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Water dimer and the atmospheric continuum

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<u>Abstract.</u> The physical origin of humidity-related atmospheric continuum absorption is examined. The existence of double water molecules (dimers) in equilibrium water vapor at room temperature is proved by direct spectroscopic experiments supported by *ab initio* calculations. It is demonstrated that diluting water vapor with air does not significantly reduce the abundance of dimers. Numerous previous studies have predicted the presence of water dimers in the atmosphere and their influence on chemical reactions, homogeneous condensation, and Earth's radiation balance. Our results provide experimental proof of the presence of dimers in the atmosphere, thus enabling a detailed study of their role in natural processes. Prospects for future research are discussed.

1. Introduction

The water molecule is one of the basic molecules determining the physical and chemical processes in Earth's atmosphere. Water makes up less than 0.5% of the atmosphere mass and is responsible for approximately 70% of radiation absorbed by the atmosphere, thus exerting dominant influence on the radiation balance (see, e.g., [1, 2] and the references therein). Furthermore, water vapor is the basic greenhouse gas of the atmosphere providing positive feedback that affects the weather and the climate of Earth [3].

Water molecules that constitute atmospheric water vapor absorb radiation in all ranges, from microwave to ultraviolet and beyond. This absorption is mostly due to the transition of

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Uspekhi Fizicheskikh Nauk **184** (11) 1199–1215 (2014) DOI: 10.3367/UFNr.0184.201411c.1199 Translated by M V Tsaplina; edited by A M Semikhatov molecules to higher rotational and vibrational energy levels corresponding to resonance spectral lines. These lines are fairly intense because the water molecule, although small in mass, has a large permanent dipole moment. This molecule is a light and quite nonrigid asymmetric top, and hence its resonance lines are rather uniformly distributed over the entire electromagnetic wave spectrum. Nevertheless, intense bands can be singled out in the water absorption spectrum, such that, with low instrumental resolution, they resemble an almost periodic sequence of peaks. These bands correspond to different vibrational modes of the molecule, i.e., to motions of the nuclei responsible for stretch of O-H bonds and variation of the angles between them. Each band consists of several hundred narrow (in atmospheric conditions) individual vibrational–rotational resonance lines.

As far back as the first half of the 20th century, water vapor was revealed to also absorb radiation in the intervals between the bands (see, e.g., [4, 5] and the references therein), and somewhat later, already in the middle and at the beginning of the second half of the 20th century, it became clear that the 'excess absorption' is also present inside the bands and shows up in the intervals between resonance lines (see, e.g., [6, 7]). This absorption remained inexplicable, in spite of the determination of increasingly more exact shapes of the resonance lines. Owing to the smooth frequency dependence, it was called nonresonance absorption, or a continuum [8]. In a broad spectral range, the water vapor continuum looks like a small pedestal only noticeable on the logarithmic scale, its shape resembling the spectrum envelope on which the resonance lines reside. Absorption in the resonance line maxima within the bands exceeds the continual absorption by about three orders of magnitude. However, in intervals between the lines, this difference is smaller and, for instance, in the millimeter wave range, in the so-called microwindows of atmospheric transparency, the contribution of the continuum can even exceed the contribution of resonance lines by a factor of 10. Because of the absence of a rigorous physical approach explaining all the known properties of the continuum, empirical formulas with experimentally determined parameters were used to account for the continuum in models of radiation propagation in the atmosphere [9, 10]. Such a description of the continuum persists in all the presently known propagation models.

The discussion of the continuum origin began from the time of its detection and has been going on to the present day (see, e.g., [11] and the references therein).

The explanation of the continuum by a large number of unknown low-intensity resonance bands of the water molecule was discussed already in the 1940s [12, 13]. Such a possibility was completely excluded only recently, when modern methods of global *ab initio* calculations of vibrational–rotational spectra virtually reached the experimental accuracy for the water molecule [14].

The far wings of intense resonance lines in the formation of the continuum were initially considered as the most probable mechanism of its formation [4]. The reason for this is the fact that the traditionally used Lorentz and Van Vlek-Weisskopf line shapes were derived in the framework of the impact approximation, in which the collision duration τ_c is assumed to be negligibly small compared to the time τ between collisions, and therefore these line shapes are only applicable when detunings from the central frequency of a line are much smaller than $(2\pi\tau_c)^{-1}$. This stimulated the development of improved models (see, e.g., [15]) which, however, were not widespread because of the presence of a number of empirical parameters. A very simple empirical correction (the γ function with parameters chosen from experiment) of the traditional line shape in the region of far wings was proposed in [16] for practical applications.

Some conclusions concerning the contribution of the far wings of the resonance lines can be drawn from the calculation of absorption in the quasistatic approximation when a colliding absorbing molecule is considered to be in the constant field of the other molecule. This approximation is only valid for the short instant of collision and is therefore indicative of absorption if the detuning from the central-line frequency is much greater than $(2\pi\tau_c)^{-1}$. For water vapor, such calculations were first done by Rosenkranz (1987) [17] and were further developed by Ma and Tipping (1990-2008) (see [18] and the references therein). The results agree satisfactorily with the observed continuum between vibrational-rotational bands, but underestimate absorption inside the bands. The contribution of the wings could be estimated more accurately by *ab initio* calculations of the line shape. However, in spite of the considerable progress in this field, such calculations are now only possible for small frequency detunings from the line centrum (see, e.g., [19]).

An essentially different approach to the explanation of the origin of the continuum is based on taking the gas nonideality into account. The key work in this direction is the theoretical paper by Stogryng and Hirschfelder (1959) analyzing inelastic collision of structureless molecules [20]. These authors were the first to point out that collisions may cause the formation of double molecules (dimers) and to derive the relation between the number of dimers and the second virial coefficient of the gas equation of state. In [21], these ideas were extended to the case of nonpolar molecules and ions in the approximation of the averaged anisotropic potential of collisional interaction. In a more general case with the properties of the multidimensional anisotropic potential of interacting molecules taken into account, this problem was addressed by Vigasin [22], who demonstrated an important role of the internal degrees of freedom of monomers in dimer formation.

Inelastic collisions of molecules thus give rise to a new absorbing entity, which should necessarily be taken into account in the analysis of absorption in a gas. For water vapor, the analysis from this standpoint, first done in [23], suggested that all the experimentally observed room-temperature continual absorption of radiation by water vapor in millimeter and submillimeter wavelength ranges (the region of the purely rotational water molecule spectrum) can be explained by the presence of dimers.

Another recognized mechanism that may lead to the occurrence of a continuum is absorption due to the transient dipole moment associated with charge redistribution in a molecule that finds itself in the electrostatic field of another molecule during the collision. This leads to the fact that even symmetric nonpolar molecules noninteracting with the electromagnetic field in a free state begin absorbing quanta in the spectral regions corresponding to the rotation and vibration of molecules. Bands occur in the spectrum whose width is inversely proportional to the induced-dipole lifetime. In its origin, this mechanism is also related to inelastic pair collisions of molecules that contribute to the second virial coefficient, and according to [20-22] it should be attributed to the result of interaction of free pairs of molecules. Obviously, for water vapor, this mechanism can only show up within resonance bands. The estimates of such absorption reported in [22, 24] suggest that for temperatures typical of Earth's atmosphere, its contribution to the observed water vapor continuum can be neglected.

Here, we present a retrospective review of the study of the dimer mechanism of continual absorption in water vapor. In Section 2, we discuss the mechanism of collisional dimer formation and estimate the abundance of dimers in equilibrium water vapor. In Section 3, we analyze the most wellknown attempts of the experimental discovery of dimers by spectroscopic methods in the laboratory, where water vapor was studied under conditions close to atmospheric, and in the real atmosphere. In Section 4, the equilibrium dimer structure is examined along with the main features of its intramolecular dynamics determined from dimer spectrum observations in low-temperature molecular beams. Sections 5 and 6 expound how, after the attempts of many researchers that lasted nearly half a century in different countries of the world, the present authors were able to reveal the specific features in the spectra, first in pure water vapor and then in a mixture of water vapor and atmospheric air, unambiguously pointing to the presence of dimers. We discuss what information can be obtained from such spectra. In conclusion (Section 7), the prospects of water vapor studies by molecular gas spectroscopy are discussed.

2. Collisional dimer formation

Questions related to dimer formation due to pair collisional interactions of molecules in the gaseous phase were considered in detail in [20–22, 25].

The result of molecular collisions is determined by the velocity v of their relative approach, the impact distance b (i.e., the minimum approach of molecules under conditions of straight-line motion), and the interaction potential U(r), where r is the intermolecular distance. Within classical mechanics, it can be rigorously shown (see, e.g., [26]) that if the distance between colliding structureless molecules is viewed as a function of time, then its kinematics is the same as in motion along one coordinate of a point mass with the reduced mass $\mu = m_1 m_2/(m_1 + m_2)$, where m_1 and m_2 are the



Figure 1. Effective potentials of intermolecular interaction for different values of rotational angular momentum of an interacting pair depending on the intermolecular spacing. The energy is normalized to the potential well depth D_e and the spacing to the equilibrium spacing r_e .

masses of colliding molecules, and with the kinetic energy $K = \mu v^2/2$ in the field of the effective potential energy

$$U_{\rm eff}(r,L) = U(r) + \frac{L}{r^2}, \qquad (1)$$

where $L = Kb^2$.

If we assume that the angular momentum of a colliding pair is $M = \mu vb$ and the moment of inertia is $I = \mu r^2$, then $L/r^2 = M^2/2I$, which corresponds to the energy of rotational motion of the pair relative to its center of mass.

A typical family of curves of effective potentials corresponding to different L values is presented in Fig. 1. The existence of a minimum and a maximum for low L implies that a colliding pair can tunnel through the potential barrier and find itself inside the potential well, forming a metastable molecular complex or a metastable dimer. The internal energy of such a dimer exceeds the energy of two free molecules ('zero' energy), and therefore it can dissociate not only when colliding with a third molecule but also by tunneling through the potential barrier. However, in a collision with a third molecule, this complex can transfer the excess kinetic energy to it and turn into a stable state, the process that is precisely the mechanism of the appearance of stable (frequently called 'bound') dimers.

The qualitative features of collisional interaction of polyatomic molecules, to which the water molecule pertains, are the same. Taking the interaction anisotropy of polyatomic molecules into account leads to the fact that quasibound pair states can occur due to not only rotation of the pair but also excitation of the internal degrees of freedom of the monomers. The excess kinetic energy of the pair is transferred, for example, to the internal monomer rotation in the dimer about the common bond or to other degrees of freedom.

The parameter characterizing the number of dimers appears from a consideration of the process of their formation as a reversible reaction of the merging of two monomers:

$$\mathbf{M} + \mathbf{M} \Leftrightarrow \mathbf{D} \,. \tag{2}$$

Obviously, the dimer formation rate is equal to the product of the probability α of the arrival of each interacting molecule at

the same spatial point, the probability β of dimer formation, and the concentrations $[M] = n_m$ of interacting molecules:

$$V_1 = \alpha \left[\mathbf{M}\right] \alpha \left[\mathbf{M}\right] \beta = \alpha^2 \beta \, n_{\rm m}^2 \,, \tag{3}$$

and the dimer decay rate is equal to the decay probability δ times the dimer concentration $[D] = n_d$:

$$V_2 = \delta\left[\mathbf{D}\right] = \delta n_{\rm d} \,. \tag{4}$$

Under equilibrium conditions, these rates are equal. The ratio derived from (3) and (4) for $V_1 = V_2$,

$$\frac{n_{\rm d}}{n_{\rm m}^2} = \frac{\alpha^2 \beta}{\delta} = K_2^{\rm c} \,, \tag{5}$$

is a constant quantity at a given temperature. This quantity is called the reaction equilibrium constant. If the interacting molecules can be regarded as an ideal gas, then, at a constant temperature, the concentration is directly proportional to pressure. The equilibrium constant can therefore be expressed in terms of the partial pressures of the initial and final reaction products:

$$\frac{p_{\rm d}}{p_{\rm m}^2} = K_2^{\rm p} = K_2 \,. \tag{6}$$

Such a definition of the equilibrium constant is conventional, but less rigorous because the merging reaction (2) is caused by the collision of molecules whose number is proportional to the number of molecules in unit volume, i.e., to the concentration rather than pressure, which is secondary.

An analytic relation exists between the equilibrium constant and the second virial coefficient of the gas equation of state (see [20, 27]):

$$B(T) = b_0 - K_2 RT, \tag{7}$$

where b_0 is the excluded volume or the region of space occupied by gas molecules.

Using the methods of statistical mechanics (see, e.g., [28]), it can be rigorously shown that the equilibrium constant can be represented as the sum of components corresponding to metastable and bound dimers:

$$K_2 = K_{\rm m} + K_{\rm b} \,. \tag{8}$$

Hence, the total number of dimers in equilibrium water vapor can be calculated using the estimate of the excluded volume and the empirical thermodynamic data on the state of water vapor, whose relative uncertainty in the range of temperatures from 273 to 1275 K and pressures from 0 to 1000 MPa (\approx 9869 atm) is presently less than 0.1% [29]. Examples of such calculations can also be found in papers of the first half of the 20th century (see, e.g., [27]) and in recent papers [25, 30]. The results of such calculations agree rather well both among themselves and with the results of present-day *ab initio* calculations [31, 32], and even with experimental data on measurements of thermal conductivity of water vapor [33] (Fig. 2).

The main conclusion following from these estimates is that rather many dimers must be produced. In water vapor in conditions typical of Earth's atmosphere, the relative dimer concentration equals $10^{-3}-10^{-4}$. Because gaseous traces of polar molecules with a relative concentration of $\sim 10^{-6}$ can



Figure 2. Temperature dependence of the water dimer equilibrium constant. The thin solid curve is a calculation by the second virial coefficient [25] (bound and metastable dimers). The bold solid curve is an *ab initio* calculation [31] (bound dimers only). The dashed curve is a calculation from association theory (bound dimers) [34]. The circles show the *ab initio* calculation in [35] (bound and metastable dimers). The cosses stand for the experimental data in [33] (bound and partially metastable dimers). The diamonds are the experimental data presented in Section 5.

readily be revealed by spectroscopic methods, it seems that the observation of water dimer spectra must not encounter any difficulties. Nevertheless, in spite of researchers' attempts, the spectra that might unambiguously be interpreted as belonging to dimers have not been observed in equilibrium water vapor at atmospheric temperatures until 2013 [36], i.e., over half a century from the time when the necessity of such observations was recognized. As is exemplified in Section 3, the main reason for such a delay and the ambiguity in the interpretation of the earlier experimental results lay in the lack of information on the dimer spectrum and insufficient accuracy of this information.

3. Experimental search for spectral manifestations of dimers

Indications that some water molecules in water vapor are in an associated (bound) state can be found, for instance, in the 1930s papers by Landsberg [37], where the analysis of the Raman spectra of water vapor showed the presence of equilibrium between isolated and associated molecules and demonstrated that varying the vapor temperature only induces a shift of this equilibrium rather than a gradual weakening of hydrogen bonds between associated molecules.

The paper by Penner and Varanasi [38] is the first known experimental study in which the 'intermolecular coupling and interactions' are mentioned as the most probable mechanisms accounting for the excess absorption in the water vapor spectrum. The authors of [38] studied the radiation absorption of the far-IR range in the region of the high-frequency wing of the band of the water vapor rotational spectrum at 400 and 500 K in the pressure range 2 to 25 atm. The integral intensity of the observed spectra increased faster than the linear pressure dependence, which could be explained by the far wings of intense water monomer lines in the model of the Lorentzian line shape. In their next work [39], the authors supplemented their experiments with the study of the temperature dependence of the observed excess absorption, which decreased with increasing temperature. This allowed estimating the binding energy of merging water molecules in the range 3 to 5 kcal mol⁻¹, which corresponds to the hydrogen binding energy.¹ As a result, they concluded that the cause of the observed excess absorption is the "association of water molecules due to hydrogen bonding." We note that the authors of [38, 39] do not mention molecular dimerization, although according to modern notions, the dimer is obviously the most widespread associate of water molecules under the conditions of their experiments.

The strong negative power-law temperature dependence of integral water vapor absorption revealed in this way and the quadratic pressure dependence of absorption have long been considered characteristic spectral features of dimers (see, e.g., [41–44]). Theoretical calculations of absorption in monomer far wings and absorption due to a collisioninduced additional dipole moment (see, e.g., [18, 24] and the references therein) showed later that such dependences are inherent not only to dimer absorption.

The hypothesis of Viktorova and Zhevakin concerning the dimer origin of the excess absorption of millimeter and submillimeter waves by water vapor [23] and their calculations of the dimer rotational spectrum (see [45] and the references therein), indicative of the presence in the spectrum of two features formed by merged lines of dimer rotational transitions at a constant total angular momentum at frequencies of about 7 and 21 cm^{-1} , stimulated an active search for and studies of the spectral peaks of water vapor near these frequencies in laboratory conditions and in the atmosphere. The most prominent in this connection is the series of studies by Gebbie et al. (see [46-48] and the references therein). A characteristic peak was revealed near the frequency 7.5 cm^{-1} (Fig. 3). The quadratic dependence of peak absorption on the water vapor pressure and its temperature dependence corresponding to the binding energy of the water dimer were demonstrated. This discovery was not supported by other studies. It was also criticized by Zhevakin as ungrounded, because the amplitude of the



Figure 3. Example of experimental data that allowed Gebbie et al. [46–48] to declare water dimer observation in the atmosphere. The dashed curve corresponds to the base line of the spectrometer. The thin solid curve is the measured water vapor transmission spectrum. The grey spectral area near the frequency of 7.5 cm^{-1} was interpreted as dimeric absorption. The bold curve shows the calculated water vapor spectrum in experimental conditions with the spectrometer resolution taken into account. The star marks the H₂O line near the wave number 6 cm⁻¹ (183 GHz), in the center of which absorption makes up $1.3 \times 10^{-3} \text{ cm}^{-1}$. The real relation of the amplitudes of this line and the dimer peaks can be seen in Fig. 11.

¹ The monomer binding energy D_e in a water dimer is 4.998 kcal mol⁻¹ = 1748 cm⁻¹ according to the current data [40].



Figure 4. High-temperature spectra of water vapor in the range of fundamental O-H bond vibrations [57]: (a) demonstrated is the correspondence between the model and the experimental data, (b) exemplified by the decomposition of one of the observed spectra into components. DM and TM are respectively metastable dimers and trimers.

discovered peak had the same magnitude as the neighboring peaks corresponding to monomer lines, which were several orders of magnitude more intense [49]. Moreover, as we show in what follows, in the dimer spectrum calculated by modern methods of quantum chemistry, characteristic features near frequencies of 7 and 21 cm⁻¹ are absent [50].

A very successful area of the search has been the study of water vapor spectra at high temperatures and pressures, i.e., in conditions when dimers (whose number is proportional to the pressure squared) must be numerous [51-56]. This work, in fact, develops and extends the investigations started by Landsberg [37] of the influence of molecule association on the vibrational frequencies of O-H bonds in water. Their results, which are fairly consistent with each other, convincingly prove that the water vapor nonideality, which shows up with increasing pressure, is due to the formation of small water clusters. Furthermore, the spectroscopic modeling of the shape of such spectra [57] suggests that the fraction of bound water dimers is substantial even under conditions more typical of a steam engine than for the atmosphere (Fig. 4). All this has confirmed the feasibility of also revealing dimers in ambient conditions. However, these studies show that the relative variation of the frequency of fundamental O-H vibrations in a water molecule upon the formation of a bound dimer is only about 3%, much less than the inhomogeneous vibrational band width due to its rotational structure. Under such conditions and with the known difficulties of work with water vapor and uncertainty in modeling the monomer spectrum, detection of a dimer band of an uncertain width on the background of a much more intense monomer band (under ambient conditions) is a rather nontrivial task.

It would seem that the problem could be solved by calculating the frequencies and intensities of overtones of the characteristic vibrations of O-H bonds in a dimer and finding the spectral range in which a sufficiently intense dimer band would lie between monomer bands. The obvious shortcomings of this approach are that (a) each subsequent overtone is about an order of magnitude weaker than the

preceding one; (b) the precision of the prediction of band parameters decreases with increasing the overtone number; (c) a dimer that is in a more and more excited metastable vibrational state as the overtone number increases dissociates increasingly fast, which may lead to a considerable additional broadening of the dimer bands, up to the complete impossibility of their observation. Nevertheless, an example of such an analysis can be found in [58], where it is pointed out that the dimer band can be revealed near a frequency of 14,800 cm^{-1} . The search for the predicted peak in the atmospheric spectrum using the Sun as a radiation source has not met with success [59]. Nothing has been revealed except absorption in the known lines of atmospheric water and oxygen, although, judging by the estimates of the dimer band intensity and the probable dimer abundance under conditions of observations, the researchers had an almost tenfold reserve in sensitivity.

A similar approach to the discovery of a dimer absorption line in the atmosphere was used in the well-known paper by Pfeilsticker et al. [60]. It was based on more accurate calculations of the frequency and intensity of a third overtone of O-H bond vibrations in a dimer, carried out by another team [61], and a long overwater path (longer than 18 km) was organized for the observations, which was saturated with water vapor and provided a higher sensitivity of detection than in the vertical atmospheric paths. The theoretically predicted dimer peak with a maximum near the frequency of 13,400 cm⁻¹ was found as the difference between the observed and calculated spectra of atmospheric absorption (Fig. 5). The revealed absorption demonstrated the expected quadratic dependence on the air humidity and agreed well with the calculated value, which allowed the authors of [60] to declare the direct detection of dimers in the atmosphere. However, a subsequent high-sensitivity study of the water vapor spectrum [62] showed a large number of previously unknown monomer lines in the region of the revealed dimer band. Taking them into account in the atmospheric absorption model resulted in complete agreement of the observed and calculated spectra, leaving no room



Figure 5. Data that allowed Pfeilsticker and colleagues to declare the observation of water dimers in atmosphere [60]. The solid curve shows the measured atmosphere transmission spectrum. The dotted curve demonstrates the result of modeling this spectrum with all water monomer lines known at that time taken into account.

to dimer absorption. Subsequent laboratory studies confirmed the absence of dimer absorption in this range, even at the water vapor pressures ensuring dimer concentration an order of magnitude higher than that attained in environmental conditions [63].

Given the absence of significant errors in the calculations of frequencies and intensities of dimer bands or the dimerization constant, this may mean that the width of spectral features in dimer absorption is strongly underestimated, possibly because the low-frequency intermolecular vibrations in the dimer are not fully taken into account. For example, it was shown in [64] that even with only two of the six strongly interacting intermolecular vibrations in the dimer included, the width of the band of a third overtone of O-H vibrations can reach 250 cm⁻¹, which exceeds the width of the peak found by Pfeilsticker by more than an order of magnitude [60]. Furthermore, we must recall that the dimer dissociation energy only makes up $1105 \pm 10 \text{ cm}^{-1}$ [65], which is an order of magnitude less than the energy of the radiation quantum absorbed by a dimer in these experiments. Consequently, the unknown band can be greatly broadened because of a rather short lifetime of the dimer metastable state.

An alternative approach to seeking dimer absorption is the study of the water vapor continuum within the vibrational-rotational monomer bands [66–68] or in the range of its rotational spectrum [69]. The absorption intensity in the peaks of monomer lines exceeds the continuum one by more than an order of magnitude, but this excess is insignificant in the numerous transparency microwindows between individual lines and can be registered, for instance, by using a multipass gas cell. An obvious advantage of the approach is the possibility of detecting intense fundamental vibration bands in the dimer, and the disadvantage is the need in a very precise monomer absorption spectrum, calculating whose line shape in the region of detuning from the line central frequency greater than $(2\pi\tau_c)^{-1}$ is still an unsolved problem.

Typical problems in the application of such an approach can be shown with the example discussed in [70], where the continuum was investigated in the range 5000 to 5600 cm⁻¹, corresponding to combinations of fundamental vibrations of



Figure 6. Data that allowed Ptashnik et al. [70] to draw a conclusion about the dimeric nature of continual absorption in water vapor within the vibrational–rotational monomer absorption band. The circles are the results of experimental measurement of continual absorption in transparency microwindows of room-temperature water vapor. The solid curve is the calculated water dimer spectrum [71]. The dashed curve shows the result of calculations of the model spectrum of the H₂O molecule at room temperature and a pressure of 20 atm by the HITRAN (High resolution TRANsmission molecular absorption) database [73].

bending and stretching of bonds in the monomer molecule. The authors of [70] believe that the evidence of dimer manifestation is the fact that a part of the residual of the monomer spectrum subtraction from the observed absorption strongly resembles the dimer absorption band shape assumed on the basis of the calculations in [71] (Fig. 6). Proceeding from this, they obtain dimerization constant values well consistent with the theoretical and experimental data. But the shape of the measured continuum coincides even better with the shape of the monomer spectrum with very low spectral resolution, which testifies to the possibility of another interpretation of the results of measurements. Nevertheless, the subsequent application of this method for the analysis of the water vapor continuum in the range of monomer fundamental vibration bands near the frequencies 1600 and 3650 cm^{-1} and a thorough analysis of temperature dependences of the observed absorption (see [72] and the references therein) allowed the authors to convincingly testify that at least part of the continuum observed inside the monomer bands can be explained by dimers. It was taken into account that some of the dimers are in metastable states, and their spectrum is estimated as a doubled monomer spectrum homogeneously broadened because of the short lifetime.

A similar method was used by the same authors to analyze the water vapor continuum in intervals between different monomer absorption bands in the frequency range 2500 to 10,000 cm^{-1} [74]. The measured continuum absorption demonstrated a quadratic dependence on the water vapor pressure and a strong negative power-law temperature dependence. The analysis of possible mechanisms of continuum formation allowed the authors to conclude that the greatest contribution to the observed absorption is made by water dimers. However, further measurements of the continuum in the frequency range 5875 to 6450 cm⁻¹, corresponding to one of the transparency windows, showed [75] that the results of absorption measurements in [74] had been overestimated by 1-2 orders of magnitude compared to the real absorption and that further investigations are needed to clarify the nature of the continuum in intervals between the monomer absorption bands.

The search for spectral manifestations of water dimers under conditions close to atmospheric had been generalized two years before their discovery at a major international conference devoted to molecular complexes in the atmosphere and beyond [76]. In the foreword to the special issue of *Molecular Physics* devoted to this conference (a special issue on a workshop by the Solvay Institutes dealing with molecular complexes in our atmosphere and beyond. Brussels—April 2010), the editors say: "Yes, the water vapor dimer is very likely to be present in our atmosphere and yes it is expected to contribute a profound fraction of the radiation budget; beware of fakes when searching for evidence of complexes and make sure that monomer contributions are accounted for up to the latest details, including all refinement in the line profile investigation" [77].

Much more successful were studies of water dimer spectra in cold molecular beams [78–80], molecular matrices [81–83], and helium nanodroplets [84]. These studies made it possible to assert the water dimer as a physical entity, to determine its equilibrium structure, to clarify its complicated internal dynamics, and to find the characteristic frequencies and intensities of fundamental vibrations. Nevertheless, in all these studies, the interaction of water molecules occurs at temperatures of several degrees Kelvin, and therefore they cannot answer the question of the dimer abundance and spectrum in Earth's atmosphere.

4. Dimer structure and spectrum

The dimer configuration was determined in the 1970s by selecting structure parameters satisfying the measured frequencies of several first rotational transitions of dimers whose lines were observed in cold molecular beams [78]. The dimer turned out to have an open structure (Fig. 7) in which water monomers are coupled by a hydrogen bond such that one of them is a donor (giving a proton) and the other is an acceptor



Figure 7. Equilibrium structure of water dimer found from ab initio calculations [85]. The left H_2O molecule plays the role of a proton acceptor and the right one of a proton donor. The dimer molecule has a symmetry plane in which the donor and the oxygen acceptor atom reside. The acceptor symmetry axis lies in the same plane. The positions of monomers relative to each other is characterized by the spacing between the oxygen atoms (2.9089 Å) and the angles between the monomer symmetry axis and the axis passing through the centers of oxygen atoms (the values of the angles are given in the figure). The positions of atoms in monomers are determined by the angle between the bonds (104.58° in the acceptor and 104.45° in the donor) and by the O-H bond lengths, which are identical in the acceptor (0.9597 Å) and somewhat different in the donor (0.9581 Å for the free proton bond and 0.9653 Å for the proton that forms the hydrogen bond). For comparison, the most exact calculations of parameters of the equilibrium configuration of the water molecule yield the angle 104.50° and the bond length 0.95785 Å [86].



Figure 8. Splitting of the lower rotational level of a water dimer, J = 0, K = 0 (*J* is the quantum number of the total angular momentum of the molecule and *K* is the quantum number of projection of the total angular momentum onto the top axis) due to the tunneling designated as AST (acceptor switch tunneling), IT (interchange tunneling), and BT (bifurcation tunneling). A, B, and E are types of level symmetry according to the adopted classification [94], given in parentheses is the statistical weight of levels due to the presence of spin in the hydrogen atom. The right-hand side of the figure shows an approximate value of splitting and shift of the levels [cm⁻¹]. For $K \neq 0$, the level parity degeneracy is removed because of the dimer asymmetry, which leads to an additional splitting of sublevels with A and B symmetry into two, and as a result, each vibrational–rotational level with $K \neq 0$ is split into ten rather than six sublevels.

(accepting this proton). Presently, the most accurate parameters of the dimer equilibrium configuration are known from high-accuracy *ab initio* calculations [85]. The details concerning the specific features of the complicated intramolecular water dimer dynamics can be found in [87–93] and the references therein.

The equilibrium dimer structure implies that it is an almost symmetric prolate top with a permanent dipole moment directed virtually along the top axis. From the possibility of permutation of identical nuclei and the presence of a symmetry plane, it follows that the dimer molecule has eight energetically equivalent configurations. Transitions from one configuration to another occur due to tunneling through three rather low potential barriers. Tunneling through the lowest barrier (about 160–170 cm⁻¹) leads to proton exchange in the acceptor. The corresponding motion (see Fig. 3 in [89]), called acceptor switch tunneling, splits each vibrational-rotational dimer level into two (Fig. 8). The second, most probable tunneling makes the monomers exchange their roles: the acceptor becomes the donor and vice versa. The corresponding motion, called interchange tunneling, can occur in two ways differing in the monomer rotation direction about their symmetry axes [87]. The barrier heights are nearly 200 and 400 to 500 cm^{-1} . This tunneling results in splitting each of the sublevels into three, occurring through the acceptor switch tunneling (see Fig. 8). The last type of tunneling in the dimer is the motion causing the donor protons to exchange places. The motion is called bifurcation tunneling. According to different estimates, the height of this barrier is from 400 to 1000 cm⁻¹. The indicated tunneling induces a small shift of the split sublevels, but does not lead to their further splitting (see Fig. 8).

The analysis of possible vibrations in water dimers was first carried out in [95]. In total, 12 normal vibrational modes exist. Six of them correspond to intramolecular vibrations of O-H bonds of monomers, each of which can contain symmetric and asymmetric bond stretching vibrations and





Figure 9. Six normal vibrational intermolecular modes of water dimers [95]. DT is donor torsion, OOS (O–O stretch) is the stretch of the O–O bond, AW is acceptor wag, AT is acceptor torsion, IPB (in-plane bend) is the hydrogen bond bend in the dimer symmetry plane, OPB (out-of-plane bend) is the hydrogen bond bend perpendicular to the symmetry plane.

bending vibrations corresponding to a change in the angle between the bonds. The frequencies of these modes are close to the frequencies of monomer modes. The other six modes correspond to low-frequency intermolecular monomer vibrations in the dimer molecule (Fig. 9). The calculated and experimentally measured frequencies of normal modes are presented in Table 1. We note that because of the strong anharmonism of intermolecular dimer vibrations, the combinational modes of low-frequency vibrations can have a substantial intensity comparable with the intensity of fundamental high-frequency vibrations. Therefore, identification of the most high-frequency modes, for example, corresponding to hydrogen-bond bending in the molecular symmetry plane and the plane perpendicular to it (in-plane and out-ofplane bend) cannot yet be considered final. The frequencies of these modes have only been measured in cold neon and hydrogen matrices, which may affect dimer vibration and, moreover, identification of these modes has not been confirmed by rigorous ab initio calculations.

Four low-frequency modes lie in the frequency range 50 to 150 cm⁻¹. These modes, their overtones, and their combinational vibrations form several thousand states, which at room temperature (thermal energy $k_{\rm B}T \sim 200 \ {\rm cm}^{-1}$) turn out to be populated to an extent sufficient to make a significant contribution to the dimer spectrum. Each of these states has a complete set of inversion-rotational levels. Such a notable inhomogeneous spectrum broadening together with the homogeneous pressure-induced line broadening leads to the fact that within its rotational-vibrational bands, the dimer spectrum is represented by continual absorption uniformly smeared about a wide spectral region [100]. The same fact explains the failure to observe the dimer spectrum in warm water vapor, even in a very well prepared laboratory experiment: a characteristic group of vibrational-rotational dimer lines (Q branch) observed at a temperature of 5 K in a cold molecular beam with a very good signal-to-noise ratio did not show up in the room-temperature water vapor spectrum (see Fig. 6 in [101]).

The most rigorous and presently accurate *ab initio* calculations of the dimer spectrum shape at temperatures typical of Earth's atmosphere and based on the summary results of previous theoretical and experimental research were published in [50]. The calculations were only performed for millimeter and submillimeter frequency ranges in which the effect of nonrigidity of the dimer on its spectrum is much less

Table 1. Frequencies $[cm^{-1}]$ of normal vibrational modes of water monomers and dimers.

H ₂	O monomer	$(H_2O)_2$ dimer			
Mode*	Experiment ** (HITRAN [73])	Mode ***	Calculation ** [93]	Experiment	
v ₁ v ₃ v ₂	3657.1 (0,4) 3755.9 (9) 1594.7 (13)	$\begin{array}{cccc} v_3 & (v_1,d) \\ v_1 & (v_3,d) \\ v_2 & (v_1,a) \\ v_9 & (v_3,a) \\ v_4 & (v_2,d) \\ v_5 & (v_2,a) \\ v_{10} & (OPB) \\ v_6 & (IPB) \\ v_7 & (OOS) \\ v_{11} & (AT) \\ v_8 & (AW) \\ v_{12} & (DT) \end{array}$	3591 (28) 3711 (12) 3634 (0,9) 3725 (11) 1614 (7) 1603 (13) 495 (14) 304 (1,3) 144 (12) 122 (21) 121 (31) 85 (10)	3601 [96] 3735 [96] 3660 [96] 3745 [97] 1616 [98] 1599 [98] 523 [98] 311 [98] 143 [99] 108 [90] 103 [90] 88 [90]	

* Notation for the normal monomer modes: v_1 is symmetric bond stretch, v_3 is asymmetric bond stretch, and v_2 is bond bend.

** Given in parentheses are the relative oscillator strengths according to the calculations in [98]. The currently most exact frequencies of low-frequency fundamental intermolecular vibrations in a dimer are given in [32].

*** Notation for the dimer normal modes [95] and their description (in parentheses) indicating the corresponding normal modes of acceptor molecules (a) and donor molecules (d) for intramolecular vibrations and notation for intermolecular vibrations (see Fig. 9).

than in the infrared. Nevertheless, all possible vibrational– rotational–inversion transitions of the dimer up to the hydrogen bond dissociation threshold were explicitly taken into account in the calculations. If we assume that the width of individual dimer lines is 0.12 cm^{-1} , i.e., approximately the same as the line width of most polar atmospheric molecules at a pressure of 760 mmHg, then using the method of calculation of the spectrum shape [50] for water vapor at the temperature 293 K and humidity 7.5 g m⁻³ (which corresponds to ordinary room conditions with relative humidity about 44%) gives the spectrum shown in Fig. 10. The figure also compares the results of calculations by Viktorova and Zhevakin [45] performed under the same conditions in a very simplified model of the dimer as a rigid top with a possibility of internal



Figure 10. Calculated room-temperature water dimer spectrum in millimeter–submillimeter wave range obtained using the currently most complete and exact quantum chemical calculations [50] (for a water vapor pressure of 7.6 mmHg) and the dimer spectrum in atmospheric air at the same temperature and water vapor partial pressure obtained in the simplified model of rigid and rigidly bound monomers with a possibility of internal rotation [45].

rotation of rigid monomers around the hydrogen bond. Surprisingly, having almost no information on dimers, the authors of [45] predicted correctly that the dimer has a linear (also referred to as open) molecular structure with one hydrogen bond [102]. This made it possible to correctly determine the general frequency dependence of the spectrum and its integral intensity [45, 103].

The approximate shape of the dimer absorption spectrum in the IR range obtained from the presently most accurate model calculations of frequencies and intensities of vibrational dimer modes including the bond and anharmonism of vibrations [93] is shown, for instance, in Fig. 3 in [72]. We note that such modeling of the dimer spectrum only provides a rough qualitative picture, because neither the width nor the shape of vibrational-rotational dimer bands is known.

An analysis of previous attempts to seek dimers in the atmosphere or in water vapor under conditions close to atmospheric suggests that an erroneous detection of dimers from their spectra can only be avoided if not a single spectral feature but a series of discrete peaks typical of dimers is observed in experiment. In [104], based on the ab initio calculations in [50], it is shown that the role of such a series can be played by the rotational dimer spectrum observed in water vapor on millimeter waves at a lowered pressure $(\sim 10 \text{ mmHg})$ when homogeneous collisional line broadening has not yet completely transformed the dense discrete dimer spectrum into smooth continual absorption. At low pressures in the spectral range 60 to 350 GHz ($2-12 \text{ cm}^{-1}$), a sequence of equidistant peaks can be seen on the background of quasi-continual absorption (Fig. 11). Calculations (see Fig. 1 in [104]) show that each peak of this series is formed of a large number of merged lines corresponding to the transitions $J \rightarrow J + 1$ between levels with symmetry E (see Fig. 8) with different K values in the various vibrational states of the dimer. It was shown in [79] that the frequencies of lines of such transitions form quasi-equidistant sequences analogous to the spectra of polar diatomic molecules. The most intense are the series with K = 0 in the vibrational ground state, which corresponds to rotation of a dimer molecule as a dumbbell about the axis with the maximum moment of inertia. Consequently, the positions of peaks observed in the spectrum are to a great extent determined by the frequencies of these particular transitions. With increasing the molecular rotation frequency, the nonrigidity effects intensify and the differences in positions of similar-type molecular transitions



Figure 11. Water dimer spectrum in water vapor calculated *ab initio* at a temperature of 270 K and a pressure of 3 mmHg (Torr) [104]. The inset gives an enlarged portion of the picture.

in various vibrational states accumulate. This causes gradual inhomogeneous broadening of rotational peaks in the dimer spectrum and their complete smearing at frequencies above 350 GHz (see Fig. 11).

An important point in choosing precisely the lowfrequency part of the rotational spectrum of a dimer for its first experimental detection, as pointed out in [104], is that the monomer spectrum does not prevent the dimer spectrum from being observed: owing to a considerable distinction between the monomer and dimer in mass and symmetry type, their rotational spectra differ considerably. The monomer spectrum in this range is studied very well. The maximum intensity of rotational monomer lines lies in the short-wave part of the submillimeter range. The millimeter range contains only one intense line near 183 GHz and several weak lines corresponding to the rotational spectrum of the main water isotopologue H216O in the first excited bending vibrational state and to the spectrum of a partly deuterated water isotopologue HDO. The parameters of all these lines are known [73]. The weak lines are comparable in intensity with the rotational peaks of dimers, but because of a noticeable difference in width, they may be attributed to useful markers in the observed spectrum rather than to obstructing factors.

Concluding this section, we note that the analysis of the *ab initio* calculated dimer spectrum in the millimeter wave range allows extending the abovementioned advantages of paper [45] to the prediction of spectrum quasi-periodicity and the correct estimate of the period of characteristic rotational peaks. However, only part of the spectrum appeared to be quasi-periodic, but as we show in Section 5, precisely this part plays a decisive role in the proof that the observed spectra belong to water dimers.

5. How the dimer was discovered

Figure 11 vividly demonstrates that observation of the 'warm' dimer spectrum with ordinary microwave spectrometers (see, e.g., recent review [105]) is problematic. The dimer concentration and hence the intensity of dimer peaks in the water vapor spectrum are directly proportional to the vapor pressure squared (see Section 2). At pressures such that the intensity of peaks turns out to be sufficient for detection, their width becomes too large for the peaks to be confidently distinguished on the background of the spectrometer baseline.²

In our opinion, the only possibility to detect the characteristic sequence of rotational dimer peaks is the use of resonator spectrometers, in which radiation absorption is registered from a variation of the Q-factor of the resonator filled with the gas under study [10, 106–108]. Such a method of measurements eliminates problems associated with separation of the absorption signal from the baseline and allows the molecular spectra, including those of continual absorption, to be examined at pressures up to the atmospheric one and higher.

This kind of spectrometer developed by our team [108– 112] registers atmospheric gas spectra in the frequency range 37 to 500 GHz, which is covered continuously. Fast digital sweeping of the radiation frequency in a phase-locked regime is first realized in such kind of spectrometers [113]. The

 $^{^2}$ The base line or the instrument function of the spectrometer is the frequency dependence of its output signal without an investigated substance. Absorption in the substance is counted from this line.



Figure 12. Simplified schematic diagram of the resonator spectrometer. The resonator is excited by coherent frequency-scanned backward wave oscillator (BWO) radiation. The resonator response is received by the detector. The resonance curve width unambiguously related to the radiation power loss in the resonator is determined from the digital response recording. The spectrometer measures the widths of responses corresponding to successive longitudinal resonator modes in the entire range of operating frequencies of the radiation source (see Fig. 13).

absence of phase discontinuities upon frequency switching allows recording the resonator response signal within a time shorter than the characteristic periods of electric and mechanical noise. Owing to this, the sensitivity to variation of the gas absorption coefficient $\sim 4 \times 10^{-9}$ cm⁻¹ was reached, which is almost an order of magnitude better than in all the known analogues. The spectrometer was successfully used to investigate the parameters of major diagnostic atmospheric lines of the millimeter and submillimeter wave ranges [114-122] and the continuum in the mixture of water vapor with nitrogen at atmospheric pressure [123]. The value of radiation absorption by the investigated gas is measured in the spectrometer at known frequencies of successive longitudinal modes of an open Fabry-Perot resonator. The spectrum recording is then analogous to recording with stepby-step scanning of the radiation frequency in ordinary microwave spectrometers. The step magnitude is equal in frequency to the intermode interval determined by a fixed resonator length and makes up about 200 MHz. Comparing this value with the characteristic width of rotational dimer peaks (see Fig. 11) shows that such frequency scanning is quite sufficient for their detection. A simplified schematic diagram of the spectrometer and a diagram illustrating the measurement method are presented in Figs 12 and 13.

For dimer detection, the spectrometer resonator was placed in a vacuum chamber where gases were examined at lowered pressures [112].

From the very start, the experiments were successful (the actual detection was reported in [124] and the details were published in [36] and in the on-line addendum to it). Recordings of the room-temperature water vapor spectrum at a pressure of about 12 mmHg in the frequency range 105 to 150 GHz, after subtraction of the monomer contribution, clearly demonstrate a sequence of four dimer peaks predicted in [104]. The peak positions exactly correspond to the frequencies of rotational dimer lines well known from low-temperature beam experiments. Numerous additional experiments showed that a series of characteristic peaks is observed in the water vapor spectrum in the course of repeated experiments and after replacement of key elements of the spectrometer and after changes in the waveguide path of the spectrometer, but not if (under the same experimental



Figure 13. Method of broadband spectrum recording using a resonator. I — the resonance width measured at frequencies of resonator eigenmodes (\approx 300 dots joined by lines) filled with an investigated gas (water vapor at a temperature of 38 °C and a pressure of 27.2 Torr). 2 — measurement I repeated under the same conditions but after deep pumping of the resonance appear at the same frequencies (baseline). 3 — resonance width variation (Δv) upon filling the resonator with the investigated gas (the difference between measurements I and 2), which for a small optical thickness is related to the gas absorption coefficient α as $\alpha = 2\pi\Delta v/c$, where c is the speed of light in the gas. Thus, curve 3 is the spectrum of the investigated gas. For comparison, the water monomer spectrum is presented (4) calculated for the experimental conditions with parameters of the lines from the HITRAN database [73].

conditions) nitrogen, which practically does not absorb radiation in this wave range, or argon was fed to the spectrometer resonator instead of water vapor. The integral intensity of the observed spectrum was consistent within the measurement error with the results of *ab initio* dimer spectrum calculations [50] and the results of measurement of continual absorption of radiation of this range in moist nitrogen [123]. All this was the first irrefutable confirmation of the fact that water dimers in a bound state are present in room-temperature water vapor in an amount agreeable with the second virial coefficient of water vapor [see Eqn (7)] [25, 30] and with the results of quantum chemical calculations [31] and that according to the preceding theoretical conclusions [23, 50, 125], it is dimers that are responsible for continual millimeter-wave absorption by water vapor.

Thus, the key step was made [126] to further the understanding of the true role of dimers in solar radiation absorption and chemical processes in the atmosphere.

The only clear distinction between the experimental and model spectra was that the observed peaks were broader than the calculated ones. In our opinion, the reason is a larger inhomogeneous broadening of the real spectrum. The narrower calculated peaks could be caused by the use of the symmetric top approximation. Furthermore, the anharmonism of poorly studied low-frequency intermolecular vibrations and the related effects of dimer structure nonrigidity might have been taken into account insufficiently. The large peak width, on the one hand, obstructed observation and the quantitative analysis of the spectrum and, on the other hand, indicated that recordings of the spectrum higher in frequency are optimum for the analysis. As the calculations show, under the same conditions, the dimer lines must be more intense, and a larger inhomogeneous broadening implies that the rotational peaks do not begin splitting into parts, as is seen in the inset in Fig. 11, but form a quasi-equidistant sequence as before.

The subsequent series of experiments investigating the water vapor spectrum carried out in the frequency range 190



Figure 14. Results of observations of the room-temperature dimer spectrum in water vapor in two frequency ranges, 105-150 and 190-260 GHz, at identical water vapor partial pressures (broken line). The solid curve shows the result of approximation of experimental spectra by a simplified model function [formula (16)]. The dashed curve demonstrates the water monomer spectrum calculated by HITRAN base line parameters [73] and subtracted from the observed spectrum. The vertical bars mark the position of rotational transitions of the series $J \rightarrow J + 1$, K = 0, of the E₁ dimer.

to 260 GHz [127] revealed another six, as had been supposed, more intense rotational dimer peaks that continued the series observed before (Fig. 14). This confirmed the results of the previous work [36] and allowed advancing the quantitative analysis of the spectrum.

Because of the complexity and high density of the dimer spectrum (see Fig. 14), ordinary spectroscopic methods based on the analysis of the shape of a separate line or a band are inapplicable for dimer concentration determination from experimental data. The *ab initio* calculation only yields a qualitative picture of the spectrum, which cannot be used for data processing. Moreover, we recall that the observed spectrum can contain considerable contributions of dimers in metastable states and far wings of the monomer lines. Therefore, for the analysis of experimental data, we have elaborated a simplified empirical model of the dimer spectrum based on *ab initio* calculations and experimental data. Construction of the model relies on the fact that rotational peaks in the spectrum of a stable dimer formed by transitions between the levels with E symmetry can be approximated by the sum of Lorentzian profiles, and the remaining part of the spectrum, mainly corresponding to transitions between the levels of A and B-type symmetry, can be approximated by a quadratic polynomial. The model empirically incorporates the pressure dependence of the peak width and the general dependence of the spectrum intensity on temperature and

pressure [128]:

$$\alpha(\nu, T, p) = \left[4.29 \times 10^{-11} \nu^2 \left(\frac{T_0}{T} \right)^{-3.8} + \sum_J \frac{I_J \gamma_J}{(\nu - \delta_J)^2 + \gamma_J^2} \right] \\ \times \left(\frac{T_0}{T} \right)^{13.5} \left(\frac{p}{p_0} \right)^2, \tag{9}$$

where α is the absorption coefficient [cm⁻¹], ν is the frequency [GHz], p is the water vapor pressure [Torr], $T_0 = 296$ K, $p_0 = 13$ Torr,

$$\gamma_J = (0.108 J - 4.43 \times 10^{-5} J^3) + 0.03(p - 13) [\text{GHz}]$$
 (10)

is the effective peak width,

$$\delta_J = 11.239 (J+1) + 8.68 \times 10^{-9} (J+1)^5 [\text{GHz}]$$
(11)

is the central peak frequency, and

$$I_J = 6.3 \times 10^{-11} J^4 \exp(-0.0872 J) [\text{cm}^{-1} \text{ GHz}]$$
(12)

is the peak intensity

Such a model agrees well with the *ab initio* calculated spectra in the frequency range from 60 to 350 GHz in the entire temperature and pressure ranges typical of Earth's atmosphere (Fig. 15). We emphasize that the intensity of the model spectrum implicitly involves the bound dimer equilibrium constant (K_2^P) , whose value can be found from the expression [31]

$$K_2(T) = 4.7856 \times 10^{-4}$$
$$\times \exp\left(\frac{1851.09}{T} - 5.10485 \times 10^{-3}T\right) [\text{atm}^{-1}], \quad (13)$$

derived using *ab initio* calculations. The equilibrium constant is in turn related to the dimer dissociation energy D_0 via the temperature dependence:

$$K_2 \sim \exp\frac{D_0}{k_{\rm B}T}\,.\tag{14}$$

Both these important parameters can be determined by comparing the model with the experimental spectra.

The experimental recordings of water dimer spectra (see Fig. 14) confirm that the positions of rotational peaks correspond well to the frequencies of E_1 type transitions



Figure 15. Water dimer spectra at different water vapor temperatures and pressures (bold curves) according to *ab initio* calculations [50] and the result of their approximation by function (9) (thin curves). The inset demonstrates the same spectra on an enlarged scale.



Figure 16. Experimental recordings of a water vapor spectrum under different conditions after subtraction of the monomer contribution (see the text) and the result of their approximation by function (16). The spectra recorded at temperatures of 6.7 and 25 °C are shown on a sevenand a twofold enlarged amplitude scale, respectively.

 $J \rightarrow J + 1$, K = 0, which can be calculated as

$$\delta_J^{\exp} = 2B(J+1) - 4D(J+1)^3, \qquad (15)$$

where B = 6.161611(21) GHz and $D = 5.0079(91) \times 10^{-5}$ GHz, are the effective rotational dimer constants found from the experimental data [79]. Frequencies (15) should be substituted in model (9) instead of frequencies (11) when the model is used for the analysis of experimental spectra. In addition, to optimize the model for improving the description of experimental water vapor spectra, three variable parameters should be added to account for the uncertainty in the values of the equilibrium constant, the width of rotational dimer peaks, and the contribution to the observed absorption of the other components of the continuum, which, according to previous studies in the millimeter wave range, can be approximated by a function quadratic in frequency [10, 123, 129]. Thus, after subtraction of the monomer contribution, the model of the water vapor spectrum must have the form

$$M(v) = A_1 \,\alpha(v, T, P, \delta_J^{\exp}, \gamma_J + A_2) + A_3 v^2 \,, \tag{16}$$

where α is given by (9).

Model (16) was fitted to the recordings of the water vapor spectrum obtained after subtraction of the monomer contribution at four different temperatures and pressures.³ The result of the fit is presented in Fig. 16. The analysis of the variable parameters obtained from the fit suggests several conclusions:

(a) the temperature dependence of the equilibrium constant of bound dimers in water vapor is approximately the same as was predicted by *ab initio* calculations [31] (see Fig. 2), but the number of dimers is 1.49(13) times less than follows from formula (13). This difference can be expected because the authors of [31] used the value $D_0 = 1234$ cm⁻¹, somewhat overestimated compared to the experimentally

found $1105 \pm 10 \text{ cm}^{-1}$ [65]. Determination of the dimer dissociation energy from the experimental data (see Fig. 16) with the use of expression (14) gives the value $1144 \pm 20 \text{ cm}^{-1}$. Bearing in mind the complexity of the object of research, this may be considered a very good agreement;

(b) approximately half of the observed nonresonance absorption cannot be attributed to stable dimers. The previous estimates [18, 22] imply that the contribution from the far wings of monomer lines, just like the contribution from absorption associated with the additional collisioninduced transient dipole moment in monomer molecules, is negligibly small in the frequency range under consideration. Hence, the source of observed absorption must be dimers in metastable states. Their number can be estimated rather accurately from the experimentally found equilibrium constant of bound dimers and the total equilibrium constant of dimers [see expressions (7) and (8)]. But modeling the spectrum of such dimers as a double spectrum of a monomer whose lines are broadened by the short lifetime of metastable states (as was proposed in [72] for the analysis of analogous data in the IR range) gives the absorption almost an order of magnitude lower than the observed one.

The best method to estimate the mean pressure-induced broadening of dense dimer spectrum lines is Pickett's method [133], within which the high-pressure spectrum is compared with the convolution of the spectrum of the same gas recorded at low pressure, with a variable-width Lorentzian profile. The mean line broadening parameter is the ratio, chosen so as to achieve the best fit, of the Lorentzian profile width to the difference of pressures corresponding to the spectrum recordings. The application of this method to the experimental spectra of water dimers is demonstrated in Fig. 17. Good agreement between the convolution model and the real spectrum gives confidence that most of the large-scale inhomogeneities in the spectrum are objective characteristic spectral features or dimer 'fingerprints' rather than the experimental noise. The parameter of dimer line broadening induced by water vapor pressure averaged over all pairs of



Figure 17. Application of the Pickett method [133] for determination of the parameter of dimer spectrum line broadening by water vapor pressure. The bold grey curve shows the result of spectrum recalculation at a pressure of 6.7 Torr and a temperature of $3.5 \,^{\circ}$ C (the lower spectrum in Fig. 15) to the spectrum at 27.2 Torr and 38 °C (the second from the top in Fig. 15) using convolution with the Lorentzian curve corresponding to the spectrum broadening by pressure and with the factors corresponding to the ratio of temperatures and pressures of both spectra taken into account. The thin broken black line gives the spectrum at 27.2 Torr and 38 °C. The vertical bars mark the position of rotational transitions of the series $J \rightarrow J + 1$, K = 0 of the E₁ dimer.

³ The resonance spectrum of the water monomer was calculated as the sum of Van Vlek–Weisskopf profiles with a line wing cutoff at the distance 25 cm^{-1} from the center for all significant lines in the range up to 1100 GHz, with five isotopologues of the H₂O molecule most widespread in ambient conditions taken into account The most exact experimental values [118, 122, 130–132] or the computational data from the HITRAN database [73] were used as parameters of the lines.

available recordings is equal to 13 ± 5 MHz Torr⁻¹. This value agrees well with the weighted (intensity-sensitive) mean (14.33 MHz Torr⁻¹ [73]) of the parameter of collisional self-broadening of the monomer rotational spectrum.

6. Water dimers in the atmosphere

Of greatest interest for atmospheric applications are the conclusions that can be drawn by analyzing the recordings of spectra with characteristic dimer peaks not in pure water vapor but with gradually added air. This would provide an unambiguous answer to the question about the existence of bound dimers in the atmosphere and the understanding of how much the collisional dimer formation in pure water vapor differs from that in air [134]. In the second collision necessary for the formation of a stable dimer, a more probable partner in this case would be not a polar water molecule with many degrees of freedom but a diatomic nonpolar nitrogen molecule or a paramagnetic oxygen molecule.

From the theoretical standpoint, the main difficulty in the analysis of such spectra is associated with different types of radiation absorption occurring in gas mixtures. We speak of absorption due to collisions of different kinds of molecules. When water vapor is mixed with air, the absorption coefficient corresponding to the spectrum of pairwise collisional interactions can be written as [135]

$$\alpha_{\text{int}} = C_{\text{H}_2\text{O}-\text{H}_2\text{O}}P_{\text{H}_2\text{O}}^2 + C_{\text{H}_2\text{O}-\text{N}_2}P_{\text{H}_2\text{O}}P_{\text{N}_2} + C_{\text{H}_2\text{O}-\text{O}_2}P_{\text{H}_2\text{O}}P_{\text{O}_2} + C_{\text{N}_2-\text{N}_2}P_{\text{N}_2}^2 + C_{\text{O}_2-\text{O}_2}P_{\text{O}_2}^2, \quad (17)$$

where the subscripts mark molecules and molecular pairs, P are partial pressures of corresponding gases, and C are normalized molecular interaction spectra including all the components of bimolecular absorption (the absorption of free pairs of molecules associated with the collision-induced dipole moment and the dimer absorption including bound and metastable states). In the case of pure water vapor considered above, only the first summand remains in the right-hand side of (17). Previous theoretical and experimental studies of molecular interaction spectra [10, 108, 123, 136, 137] allow a rather good quantitative modeling of this absorption using its approximation by a smooth quadratic frequency dependence in the millimeter wave range. But the detailed form of the interaction spectra is unknown. Most of these spectra can be due to the corresponding dimer spectra [138, 139] exhibiting characteristic spectral single features.

From the experimental standpoint, obtaining and analyzing such spectra is mainly obstructed by water molecule absorption and desorption by spectrometer elements. Reaching a stable pressure at a constant temperature in a chamber after it is filled with water vapor takes a very long time (nearly 10 hours in our spectrometer). The partial pressure of the water vapor then corresponds to the total pressure measured by the gauge. But when any other gas is added to the chamber, the equilibrium between absorption and desorption is again violated. The new equilibrium value of the total pressure established in the chamber can, as before, be measured by the gauge, but the partial water vapor pressure becomes unknown. The only reliable way to find it is the analysis of the integral intensity of any known water vapor line, which is uniquely related to the number of absorbing molecules. Such an analysis is a fairly complicated task in and of itself (see,



Figure 18. Water dimer spectrum variation in water vapor mixed with air at room temperature. Records I-3 were made at respective partial air pressures 0, 61, and 530 Torr. Spectra 2 and 3 are shifted vertically for clarity by 0.8 and 1.6 points. The thin curves above spectra 2 and 3 demonstrate the results of convolution of spectrum *I* with the Lorentzian profile. The vertical bars mark the position of rotational transitions of the series $J \rightarrow J + 1$, K = 0 of the E₁ dimer.

e.g., [115]). A less essential but no less important aspect is the necessity of maintaining stable conditions not only of the investigated gas but also of the stable operation of the whole equipment setup during the entire measurement cycle. The specificities of the spectrometer construction result in the fact that variations of the air temperature in the laboratory or the coolant temperature in the radiation source can change the baseline of the spectrometer and show up as smooth variations of the recorded spectrum amplitude.

We performed a series of experiments where, despite the complications, three satisfactory water vapor spectra were recorded with a partial pressure ~ 11 Torr in a mixture with atmospheric air and the total pressure 72, 246, and 551 Torr in the chamber. The gas mixture temperature was ~ 296 K. The mixture preparation and registration of each spectrum took about 24 hours, after which the chamber was completely pumped out to a high vacuum and was further prepared for the next experiment. The partial pressure of water vapor during spectrum recording was determined from the wing of the H₂¹⁶O intense line centered near a frequency of 183 GHz (see Figs 13 and 14), which is within the frequency range under consideration.

Because the aim of this experiment was only to reveal the presence of bound water dimers in atmospheric air, only the most informative component of the obtained spectra was used for the analysis (Fig. 18): apart from the contribution of the monomer, the calculated absorption linear in humidity and quadratic in frequency was subtracted from each spectrum. From the spectra we also subtracted the empirically found component slowly varying with frequency due to the above-discussed absorption variations unrelated to water dimers. This component was identified in accordance with the condition that the characteristic scale of its frequency variations substantially exceeds the water dimer peak width.

The spectra obtained were analyzed using a model function, a convolution of the experimental water dimer spectrum at the same partial pressure of water vapor as that in the mixture with air, with the Lorentzian profile of unit area. The variable parameters were the amplitude factor before the convolution, whose physical meaning is the relative number of dimers, the width of the Lorentzian profile, which determines the mean parameter of water dimer line broadening by air pressure, and the amplitude of the absorption component, changing quadratically with frequency.

At a mixture pressure of 540 Torr, the dimer peaks broaden so much that their amplitude becomes smaller than the experimental noise. An analysis of the spectra recorded at 72 and 246 Torr showed that the characteristic dimer peaks in the spectrum of water vapor mixed with air broaden expectedly by the air pressure (the broadening parameter is 6 ± 2 MHz Torr⁻¹), but their integral intensity barely lowers (the parameter of the relative number of water dimers in air is 0.9 ± 0.2). This suggests the conclusion, very important for practical applications, that at a given partial water vapor pressure, the number of water dimers in the atmosphere is about the same as in pure water vapor.

The conducted experiment is in fact the first direct observation of water dimers in ambient conditions that gives real grounds to the previous hypotheses concerning the important role of dimers in atmospheric processes, including the radiation balance [140], the atmospheric chemistry [141, 142], and the homogeneous condensation [143]. This experiment confirms that water dimers are responsible for the quadratic part of the experimentally observed atmospheric continuum in the millimeter wave range (quadratic in the partial water pressure) [23]. The dimers absorbing millimeter radiation also absorb infrared and visible radiation. Hence, our study indirectly confirms the conclusions in [72] that dimers contribute considerably to this part of the continuum also in the IR range, at least within the bands of fundamental vibrations of the monomer.

The results of water dimer spectrum observation in atmospheric air allow estimating the possibility of direct observation of dimer spectral manifestations in the atmosphere using radiometers. A radiometer measures the power of radiation flux in the direction of observation, which is typically expressed in brightness temperature. The simplest estimation of temperature variations in Earth's atmosphere due to rotational peaks of the dimer spectrum was made in [128]. It turned out that during zenith observation by a ground-based radiometer in average summer conditions, the difference between temperatures corresponding to frequencies of maxima and minima of the quasiperiodic dimer spectrum in the short-wave part of the millimeter range must be nearly one degree, which greatly exceeds the sensitivity of modern radiometers.

7. Conclusion

We have shown how two steps of paramount importance were made: (1) obtaining the dimer spectrum in room-temperature water vapor and (2) passing from the observation of the dimer spectrum in water vapor to the observation of this spectrum in ambient conditions. The first step was the observation, expected for almost half a century, of the fairly complicated spectrum of the important atmospheric component — the water dimer — in equilibrium under conditions close to atmospheric. The second step showed the possibility of observing the dimer spectrum directly in atmospheric air, which is the key point for an experimental determination of the true role of the water dimer in natural atmospheric processes, from radiation absorption, atmospheric chemistry, and homogeneous condensation to the radiation balance and the prediction of Earth's climate variation.

Our experimental results presented in this review are in fact a demonstration of a path open to extensive quantitative

studies of the spectrum of the warm water dimer in laboratory and field conditions.

Optimization of experimental methods and technical improvement of laboratory equipment will help in extending the range of temperatures, frequencies, and pressures involved in the research and in increasing the reliability of obtained data. The development of the methods of *ab initio* dimer spectrum calculations [32] opens up prospects for a high-precision experimental determination of the equilibrium constants (including their temperature dependence) of water dimers in mixtures with the main atmospheric gases, a spectroscopic determination of the dimer dissociation energy, separation of the contribution of metastable states, and many others.

In concluding, we note another repeatedly mentioned aspect of water dimer study (see, e.g., [144]): owing to its unique properties, water as a substance plays one of the key roles in the evolution of life on our planet. The hydrogen bond joining two H₂O molecules in a dimer determines the properties of liquid and solid water. The dimer is the simplest object containing such a hydrogen bond, and therefore its study is exceedingly important for a comprehensive scientific description of water properties in all its phases at the molecular level. Microwave low-temperature beam studies of small water clusters containing an increasingly large number of water molecules (see [144, 145] and the references therein) provide more and more exact information on the rigid crystal lattice of water clusters near the equilibrium. The number of monomers in the investigated clusters now reaches 15 [146], but these studies fail to provide information on the atmospheric-temperature cluster dynamics. Thus, the investigations of 'warm' dimer spectra allow us not only to examine its role in natural processes but also to further the understanding of water properties.

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