Review

Evidence for the contribution of water dimers to the near-IR water vapour self-continuum

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Abstract

The nature of the water vapour continuum absorption and the possible contribution of water dimers (WD) to this phenomenon have been a matter of debate for many years. The current work presents an overview and analysis of a number of experiments, both recent and old, where spectral signatures, similar to recent theoretical predictions for WD, have been observed in *equilibrium* laboratory conditions within near-infra-red (IR) water vapour absorption bands. These experiments, in contrast to those where water complexes are usually studied in non-equilibrium and low-temperature conditions, can give direct information about the possible WD amount in atmospheric conditions. Intercomparison of the results of these works and the recent *ab initio* prediction for WD band intensities and positions testifies in favour of a significant contribution of WD absorption to the water vapour self-continuum in the centre of the strongest near-IR water vapour absorption bands.
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Keywords: Water clusters; Dimerization equilibrium constant; CKD continuum model

Contents

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1. Prehistory and introduction

Despite decades of extensive studies, the role of the *water dimer* (WD) (i.e., a complex consisting of two hydrogen-bonded water molecules (Fig. 1)) in the atmospheric radiation budget is still controversial. By different assessments WD may contribute from 0.5% to 1.5% to the total absorption of solar radiation in the atmosphere [1,2]. According to the calculation [3,4] of water *dimerization equilibrium constant* K_{eq}, that defines WD pressure p_{WD} for a given water monomer (WM) pressure p_{WM} as $p_{WD} = K_{eq}p_{WM}^2$, the value of WD radiative absorption could be even higher. WDs were also postulated as playing an important role in atmospheric chemistry, for example, in catalysing the formation of atmospheric H_2SO_4 [5].

Another point at issue associated with WD, which is the main question discussed in this paper, is the possible contribution to the water vapour *continuum absorption* (henceforth "continuum"). Discovered by Hettner [6] as a low-frequency component of water vapour absorption in the atmospheric window 8–14 μm, this phenomenon remained unexplained for 20 years, until Elsasser [7] suggested that the continuum is an accumulated *far-wing* contribution of strong water vapour spectral lines from neighbouring bands. This hypothesis was generally accepted until the end of 70 years when the strong quadratic pressure dependence of the continuum absorption (which could not be explained by the Lorentzian line profile [8] based on the impact approximation[2]) as well as the strong negative temperature dependence was detected [9,10]. In this connection, Penner and Varanasi [10] and Varanasi et al. [11] suggested that the main contribution to the *self-continuum*[3] could be due to WDs, rather than by far wings of WM lines. A similar assumption was also made by Victorova and Zhevakin [12] for the microwave spectral region. The dimer model could explain quite easily the pressure and temperature dependencies of the self-continuum absorption observed in many experiments since then [11,13–16].

Since the works [10–12] a long scientific discussion has started between adherents of the "monomer" (or "far wings") and the "dimer" explanation for the water vapour self-continuum, which continues to the present day. On the one hand, more sophisticated (than Lorentz theory) *ab initio* [17–19] and semiempirical [20,21] line-shape models have been developed, which could explain quite well the experimental facts mentioned above; because of this, the dominating role of the far wings of water vapour lines in the continuum absorption, especially in atmospheric conditions, is most commonly accepted today. On the other hand, WDs have been and are often discussed as a possible component of the water self-continuum absorption [22–33].

It is worth mentioning, however, that most of the work on the water continuum has been considered so far only for the 8–25 μm spectral region (far band wings or "atmospheric window") that is most important for the atmospheric radiation balance, but where large uncertainties in the magnitude and spectral structure of WD absorption still exist. Thus, no spectral features unambiguously assigned to WD have yet been identified in the room-temperature laboratory or in atmospheric measurements; as a consequence, all results obtained in this spectral region are not conclusive enough to either support or disprove the dimer hypothesis.

The difficulties in detecting WD absorption in the atmosphere are exacerbated also by very small WD amounts at standard conditions (no more than 0.1% of the water vapour pressure) and by strong overlapping by air-broadened WM spectral lines. That is why the spectroscopic properties of WDs, like any other clusters, were and are usually studied only in *non-equilibrium* or *non-gaseous* conditions like supersonic molecular beams or in solid matrices at very low temperatures. In all these works, absorption spectral features of WDs and higher water clusters were clearly detected and investigated at low temperatures from infra-red (IR) ($7200\,cm^{-1}$ [34], $1600–7200\,cm^{-1}$ in matrix [35,36], $3600\,cm^{-1}$ [37–41], $1600\,cm^{-1}$ [42]) to far-infrared ($140–145\,cm^{-1}$ [43], $87–108\,cm^{-1}$ [44], $70–80\,cm^{-1}$ [45], $22\,cm^{-1}$ [46]) and microwave [47,48] spectral regions. This, in turn, stimulated *ab initio* determination of the reliable water pair potential [4,49,50], as well as positions and strengths of near-IR [51,52] and millimetre and far-IR [53] WD bands.

These investigations, however, for all their importance, can give only indirect information about possible WD amount and absorption in *atmospheric* conditions. This amount is dependent on the dimerization

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[2] I.e., "instant collisions" approximation.

[3] Historically, water continuum absorption is often described as consisting of two additive components: "self-continuum" (also called "self-broadening" continuum), attributed only to the interactions between water molecules; and "foreign-continuum", attributed to the interactions between water molecules and any other ("foreign") molecule (in atmospheric conditions it is mostly N_2).
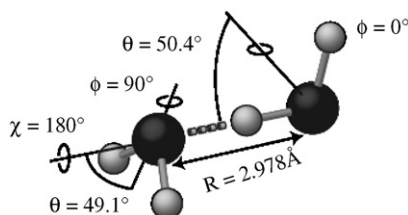
Fig. 1. Equilibrium structure of the water dimer determined from the VRT(ASP-W)III potential surface [4]. The figure is adopted from [56] (Courtesy of R. Saykally).

equilibrium constant, the value of which at near-room temperatures was a subject of big uncertainty until very recently [4,54]. Another problem of applying the low-temperature results to the atmospheric conditions is that room-temperature WD absorption signatures are expected to be rather different from those at low temperatures, because of strong overlapping of WD lines at atmospheric conditions and because of the probable strong contribution of short-lived *metastable*[4] WDs at near-room temperatures [55]. Similar to the water continuum, metastable WDs are also expected to show very broad continuum-like spectral features at standard conditions, caused by strong vibrational and pre-dissociative, and hence short-lived, WD states [40,56].

A comparison of the near-IR water vapour continuum model CKD-2.4 [21] with WD absorption features, calculated on the basis of the recent Schofield and Kjaergaard [52] *ab initio* prediction for WD band intensities and positions, is presented in Fig. 2.[5] Because of a lack of information, at present the simple Lorentz profile is used here to simulate WD band shape. Although the assumption of a simple Lorentzian line shape can overestimate WD absorption in far band wings, a discussion of these spectral regions is beyond the scope of this work and does not affect its main conclusions. The general spectral similarity of the CKD continuum model and expected WD absorption within near-IR water vapour absorption bands were mentioned in [54] and investigated in more detail in [58]. The temperature extrapolation of Curtiss et al.'s [59] data is given by

$$K_{eq} = \exp(\Delta S/R - \Delta H/RT),$$

with the enthalpy and entropy parameters: $\Delta H = -3590\,\mathrm{cal\,mol^{-1}}$, $\Delta S = -18.59\,\mathrm{cal\,K^{-1}\,mol^{-1}}$, derived in [59] from the hot steam thermal conductivity measurements, is used in Fig. 2 and throughout this paper unless stated otherwise. These parameters are on average in a good agreement with some results obtained from the theory [3,60], especially, given the existing uncertainty in theoretical prediction of these values (compare, for example, [3,4]), and, as will be shown later, produce $K_{eq}(T)$, which lies just between different theoretical and recent experimental predictions by different authors.[6]

The lack of direct experimental evidence for WD absorption in equilibrium room-temperature gaseous conditions is probably one of the reasons why, so far, known continuum models are based purely on WM line-shape theories [17–21]. The CKD continuum model [20], most widely used today in the atmospheric community, also does not employ a dimer formulation. According to the early CKD continuum definition by Clough et al. [20], the deviation of absorption in spectral line wings from Lorentzian profile was caused by finite duration of the collisions, in contrast to the impact approximation. However, because metastable WD can be described to certain degree as two water molecules undergoing extra-long collisions, it is clear that the external appearance of these two phenomena can be qualitatively very similar. Taking into account the semi-empirical character of the CKD continuum model,[7] it is evident that in some spectral regions WD absorption may be implicitly included in CKD self-continuum. The first experimental evidence in favour of this

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[4]I.e., with the total energy greater than the dissociation energy of WD ($D_0 \sim 15.7\,\mathrm{kJ/mol}$ [3]) by contrast with the *truly bound* water molecules (i.e., "true" or "stable" dimer).

[5]All line-by-line calculations in this work are performed with the code of Mitsel et al. [57].

[6]The author does not take into account here any possible temperature dependence of the thermodynamic parameters ΔS and ΔH, as the uncertainty in theoretical prediction of these dependencies is still rather large.

[7]Though the CKD-continuum is based on a rather solid physical model, it applies a few ad hoc line-shape parameters, which do not have clear relation to any physical value and are derived by fitting the CKD-model to "experimental continuum". The latter is derived as a total absorption minus "local contribution" of spectral lines [20].
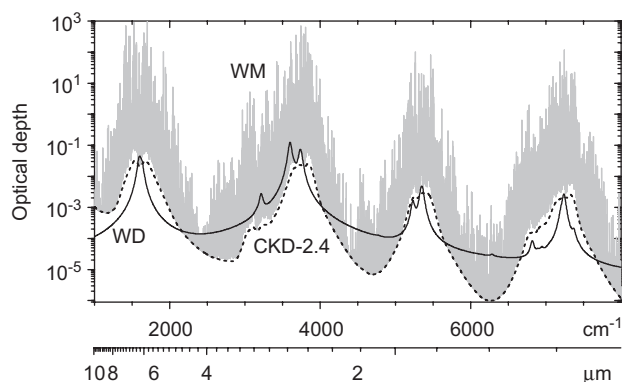
Fig. 2. Spectra of optical depth calculated for pure water vapour ($L = 10$ m, $P_{H_2O} = 15$ mbar, $T = 293$ K). WM: water monomer spectrum (grey), simulated using HITRAN-2001 [77] and CKD-2.4 [21] continuum model; CKD-2.4: continuum model separately (dashed); WD: water dimer spectrum (solid line), simulated according to the WD *ab initio* intensities and band positions [52], using WD bands width HWHM $= 25$ cm^{-1} (Lorentzian profile) and equilibrium constant $K_{eq} = 0.041$ atm^{-1} according to the Curtiss et al. [59] extrapolation (see Fig. 5).

suggestion was obtained in [54] for continuum absorption in the centre of $v + \delta$ water vapour band (~ 5300 cm^{-1}).

The most recent version of the CKD continuum model: MT_CKD [61], added a new mechanism to explanation of the water continuum. In addition to the superposition of far wings of allowed WM transitions (which, according to MT_CKD formulation, is dominant in between water vapour bands), the new model also introduced *collision-induced* absorption (dominant within water vapour bands), i.e., forbidden transitions for free water molecules, resulting from the generation of a *short-lived complex* of water vapour and colliding molecules. Although the authors of MT_CKD still prefer to explain the self-continuum only in terms of WM absorption, it is clear that the term "short-lived complex" can also be equally well attributed to the metastable WDs [55]. Moreover, the contribution of metastable WDs is often "by definition" included in the term "collision-induced absorption" together with *free–free*[8] transitions [62]. Thus, after the second mechanism was added to CKD, discussions about the possible WD contribution to the water vapour continuum may be partly semantic, unless one means to distinguish between *free–free* transitions and the *true-bound* or *metastable* WD contribution.

The possibility of any noticeable contribution of collision-induced absorption, including WDs, to the water continuum at atmospheric conditions is however strongly disputed by Tipping; at least for 1600 and 3600 cm^{-1} water vapour bands [63,64] (also personal communication, 2005, 2006). This point of view is shared by Vigasin only in respect to the *free* pair states, whose negligible role as compared with the *metastable* and *true-bound* WDs at near-room temperatures has been shown in [65,66] by preliminary statistical partitioning of the pair states in water vapour. A similar result was also obtained in [67].

A possible way to discriminate between these different phenomena in experiment (apart from the temperature dependence, usually applied to distinguish between far wings of WM lines and WD absorption in band wing spectral region [33]) can be based on the different character of the spectral signatures, they must produce. Absorption lines of truly bound WDs must be quite narrow (0.5–1 cm^{-1}) at standard conditions, assuming collision broadening (although overlapped WD lines may form spectrally unresolved continual-like features in some spectral regions; see for example the recent *ab initio* analysis [53]). Metastable dimers and free–free collisions, by contrast, must form smooth and wide spectral features with half-width of few tens of centimetres [1,68]. The spectral features of metastable dimers, however, may have some signature of WD band structure often shifted[9] as compared with more diffuse collision-induced absorption.

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[8] I.e., caused by transitions between perturbed energy levels of unbound ("free") water molecules experiencing short collisions.

[9] It is well established in low-temperature experiments that the frequencies of proton-acceptor molecule of WD are weakly shifted with respect to those of the monomer (~ 10 cm^{-1} red shift is expected for v_1 and v_3 transitions and ~ 4 cm^{-1} blue shift for v_2). A large red shift (~ 100 cm^{-1}) is expected for hydrogen-bonded O–H oscillator of proton-donor molecules, while the other O–H oscillator is quasi-free [35].

The first reports claiming detection of WD absorption in atmospheric [69] and in *equilibrium* room-temperature laboratory conditions [54] have appeared only recently. The result of [69], however, was criticized in [68] and has not been confirmed in the series of later experiments [70–72], while the result [54] still needs independent verification. On the other hand, a focused review of older works on the measurements of the water vapour continuum absorption in the *centres* of the strongest near-IR bands reveals at least two more experiments where spectral signatures, similar to those predicted for WD, have been clearly observed in equilibrium laboratory conditions. One of these works is a set of high-pressure and high-temperature measurements by Poberovsky [73,74] in the absorption bands near $3700\,cm^{-1}$ ($2.7\,\mu m$), $5350\,cm^{-1}$ ($1.87\,\mu m$) and $7250\,cm^{-1}$ ($1.38\,\mu m$) that appears to have remained unknown to the international community for a long time. The other study is the better-known measurements of Burch [75] in the spectral region $3000–4200\,cm^{-1}$, which, however, was never previously regarded as evidence of WD signature detection, apart from the recent work [76].

This paper presents an analysis and intercomparison of the results of these experiments and the recent *ab-initio* prediction [52] for WD band intensities and positions. The main aim is to show that experimental and theoretical data accumulated to date seem quite sufficient to make a firm conclusion on significant WD contribution to the self-continuum absorption, at least within strongest near-IR water vapour bands.

2. Recent laboratory measurement (2004), 5000–5600 cm^{-1}

Ptashnik et al. [54] performed high spectral resolution Fourier transform spectroscopy measurements at the Rutherford Appleton Laboratory (RAL) Molecular Spectroscopy Facility in the water vapour absorption band $5000–5600\,cm^{-1}$ ($1.785–2\,\mu m$) for two different water vapour pressures and temperatures. Fig. 3 shows the simulated WM absorption spectrum for this band for 20 mbar pure water vapour at 294 K together with the CKD-2.4 continuum model and the simulated WD signature. It is clear from Fig. 3 that the CKD continuum and WDs should form a noticeable part of the total absorption in numerous micro-windows between the WM spectral lines, and, thus, their contribution should be accessible for absorption paths larger than 10 m (i.e., optical depths $\geqslant 0.01$ in the micro-windows, which is confidently detectable with the modern Fourier spectrometers).

In [54], a path length of 128 m was used for the pure water vapour measurements at pressures $P_{H_2O} = 20$ and 98 mbar and temperatures $T = 299$ and 342 K. In both cases the residuals, calculated initially as

$$\text{"Measurement"} - \text{"HITRAN-2001(m)\_with\_CKD-2.4\_continuum"}, \tag{1}$$

were found to be similar.

Calculation of the water vapour absorption coefficient with the spectral line parameters in HITRAN was performed according to the standard formula

$$\alpha(v, T) = N_{H_2O} \sum_i S_i \frac{Q_{VR}(T_o)}{Q_{VR}(T)} \exp\left[\frac{hcE_i''}{k_B}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right]\left[\frac{1 - \exp(-hcv_i/k_B T)}{1 - \exp(-hcv_i/k_B T_o)}\right] V\left(\frac{\Delta v}{\gamma_D}, \frac{\gamma_L}{\gamma_D}\right),$$

where α is absorption coefficient (cm^{-1}) at wavenumber v (cm^{-1}) and temperature T (K); N_{H_2O} is concentration of water vapour molecules (molecules/cm^3); S_i is intensity of the *i*-th spectral line in HITRAN (cm/molecule); $Q_{VR}(T)$ is vibrational–rotational partition sum (available in HITRAN in the file "parsum.dat"); $T_0 = 296$ K is the reference temperature for HITRAN parameters; h, c and k_B are respectively Planck's constant, the speed of light in vacuum and Boltzmann's constant ($hc/k_B \approx 1.43878$ (cm K)); E'' is the transition's low-level energy (cm^{-1}); v_i is wavenumber of the centre of the *i*-th line (cm^{-1}); V is the Voigt function (cm), normalized to unit area, and calculated only within $25\,cm^{-1}$ from the line centre when CKD is included in the simulation[10]; $\Delta v = |v - v_i|$; γ_L and γ_D are Lorentz and Doppler line half-width (HWHM), respectively (cm^{-1}).

The smoothed spectrum of the residual obtained in the work [54] is shown in Fig. 4(a) by dots. "HITRAN-2001(m)" implies here HITRAN-2001 database [77] with the intensities and half-widths of ~500 strongest WM lines replaced by those derived from fitting to the measured high-resolution spectrum (see below).

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[10]Apart from $25\,cm^{-1}$ cut-off the line profile must also be reduced by its value at the edges of this interval [20].
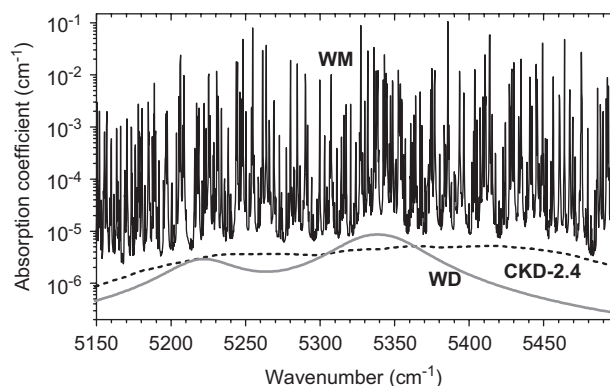
Fig. 3. The simulated spectrum of WM lines absorption for pure water vapour (20 mbar, 294 K) according to HITRAN-2001 [77] with the CKD-2.4 [21] continuum model included. The CKD-2.4 continuum and WD *ab initio* model [52] (WD bands HWHM = 25 cm^{-1}, $K_{eq} = 0.04$ atm^{-1}) are shown separately for comparison.

The value and spectral dependence of the residual was found to be very similar to that predicted for WD absorption [52]. The WD bandwidth and equilibrium constants K_{eq} were derived from the best fitting to the central residual peak near 5340 cm^{-1} and using WD line strength from [52] (Fig. 4). A peak of the residual, centred between 5400 and 5500 cm^{-1}, might be due to transitions to states involving other low-frequency modes (like combined intra- and inter-molecular vibrations), not included in the current OH-stretch and HOH-bending calculations[11] [52], or might still be caused by inaccuracies in WM continuum in CKD model.

However, as has been shown in [54], the definition of the WD residual in form (1), i.e., by subtracting the CKD continuum, would lead to the very weak dependence of K_{eq} on temperature (grey squares in Fig. 5), causing unphysical values of the WD enthalpy ΔH and entropy ΔS parameters retrieved from the equation $K_{eq} = \exp(\Delta S/R – \Delta H/RT)$. On the other hand, the residual calculated as

"Measurement" − "HITRAN-2001(m)_with_Ma&Tipping_continuum"   (2)

(see Fig. 4(b)), i.e., by subtracting *ab initio* continuum of Ma and Tipping [19,79] (which does not contain WD absorption) gives a much more physical $K_{eq}(T)$ behaviour (open squares in Fig. 5) that correspond well to the temperature dependence predicted by theory and by extrapolation of Curtiss et al.'s data [59]. This fact led authors of [54] to the conclusion that WD gives a significant contribution to the total self-continuum absorption in this spectral region, and most probably is implicitly partly included within the CKD continuum model as a result of fitting its parameters to the experimental continuum in middle IR; for example, within 1600 cm^{-1} water vapour band that may include some absorption by WDs (see Section 3.3). Fig. 8(b) shows also the most recent CKD continuum model MT_CKD [61] that was not available during submission of [54] for publication. It is clear that the MT_CKD model, though having slightly higher (but smoother) absorption structure than CKD-2.4, still cannot explain the spectral features detected in [54] (Fig. 4(b)); in particular, a quite pronounced and much narrower residual peak near 5340 cm^{-1}. The higher value of the MT_CKD absorption (as compared with the CKD-2.4 version) in the centre of this band still correlates well with the idea of implicit WD contribution to the CKD/MT_CKD model and is also discussed in Section 3.3.

The main problem in the correct assessment of the residual in [54] was the lack of WM line self-broadening parameters in HITRAN-2001 (the recent HITRAN update at that time). This problem was found to be rather important, because systematic underestimation either in WM line intensities or self-broadening coefficients in HITRAN by about 15% could produce a very similar residual signature (see Fig. 4(a)). However, the main peak of this residual would be blue-shifted compared with the one detected by about 5–10 cm^{-1}, which, in fact, can be treated as an additional argument in favour of the WD nature of the residual detected in [54].

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[11]In fact, the recent calculations, employing *ab initio* molecular dynamics technique to simulate WD spectrum at room temperatures [78], predict the presence of WD absorption near 5400–5500 cm^{-1} with relative intensity and spectral shape in reasonable agreement with the respected residual feature detected at RAL (Fig. 4(b)).
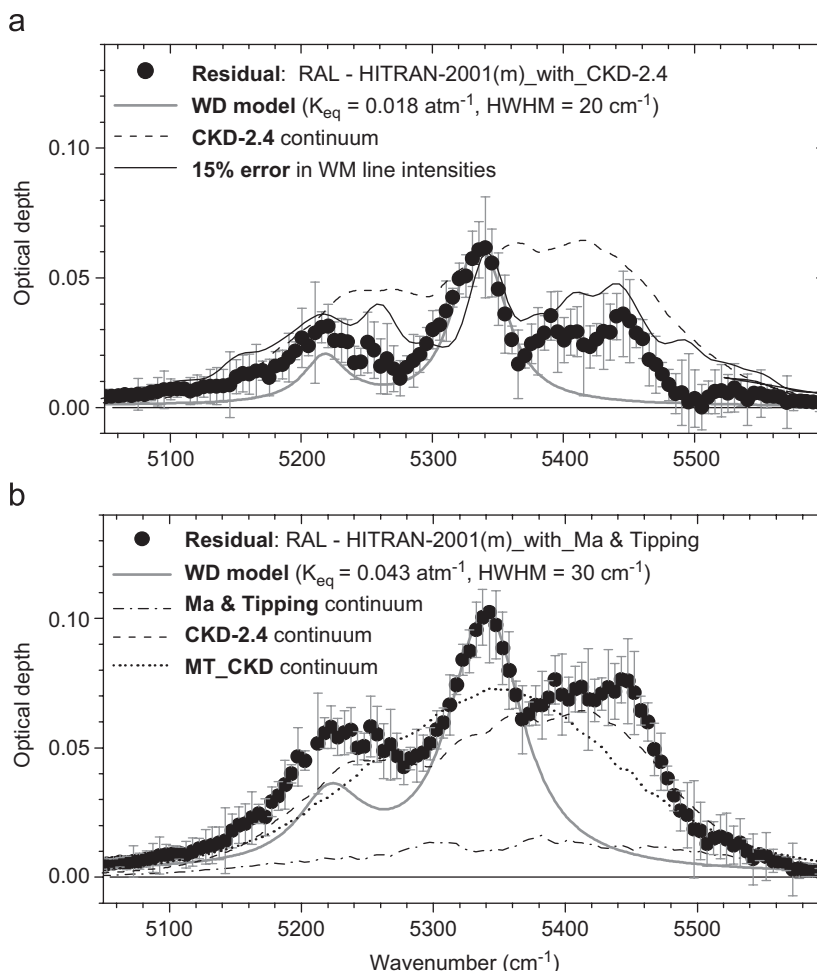
Fig. 4. Smoothed residual optical depths of pure water vapour from the RAL experiment [54] (20.5 mbar, 128.7 m, 299 K) for two different methods for obtaining the residual: (a) the CKD-2.4 [21] continuum model is subtracted from the measurement; (b) Ma and Tipping [79] continuum is subtracted. For comparison both continuum models are shown separately as well as the recent MT_CKD [61] model. The WD model absorption [52] is plotted with K_{eq} and WD bands width derived from a best fit to the central residual peak. The solid black line in (a) shows residual that would be caused by a 15% systematic underestimation either in HITRAN line intensities or self-broadening coefficients (except for small modifications, the figures are adopted from [54]).

Although some additional steps were undertaken in [54] to minimize the possible impact of WM line parameter errors on the residual (for example, excluding the central part of lines from the residual retrieval), to be fully consistent, the line intensities and self-broadening coefficients of about 500 strongest lines were finally derived by fitting to the measured spectrum, forming the HITRAN-2001(m) linelist [54]. The local baseline for each spectral line was included in the fitting procedure together with the line parameters: intensity, centre and half-width. This made the authors of [54] sure that the continuum absorption, caused by WD and/or by far wings of neighbouring WM lines, did not affect the derived WM line parameters.[12]

A thorough analysis and comparison with HITRAN-2001 and HITRAN-2004 [80] made later in [81] confirmed the validity of the WM line parameters retrieved in [54]. Moreover, this analysis indicated significant systematic overestimation in HITRAN-2004 self-broadening water vapour line parameters in the spectral region 5000–5600 cm^{-1} [81]. This discrepancy would reduce the residual in Fig. 4(a) by a factor ~1.5 if

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[12]Not accounting for the local baseline in the fitting procedure, according to the results obtained in [81], can lead to an overestimation of the intensities and widths of the weak WM lines by implicit including part of the continuum (and possible WD absorption) into derived line parameters.
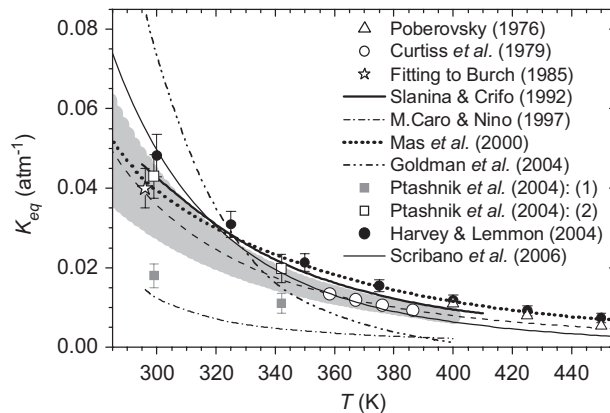
Fig. 5. Dimerization equilibrium constant by different authors. The symbols correspond to experimental data, while curves represent *ab-initio* predictions: Poberovsky [73] spectro-photometric measurement in pressurized steam; Curtiss et al. [59] measurement of the hot steam thermal conductivity; Fitting to the Burch [75] continuum, performed in the current work using WD line strengths from Schofield and Kjaergaard [52]; Slanina and Crifo [91] prediction using BGH/G pair potential; Munoz-Caro and Nino calculation [92]; Goldman et al. [3] calculation, based on the rigid VRT(ASP-W)III potential; Ptashnik et al. [54] fitting to the experimental residual obtained with the formula (1) and (2) and using WD line strengths from [52]; Harvey and Lemon [93] and Mas et al. [49] second virial coefficients $B(T)$, derived from experiment and from *ab initio* SAPT-5s pair potential respectively, are used to calculate $K_{eq}(T) = -[B(T)-b_o]/RT$, with $b_o = 38.5\,cm^3\,mol$ [59]; Scribano et al. [4] calculation using flexible VRT-MCYf potential energy surface. The dashed line shows extrapolation of Curtiss et al. [59] data as $K_{eq} = \exp(\Delta S/R - \Delta H/RT)$ with the enthalpy and entropy parameters derived in [59] ($\Delta H = -3590\,cal\,mol^{-1}$, $\Delta S = -18.59\,cal\,K^{-1}\,mol^{-1}$). The grey shadow represents a confidence interval for this extrapolation according to the errors in ΔH and ΔS retrieval [59].

HITRAN-2004 were used in expression (1) instead of HITRAN-2001(m) or HITRAN-2001. Thus, it should be a matter of concern that in some spectral regions (mostly within water vapour absorption bands, where WD signatures may be quite pronounced) the intensities and widths of relatively weak WM lines in spectral line databases are possible significantly overestimated as a result of implicitly including part of the continuum absorption if *local baseline* was not fitted along with the other line parameters [81].

It will be shown in Section 3 that both the value and the spectral dependence of the residual derived in the room-temperature RAL experiment [54] are in a good agreement with the results obtained earlier by Poberovsky at high water vapour pressures and temperatures [73,74].

3. Older experiments

Already in 1937 in pressurized steam measurements of Landsberg and Ukholin [82] the *shifted* bands compared with WM absorption were observed and attributed to water complexes. This conclusion was confirmed in similar measurements by Franck and Rott [83]. Later, in a series of experiments by Yukhnevich and Vetrov [84,85], Styrikovich et al. [86] (see Fig. 6) and Vetrov [87] (see also the recent analysis by Vigasin et al. [88] of high-pressure water vapour measurements by Vetrov [87] and Jin and Ikawa [89]) the *red-shifted* absorption bands of water complexes were clearly identified and investigated in pressurized steam at high temperatures in the spectral regions near $3600\,cm^{-1}$ ($2.78\,\mu m$), $5300\,cm^{-1}$ ($1.89\,\mu m$) and $7300\,cm^{-1}$ ($1.37\,\mu m$). The most effective method to retrieve the pure contribution of water clusters in this kind of measurement was suggested by Poberovsky [73,74].

3.1. High-pressure measurements of Poberovsky (1976)

3.1.1. 5000–5600 cm^{-1}

The spectro-photometric low-resolution (FWHM $\approx 15\,cm^{-1}$) laboratory measurements were made by Poberovsky [73] at water vapour pressures from 4 to 41 atm and temperatures from 400 to 550 K. To extract
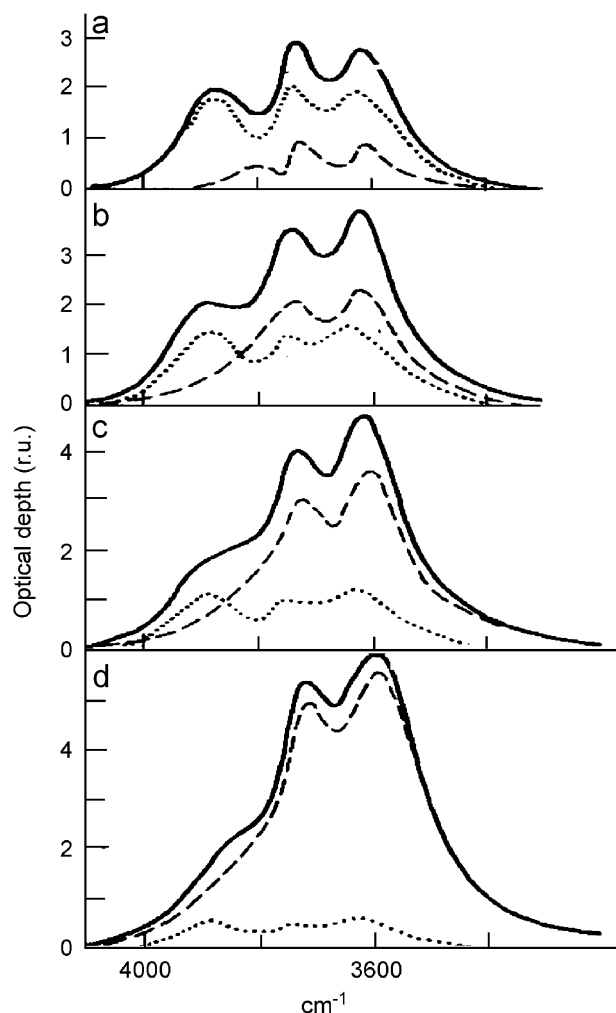
Fig. 6. The figure, adopted from the work of Styrikovich et al. [86] (courtesy of A. Vigasin), shows the spectra of pure water vapour (solid line) obtained in high-pressure measurements ($T = 360\,°C$, $a = 65\,atm$, $b = 114\,atm$, $c = 143\,atm$, $d = 177\,atm$). The dotted and dashed lines show contribution of water monomers and water complexes, respectively, estimated in [86].

the pure absorption by water complexes and *exclude the WM contribution,* two kinds of measurements were used at each temperature (see Fig. 7(a)):

(1) relatively low pressure of water vapour (4.2 atm) with high pressure of nitrogen (115 atm);
(2) high pure water vapour pressure (41.4 atm).

The physical reasoning for such an arrangement is based on the fact that the self-broadening coefficient is typically 5–6 times larger than the foreign broadening for water vapour lines. The high-pressure nitrogen in case 1 was used to produce WM lines with a pressure broadening similar to that for the 41 atm pure H_2O (case 2). The water vapour total path amount was chosen to be the same in these two cases by using different cell lengths ($L = 4.83$ and $0.49\,cm$ in cases 1 and 2, respectively). Under such conditions, it can be found from numerical line-by-line simulation that the optical depths must be almost the same for these two different cases if only local contribution (within $25\,cm^{-1}$) from water vapour lines is taken into account (i.e., not any continuum absorption is included). Thus, the differential absorption between these two cases, assuming about a two orders of magnitude higher WD abundance expected in case 2, was attributed in [73] entirely to the
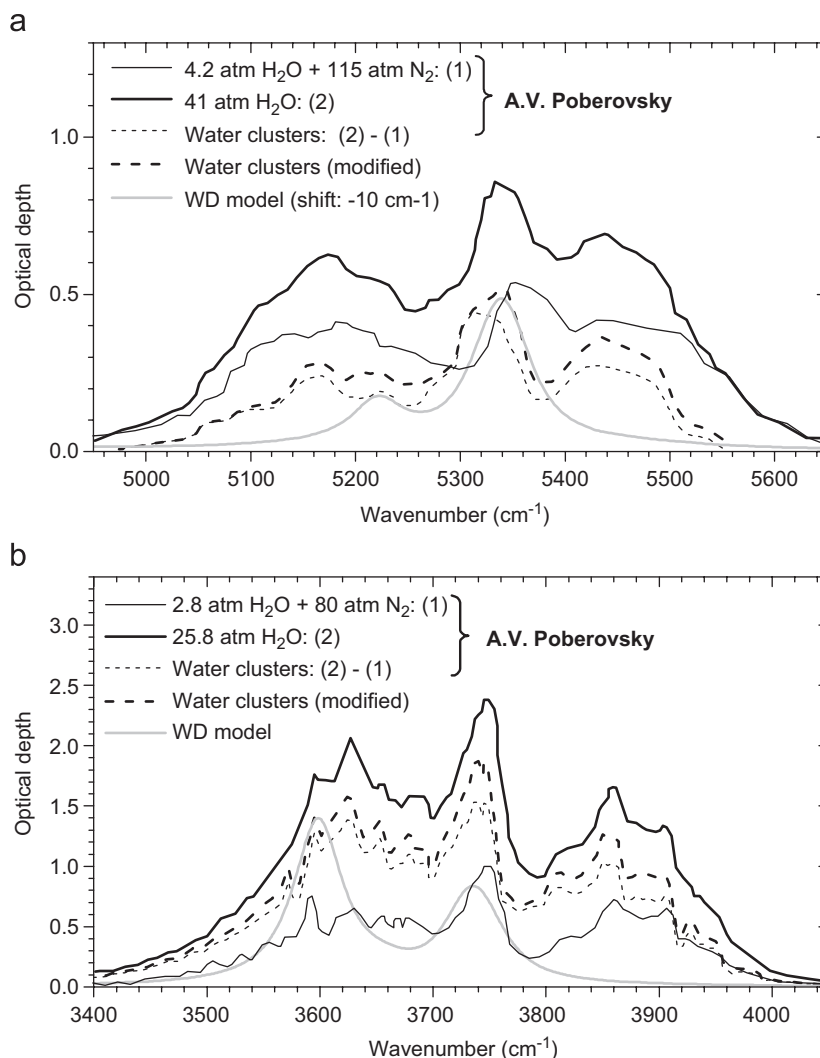
Fig. 7. The spectra of water vapour in $5300\,cm^{-1}$ (a), and $3700\,cm^{-1}$ (b) absorption bands, obtained in the experiments of Poberovsky [73,74] for the cases (1): $H_2O + N_2$, and (2): pure H_2O (see text); the difference spectrum (2)−(1), attributed by Poberovsky to water clusters; the difference spectrum of Poberovsky, modified in this work; WD according to the model [52]. (a) Experiment [73]: $T = 530\,K$, spectral resolution FWHM $= 15\,cm^{-1}$, $L = 4.83\,cm$ (1) and $0.49\,cm$ (2); WD simulation: line strengths and positions from [52], HWHM $= 28\,cm^{-1}$ [54], $K_{eq}(530\,K) = 0.0023\,atm^{-1}$ (Curtiss et al. [59] extrapolation). (b): Experiment [74]: $T = 503\,K$, spectral resolution FWHM $= 10\,cm^{-1}$; $L = 0.88\,cm$ (1) and $0.08\,cm$ (2); WD simulation: HWHM $= 25\,cm^{-1}$, $K_{eq}(503\,K) = 0.0032\,atm^{-1}$.

water clusters (the thin dashed line in Fig. 7), mostly to WD.[13] The thick dashed line in Fig. 7 accounts for a small modification to the results of Poberovsky, as the recalculations here using a line-by-line simulation found that $\sim170\,atm\ N_2$ pressure and $L = 4.4\,cm$ should be used instead of 115 atm and 4.83 cm in case 1 for the exact simulation of the 41 atm pure water vapour line broadening.

Numerical simulation of the experiment [73], performed using the HITRAN-2001 database and the WD band intensities [52], is presented in Fig. 8(a). The result of the simulation is in a good qualitative agreement with that obtained by Poberovsky (compare Fig. 7(a) and 8(a)). In both, the Poberovsky experiment and in the

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[13]This assumption made by Poberovsky is that the probability of formation of $H_2O–N_2$ complexes is much less then that of $H_2O–H_2O$. This must be true taking into account that the dissociation energy of the water–nitrogen complex $\sim2.7\,kJ/mol$ [32], which corresponds to about 350 K, is less than the ambient temperature of the experiments [73] (400–550 K). The dissociation energy of WD is about $15.7\,kJ/mol$ [3], for which the equivalent temperature is $\sim1900\,K$.
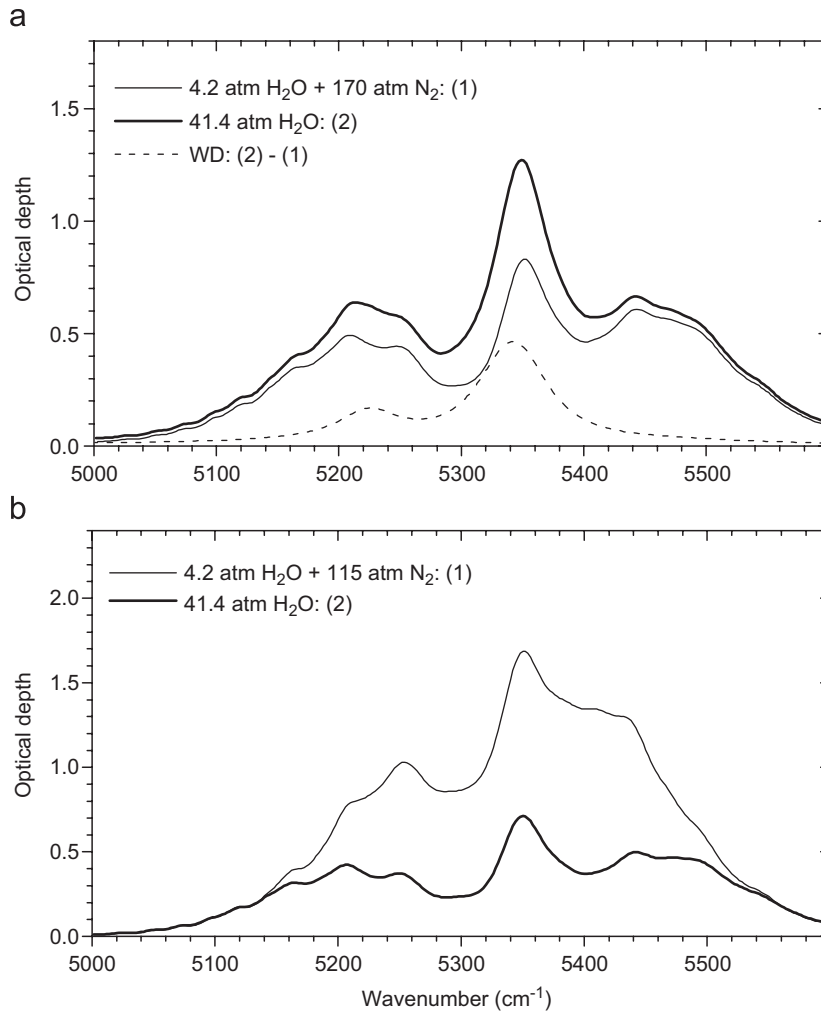
Fig. 8. Spectra of water vapour, simulated in this work for cases (1) and (2), similar to those in the experiment of Poberovsky [73]. Spectral resolution FWHM $= 15\,cm^{-1}$. (a) HITRAN-2001 [77] with the WD model [52] (WD band HWHM $= 28\,cm^{-1}$ [54], $K_{eq}(530\,K) = 0.0023\,atm^{-1}$ [59]), (1) $L = 4.4\,cm$, (2) $L = 0.49\,cm$. (b) HITRAN-2001 with the MT_CKD [61] continuum model, (1) $L = 4.83\,cm$, (2) $L = 0.49\,cm$. The difference spectrum (2)−(1) in case (a) coincides with the original WD model used in the simulation.

present simulation, the total optical depth τ for case 2 of high water vapour pressure is larger than for the low water vapour pressure with nitrogen (case 1):

$$\text{HITRAN} + \text{WD}: \tau_{41.4\,\text{atm }H_2O} > \tau_{4.2\,\text{atm }H_2O + 115\,\text{atm }N_2}.$$

On the other hand, a simulation performed using HITRAN-2001 with MT_CKD continuum model (Fig. 8(b)) shows quite the contrary result. The total optical depth is larger in case 1 (nitrogen broadening) than in pure water vapour case 2:

$$\text{HITRAN} + \text{MT\_CKD}: \tau_{41.4\,\text{atm }H_2O} < \tau_{4.2\,\text{atm }H_2O + 115\,\text{atm }N_2}.$$

This means that the modern MT_CKD continuum model (and CKD-2.4 gives a similar result) contradicts the results of Poberovsky experiments [73,74], apparently overestimating the foreign-continuum and underestimating the self-continuum in band centres at high pressures.

Although the CKD/MT_CKD continuum model was not originally designed to be used at the temperature region far from 260 to 296 K where its parameters were derived, such a significant deviation from the real behaviour of water vapour spectrum at elevated temperatures causes serious doubts about the completeness of
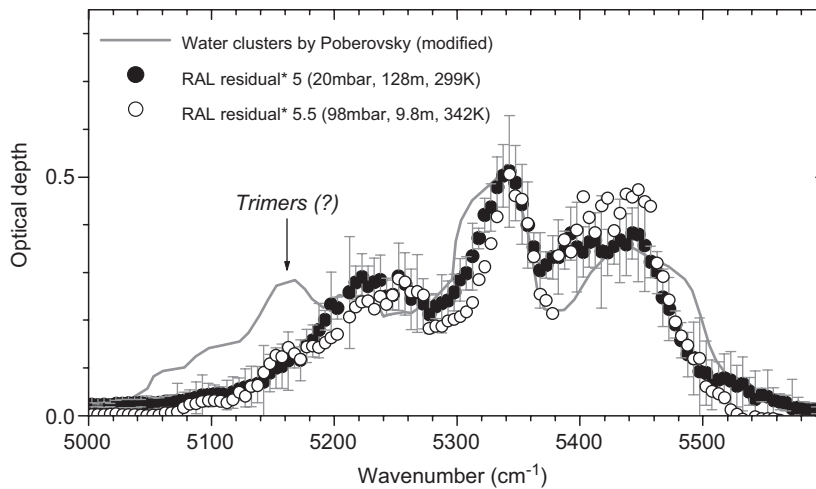
Fig. 9. Comparison of the residuals obtained in high-pressure measurement by Poberovsky [73] (modified) and in RAL experiments [54] (calculated as "Measurement–HITRAN-2001(m)$_{with\ Ma\&Tipping\ continuum}$") for two pressures.

the physics incorporated into these models. For example, the recent experiments by Baranov et al. [90] show that the MT_CKD model underestimates the experimental self-continuum up to 50% when temperature increases to 350 K, i.e., only by 40–50° above the upper temperature point at which the CKD model is regarded to be applicable. It is worth mentioning in this connection that the great advantage of the CKD/MT_CKD model is that, in spite of being fitted only in middle and far-IR, it works reasonably well (especially for the foreign-continuum) in many other spectral intervals from near-IR up to the visible region. Therefore, appropriate extension of its validity to higher (than atmospheric) temperatures is rather desirable and would increase the applicability of this model. The current review shows, however, that such an extension may be impossible without explicit incorporation of WD mechanism into the MT_CKD model.

In Fig. 9, the optical depth for water clusters, derived in [73], is compared with the residual from the RAL experiment [54], scaled to the same amplitude (i.e., by a factor of 5, see below). The agreement between the residual spectral signatures of the two independent experiments is striking. The most convincing argument for a dimer explanation is that these residuals were obtained by very different methods. In the work of Ptashnik et al. [54], the residual is calculated as the difference between measurement and simulation using modern spectral line database, while in [73] the residual was derived as the difference between two measurements, so no calculation (apart from the simple estimation of the equivalent broadening N_2 pressure) was applied.

The agreement in amplitudes of the residuals is also quite reasonable, considering the different conditions at which the residuals were obtained. Taking into account that WD optical depth is proportional to WD concentration $n_{WD} = K_{eq}p^2_{WM}/kT$ and to the path length L, and assuming the following relations of parameters in the works [73,54]: $L^{[73]}/L^{[54]} = 0.49\,cm/12{,}800\,cm$; $p_{WM}^{[73]}/p_{WM}^{[54]} = 41\,atm/0.02\,atm$; $K_{eq}(530\,K)^{[73]}/K_{eq}(299\,K)^{[54]} = 0.002\,atm^{-1}/0.043\,atm^{-1}$; $T^{[73]}/T^{[54]} = 530\,K/299\,K$, the expected ratio of the optical depths can be estimated as $\tau^{[73]}/\tau^{[54]} = 4.2$. This value is rather close (considering the very approximate character of the K_{eq} estimation) to the scaling factor 5, used in Fig. 9 to bring the residual from the experiment [54] in agreement with the result of Poberovsky [73]. The equilibrium constants, derived in [73] at a few temperatures, are presented in Fig. 5 and are also in a good agreement with the extrapolation of Curtiss et al.'s [59] data.

The additional peak near 5160 cm^{-1} in the residual of Poberovsky, as compared with the low-pressure residual obtained at RAL (Fig. 9), might be caused by a contribution of higher-order water complexes (for example, trimers,[14] whose abundance is proportional to the cube of the water vapour pressure). There is a hint

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[14]Calculations performed in [51] have shown ∼50 cm^{-1} shift to lower wavenumbers for fundamental water trimer band compared to the dimer, which is in a good agreement with the position of the high-pressure residual peak near 5160 cm^{-1} in Fig. 9.

of a similar peak, though much less pronounced, in the residual obtained at higher-pressure (98 mbar) RAL measurements (see the open circles in the Fig. 9).

3.1.2. 3400– 4000 cm^{-1}

Similar measurements were also performed by Poberovsky in the first and in the third water vapour polyads, centred near 3600 cm^{-1} (2.78 μm) and 7300 cm^{-1} (1.37 μm), respectively [74]. The first spectral region is most interesting concerning WD because the more pronounced WD absorption is expected compared with the WM (see Fig. 2). The resulting absorption by water clusters, obtained in [74] in the spectral region 3400–4050 cm^{-1} with a similar approach to that described above, is presented in Fig. 7(b). Again, some slight correction is applied to the residual of Poberovsky (which, however, does not change it markedly) according to the result of numerical simulations for the cases 1 and 2 in Fig. 7(b). Very similar WD absorption signatures for this band were obtained in the work of Vigasin et al. [88] from a comparison of quantum-chemical *ab initio* calculations for WD with high-density experiments of Vetrov [87].

In order to put into context the results of Poberovsky for this band (Fig. 7(b)), they are compared below with the water vapour continuum measurements of Burch [75] for the same absorption band.

3.2. Experiment of Burch (1985), 3100– 4200 cm^{-1}

The work of Burch [75] describes laboratory measurements of water vapour continuum absorption in numerous micro-windows in the spectral region of 3100–4200 cm^{-1}. The measurements were made at the temperature 296 K and 23 mbar pure water vapour pressure. Although Burch was not disposed to assign the extra continuum absorption obtained in [75] to the WD, however, the analysis here strongly supports a WD explanation.

Fig. 10 shows the following spectral dependencies related to the work [75]:

(a) the high-resolution spectrum of WM absorption, calculated using HITRAN-2004 [80] with MT_CKD, and convoluted with a triangular instrumental line shape (ILS) function according to [75] (ILS HWHM ~0.8 cm^{-1}); the smoothed form of the spectrum (filter width of 30 cm^{-1}) is also presented;

(b) the spectra of the two recent versions of CKD continuum: CKD-2.4 [21] and MT_CKD [61];

(c) WD absorption spectrum, simulated using *ab initio* prediction [52] for WD band intensities and positions, dimerization constant $K_{eq} = 0.043$ atm^{-1} [54], and HWHM = 25 cm^{-1} for WD absorption bands: $|0\rangle_f|0\rangle_b|2\rangle, |0\rangle_f|1\rangle_b|0\rangle, |10\rangle_+|0\rangle, |1\rangle_f |0\rangle_b|0\rangle$ and $|10\rangle-|0\rangle$, centred near 3215, 3600, 3656, 3730 and 3745 cm^{-1} respectively [52][15];

(d) monochromatic WM lines contribution (i.e., with no convolution with the ILS or any continuum model included) in micro-windows, calculated by Burch [75] using AFGL [94] spectral lines database, and calculated in this work using HITRAN-2004[16] (both calculations employ only Voigt line profile with wings up to 1000 cm^{-1});

(e) empirical self-continuum absorption, obtained by Burch from the ratio of the measured transmissions to the calculated ones, using AFGL [94] line parameters and Voigt profile with the ILS function taken into account.[17]

The absorption coefficient k in Fig. 10 is given in the units of "cm^2 molecule^{-1} atm^{-1}" that were introduced originally only for the "far-wing" water vapour continuum model [75], and reflected the direct proportionality

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[15]According to the notation [52] $|x\rangle_f |y\rangle_b |z\rangle$ and $|xy\rangle \pm |z\rangle$ labels 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 HOH bending mode, while "±" refers to the symmetry of the stretching vibrations in the acceptor unit.

[16]Calculation of the monochromatic absorption, performed with HITRAN-2001, gives very close values to those obtained by Burch [75] using AFGL [94].

[17]In the traditional CKD approach [97], the contribution of single WM line to the continuum is derived by subtracting from the CKD line profile the central part (within 25 cm^{-1}) of Voigt shape, reduced by its value at the 25 cm^{-1}. In the work of Burch [75], the empirical continuum was derived by subtracting from the measured spectrum the whole Voigt profile contribution, including far wings. Applying the same approach to the CKD continuum models in Fig. 10 would reduce their strength compared to the unmodified CKD values by about 10% in the band centre to ~20% in the wings, which could only strengthen our conclusions concerning the dimer origin of the absorption.

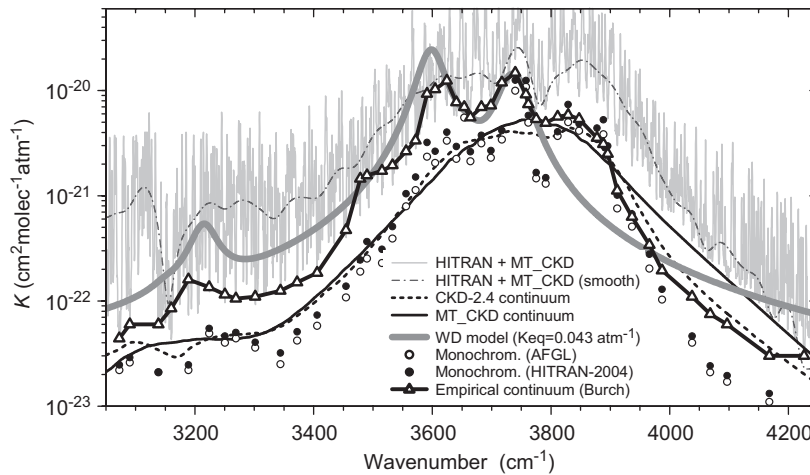Fig. 10. Spectra of absorption coefficients, simulated in this work and obtained in the Burch [75] pure water vapour experiment ($P_{H_2O} = 23$ mbar, $T = 296$ K): high-resolution spectrum of WM absorption, simulated using HITRAN-2004 [80] with the MT_CKD [61] continuum included, and convoluted with the instrumental line-shape function from [75]; smoothed WM absorption; CKD-2.4 [21] and MT_CKD continuum models; WD model spectrum simulated using *ab initio* intensities and positions from [52] and band HWHM $= 25$ cm^{-1}; monochromatic WM lines absorption, calculated in [75] for separate micro-windows using AFGL [94] spectral lines database, and calculated in this work using HITRAN-2004; Empirical continuum of Burch [75] (see text for details).

of the continuum absorption (described as far Lorentzian wings of spectral lines) to the ambient pressure, in addition to the proportionality to the water vapour concentration. The absorption coefficient for the continuum is given by

$$\alpha_c \propto N_{H_2O} \frac{S}{\pi} \frac{\gamma}{\Delta v^2 + \gamma^2} \xrightarrow{\Delta v \gg \gamma} N_{H_2O} \frac{S\gamma}{\pi \Delta v^2} = N_{H_2O} \frac{S(\gamma_s P_s + \gamma_f P_f)}{\pi \Delta v^2} \propto N_{H_2O}(k_s P_s + k_f P_f),$$

where S, like earlier, is line intensity (cm/molecule), $\gamma_{s,f}$ is, respectively self- and foreign-broadening coefficient (cm^{-1}/atm), and $P_{s,f}$ stands for water vapour and foreign-gas pressure. Meaning "per one molecule of H$_2$O and per one atmosphere of ambient pressure" the unit "cm^2 molecule^{-1} atm^{-1}" has a rather formal sense for WDs and for WM absorption near line centres and is used here only for consistency.

Fig. 11(a) is the same as Fig. 10, but with a linear scale for the absorption coefficient to underline the two strongest peaks of continuum absorption detected by Burch [75]. The shift between the smoothed WM signature near 3750 cm^{-1} and the detected peaks of absorption (supposed $|1\rangle_f|0\rangle_b|0\rangle$ and $|10\rangle_-|0\rangle$ WD stretching vibrations [52]) is about 10–15 cm^{-1}. Fig. 11(a) also presents the empirical continuum of Burch modified in this work to account for updated spectral line parameters in HITRAN-2004 [80] as compared with the AFGL [94].

Analysis of the spectra presented in Figs. 10 and 11(a) leads to the following conclusions:

(1) Despite the fact that the measurements of Burch [75] have been cited in the work [20] as those used to develop the first CKD continuum model,[18] all CKD continuum versions including the two recent ones, fail to describe most of the continuum absorption detected by Burch. The empirical continuum of Burch exceeds the CKD-2.4 and MT_CKD continuum models on average by 3–4 times in the spectral region of 3150–3750 cm^{-1}, and is, respectively, 1.5–2 and 2–3 times smaller than these models in the region of 3900–4200 cm^{-1}.

(2) The empirical continuum of Burch demonstrates distinct spectral features near 3200, 3610 and 3730 cm^{-1} that are not explained by any CKD continuum model, but are in reasonable agreement with the WD bands according to the *ab initio* prediction [52]. As with the predicted WD bands all peaks of the Burch empirical

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[18]According to Eli Mlawer (personal communication), however, the work of Burch [75] is most likely cited by mistake in the paper of Clough et al. [20].
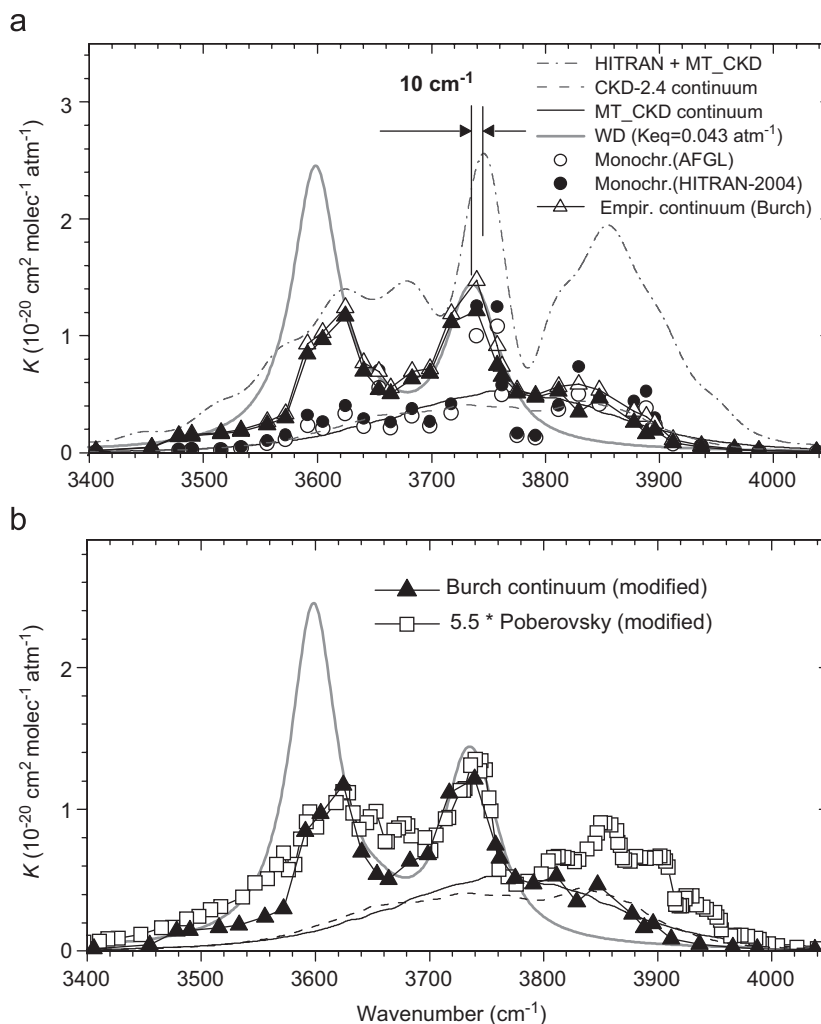
Fig. 11. (a) Same as Fig. 10 but in linear scale for absorption coefficient. Empirical continuum of Burch [75], modified in this work to account for the updated spectral line parameters in HITRAN-2004 [80], as compared with AFGL [94] is shown by solid triangles; (b) similar to (a), but the water clusters signature from Poberovsky's [74] experiment at 503 K is also shown for comparison.

continuum have a 10–30 cm^{-1} red shift with respect to the smoothed absorption spectrum of WM, which also points to their dimer origin. A feature of the Burch continuum absorption near 3490 cm^{-1} could also be caused by the WD because of its noticeable shift ($\sim$20 cm^{-1}) to the IR region with respect to the similar WM absorption feature.

(3) Comparison of the Burch empirical continuum with the WD model [52] shows that the latter clearly overestimates the intensity of the $0\rangle_f|1\rangle_b|0\rangle$ WD band (centred near 3600 cm^{-1}) as compared with the joint intensity of the bands $|1\rangle_f|0\rangle_b|0\rangle$ and $|10\rangle_-|0\rangle$ (near 3730 cm^{-1}). Like earlier (i.e., in case for 5300 cm^{-1} band) the WD model [52] cannot explain the 'third bump-like' feature of the Burch continuum near 3850 cm^{-1}, which can be attributed either to additional low-frequency modes, not accounted for in this WD model, or to the WM self-continuum.

It is worth mentioning that Burch [75] discussed briefly the possibility that the detected features had the WD nature. However, he rejected this idea because of the apparent good correlation between these peaks and WM bands' signature. Burch obviously expected rather bigger ("significant" [75]) shifts of WD bands as compared with the modern predictions and low-temperature observations.

A similar line-by-line analysis shows that in the foreign-broadening case (which was also investigated by Burch [75]) the absorption by WM line wings markedly exceeds WD absorption. This explains why Burch could not have detected marked extra WD absorption for the foreign-broadened continuum (compared with the FASCOD continuum model [95]), in contrast to the self-broadening case described above.

Fig. 11(b) presents a comparison between the empirical continuum Burch [75] and the water clusters signature obtained by Poberovsky [74] for the same spectral region. Again, there is very good spectral agreement between these two independent experiments and approaches, apart from some additional features at 3800–3900 cm^{-1} in [74] as compared with [75], which can be attributed to the higher-order water clusters that become more pronounced at elevated water vapour partial pressures.

During the revision of this paper, the results of low-resolution study by Burch [75] have been generally well supported in recent high-resolution measurements of the water vapour continuum by Paynter et al. [96] at a range of near-room temperatures.

It is seen from Figs. 10 and 11(a) that WM line absorption (the monochromatic absorption coefficients in the micro-windows), calculated using only a Lorentzian profile, contributes generally much less within selected micro-windows than the detected features of the continuum absorption. This means that uncertainty in line parameters, still remaining in the modern databases, is very unlikely to be the reason for these features. This emphasizes the high reliability of these measurements for retrieval of the continuum, and means that the experiment of Burch [75] and Paynter et al. [96] can be treated as the strongest evidence today for a dominant role of WD in causing the water vapour continuum within absorption bands.

It must be noted that no line-mixing effect was taken into account in the present analysis of the high-pressure measurements of Poberovsky [73,74] (Section 3.1). However, if this effect were important and gave significant contribution to the high-pressure water vapour absorption signatures detected in [73,74], it would be very unlikely to expect a similar residual for the low-pressure water vapour measurements [54,75], unless the impact of line-mixing effect was compensated by the specific differential approach used by Poberovsky to obtain the WD signature. In any case it means that line mixing is very unlikely to affect the main conclusions.

3.3. 1600 cm^{-1} water vapour absorption band

The possible WD contribution to the "in-band" water vapour continuum absorption can be discussed semi-quantitatively also (though with much weaker evidence) on the basis of the measurements of Burch [97] and Tobin et al. [98] in the 1600 cm^{-1} absorption band. Fig. 12 shows the continuum absorption coefficients obtained in these works as well as the two CKD continuum versions that are based on the fitting of CKD line-shape parameters to these different measurements.

The minimum in the spectral dependence of the absorption coefficient near 1600 cm^{-1} was present in all former CKD self-continuum versions including CKD-2.4, reflecting the similar minimum obtained in the work [97] (see Fig. 12).[19] This minimum has vanished, however, in the recent MT_CKD continuum model, which corresponds to the results of Tobin et al.'s measurement [98] performed at lower temperatures than in [97]. On the other hand, the *ab initio* prediction [52] (see the Figs. 1 and 12) and supersonic measurement of Paul et al. [42] show strong WD absorption bands in this spectral region ($|00\rangle|1\rangle$ and $|0\rangle_f|0\rangle_b|1\rangle$ bands, centred, respectively, near 1600 and 1626 cm^{-1} [52]).

Thus, the significant disagreement between the self-broadened continuum near 1600 cm^{-1}, obtained in the works [97,98], can be caused by the different temperatures at which these experiments were carried out, in conjunction with the strong negative temperature dependence of the expected WD absorption (see the dashed lines in Fig. 12). $K_{eq}(296 \text{ K}) = 0.04$ and $K_{eq}(308 \text{ K}) = 0.03 \text{ atm}^{-1}$, chosen for this plots, agree well with the Curtiss et al. [59] extrapolation.

Some experimental facts in favour of the possible significant WD contribution to the high-pressure self-continuum absorption in the centre of the 1600 cm^{-1} water vapour band have also been obtained in experiments [87] and are discussed by Vigasin [99].

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[19]It should be mentioned, however, that there seems to be only one point in the Burch [97] data which represents this minimum (see Fig. 12).
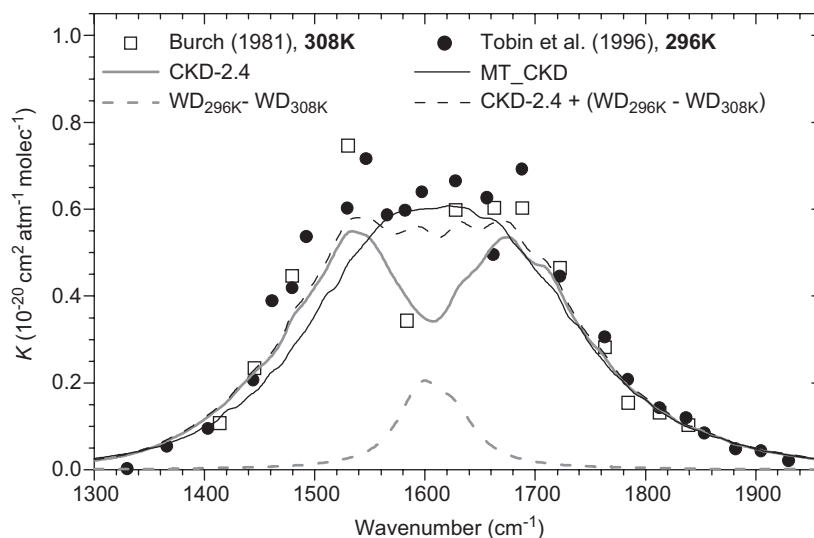
Fig. 12. Self-continuum absorption obtained by Burch [97] and Tobin et al. [98] at 308 and 296 K, respectively; CKD-2.4 [21] and MT_CKD [61] models. 'WD$_{296K}$–WD$_{308K}$' shows the difference between WD absorption at the two temperatures, simulated on the basis of the model [52], WD band HWHM = 25 cm^{-1}, K_{eq}(296 K) = 0.04 and K_{eq}(308 K) = 0.03 atm^{-1}. The thin dashed line shows the CKD-2.4 continuum model plus the "temperature correction" for water dimer absorption.

4. Atmospheric measurements

It is known that so far all attempts to detect WD absorption in the atmosphere have failed [100,101].[20] It is not surprising taking into account that far wings of air-broadened water vapour lines (foreign-continuum) should strongly overlap the possible contribution of WDs in the band centres.

In the recent work of Pfeilsticker et al. [69] (long-path (18.3 km) ground-based measurements of atmospheric absorption near 13340 cm^{-1} (0.75 μm)), the authors claimed possible detection of WD absorption in the out-of-band spectral region, where the impact of the foreign-continuum is relatively small. The residual, attributed to the WD absorption (see Fig. 13), was obtained in [69] by comparison of the experiment with calculation using the WM linelist of Coheur et al. [103] (which was included in the 2004 edition of the HITRAN database [80]).

However, the failure of Pfeilsticker et al. [71,72] to observe the similar residual in a new set of measurements with higher water vapour amount casts serious doubts on the dimer nature of the signature detected in [69]. The result obtained in [69] has also received some criticism from Suhm [68], primarily due to arguments in favour of very short WD lifetimes at normal conditions and hence a wider band for WD transitions than reported by [69]. Thus, the question about detection of WD absorption in atmospheric conditions still remains open and requires further investigations.[21]

It is worth mentioning that the work [69] revealed again the problem (already mentioned above) related to retrieval of smooth and relatively weak continual absorption masked by local spectral lines contribution. The problem is that HITRAN-2004 may not reflect exactly the line absorption in some spectral regions. For comparison, Fig. 13 shows the water vapour absorption spectrum calculated using the *ab initio* Schwenke and Partridge (S&P) linelist [104], which includes a large number of very weak water vapour lines not catalogued in HITRAN. The S&P database shows double the WM absorption than HITRAN-2004 and is rather close to the total absorption detected in [69], including a spectral feature similar to WD. The same conclusion was made recently in the work of Kassi et al. [70], although their ring-down measurements have shown much less WM

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[20]The possible explanation of this failure could be the wrong spectral region for WD detection selected in [100,101] on the basis of *ab-initio* prediction [102]. Vaida et al. [1] attribute this mostly to the lack of a suitable dipole moment function in the model [102].

[21]In [71,72], the authors report a possible detection $|0\rangle_f|5\rangle_b|0\rangle$ overtone of WD bending transition near 614 nm (~16,290 cm^{-1} versus 16,312 cm^{-1} predicted in [52]).
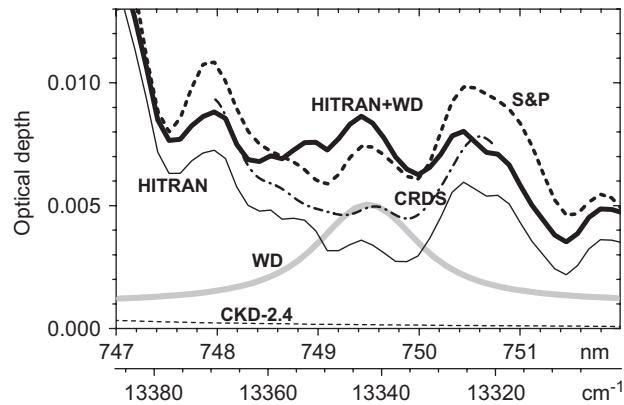
Fig. 13. Spectra simulated for the conditions of Pfeilsticker et al.'s [69] experiment ($P_{H_2O} = 14.4$ mbar, $L = 18.3$ km, $T = 292$ K, spectral resolution 10 cm^{-1}). CKD-2.4: continuum model [21]; WD: water dimers model [52] with band FWHM $= 19.4$ cm^{-1} and $K_{eq} = 0.047$ atm^{-1} (which corresponds well to the smoothed residual derived in [69]); HITRAN: WM absorption according to HITRAN-2004 [80]; HITRAN + WD: HITRAN-2004 with WD absorption included (simulates the total absorption detected in [69]); S&P: Schwenke and Partridge database [104]; CRDS: WM lines absorption according to the cavity ring-down measurements by Kassi et al. [70] (The style of the figure is adopted from [70]).

absorption than the S&P database, however, it was still markedly higher than in HITRAN-2004 (Fig. 13). This fact confirms again the importance of using *high-resolution* measurements for correct water continuum retrieval, which may allow correction of spectral line parameters (as compared with HITRAN or S&P database) in some spectral regions by direct fitting to the high-resolution experimental spectrum.

5. Far band wings

Although the significant contribution of WDs in the formation of *in-band* water vapour self-continuum seems clear in the light of the analysis presented here, this contribution itself is not of much importance for absorption of solar radiation. There are two main reasons for this. First, as mentioned above, the foreign-continuum dominates within water vapour bands in atmospheric conditions. Second, absorption of solar radiation within the strongest near-IR water vapour bands is highly saturated by water vapour lines, so even the contribution of the foreign-continuum to the total absorption is quite small. That is why most debate about the nature of the water vapour continuum has concerned *out-of-band* spectral regions (or atmospheric windows) where the question about possible contribution of WDs to the continuum still remains open.

The problem is caused mainly by the absence of clear spectral signatures and/or relevant predictions for WD absorption in the band wings, and by the very small values of the out-of-band absorption in the near-IR. As was discussed in the introduction, in spite of the most commonly accepted today far-line-wings theory, there are a great number of works suggesting WD as the possible origin of (or, at least, contributor to) the out-of-band self-continuum absorption. Most of these papers considered the spectral region 8–20 μm. A thorough overview of these works deserves a separate paper. In the light of the discussion above, the author would like to mention only two of these works, demonstrating that the discussion about possible marked WD contribution to the continuum in atmospheric windows is not over.

In Vigasin [32] paper, a model of temperature dependence of mm-wave and IR continua absorption is suggested in terms of absorption by weakly bound binary complexes. The model is verified for $(H_2O)_2$ dimers and for H_2O–N_2, H_2O–CO_2 and H_2O–Ar complexes, and shows very good agreement with a series of different experiments in mm-wave and far-IR spectral regions by fitting only two physically clear parameters for each type of complex.

The new high-accuracy cavity ring-down measurements, carried out by Cormier et al. [33], have shown that the temperature dependence of the detected self- and foreign-broadened continuum absorption at 944 cm^{-1} is in excellent agreement with that predicted for water complexes in [32]. The temperature dependence derived from far-wing theory [18,19] was found to be less satisfactory. Along with the detected quadratic partial

pressure dependence this allowed Cormier et al. [33] to suggest the high probability of dominating contribution of water complexes in the detected continuum absorption. However, the authors were reluctant to make a firm conclusion, and pointed to the need for further research.

6. Conclusion

There are some spectral regions (here mainly near-infra-red (IR) in-band locations were discussed) and temperature–pressure conditions, where the modern CKD-2.4 or MT_CKD water vapour continuum models cannot describe properly the measured continuum absorption. By contrast, the analysis presented here of the different equilibrium pure water vapour measurements within the 3700 and 5300 cm^{-1} absorption bands, shows that the particular continuum anomalies obtained there can be satisfactory explained by water dimer (WD) stretching fundamental and first overtone bands, respectively, according to the up-to-date WD *ab initio* model of Schofield and Kjaergaard [52] and dimerization equilibrium constants close to those estimated by Curtiss et al. [59]. It was shown that the high-pressure water vapour measurements of Poberovsky [73,74] and Vetrov et al. [84–87], as well as more recent studies [88,89], reveal distinct WD signatures that are in an excellent agreement with the results of independent low-pressure measurements by Burch [75] and Ptashnik et al. [54]. These facts indicate that the water vapour self-continuum within near-IR absorption bands is strongly affected by WDs.

Despite the wide discrepancy still existing between different theoretical predictions for the temperature dependence of dimerization equilibrium constant, the values obtained from different experiments seem to be in reasonable agreement with each other and with the theoretical predictions by Slanina and Crifo [91], Mas et al. [49] and Scribano et al. [4] (Fig. 5).

The overview and analysis presented in this work was formed as a result of experimental evidence that cannot be ignored but that still requires further verification. Thus, additional thorough and independent measurements of the continuum absorption are necessary (preferably in laboratory conditions in order to minimize the impact of unknown atmospheric factors), both within and (especially) between vibrational water vapour bands in the near-IR, where the CKD continuum model is poorly evaluated at present and where WD band wings may contribute to absorption of solar radiation in the atmosphere [1,2,54,58].

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