Water dimers: an "unknown" experiment

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It is shown that reliable evidences of significant contribution of water dimer absorption to the water vapor continuum in the spectral range of 3000–4200 cm^{-1} can be revealed from well-known Burch's measurements.

Despite the decades of intensive investigations, the role of water dimers (WDs) (short-lived clusters consisting of two water molecules) in the radiation budget of the atmosphere is still under discussion. According to different estimates, WDs can contribute from 0.5 to 1.5% to the total atmospheric absorption of the solar radiation.[1–3] Moreover, according to the calculation of the dimerization constant by Goldman et al.,[4] the contribution of WDs to the atmospheric absorption of radiation can be even 1.5–2 times higher than the above estimates.

Water dimers are also interesting from the theoretical point of view. Water dimers were discussed many times in the context of their possible contribution to the *continuum absorption* of radiation by water vapor,[5,6] because the theoretical dependence of WD absorption on water vapor temperature and pressure is similar to that of the self-broadening continuum (from here on in this paper, we mean under the water continuum only its part caused by self-broadening).

According to the CKD (Clough, Kneizys, Davies) model of continuum,[7] the deviation of the spectral dependence of absorption in line wings from the Lorentz profile is caused by the finite time of collision of water molecules. Since the WD cluster can be described, to a certain degree, as two water molecules with the long collision time, the differences between these two phenomena are largely leveled out.

In the recent version of the CKD continuum – MT_CKD,[8] the water continuum absorption is explained by a combination of two factors: 1) far line wings, corresponding to "allowed" transitions and 2) strongly broadened lines of collision-induced transitions caused by the appearance of the short-lived dipole moment for the time of collision. In the authors' opinion, the second mechanism is the main contributor to the continuum absorption at the centers of absorption bands (see, for example, Refs. 9 and 10). As earlier in Ref. 7, the authors of the MT_CKD model of continuum negate the possibility of *considerable* WD contribution to the continuum absorption, acknowledging only the possibility of some weak spectral dimer "signatures" (such as, for example, an absorption feature nearby 930 cm^{-1}, mentioned in Ref. 10). The main evidence in favor of this was the argument that the spectral dependence of continuum absorption in the IR water vapor bands, measured by Burch[11,12] and more recently by Tobin with co-workers,[13] correlates well with the selective absorption of water monomers (WMs).

The "good correlation" is understood there probably as the absence of "any" shift with respect to the centers of monomer vibrational bands, which is characteristic of dimer bands and caused by the "damping" influence of the hydrogen bond between water molecules on their vibrational frequencies.

In spite of active investigations into WDs, the observations of WD absorption in the atmosphere[14] and under equilibrium laboratory conditions[15] at the water vapor pressure and temperature close to the atmospheric one have not been reported until recently. (WD physical–chemical properties and spectral characteristics were studied earlier only in dimers obtained artificially in the ultrasonic jets or in gases at ultralow temperatures). However, the results of these experiments are not strictly unambiguous and, in principle, admit, to some extent, double interpretation. On the other hand, our analysis has revealed one more experimental paper, which has become a classical one, whose author detected nonselective absorption, being in a good agreement with the recent calculation[16] for WDs. It is Burch's paper,[17] which presents the results of laboratory measurements of water vapor continuum absorption in the spectral region of 3000–4200 cm^{-1}. Despite the author of Ref. 17 himself was not disposed to assign the found discrepancy between the residual absorption and the available model of continuum to water dimers, our analysis proves the contrary.

Figure 1 shows the following spectral dependences:

a) convolution of the spectrum of water vapor absorption coefficient, calculated based on the HITRAN-2004 database of spectral line parameters[18] and the MT_CKD model of continuum, with the instrumental function used in the experiment,[17] along with the smoothed form of this spectrum;

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b) absorption coefficients of two last versions of the CKD continuum model: CKD-2.4[10] and MT_CKD[8];

c) WD absorption simulated based on *ab initio* calculations of band intensities,[16] dimerization constant Keq = 0.04 atm^{-1} (according to Ref. 15 for the temperature of 296 K), and half-widths of dimer absorption bands of 25, 20, and 20 cm^{-1} (from the left to the right in Fig. 1);

d) monochromatic WD absorption coefficients in microwindows, obtained in Ref. 17 on the basis of the AFGL database of spectral lines[19] and calculated by us using HITRAN-2004 (both of the calculations use only Voigt line profile and ignore the continuum absorption);

e) empirical continuum absorption coefficients obtained in Ref. 17 from the ratio of the measured transmission to the transmission calculated on the basis of AFGL line parameters[19] and Voigt profile with the allowance for the instrumental function, as well as the corrected empirical coefficients of Burch[17] with the allowance for the updated spectral line parameters in HITRAN-2004 as compared to the AFGL database.

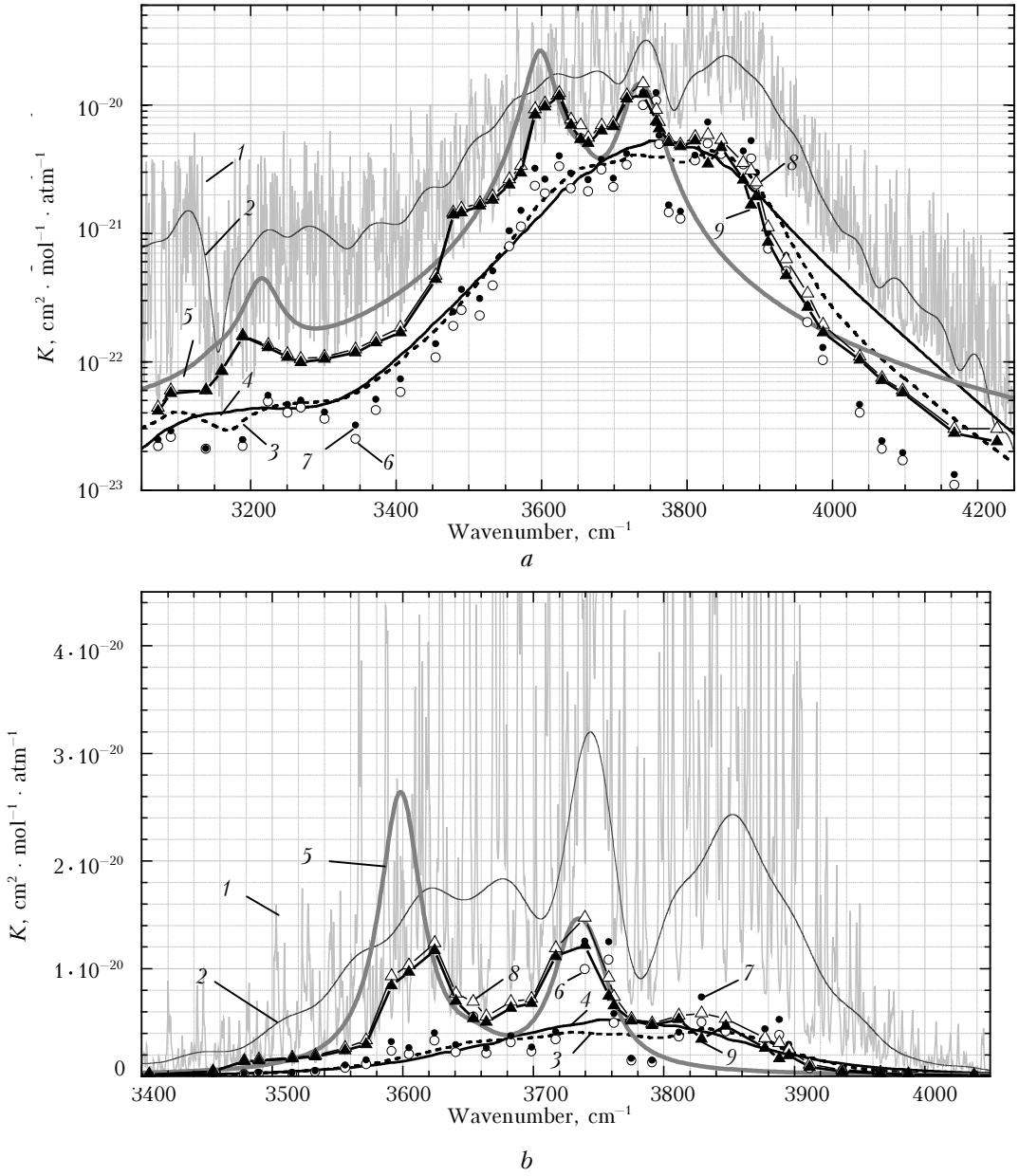

Fig. 1. Absorption spectra in microwindows in the region of 3000–4200 cm^{-1} in the log (*a*) and linear (*b*) scales: HITRAN-2004 + MT_CKD (IF = 0.4 cm^{-1} is the width of a triangular instrumental function, used in Ref. 17 and in this work) (curve *1*); HITRAN-2004 + MT_CKD (smoothed) (*2*); CKD-2.4 (*3*); MT_CKD (*4*); water dimers[16] (Keq = 0.04 atm^{-1}) (*5*); monochromatic absorption (AFGL,[18] Voigt profile); monochromatic absorption (HITRAN-2004, Voigt profile) (*7*); empirical continuum (Burch, Ref. 17) (*8*); corrected empirical continuum of Burch (*9*).

Analyzing the spectra presented, it is possible to conclude the following.

1. Despite the measurements from Ref. 17 were used in Ref. 7 to develop the first CKD model of continuum, any version of this model, even the latest one, fails to describe the most part of the continuum absorption detected in Ref. 17.

2. Burch's empiric continuum exceeds the CKD-2.4 and MT_CKD continuum, on average, by 3–4 times in the spectral region of 3150–3750 cm^{-1} and is 1.5–2 and 2–3 times smaller than the continuum in these models, respectively, in the region of 3900–4200 cm^{-1}. In the region of 3150–3800 cm^{-1}, Burch's empiric continuum demonstrates spectral features with the centers near 3200, 3610, and 3730 cm^{-1}, which are in a good agreement with WD bands, predicted in Ref. 16, namely $|0\rangle_f|0\rangle_b|2\rangle$, $|0\rangle_f|1\rangle_b|0\rangle$ and a pair of close bands $|1\rangle_f|0\rangle_b|0\rangle$ and $|10\rangle\_|0\rangle$ (designations are the same as in Ref. 16).

3. Similarly to the calculated WD bands, all these absorption peaks have a 10–30 cm^{-1} shift toward the IR spectral region with respect to the water monomer absorption spectrum (see the smoothed spectrum of monomers), which confirms their dimer origin.

4. It should be expected that the WD band $|0\rangle_f|1\rangle_b|0\rangle$ (centered near 3600 cm^{-1}) should have lower intensity than that predicted in Ref. 16 and smaller shift to the IR region. A feature of the continuum absorption near 3490 cm^{-1} is likely caused by the dimer band (missed in Ref. 16) as well, because it is markedly shifted (~20 cm^{-1}) to the IR region with respect to the similar feature in the absorption of water monomers.

It should be also noted that the value of the dimerization constant (0.04 atm^{-1}), used in this work to simulate the WD absorption in the 3000–4200 cm^{-1} band, is in a good agreement with the value used in Ref. 15 for describing absorption by WD in the 5000–5600 cm^{-1} band.

It is seen from Fig. 1 that the selective part of the absorption (see monochromatic absorption coefficients in microwindows), that is, the calculation with the use of only the Lorentz profile, contributes generally much less to the total absorption in selected microwindows within these spectral region. This emphasizes the high reliability of these measurements for determination of the continuum absorption.

Thus, we can assert that Burch's experiment[17] considered in this paper is now the most reliable proof of the significant contribution of WDs to the water vapor continuum absorption.

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