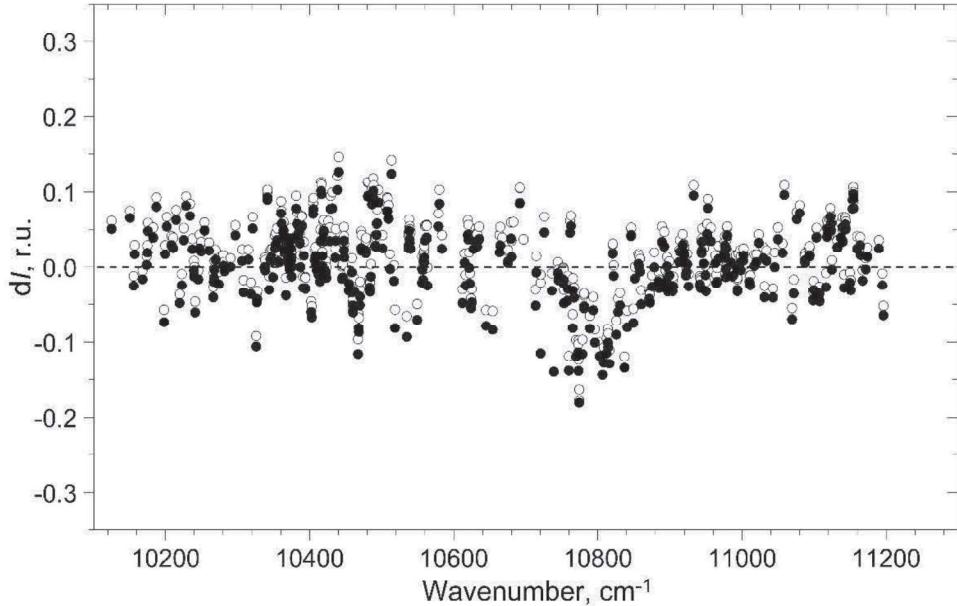
232 those calculated line-by-line using the HITRAN-2016 parameters within a distance of a few
 233 halfwidths from the line centre. Figure 2 shows an example of a distribution of relative deviation for
 234 each selected i-th line ($\delta I(v_i)$) in the investigated spectral region calculated using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

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

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



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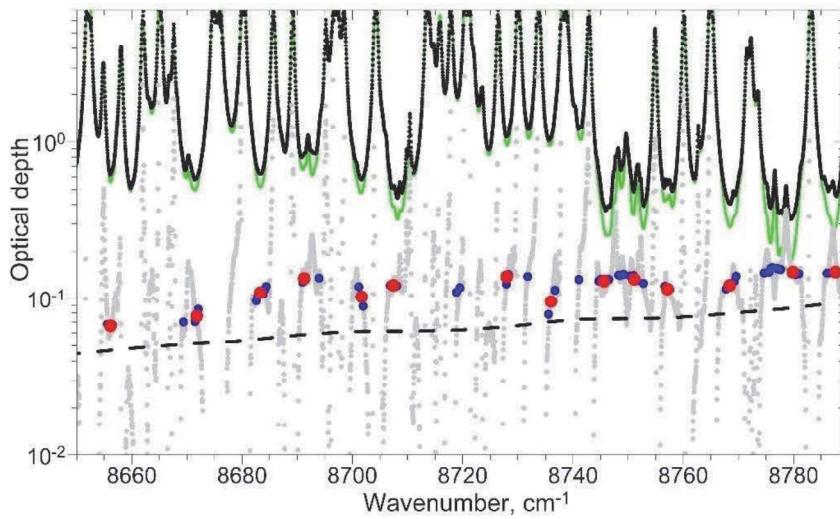
250 **Fig. 2.** Relative deviation of line intensities in the spectral region under investigation for measurements at 431K and 2070
 251 mbar: empty circles – before pressure adjustment (2039 mbar), black points – after pressure adjustment (increased by
 252 1.5%).

253

254 **4. Retrieval of the water vapour continuum absorption**

255 At the first stage of the analysis, the water vapour continuum optical depth $\tau_c(v)$ was derived as
 256 a difference between the experimental optical depth spectrum $\tau(v)$ (see Section 2) and the cumulative
 257 local contribution of water monomer lines $\tau_{\text{mon}}(v)$ calculated with the line-by-line technique [34]. An
 258 example of the preliminary retrieval of the continuum absorption is given in Fig.3 (grey points).
 259 Fluctuations of the continuum at frequencies corresponding to water monomer line centres are caused
 260 by uncertainties in spectral line parameters. Generally, the retrieval of the continuum is not possible
 261 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 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



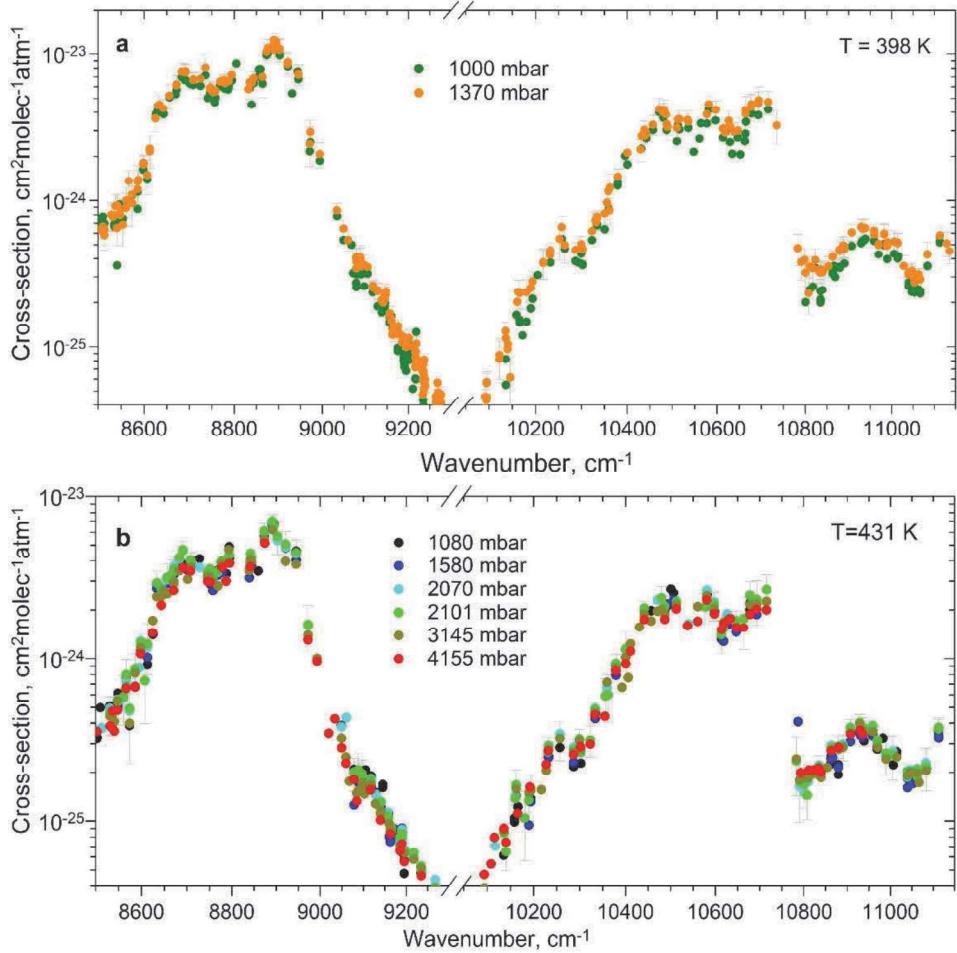
277
 278 **Fig. 3.** Example of the continuum absorption spectrum retrieved from the experimental data (431K, 1080 mbar):
 279 measured absorption spectrum of pure water vapour($\tau(v)$, black points), MT_CKD-3.2 model (dashed line), calculated
 280 spectrum of the local line absorption $\tau_{\text{mon}}(v)$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

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

286

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

287 where ρ_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, $\alpha(v)$ 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).
 291



292

293

294 **Fig. 4.** Cross-section spectra of the water vapour continuum absorption obtained using eq. (2) for two pressure sets: 1000
295 and 1370 mbar at 398 K (a) and six pressures from 1080 to 4155 mbar at 431 (b) K. The error bars are given for the
296 continuum cross-section spectra corresponding to 1370 mbar, 398 K (a), and 2101 mbar, 431 K (b).

297

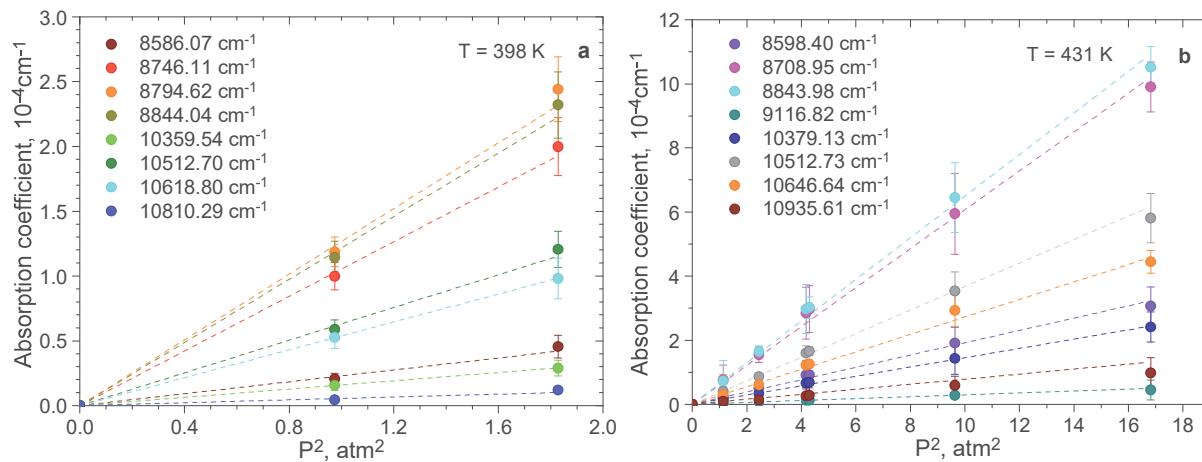
298 A linear fitting was performed to confirm the pressure-squared dependence of the measured
299 water vapour continuum absorption. The continuum absorption coefficients $\alpha(v)$ versus P^2 are
300 presented in Fig. 5 for some microwindows. There is good agreement between the experimental
301 points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

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

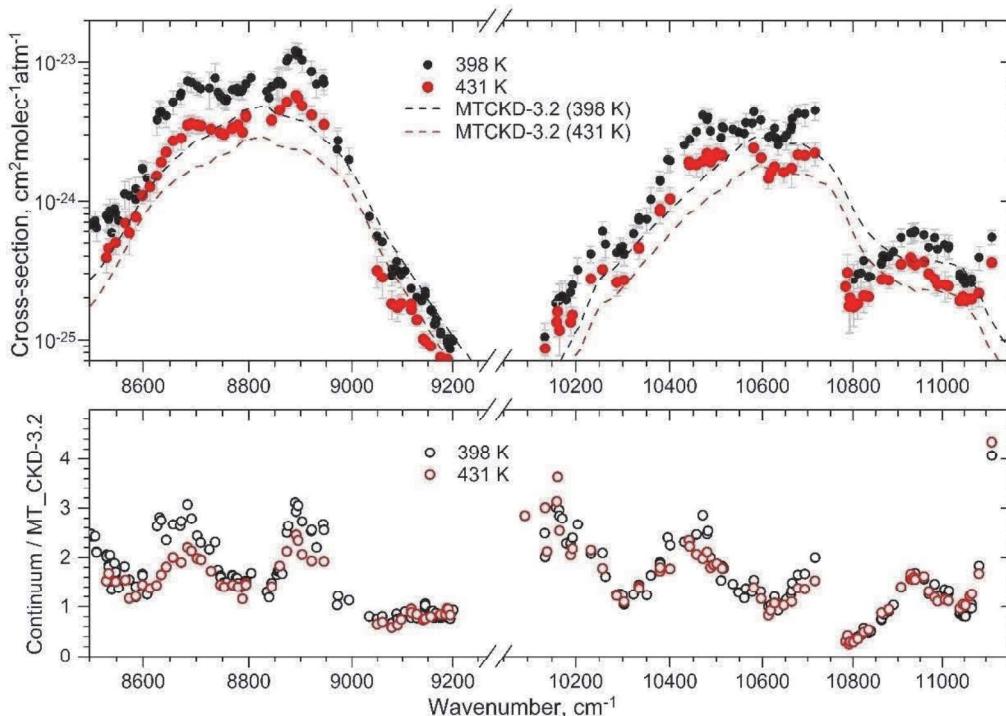
316 We acknowledge that MT_CKD was not designed for application at such high temperatures, as
 317 it was intended for use in atmospheric conditions, although as noted in Section 1, the temperature
 318 dependence was defined using measurements at elevated temperatures at lower wavenumbers.

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 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:

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

343 where K_{eq}^b and K_{eq}^q are the equilibrium constants of b- and q-dimers (in $[\text{atm}^{-1}] \equiv [\text{n}_{\text{dimers}}/\text{n}_{\text{monomers}}$ per
 344 1 atm of water monomers]); S_i^b is the intensity of i-th subband of b-dimers [cm/dimer]; S_i^q is the
 345 intensity of i-th line of q-dimers [cm/dimer]; $f_i^b(\Delta\nu_i, \gamma^b)$ and $f_i^q(\Delta\nu_i, \gamma^q)$ are Voigt profiles [cm]
 346 with halfwidths at half-maximum intensity γ^b and γ^q [cm^{-1}] of b- and q-dimers, respectively; $\Delta\nu_i$ is the
 347 distance from the centres of b-dimer subbands; $\Delta\nu_j$ [cm^{-1}] is a distance from q-dimer line centre. The
 348 calculation was carried out using the LBL_{IAO} 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 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 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, cm^{-1}	Intensity, cm/molec
$ 0>_f 2>_b 1>$	8530.5	2.35E-21
$ 20>_+ 1>(70\%)+ 11>_+ 1>(16\%)$	8754.9	6E-22
$ 2>_f 0>_b 1>(63\%)+ 1>_f 1>_b 1>(22\%)$	8804.8	7E-21

$ 20> 1>$	8806.9	5.5E-20
$ 1>_f 1>_b 1>(66\%)+ 2>_f0>_b 1>(25\%)$	8930.1	1.9E-21
$ 11>_+ 1>(74\%)+ 20>_+ 1>(18\%)$	9006.9	4.85E-24
$ 0>_f2>_b 2>(69\%)+ 0>_f3>_b 0>(13\%)$	10057.5	2.65E-22
$ 0>_f3>_b 0>(80\%)+ 0>_f2>_b 2>(12\%)$	10161.1	1.95E-21
$ 30>_+ 0>(77\%)+ 21>_+ 0>(9\%)$	10601	1.85E-21
$ 3>_f0>_b 0>(67\%)+ 2>_f1>_b 0>(12\%)$	10611	6.5E-21
$ 30>_+ 0>$	10615.3	1.8E-20
$ 1>_f2>_b 0>(68\%)+ 3>_f0>_b 0>(15\%)$	10673.7	9.5E-21
$ 21>_+ 0>(80\%)+ 30>_+ 0>(10\%)$	10869.7	8E-22
$ 2>_f1>_b 0>(74\%)+ 1>_f2>_b 0>(15\%)$	10889.1	3.5E-21
$ 21>_+ 0>$	11042	2.25E-21

373

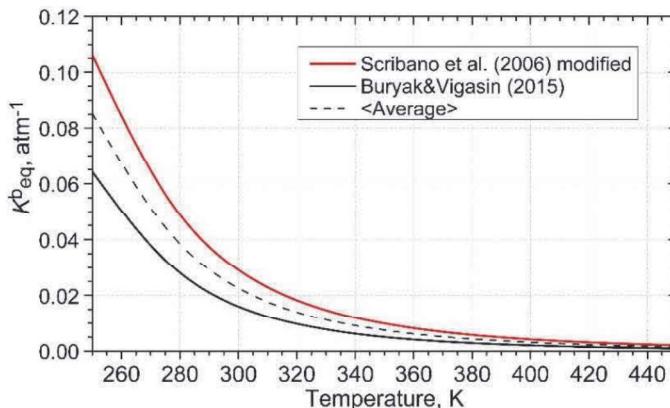
374 * According to the notation [28], $|x>_f|y>_b|z>$ and $|xy>_{\pm}|z>$ label the vibrational modes in the donor and acceptor water unit respectively.
 375 Here, x and y denote number of the vibrational quanta respectively in the free ('f') and bound ('b') OH-stretching mode in the donor
 376 unit, z is the quanta in the H_2OH_b bending mode, while “ \pm ” refers to the symmetry of the stretching vibrations in the acceptor unit.
 377

378 Quasibound dimers, which can be considered as a transitional state between free-pairs and b-
 379 dimers, have not been studied as much as the bound states. Therefore, a very simple approximate
 380 model of q-dimer lines was used here. In a similar way to [9], the q-dimer absorption spectrum was
 381 simulated as a sum of strongly broadened water monomer lines with doubled intensity S_i (i.e.
 382 $S^q_i = 2S_i$). Strong broadening occurs because the lifetime of q-dimers is rather short ($\sim 10^{-12}$ s). The
 383 halfwidth of q-dimer lines was set to 10 cm^{-1} , which corresponds to estimates of their average
 384 lifetime (see [9]). Intensities of q-dimer lines were assumed to be equal to double the intensities of
 385 the corresponding water monomer lines, as an approximation for two slightly interacting water
 386 monomers in a short-lived metastable state. For simulation of the q-dimer spectrum, intensities and
 387 centres of monomer lines were taken from the HITRAN-2016 database [35]. It was shown that the
 388 total dimer spectrum agrees well with the measured continuum within 1600 and 3600 cm^{-1} absorption
 389 bands [9] despite using this quite simple model for the description of the q-dimer spectrum.

390 The main challenge in parameterization of the dimer model (Eq. (3)) is to determine the
 391 equilibrium constant of q-dimers. Direct quantum-chemical calculations of this value, especially for
 392 the high temperatures observed here, are not available at present. In this work, an attempt was made
 393 to derive both K^b_{eq} and K^q_{eq} values by fitting the model (Eq. (3)) to the retrieved continuum within
 394 8800 and 10600 cm^{-1} absorption bands. As a result, a satisfactory spectral agreement between the
 395 dimer model and the continuum absorption spectrum was established. A significant difference in the
 396 expected contribution of b- and q-dimers at the measurement temperatures was also observed, with a
 397 strong prevalence of q-dimers. This result supports the conclusion made on the basis of the statistical
 398 approach [19,21] for the temperature dependence of K^b_{eq} and K^q_{eq} . However, K^b_{eq} values derived from
 399 this fitting were characterized by significant estimated errors that exceed 100% in some cases. This is
 400 due to the very small relative contribution of b-dimers to the total absorption at the investigated
 401 temperatures, so that a simultaneous fitting of b- and q-dimer spectra to the continuum leads to large
 402 estimated errors in the derived K^b_{eq} values and in the fitting itself.

403 Currently two relatively recent independent estimates of K^b_{eq} temperature dependence are
 404 available [40,41]. The first [40] requires recalculation adjusted for a more accurate value of the
 405 dissociation energy obtained from measurements [44] ($D_0^{\text{new}} = 1105 \text{ cm}^{-1}$ instead of $D_0 = 1234 \text{ cm}^{-1}$
 406 used in [40]). In our work, the adjusting factor $e^{(D_0^{\text{new}} - D_0)/kT}$ was applied to K^b_{eq} from [40]. The
 407 available calculated temperature dependences of K^b_{eq} (Fig.7, red [40] (modified) and black [41] (with
 408 $D_0 = 1105 \text{ cm}^{-1}$) solid curves) noticeably differ from each other at low temperatures. Moreover, both
 409 estimates are partially confirmed by different experimental data at temperature up to 350 K (see, for
 410 example, Fig.6 (left panel) in [24]). Therefore, in the next step, the average value of these two

411 estimates (further denoted as $K^{b(\text{aver})}_{\text{eq}}$) 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^q_{eq} values as a result of fitting the dimer model (Eq. (3)) to the retrieved continuum
 415 spectra with $K^{b(\text{aver})}_{\text{eq}}$ values from theoretical calculations (Table 3a, column 5) using the least square
 416 method. The rms deviation of K^q_{eq} 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^b_{eq} (see details above).

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

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

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

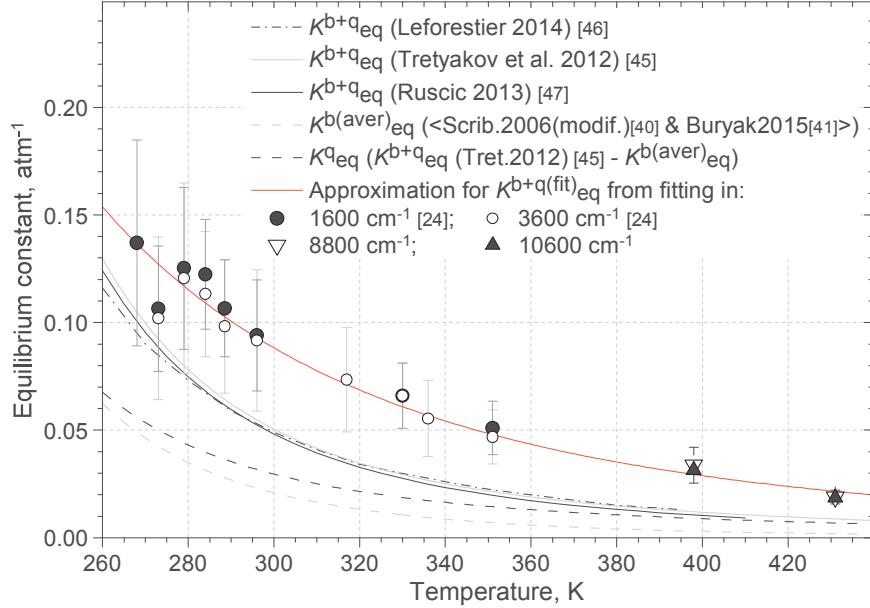
430 6. Discussion

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

434
$$K_{\text{eq}}^{b+q} = K_{\text{eq}}^b + K_{\text{eq}}^q. \quad (4)$$

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

other (see Fig.8, solid grey, solid black, and dash-dot black curves). In this work, we apply the temperature dependence of K^{b+q}_{eq} derived from the virial equation of state for real gases, using highly accurate measurements of water vapour thermodynamic properties [45]. The difference between K^{b+q}_{eq} [45] and $K^{b(aver)}_{eq}$ was taken to get approximate temperature dependence of $K^{q(calc)}_{eq}$ (see black dashed curve in Fig.8 and values in column 6 of Tab.3b). Column 5 in Tab.3b contains the values of $K^{q(fit)}_{eq}$ obtained as a result of the dimer model fitting to the retrieved water vapour self-continuum 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 cm^{-1} bands (black and white circles) [24]; K^{b+q}_{eq} obtained from the fitting within 8800 and 10600 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 cm^{-1} bands [24] and at elevated temperatures within 8800 and 10600 cm^{-1} absorption bands
470 was interpolated in this work using the empirical fit

471

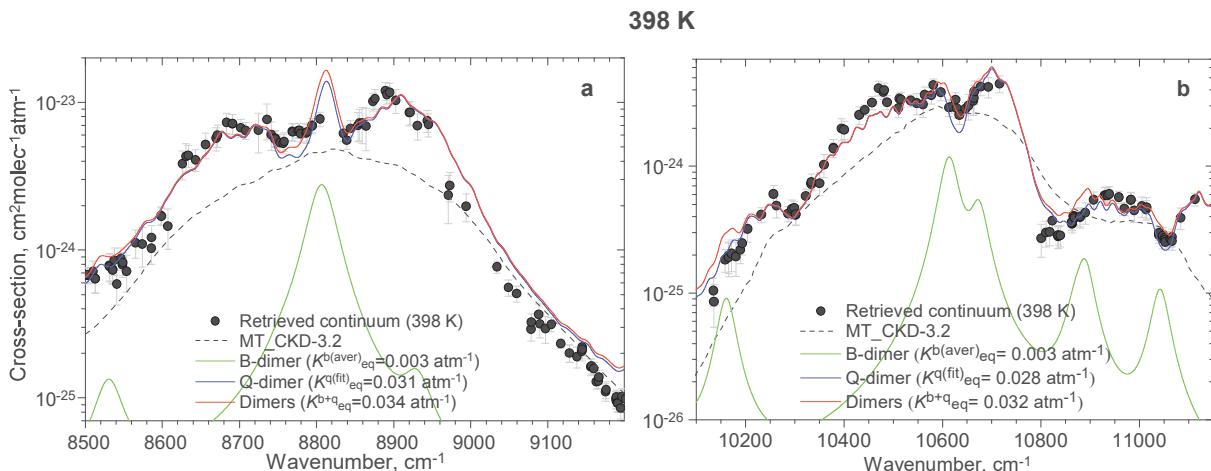
$$K_{eq}^{b+q}(T) = 3.717 \cdot 10^8 \cdot T^{-3.886}. \quad (5)$$

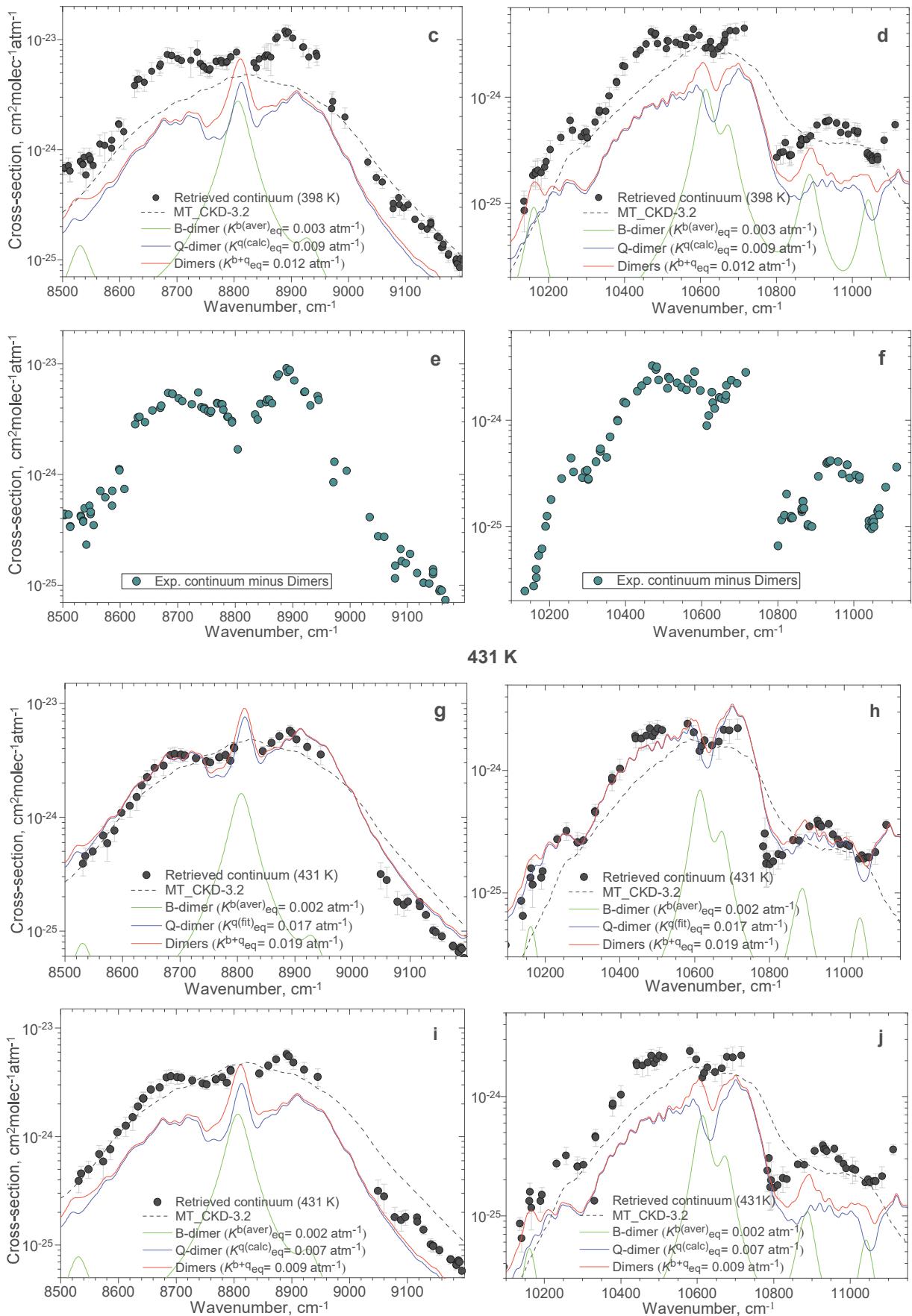
472 This can be considered as the temperature dependence of some *effective* total dimerization constant
 473 (solid red curve in Fig. 8); i.e. it is the constant that gives a satisfactory description of spectral
 474 behaviour and strength of the water vapour self-continuum in the investigated spectral 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”.

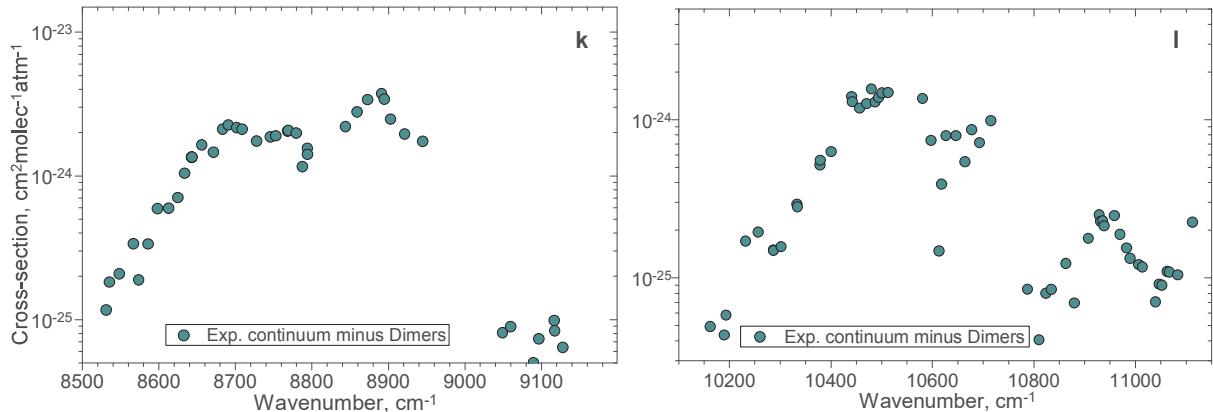
479 The effective equilibrium constant $K^{b+q(\text{fit})}_{eq}$ obtained in this work is a factor of 1.5-2.5 greater
 480 than values of K^{b+q}_{eq} from prior estimates [45–47] across the entire temperature range. This means
 481 the best fitting of the dimer model (Eq. (3)) requires a larger quantity of water dimers than can be
 482 objectively explained at the considered thermodynamic conditions (according to the independent
 483 estimates), and it is K^q_{eq} 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⁻¹ band at 296 K reached
 487 a broadly similar conclusion, finding a factor of about 1.35 greater $K^{b+q(\text{fit})}_{eq}$ (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 $K^{q(\text{fit})}_{eq}$ in our current fitting that
 496 leads to the overestimation of the total $K^{b+q(\text{fit})}_{eq}$.

497 Fig. 9 (c,d,i,j) contains the simulated water dimer absorption spectra using the values of
 498 $K^{b(\text{aver})}_{eq}$ (Table 3a, 5 column) and $K^{q(\text{calc})}_{eq}$ (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).

503







504 **Fig. 9.** Result of the water dimer model (Eq. (3)) fitting within the 8800 cm^{-1} (left panels) and 10600 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 at
510 431 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.

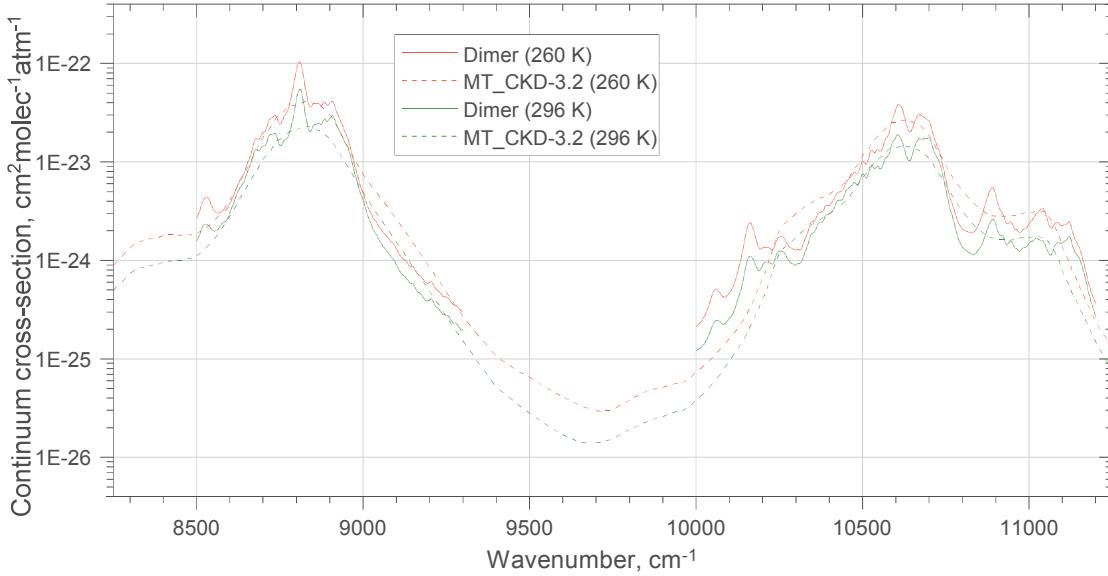
514

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 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 H_2O 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}_{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 $\sim 1.5\text{-}2$ 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}_{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 each 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

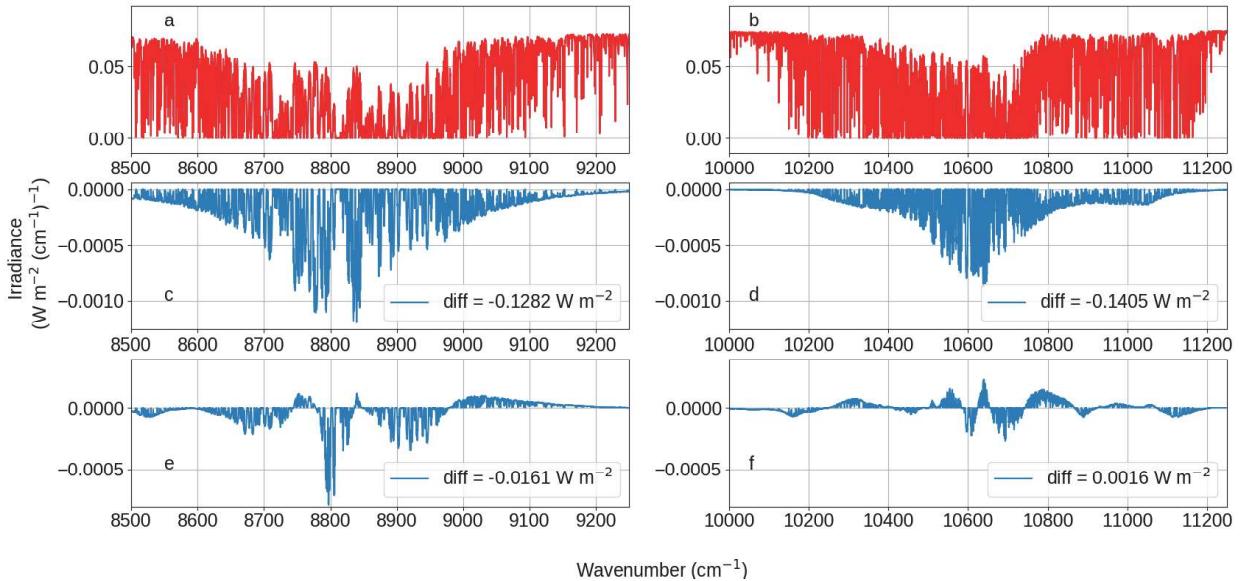
548

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

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 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 H₂O, CO₂ (at 380 ppmv), CH₄ (1.7 ppmv), O₂, N₂ and O₃. 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 ~ 0.26 W m⁻² in MLS conditions compared
 568 to the no-continuum case across the 8500-9250 cm⁻¹ and 10000-112000 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 ~0.014 W m⁻², but as high as ~0.46 W m⁻² for TRO. This makes up ~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 cm⁻¹ (panels a, c and e) and 10000-11200 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} 587 and $I_{no\ self-continuum}$ 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 cm⁻¹ region) between the two in this case is relatively small (roughly 0.021 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 ~12.5% in the 8500-9250 596 cm⁻¹ region, with a much smaller decrease (~1%) in irradiance in the 10000-11200 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 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 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 ~ 8530 and 10160 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 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 b) 10000-11200 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 * Values are in W m^{-2} integrated over each band. Values in brackets indicate the percentage change in the surface
 630 irradiance due to self-continuum absorption within each band using the dimer-based model rather than MT_CKD-3.2. A
 631 negative number indicates that the surface irradiance has decreased (i.e. absorption has increased) when making this
 632 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 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 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 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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685

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845

846 Appendix

847

848 **Table 1.** Cross-section absorption, $C_s(v)$ [$\text{cm}^2 \text{molec}^{-1} \text{atm}^{-1}$], of water vapour self-continuum experimentally
849 retrieved in this work at 398 and 431 K within 8800 and 10600 cm^{-1} absorption bands.

398 K						431 K					
v, cm^{-1}	$C_s(v)$	$C_{\text{err}}(v)$									
8502.76	6.85E-25	8.23E-26	10135.45	1.04E-25	2.62E-26	8531.26	3.9E-25	8.61E-26	10052.73	2.41E-26	3.01E-27
8503.12	6.73E-25	8.19E-26	10136.23	8.55E-26	3.19E-26	8535.51	4.57E-25	7.71E-26	10094.07	3.74E-26	7.38E-27
8503.18	6.84E-25	8.23E-26	10158.86	1.83E-25	3.70E-26	8548.44	5.00E-25	8.92E-26	10136.20	8.61E-26	1.06E-26
8510.23	7.16E-25	1.25E-25	10165.49	1.97E-25	5.53E-26	8566.64	6.90E-25	1.42E-25	10140.36	6.48E-26	1.51E-26
8512.94	6.43E-25	1.30E-25	10165.88	1.91E-25	5.63E-26	8573.81	5.89E-25	1.80E-25	10160.61	1.33E-25	2.81E-26
8513.09	6.40E-25	1.30E-25	10171.94	2.05E-25	5.72E-26	8586.10	7.64E-25	1.52E-25	10162.35	1.59E-25	2.86E-26
8531.32	7.85E-25	1.66E-25	10180.58	1.94E-25	5.81E-26	8598.40	1.09E-24	1.36E-25	10166.23	1.17E-25	4.08E-26
8531.69	7.75E-25	1.65E-25	10189.74	2.19E-25	4.83E-26	8612.80	1.26E-24	2.58E-25	10189.83	1.33E-25	2.64E-26
8535.36	7.42E-25	1.44E-25	10193.60	2.47E-25	4.69E-26	8624.98	1.51E-24	3.64E-25	10193.45	1.50E-25	2.28E-26
8535.51	7.36E-25	1.44E-25	10204.45	3.20E-25	6.90E-26	8633.68	1.90E-24	3.70E-25	10232.14	2.74E-25	2.80E-26
8535.60	7.32E-25	1.45E-25	10232.14	4.15E-25	5.68E-26	8643.08	2.24E-24	3.17E-25	10256.85	3.21E-25	5.20E-26
8537.83	8.53E-25	1.80E-25	10256.82	6.04E-25	1.00E-25	8643.17	2.24E-24	3.17E-25	10286.62	2.59E-25	3.37E-26
8541.11	5.89E-25	1.64E-25	10263.09	4.88E-25	9.67E-26	8643.30	2.25E-24	3.16E-25	10286.77	2.58E-25	5.29E-26
8546.57	8.81E-25	1.52E-25	10286.65	4.23E-25	5.84E-26	8656.13	2.71E-24	4.71E-25	10302.29	2.68E-25	3.62E-26
8548.44	7.99E-25	1.45E-25	10294.42	4.62E-25	8.09E-26	8671.47	2.84E-24	5.23E-25	10333.50	4.63E-25	4.14E-26
8548.68	8.21E-25	1.46E-25	10299.28	4.70E-25	5.95E-26	8683.28	3.51E-24	5.42E-25	10334.02	4.55E-25	7.39E-26
8553.83	7.20E-25	2.01E-25	10302.29	4.13E-25	7.27E-26	8690.75	3.61E-24	5.18E-25	10378.85	8.37E-25	1.54E-25
8565.37	1.12E-24	2.43E-25	10302.47	4.17E-25	7.23E-26	8701.60	3.53E-24	4.79E-25	10379.13	8.74E-25	9.39E-26
8573.87	1.10E-24	3.27E-25	10322.60	5.81E-25	7.98E-26	8701.66	3.53E-24	4.78E-25	10400.43	1.03E-24	2.00E-25
8585.92	1.03E-24	2.26E-25	10333.78	7.29E-25	7.12E-26	8708.95	3.48E-24	3.86E-25	10441.20	1.91E-24	1.69E-25
8586.07	1.22E-24	2.48E-25	10333.93	7.22E-25	7.52E-26	8727.97	3.29E-24	3.67E-25	10442.34	1.82E-24	2.92E-25
8598.37	1.72E-24	2.39E-25	10334.14	7.53E-25	1.14E-25	8745.99	3.10E-24	3.49E-25	10457.05	1.82E-24	3.59E-25
8598.85	1.70E-24	2.30E-25	10350.62	7.37E-25	1.53E-25	8752.80	3.02E-24	3.14E-25	10470.67	1.93E-24	4.29E-25
8607.14	1.45E-24	4.44E-25	10359.54	1.03E-24	2.10E-25	8768.43	3.35E-24	3.71E-25	10480.01	2.20E-24	2.84E-25
8626.03	3.83E-24	8.44E-25	10378.92	1.40E-24	2.27E-25	8769.37	3.37E-24	3.71E-25	10487.24	1.90E-24	2.43E-25
8630.64	4.31E-24	9.40E-25	10379.28	1.38E-24	1.49E-25	8779.55	3.52E-24	3.57E-25	10494.26	2.06E-24	3.72E-25
8633.74	4.37E-24	7.43E-25	10395.52	1.98E-24	3.90E-25	8787.75	3.14E-24	3.74E-25	10500.87	2.20E-24	3.63E-25
8643.17	4.08E-24	6.79E-25	10400.64	1.95E-24	3.24E-25	8794.05	4.11E-24	4.10E-25	10512.73	2.13E-24	1.83E-25
8656.13	5.16E-24	1.01E-24	10431.01	2.53E-24	4.05E-25	8794.59	4.04E-24	4.06E-25	10581.00	2.40E-24	2.92E-25
8669.69	5.71E-24	1.02E-24	10442.28	2.78E-24	2.62E-25	8843.98	3.81E-24	3.55E-25	10597.46	2.04E-24	2.84E-25
8671.41	5.98E-24	1.03E-24	10457.05	3.17E-24	3.82E-25	8859.34	4.51E-24	4.75E-25	10613.25	1.44E-24	2.27E-25
8683.28	7.30E-24	1.15E-24	10470.70	4.13E-24	5.58E-25	8873.02	5.15E-24	5.85E-25	10618.25	1.58E-24	2.11E-25
8690.87	7.15E-24	1.11E-24	10479.98	3.85E-24	4.83E-25	8891.16	5.75E-24	6.61E-25	10626.69	1.76E-24	2.21E-25
8690.96	7.17E-24	1.11E-24	10482.03	3.99E-24	5.41E-25	8894.84	5.50E-24	6.63E-25	10646.64	1.60E-24	2.65E-25
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8708.17	6.44E-24	8.43E-25	10510.41	2.87E-24	4.61E-25	8921.35	4.14E-24	7.08E-25	10677.86	2.14E-24	3.83E-25
8724.71	6.49E-24	1.95E-24	10512.70	3.42E-24	3.31E-25	8945.07	3.55E-24	6.54E-25	10693.04	2.13E-24	4.68E-25
8735.68	7.67E-24	2.08E-24	10515.78	3.37E-24	4.67E-25	9049.21	3.16E-25	8.20E-26	10715.40	2.21E-24	4.17E-25
8741.22	6.05E-24	1.33E-24	10535.78	3.29E-24	3.57E-25	9059.81	2.81E-25	8.33E-26	10783.20	2.40E-25	8.05E-26
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9089.58	3.16E-25	6.15E-26	10958.78	5.70E-25	6.23E-26	--	--	--	--	--	--
9096.85	2.95E-25	6.07E-26	10969.45	4.64E-25	5.59E-26	--	--	--	--	--	--
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9144.27	2.07E-25	2.89E-26	11014.92	4.75E-25	9.05E-26	--	--	--	--	--	--
9144.49	2.21E-25	2.94E-26	11039.59	2.86E-25	3.94E-26	--	--	--	--	--	--
9144.70	2.13E-25	2.93E-26	11039.84	2.98E-25	3.81E-26	--	--	--	--	--	--
9155.65	1.62E-25	2.05E-26	11046.83	2.68E-25	4.53E-26	--	--	--	--	--	--
9156.55	1.64E-25	1.95E-26	11047.22	2.84E-25	4.60E-26	--	--	--	--	--	--
9159.71	1.58E-25	1.63E-26	11052.31	2.74E-25	2.43E-26	--	--	--	--	--	--
9162.87	1.29E-25	1.40E-26	11052.46	2.64E-25	2.80E-26	--	--	--	--	--	--
9165.45	1.3E-25	1.49E-26	11052.73	2.53E-25	3.05E-26	--	--	--	--	--	--
9166.14	1.38E-25	1.53E-26	11062.89	2.69E-25	3.69E-26	--	--	--	--	--	--
9175.04	1.10E-25	1.50E-26	11063.16	2.65E-25	3.76E-26	--	--	--	--	--	--
9175.40	1.14E-25	1.51E-26	11066.56	2.76E-25	4.37E-26	--	--	--	--	--	--
9188.51	9.91E-26	1.18E-26	11066.68	2.56E-25	3.77E-26	--	--	--	--	--	--
9188.69	9.56E-26	1.17E-26	11083.74	3.93E-25	7.52E-26	--	--	--	--	--	--
9188.93	9.62E-26	1.16E-26	11112.82	5.48E-25	6.26E-26	--	--	--	--	--	--
9189.14	1.01E-25	1.19E-26	--	--	--	--	--	--	--	--	--
9190.44	9.25E-26	1.20E-26	--	--	--	--	--	--	--	--	--
9190.59	9.18E-26	1.21E-26	--	--	--	--	--	--	--	--	--
9194.50	8.53E-26	1.34E-26	--	--	--	--	--	--	--	--	--
9196.16	1.02E-25	1.43E-26	--	--	--	--	--	--	--	--	--
9200.35	9.83E-26	1.67E-26	--	--	--	--	--	--	--	--	--

Figure 1

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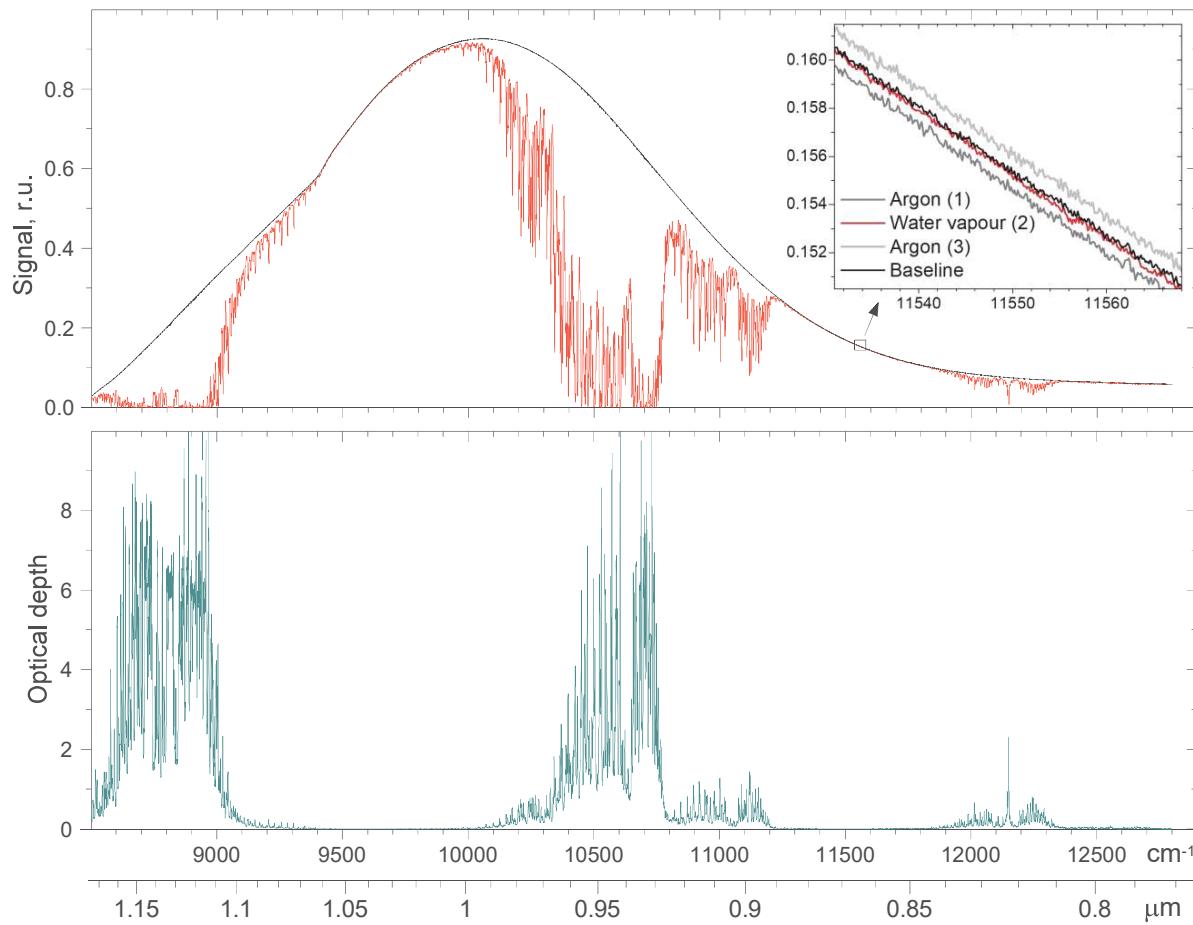
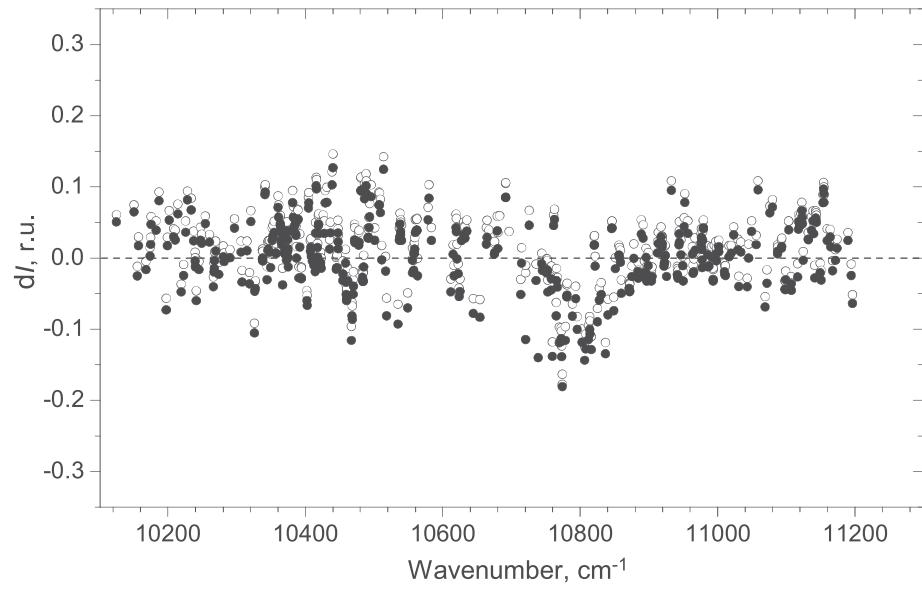


Figure 2

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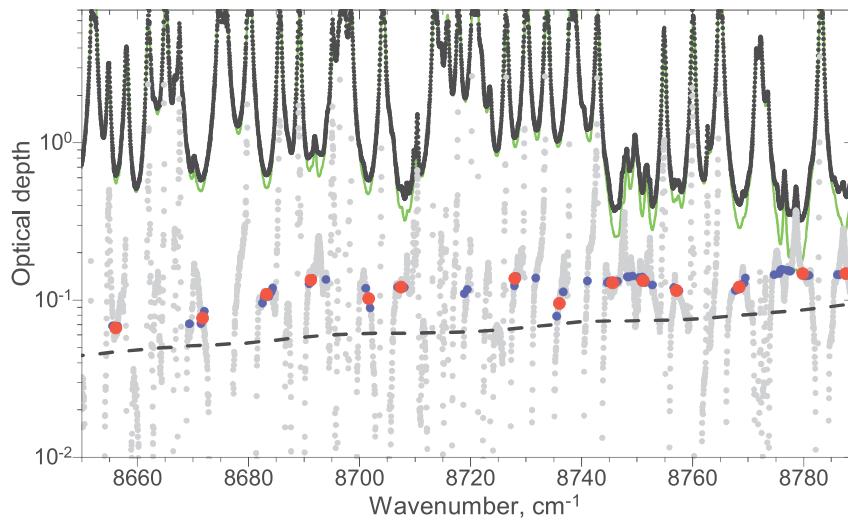


Figure 4

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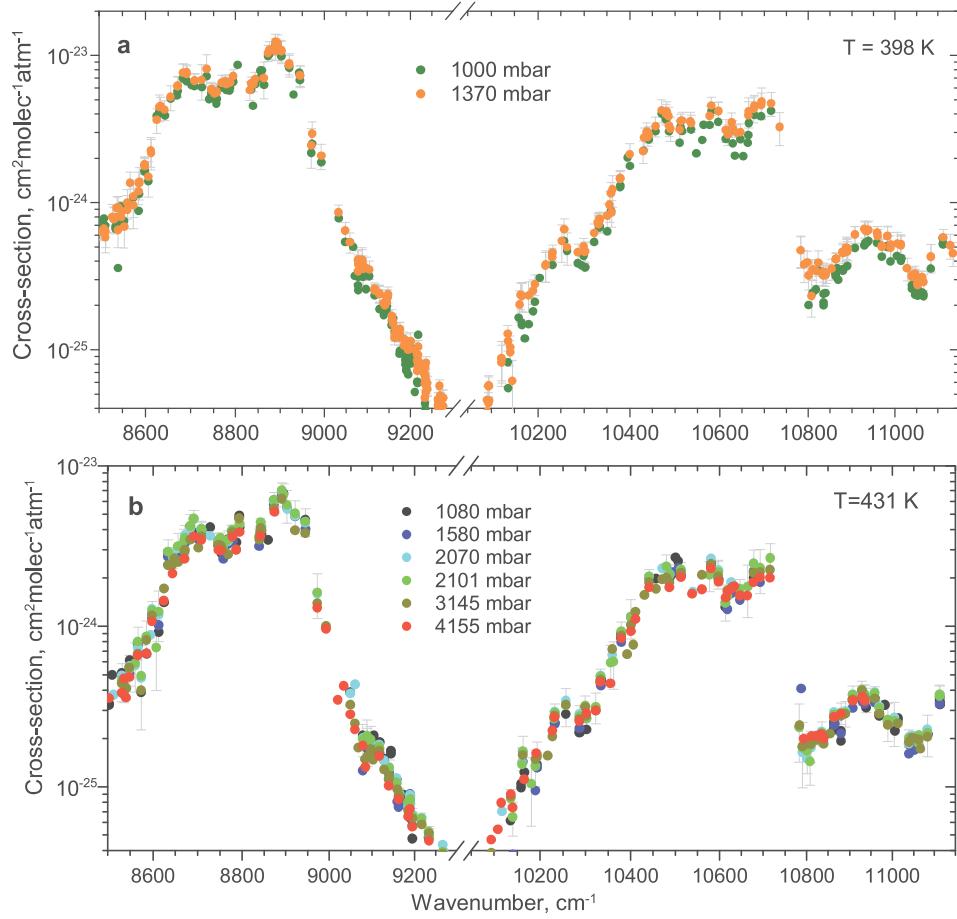


Figure 5

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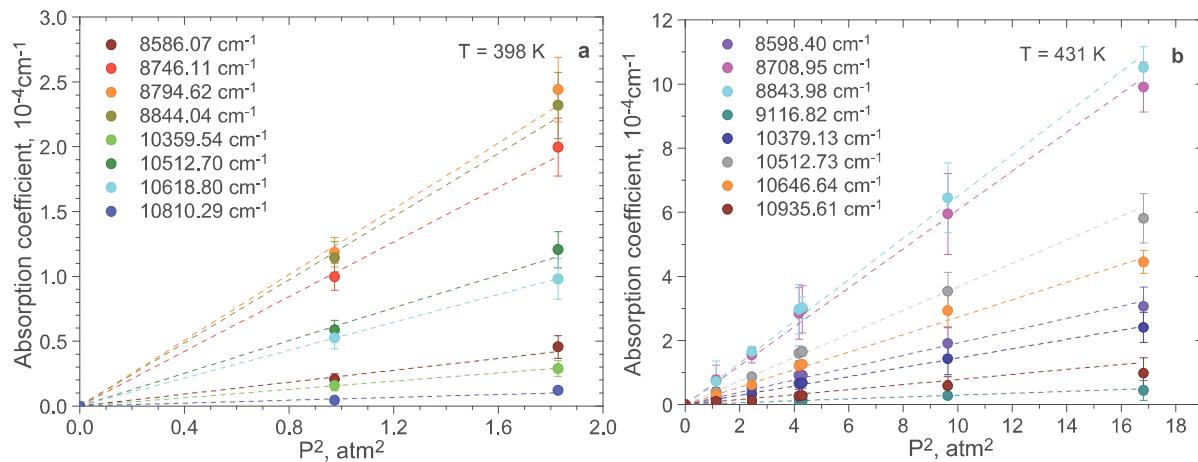
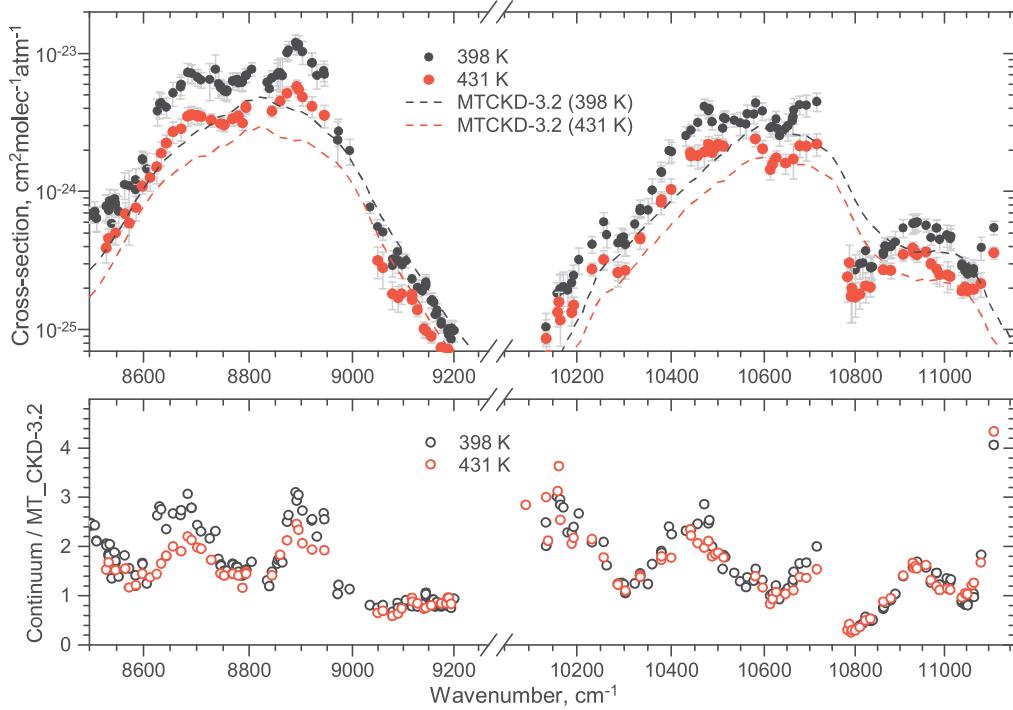
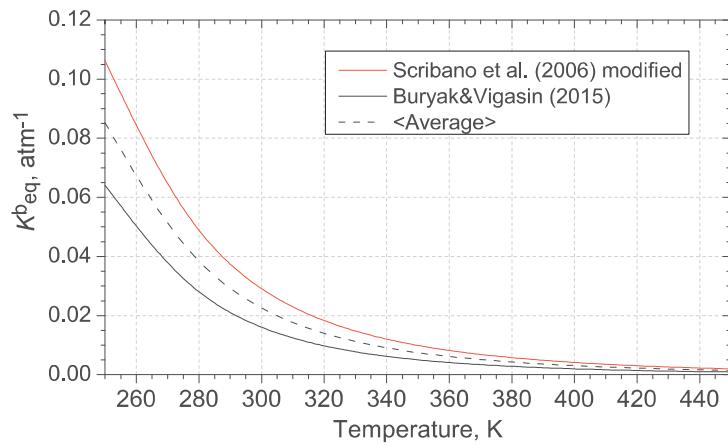
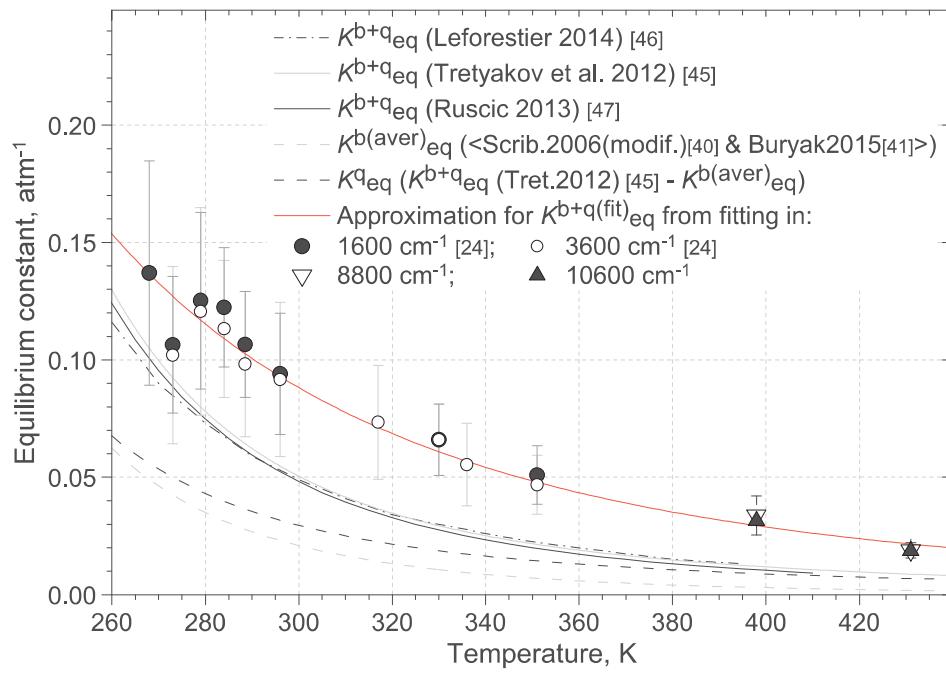


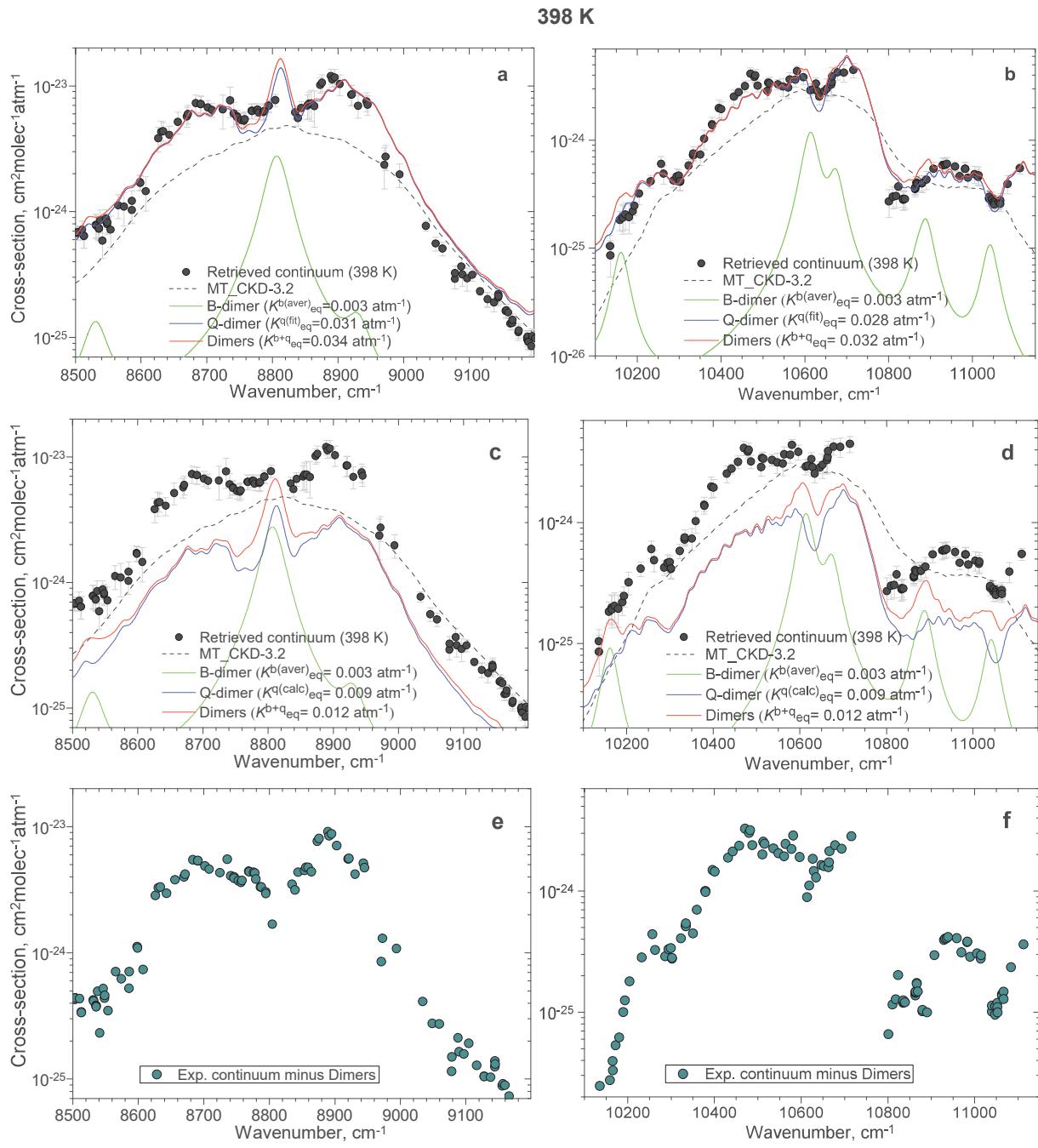
Figure 6

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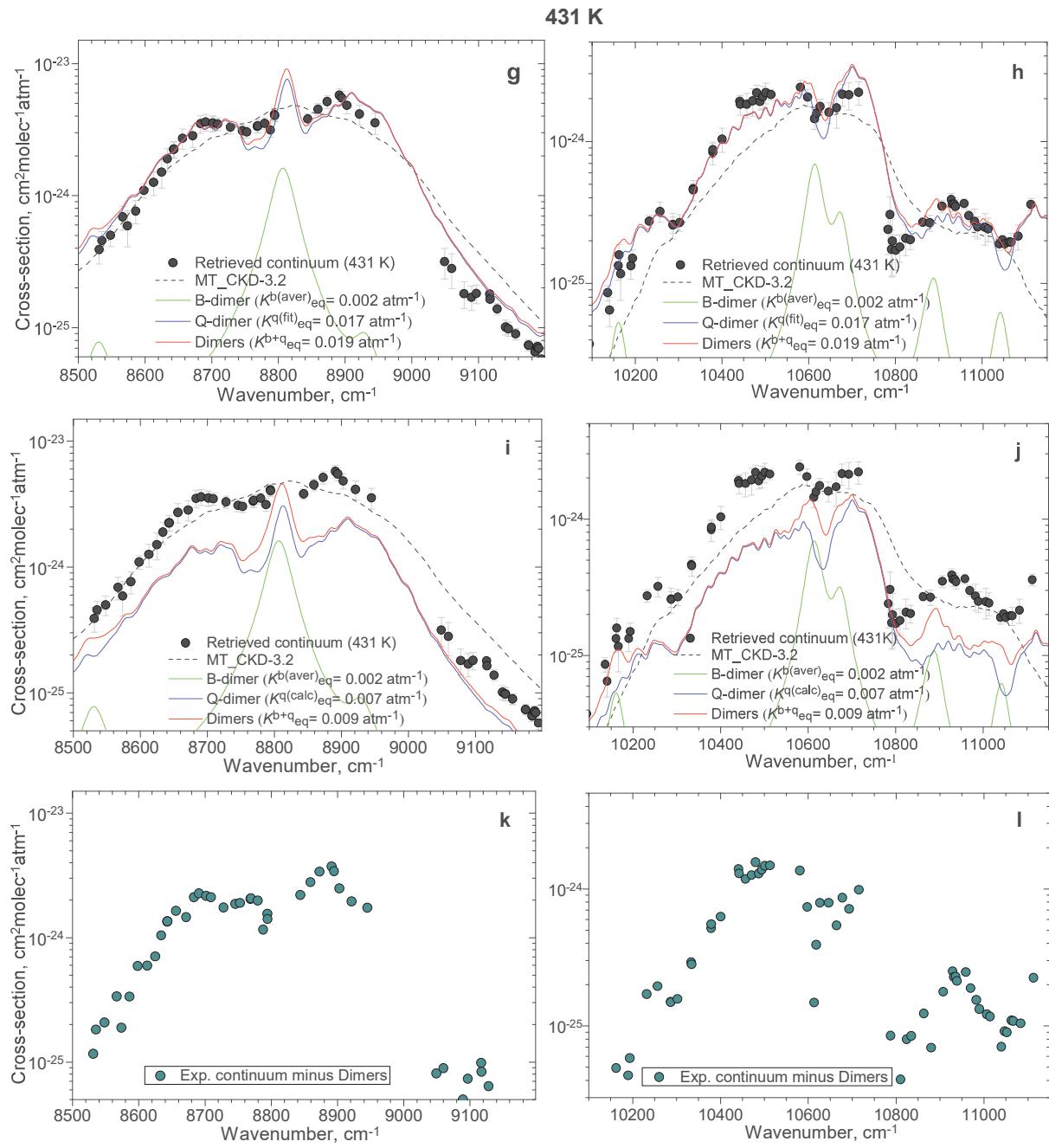


Figure 10

