



Possibilities of the observation of the discrete spectrum of the water dimer at equilibrium in millimeter-wave band

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ABSTRACT

Attempts of experimental observations of the water dimer spectrum at equilibrium conditions have lasted for more than 40 years since the dimeric hypothesis for extra absorption, but have not yielded any positive confirmed result. In the present paper a new approach is considered: using a high-resolution millimeter-wave spectrum of the water dimer at equilibrium, calculated by a rigorous fully quantum method, we show the potential existence of discernible spectral series of discrete features of the water dimer, which correspond to $J+1 \leftarrow J$, K lines of E_1 symmetry, already observed in cold molecular beam experiments and having, therefore, well-defined positions. The intensity of spectral series and contrast to the remaining continuum-like spectrum of the dimer are calculated and compared with the monomer absorption. The suitability of two types of microwave spectrometers for observing these series is considered. The collisional line-width of millimeter lines of the dimer at equilibrium is estimated and the width of IR dimer bands is discussed. It is pointed out that the large width of IR dimer bands may pose difficulties for their reliable observation and conclusive separation from the rest of absorption in water vapor. This situation contrasts with the suggested approach of dimer detection in millimeter-waves.

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1. Introduction

The importance of water as an atmospheric absorber of radiation is well known. Also, the problem of extra absorption in water vapor has been known for a long time, which does not result from absorption by water monomers. The tendency of water molecules to aggregate, even in gas (vapor) phase was known well before the appearance of the problem of extra absorption of radiation in water vapor. The dimeric hypothesis of extra absorption of radiation by water vapor appeared in the 60's, and was first exactly formulated in 1966 by Viktorova and Zhevakin [1] for millimeter-wave radiation in atmosphere. However, the first reliable observation of the water dimer spectrum was done not at equilibrium conditions, corresponding to the atmosphere, but in cold molecular beams by Dyke and Muenster [2] in 1974. This direction of studies of the dimer became very successful, and the results of Ref. [2] were confirmed and extended in a series of studies by several groups. To avoid overloading a reader by numerous references we can point out two papers [3,4] in which (and references therein) most of the cold-beam rotational and low-frequency vibrational data of the water dimer used in our papers are summarized. Nevertheless, attempts to observe the water dimer spectra at equilibrium conditions aiming at

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atmospheric applications continued but were not so successful. As an example one can cite earlier work of Harries et al. [5] or the recent publication of Pfeilsticker et al. [6]. The most recent publications on the subject are a series of papers of Ptashnik et al. [7], Paynter et al. [8] and Ptashnik [9]. Despite all these efforts, one cannot draw definite conclusions as the works [7–9] were not confirmed and the study of Pfeilsticker et al. [6] received some critical comments [10–12]. The conclusion made by Lotter [12], for example, was that “the first evidence for atmospheric water dimer detection as reported recently by Pfeilsticker et al. [6], has to be revoked, as the findings cannot be confirmed by subsequent measurements, especially by those carried out in the tropics”. All these comments were well-grounded and it is worth mentioning in particular the comment made by Suhm [10] who pointed out that the feature observed in this work [6] “appears to be too narrow by up to an order of magnitude” for the dimer band, which is inhomogeneously broadened at ambient temperatures due to continuous range of possible vibrations “spanned by the corresponding water monomer vibration and cold dimer vibration”. This comment was then supported by the results of Scribano and Leforestier [13], hereafter referred to as Paper I, and also addresses the results presented by Ptashnik et al. [7–9]; in fact, the author of this latter review stated himself that his results “still require further verification. Thus, additional and independent thorough measurements of the continuum are necessary...”. One of the main difficulties in papers [7–9] is that the authors are trying to find the spectrum of the dimer as a small difference of two large values, namely the experimental spectrum of water vapor and the calculated spectrum of water monomer. The intensity of each of them exceeds by several orders of magnitude the effect the authors are looking for. Such a procedure requires the highest precision in knowledge of each spectrum that is difficult to fulfill for both of them. We also can point out an unsuccessful attempt by McKellar [14] to observe directly the equilibrium discrete spectral features of the water dimer by infrared spectroscopy methods.

Summing up, we can state that, despite 40 years of experimental studies, up to the moment there is no confirmed experimental observation of spectral lines or spectral features of the water dimer at equilibrium conditions, thus making uncertain, e.g., its role in the atmospheric absorption of radiation and in the radiative balance of Earth.

In view of these difficulties, Krupnov and Zobov [15], hereafter referred to as Paper II, recently proposed to observe the discrete spectrum of the water dimer at equilibrium by high-resolution microwave spectroscopy methods in the millimeter-wave band, as will be considered in the present paper. They used rotational constants from Ref. [3], the statistical sum of the dimer from Ref. [16] and the assumption of collisional line width of the dimer lines in the millimeter-wave range.

In our subsequent paper [17], the relation between the intensities of the dimer lines and the water-induced continuum in the millimeter wave band was discussed according to the published papers. The data from all most familiar works on the subject [18–22] were analyzed. As a result, it was found that the intensity of the considered dimer line should constitute a significant portion of the observed intensity of the water continuum at the line frequency. Calculations of Scribano and Leforestier in Paper I also showed that “in the millimeter range, water dimer absorption alone reproduces the experimentally determined water vapor continuum absorption”.

The *ab initio* approach developed by Scribano and Leforestier in Paper I enables calculating the full water dimer spectrum in the millimeter-wave range at high resolution. In Paper I the dimer spectrum was calculated at low resolution, giving only the envelope of the spectrum. At high resolution (e.g., under conditions proposed in Paper II) this *ab initio* method allows obtaining a qualitative “global” picture of the spectrum of the dimer, which is invaluable for the estimation of the possibility of experimental observation of the spectrum in spite of possible inaccuracy in frequencies of separate spectral lines. This global picture may reveal spectral series discernible in the spectrum, and contrasts between separate lines (or separate spectral features) of the dimer and the rest of the “continuum” produced by unresolved dimer lines. Also of interest are the calculations of partial spectra produced by lines pertaining to a given symmetry type.

The major goal of our present paper is the demonstration that the millimeter-wave spectrum of the water dimer at equilibrium conditions may really have regular discrete features that could be observed by existing spectrometers. Analysis of necessary parameters to be considered for a possible detection of those spectral features is given in the paper. These parameters involve (a) the water dimer line-widths, (b) the line strengths and positions, (c) the dimer equilibrium constant, (d) contrast of the features to the rest of water vapor absorption and finally (e) a sensitivity of experimental instruments. Although some theoretical calculations and estimations exist, most of these parameters for ambient temperature and pressures are still unknown and this is one of the reasons of the aforementioned problems of the dimer detection at equilibrium conditions. The width item is analyzed in Section 2; strengths and positions of lines as well as the equilibrium constant and the contrast of the dimer features to the rest of water vapor absorption are considered in Section 3; quantitative comparison of the calculated water dimer spectrum with other constituents of the total water vapor absorption in the considered wave range is also given in Section 3; sufficiency of some existent spectrometers is reviewed in Section 4.

2. Expected widths of the dimer lines and bands

Before calculating the dimer spectrum, the important question of expected widths of the dimer lines and bands deserves some consideration. The width also plays a crucial role concerning the better observation range for the dimer discrete spectrum.

First of all, we assume that collisional broadening will prevail for water dimer lines at least for the states located well below the dissociation threshold D_0 (calculated to be 1230 cm^{-1} [16]; more recent calculations lead to somewhat smaller value of 1125 cm^{-1} [23]). Confirmation of this assumption could be found, e.g., in McKellar's work [14], where the spectrum of the Ar–CO complex was recorded at two different pressures, clearly showing an increase of the line broadening with increase of pressure. In Paper I, a somewhat arbitrary value of 2 cm^{-1} FWHM was used for the water dimer line-width at a pressure $\sim 0.02\text{ atm}$ without suggestion of any broadening mechanism. A corresponding broadening parameter value, assuming a collisional broadening, would be $\sim 2\text{ GHz/Torr}$ ($51\text{ cm}^{-1}/\text{atm}$). Such large values of broadening were not observed for any molecule before. In Paper II instead, we used a line broadening parameter of (very approximately) $\sim 30\text{ MHz/Torr}$ ($0.76\text{ cm}^{-1}/\text{atm}$) for the dimer lines in pure water vapor. We will also use this value in the present paper. We estimate the uncertainty of this parameter as not more than 30%. The broadening parameter value estimation followed from: (i) the assumption of a prevailing contribution of the dipole–dipole interaction between strongly polar water dimer and water monomer molecules to the collisional line-width, (ii) the assumption of a rough proportionality of the broadening parameter to the dipole moments of the collisional partners, (iii) reference to collisional line-width parameters for molecules with similar dipole moments, such as for self-broadening of water ($\sim 20\text{ MHz/Torr}$ or $\sim 0.51\text{ cm}^{-1}/\text{atm}$ for a 1.87 D dipole moment), self-broadening of CH_3CN ($\sim 50\text{ MHz/Torr}$ or $\sim 1.27\text{ cm}^{-1}/\text{atm}$ for a 3.9 D dipole moment [24]) etc., and (iv) a measured dipole moment of the water dimer of about 2.6 D [25]. We would like to recall that collisional broadening is so-called homogeneous broadening.

The width (FWHM) of the whole spectrum, only due to intermolecular excitation, as calculated in Paper I, extends to ca. 200 cm^{-1} without any prominent narrow feature at a resolution of 0.12 cm^{-1} (Fig. 8 of Paper I). This is easy to understand because there are four different low frequency intermolecular modes in the range $50\text{--}150\text{ cm}^{-1}$, to each of which a whole manifold of rotational levels is associated. Thus, a very large number of rovibrational levels are populated at near room temperature ($kT \sim 200\text{ cm}^{-1}$). The *synthetic* spectrum calculated in Paper I corresponds to transitions originating from these levels and comprises three different contributions: (i) the pure rotational spectrum at very low frequencies, coinciding with the one for molecules having a rotational constant of ca. 6 GHz or 0.2 cm^{-1} [26]); (ii) the acceptor-donor tunneling splitting spectrum (these two constituents are evidenced by the “hump” at ca. 15 cm^{-1} in Figs. 8 and 13 of Paper I) and (iii) the *P*, *Q*, *R* branches of the low intermolecular modes and their combinations up to the point where the increase in intensity with frequency is canceled by the decrease in the associated dipole matrix elements. The spectrum complexity is also increased by the strong couplings between the highly anharmonic dimer modes of motion with large amplitude. Thus, the width of the dimer spectrum is determined by the spread and overlapping of many separate lines, i.e. by inhomogeneous broadening.

The calculated spectrum in Paper I allows us to make some comments about the width of the IR bands associated with excited bending or stretching vibrations of the constituting monomers of the dimer, which were the subject of numerous investigations. Consideration of this width issue should be very useful for further discussions concerning the possibility of observing water dimer discrete lines or spectral features.

The width of an IR band of the water dimer can hardly be narrower than the width of the spectrum (ca. 200 cm^{-1}) calculated in Paper I for the far-infrared region. Actually, each line in the IR band originates from one of the numerous aforementioned rovibrational states populated at room temperature. An analogous system of intermolecular rovibrational states is associated with each intramolecular bending or stretching excited mode. If one supposes that to each transition calculated in the far infrared region there corresponds a similar transition to an excited intramolecular mode, the resulting width of that IR band should be roughly the same as in the far-infrared spectrum. Actually, there are also numerous lines corresponding to transitions to intermolecular states, allowed by the large intramolecular energy shift, which should lead to a further increase of the IR band-width. The real spectrum will be even more complex due to the different values of the vibrational and rotational constants in the lower and upper states. Some limitations on the number of lines can in principle result from selection rules, but their effect can hardly be fully estimated in such a complex and non-rigid system as the water dimer.

Therefore the actual shape of the IR bands remains essentially unknown. It should differ from the dimer ground state band-shape due to the aforementioned additional transitions, the existence of some *Q*-branches of vibration, etc. The spectrum of the dimer in the ground state [13] looks featureless, though it includes several low frequency vibrations. No *Q*-branch was ever observed by McKellar at equilibrium [14], though it was visible in cold beams. The question of the dimer IR band-shape can only be answered at the moment by a full quantum calculation as performed in Paper I.

Many papers dealing with the width and shape of the IR transitions of the dimer [6–9,12] refer to the work of Low and Kjaergaard [27], and its continuation by Schofield and Kjaergaard [28], as theoretical grounds for the spectrum of the dimer bands. These authors in turn took their estimations from the work of Vaida et al. [29]. All these authors [27–29] assert in similar words the absence of any information about the width and shape of the water dimer bands at equilibrium, and just assume some values and the Lorentzian shape. A most extensive consideration of this subject has been reported by Vaida et al. [29]. In this work, the authors state, that “no experimental or theoretical information is available concerning the line-width or line-shape of vibrational overtone transitions of water clusters”, and a taking a Lorentzian band-shape, cautiously specified a width for the dimer bands ranging from 15 to 200 cm^{-1} , mentioning that they assumed these limits from very simple considerations. They used information about the width of the dimer bands observed in cold-beams, which was measured in different experiments as 11.5 and 13 cm^{-1} , and took 15 cm^{-1} as a lower limit. They took an upper limit of 200 cm^{-1} as a large excess from measured widths of bands in “polyatomic molecules of size similar to the water

dimer". As an example of molecules of similar size they pointed to dimethyl ether, acetone, and butadiene. This choice cannot be considered as adequate, because these molecules do not display a hydrogen bond between moieties of significant masses. As a consequence, these molecules do not present such low frequency vibrational modes as the water dimer does. Three calculated curves of the water dimer absorption are presented in Fig. 3 of [29] for assumed band-widths of 15, 40 and 200 cm^{-1} (FWHM) respectively, the 40 cm^{-1} one represented the most likely case. However, from the preceding considerations, such a width of 40 cm^{-1} just appears as the authors choice, and the actual band-shape is hardly Lorentzian.

The synthetic spectrum calculated in Paper I and the discussion given above may suggest that an "upper" bound of the width of a bending or stretching band of the water dimer, assumed to be 200 cm^{-1} in Ref. [29], actually may exceed this value, and this width results from inhomogeneous broadening. This conclusion supports the comment made by Suhm [10] that the width of the dimer band found by Pfeilsticker et al. [6] to be 19.4 cm^{-1} FWHM "appears to be too narrow by an order of magnitude". Consequently, one may question the recent findings of dimer band-widths ranging from 32 to 60 cm^{-1} FWHM by Ptashnik et al. [7–9]. Pfeilsticker [30] and Ptashnik [9] took the comment of Suhm [10] as an "argument in favor of very short WD lifetimes at normal conditions and hence a wider band for WD transitions than reported by [Pfeilsticker et al.]" [9], and "[from] the Heisenberg uncertainty principle, our finding of a 19.4 cm^{-1} band-width points to a lifetime of $2.7 \times 10^{-13}\text{ s}$ for the water dimer fourth overtone transitions" [30], whereas Suhm definitely mentioned "prediction of substantial inhomogeneous broadening" [10]. Vaida et al. [29] did not consider the life time, but mentioned "these lower-frequency modes [having] vibrational frequencies of the order of 100 cm^{-1} ... [which] could contribute to an increase in the overall width of the transitions", i.e. an inhomogeneous mechanism of broadening.

Of course, the finite dimer life time in its intramolecular excited states (the dissociation energy of the dimer, ca. 1125 cm^{-1} , is less than the excitation energy of the low frequency bending motion, ca. 1600 cm^{-1} , or the stretch overtone excitation energy around $13\,400\text{ cm}^{-1}$, observed by Pfeilsticker et al. [6]) will contribute to the dimer lines broadening, but this broadening mechanism will only lead to further smearing of the IR dimer bands.

An increase of the estimated width of the bands in comparison with those assumed in Refs. [6–9] may make more difficult the observation of these broader dimer features in the IR range as well as their reliable separation from the collision-induced continuum and hamper any conclusive proof that they belong to the dimer. This in turn makes more perspective the attempts to observe spectral series of discrete lines or features of the dimer in the millimeter-wave range, using predictions from cold-beam studies, which is the focus of the present paper. It should also be mentioned that the number of water monomer lines in this range is very modest in comparison with the situation in the IR range, and that their parameters are well known. We will consider this point in Section 3.

Another consequence of the increased water dimer IR band-width should be an increase in the expected absorption intensity of solar radiation by the dimers in the atmosphere, as was pointed out by Vaida et al. [29]. An increase of the dimer band from 40 to 200 cm^{-1} FWHM leads to a fivefold increase in the absorption of solar radiation by the dimers (Table 2 of Ref. [29]), thus increasing the role of the water dimers in, e.g., a global warming scenario.

3. The millimeter-wave spectrum of the water dimer

Calculated partial millimeter-wave spectra of the water dimer produced by lines of symmetries A_1 , A_2 , B_2 and E_1 , respectively, are shown in Fig. 1. These calculations were made as described in Paper I, for conditions specified in Paper II, namely a pressure of 3 Torr or 0.004 atm, a temperature of 270 K and a line-width of 180 MHz or 0.006 cm^{-1} (FWHM). For the calculation of the spectrum we adopted the value of the dimer equilibrium constant from work [16], where it was calculated in the range 190–390 K, using a flexible potential energy surface fitted to reliable experimental cold-beam spectroscopic data. It was shown in Ref. [16] that the calculated values of the constant are in good agreement with approximations of the most reliable measurements of the constant by Curtiss [31] through thermal conductivity of water vapor. However, it should be pointed out that the value of the constant affects first of all the general intensity of the spectrum and cannot change relative amplitude of the spectrum constituents shown in Fig. 1. So a change of the constant would change only the required sensitivity of the spectrometer which will be discussed later.

The summed up millimeter-wave spectrum of the water dimer in these conditions is presented in Fig. 2. Its most important feature is the existence of a clearly distinguishable series of equally spaced groups of lines belonging to the E_1 symmetry. The rest of the spectrum displays an irregular ("noise like") pattern produced by many unresolved lines. This confirms our choice of the E_1 series as an observable object in the millimeter-wave water dimer spectrum suggested in Paper II. Each group corresponds to several unresolved lines constituting the $J+1 \leftarrow J$ transition with different K values (which are resolved in the cold-beam spectrum as seen in Fig. 3 of Ref. [3]). A spread of the most intense K components in a group is of the same order of magnitude as our estimated line-width at 0.004 atm. This somewhat broadens the feature to be observed, but at the same time increases its intensity. The contrast of the features (ratio of the feature peak absorption to the rest continuum-like absorption at the feature frequency) is about 2. The absolute difference between the feature peak amplitude and the "continuum" increases with frequency and is about 10^{-7} cm^{-1} at 120 GHz. A more careful investigation of Figs. 1 and 2 reveals that the periodicity in E_1 groups is ca. 11 GHz, instead of 12.3 GHz as could be expected for this series. This mismatch is due to the inaccuracy of the semi-empirical flexible potential energy surface [32] used in the synthetic spectrum calculation. This spectrum should thus be considered as semi quantitative, revealing however invaluable information on the existence, *under equilibrium conditions*, of a distinguishable spectral series of the water dimer.

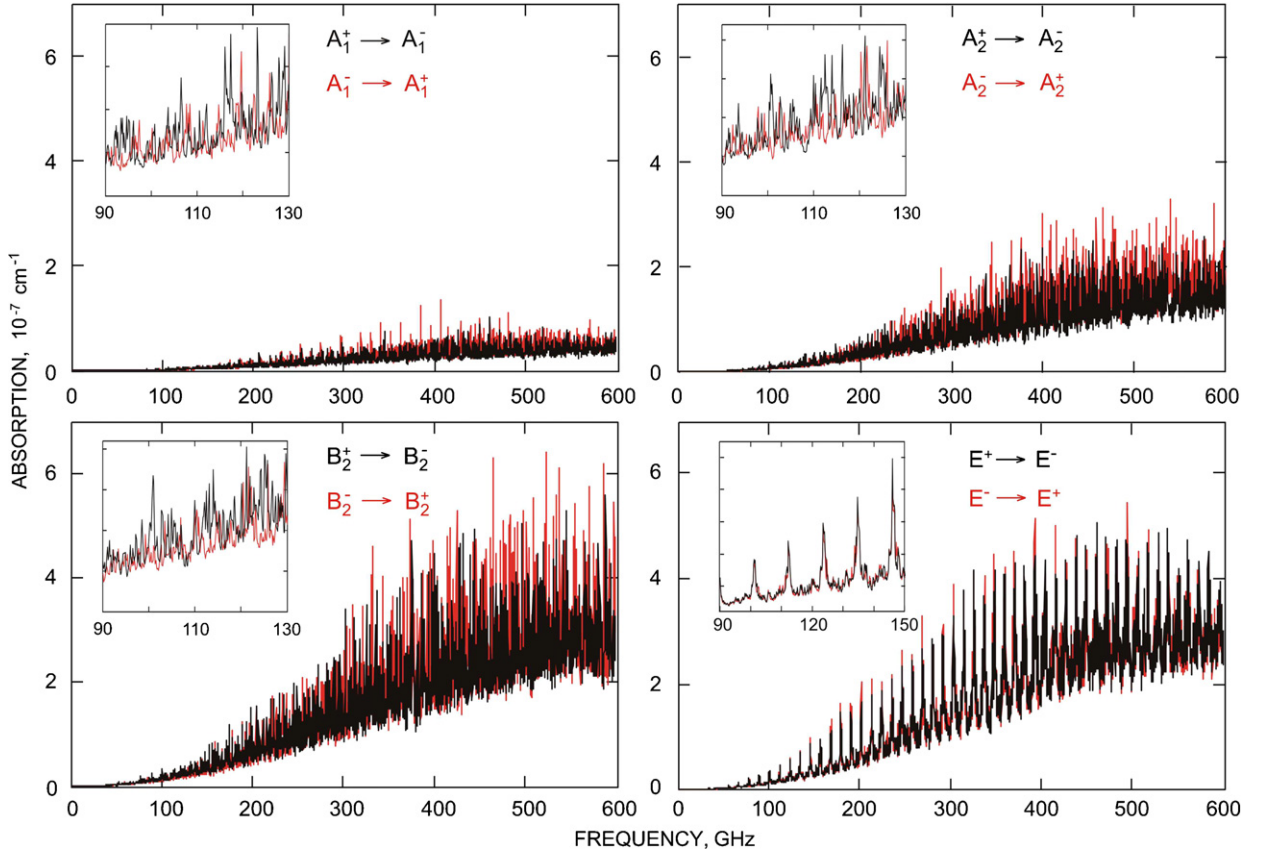


Fig. 1. Calculated separated components of the millimeter-wave absorption spectrum of the water dimer at equilibrium conditions ($T = 270$ K and a water vapor pressure of 3 Torr = 0.004 atm): (a) $A_1^+ \rightarrow A_1^-$ and $A_1^- \rightarrow A_1^+$ transitions; (b) $A_2^+ \rightarrow A_2^-$ and $A_2^- \rightarrow A_2^+$ transitions; (c) $B_2^+ \rightarrow B_2^-$ and $B_2^- \rightarrow B_2^+$ transitions and (d) $E_1^+ \rightarrow E_1^-$ and $E_1^- \rightarrow E_1^+$ transitions. A Lorentz line-shape with 180 MHz (0.006 cm^{-1}) FWHM was assumed for each individual line.

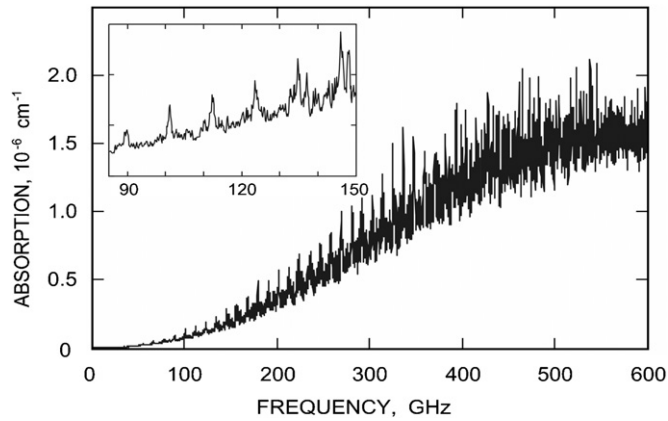


Fig. 2. Total absorption spectrum of the water dimer corresponding to the sum of the different components presented in Fig. 1.

However, for planning the experiment, the line frequencies calculated in Paper II corresponding to positions of peaks of the aforementioned series should be used. The frequencies of the $J+1 \leftarrow J$, $K = 0$, E_1 -type transitions were calculated on the basis of data obtained from cold molecular beam experiments (all parameters required for the calculation can be found in Refs. [3,4], frequencies are given in Ref. [15]). The uncertainty of the frequency calculation is much less than the single line-width discussed above. Another important point that Fig. 2 reveals is that this regular E_1 series tends to disappear at higher frequencies. One can then define the optimal range of observation of these dimer lines as the 90–400 GHz (3–13 cm^{-1}) domain.

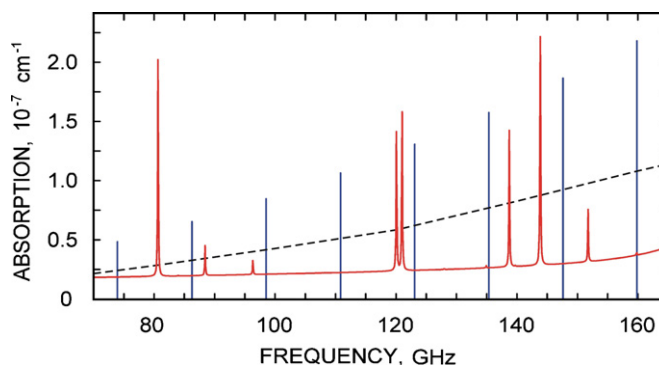


Fig. 3. Calculated components of water vapor absorption at 270 K and 3 Torr (0.004 atm). Absorption by discrete lines of monomer is shown by the solid line. The dashed line presents the continuum absorption induced by collisions between monomers. Vertical bars correspond to predicted positions and amplitudes of the dimer spectral features.

It is of interest to analyze how the calculated spectrum of the dimer relates to other spectral constituents of water vapor at equilibrium conditions. In particular the absorption in the discrete monomer lines and the collision-induced continuum should be considered. Calculated spectra of these constituents in the 70–165 GHz ($2.4\text{--}5.5\text{ cm}^{-1}$) window of the considered frequency range are presented in Fig. 3. Rotational lines of all the most abundant water isotopologues in the ground and thermally populated lowest excited vibrational state (ν_2) should be accounted. Two sources were used for the water molecule line list. For the ground and ν_2 state of H_2^{16}O we used HITRAN [33] data. For the H_2^{17}O , H_2^{18}O , HD^{16}O and D_2^{16}O isotopologues the most complete to date line list calculated on the basis of Partridge and Schwenke *ab-initio* calculations of the potential energy surface [34] and dipole moment surface [35] of water molecule was used. Line positions and intensities in the second source are somewhat less accurate (expected uncertainties are $\sim 300\text{ MHz}$ or 0.01 cm^{-1} and $\sim 20\%$, respectively) than in HITRAN. Nevertheless we may sacrifice that in favor of the completeness of the line list. The Lorentz line-shape and, typical for a water lines, a self-pressure broadening parameter of 20 MHz/Torr ($0.51\text{ cm}^{-1}/\text{atm}$) was used for all lines. The resulting absorption is shown in Fig. 3 by solid line. The continuum absorption induced by collisions between water monomers was calculated using the MT_CKD_2.4 program [21]. This absorption is shown in Fig. 3 by the dashed line. Vertical bars in the figure demonstrate positions and amplitudes of expected water dimer spectral features. Analysis of Fig. 3 leads to two conclusions: (1) the aforementioned series of the dimer features will be observed on a smooth slope of the monomer collision-induced absorption. This absorption lifts up the predicted dimer absorption spectrum by about 50% at all frequencies decreasing the contrast of the dimer features (Fig. 2) but does not change the shape of the features and absolute difference between their peak amplitude and the remaining continuum and (2) the monomer spectral lines do not prevent observation of the dimer features, making their subtraction from the spectrum unnecessary. On the contrary, known position, intensity and width of the monomer lines might help in the experiment for the spectrometer calibration.

4. Analysis of existing spectrometers

For reliable observation of the millimeter-wave spectral lines of the water dimer under equilibrium conditions, the spectrometer should have a high sensitivity (of the order of 10^{-9} cm^{-1}) at relatively high pressures for microwave spectroscopy (of the order of several hPa), and also display broadband properties (e.g., $\sim 30\text{ GHz}$ working band-width is desirable for the successive observation of three consequential members in the E_1 series mentioned above). The most widely used video spectrometers reach a comparable sensitivity only at lower pressures (a few tenths of hPa), at which the dimer concentration (and consequently its line intensity) is much lower. We can point out two spectrometers satisfying the aforementioned demands. The first one is the resonator spectrometer [36], having the highest to date (for this type of the instrument) absorption variation sensitivity of $4 \times 10^{-9}\text{ cm}^{-1}$, due to the fast precise backward-wave oscillator (BWO) phase lock-in loop (PLL) used in it. The spectrometer works at atmospheric pressure but there is no limitation in principle to its operating at lower pressures. Another one is a spectrometer with BWO (and also with PLL) and an acoustic detection of absorption (RAD-spectrometer-its modern version is described, e.g., in Ref. [37]) working at pressures up to about 7 hPa. It was demonstrated by Kazakov [38] that this spectrometer can reach a sensitivity of $6 \times 10^{-10}\text{ cm}^{-1}$. Both spectrometers have some specifics for their use in the proposed experiment. For the resonator spectrometer some further increase in sensitivity can be achieved by changing the currently used Schottky diode receiver to a liquid helium temperature bolometer or to a superheterodyne receiver. An increase of the resonator length up to at least 2–3 m is desirable, as required by our experimental method. To achieve the aforementioned high sensitivity, relative changes of the resonator quality factor of the order of $10^{-4}\text{--}10^{-5}$ should be detected. A mechanical tuning cannot provide such a reproducibility of the quality factor in two scans (with the resonator filled either by the sample or by a non-absorbing gas (nitrogen) to subtract the apparatus function, as described, e.g., in Ref. [39]). In the spectrometer, the quality factors of consecutive longitudinal modes of a Fabry–Perot resonator are measured without any mechanical tuning for recording broad lines at atmospheric

pressure. The distance between the modes in frequency units is about $c/2L$ (where c is the velocity of light, and L is the resonator length), which corresponds in the existing spectrometer to about 380 MHz (0.013 cm^{-1}), which is enough for a detailed recording of atmospheric lines displaying a 3–6 GHz ($0.1\text{--}0.2\text{ cm}^{-1}$) FWHM. For observing the narrower features of the order of several hundreds MHz as expected in the proposed experiment, the distance between two consecutive modes of the resonator must be, say, 5–10 times lower, which gives the aforementioned values for the resonator length. A further increase in the length may be counterproductive as it would lead to a more complicated higher order modes pattern; however even 10-m resonator placed in a vacuum chamber is known [40]. The RAD spectrometer, which does not require any mechanical tuning, would be very convenient for the proposed experiment, but the associated sensitivity of $6 \times 10^{-10}\text{ cm}^{-1}$ was achieved in Ref. [38] by the use of a high power BWO (and a nontunable resonator cell). Such a high power BWO is not available at the moment from the manufacturer [41]. Sufficiently powerful (1–2 W) millimeter-wave clinotrons sources exist [42], but they have much narrower tuning possibilities (say, 14 GHz in comparison with 80-GHz BWO tuning range), so several clinotrons would be necessary to cover the spectral range required. A method for subtracting the apparatus function (baseline) for the RAD spectrometer has been developed by Golubiatnikov et al. [43], which may be helpful for observation of broad spectral features.

5. Conclusions

For the discovery of spectral lines or features of the water dimer in equilibrium gas phase the direct observation of high resolution spectrum of water vapor by microwave spectroscopy methods is suggested. Suggested experimental conditions are the following: pressure $\sim 0.004\text{ atm}$, temperature $\sim 270\text{ K}$, frequency range 90–400 GHz ($3\text{--}13\text{ cm}^{-1}$).

The possibility of existence, under these experimental conditions, of distinguishable spectral series of discrete features pertaining to the water dimer has been shown. Those features correspond to the $J+1 \leftarrow J$, K lines of E_1 type of symmetry. The distance between these features is expected to be ca. 12.3 GHz (0.41 cm^{-1}), which is supported by accurate spectroscopic constants obtained from reliable experimental studies of the dimer in cold molecular beams.

A synthetic spectrum of the dimer has been calculated using a fully quantum approach developed previously [13]. These calculations confirm our simple estimations [15,17]. A collisional line broadening mechanism has been assumed in the millimeter range considered. This synthetic spectrum allowed us to assess the magnitude of the discrete features of interest as well as their contrast with respect to the remaining continuum-like part of the water vapor spectrum. It is shown that discrete lines of monomer do not prevent observation of the dimer features in the frequency range considered.

The very important issue of the widths of IR bands of the dimer has been discussed. It was concluded that the value of 200 cm^{-1} FWHM for the band-width, considered earlier as an upper bound of band-width, may happen to be nearer to the lower bound.

Large width of the dimer IR absorption bands at equilibrium may make difficult their reliable observation and their conclusive separation from the other kind of absorptions of the water vapor spectrum. We propose to overcome this problem by looking for discrete lines or features of the dimer at equilibrium in the millimeter range. Two different types of existing millimeter-wave spectrometers were suggested for the observation of the water dimer discrete spectrum at equilibrium conditions: a resonator spectrometer with a fast precise continuous-phase BWO PLL, and a spectrometer using also a BWO PLL and an acoustic detection. The required modifications of these apparatuses have been discussed.

Proposed direct observation of spectral series of the dimer under equilibrium conditions would unquestionably demonstrate their presence in the atmosphere. Furthermore, the measurement of their intensities and widths will bring a long-awaited quantitative answer and remove uncertainties concerning the abundance of the water dimer in the atmosphere, and its possible role in the energy balance of Earth in relation with the weather prediction and global warming.

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