On a possibility of experimental observation of individual rotational lines of water dimer in the equilibrium gas phase

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The necessity to observe individual lines of a water dimer in the equilibrium gas phase for solving the problem of the dimer absorption of radiation in the Earth's atmosphere is discussed. Intensities of the series of rotational transitions between $E_1^{\pm}$-states in the millimeter range of line widths are calculated. The experimentally reachable sensitivities are considered as applied to a resonant spectrometer of a new type and to a radiospectrometer with acoustic detector for observation of calculated lines. The absorption coefficient and broadening parameter can be measured under the pressure of an individual line of a water dimer with the known quantum number of transition under equilibrium conditions.

The presumption that water dimers can play a part in excessive absorption of radiation by the Earth's atmosphere was put forward more than forty years ago.[1]

This hypothesis evoked the interest in the scientific community and stimulated a wave of investigations. In particular, microwave spectrum of a water dimer was observed in cold supersonic beams[2] (chronology of investigations and all the experimental data available to the time of the publication are collected in Ref. 3; new experimental data are presented in Ref. 4). This made it possible to determine the structure, rotational and centrifugal constants, inversion frequencies, and dipole moment of a dimer. The present-day estimates of the dimer energy range and calculations of the statistical sum of a water dimer by variation methods are presented in Ref. 5.

However, the discussions of the role of water dimers in the observed atmospheric absorption are being continued. This is caused by the fact that nobody has ever observed an individual spectral line of a water dimer in the equilibrium gas phase; the theoretical calculations are ambiguous. Under atmospheric conditions, individual lines of a dimer coalesce and form a continuum. Moreover, this continuum coalesces with other forms of continuous absorption, which are caused by spectra induced by molecular collisions, far wings of monomer lines; and in the presence of foreign gases, as, for instant, in the atmosphere, by spectra of complexes "water molecule — foreign gas" (see, for instance, Refs. 6—8). In this case, it is almost impossible to separate uniquely the contribution of the dimer spectrum itself from the continuous part of absorption, which is all the more uncertain.

Under these conditions, observation of an individual reliably identified line of a water dimer in the equilibrium gas phase is the most important problem. Measurement of the absorption index and the width of a dimer line with known quantum numbers of transition at the known temperature and pressure of the sample would give the important deficient information to calculate dimer spectrum under equilibrium conditions, which are characteristic of the atmosphere. This would also help to determine the continuous part of radiation absorption in the atmosphere. The discussion of the experiment on observing an individual line of a water dimer in the equilibrium gas phase requires the estimate (on the base of available data and reasonable assumptions) of possible frequencies, intensities, and broadening of particular rotational lines of the dimer, as well as estimates of possibilities to observe these lines with the use of corresponding sprectroscopy instrumentation.

This paper is devoted to calculation of the water dimer line series, which is reliably predicted and one of the most intensive in the millimeter rotational spectrum; as well as the discussion of possibilities to observe it with spectrometers of millimeter and submillimeter ranges: recently designed resonance spectrometer of a new type [Ref. 9] and radiospectrometer with an acoustic detector (RAD) (present-day version, see, for instance, Ref. 10). These spectrometers were chosen due to their very high sensitivity in observations of rather wide spectral lines, which can be dimer lines at acceptable intensities. Recall that intensities of dimer lines squarely depend on the pressure of the sample under study. The resonant spectrometer[9] operates at pressures up to atmospheric. The spectrometer RAD [Ref. 10] operates at a pressure up to ~ 5 Torr. Videospectrometers reach comparable sensitivity at much less pressures (~ 0.1 Torr), at which considerably less intensity of dimer spectral lines can be expected. Both spectrometers[9,10] are also close to the "zero" principle of receiving signals from lines. This makes it easier to separate the "base line" or the spectrometer's instrumental function. Estimates demonstrate that at present it is possible to design an experimental unit for observing rotational spectral lines of the water dimer in the equilibrium gas phase

with sufficient signal-to-noise ratio and sufficient accuracy of amplitude and frequency measurements.

The calculation of the rotational spectrum of a water dimer is presented in Refs. 11 and 12. Not all molecular parameters of the dimer were known at that time,[11] therefore, only very rough estimates could be made. In Ref. 12, only the rotational spectrum envelope was calculated for atmospheric conditions on the base of a few molecular parameters known for the water dimer. For our purposes, this is not sufficient because we need calculations of a particular rotational line (more exactly, a series of lines because a single line can be observed under unfavorable conditions). Now we can use experimentally measured frequencies for several tens of dimer's lines and their dipole moments, as well as theoretical analysis of the spectrum.[2–5]

The whole millimeter spectrum of the dimer still cannot be calculated because of a large number of missing or badly defined parameters. However, it is possible to extrapolate some individual series of spectral lines. We choose the line series $E_1^{\pm}$, $J + 1 \leftarrow J$, $K = 0$, beginning with 12.3 GHz, which can be described most simply using the measured frequencies of nine lower rotational transitions.[2–4] Line frequencies in this series of transitions $J + 1 \leftarrow J$, $K = 0$ for an elongated, weakly asymmetrical top, such as a water dimer, can be described almost in the same way as frequencies of the rotational spectrum of a diatomic molecule, differing only by the introduced efficient rotational constant B_{eff}:

$$\nu \cong 2B_{\text{eff}}(J + 1) - 4D_J(J + 1)^3, \qquad (1)$$

where for the states $E_1^{\pm}$: $B_{\text{eff}} = 6160.6011(21)$ MHz; $D_J = 0.050079(91)$ MHz [Ref. 3].

For definiteness of further calculations, we have chosen the following parameters: a frequency range of 200 GHz, convenient for both spectrometers; a water vapor pressure of 3 Torr; a temperature of 270 K, under which the pressure is equal to that of saturated water vapors. The presented formulas make it easy to recalculate the necessary parameters for other conditions. Note that rapid condensation of water vapors at the temperature decrease leaves little freedom in choosing parameters of the sample if we require a sufficiently high (as compared to atmospheric) resolution.

Table presents measured frequencies for the lines of the considered series, and our calculations by formula (1).

The maximal error in predicted frequencies of transitions due to errors[3] in determining B_{eff} and D_J is equal to 3.3 MHz. Of principal for us is the fact that the error in predicted accuracy for line frequencies is much less than line width estimated below.

To calculate the absorption index, we apply the usual expression[13]:

$$\alpha_{\max}(\text{cm}^{-1}) = \frac{8\pi^2 n_{\text{D}} f_m \nu_0^{\,2} \, |\mu_{nm}|^2}{3ckT\Delta\nu}, \qquad (2)$$

where n_{D} is the number of dimers in 1 cm³; f_m is the part of dimers in the lower of two states of transition;

ν_0 is the central transition frequency; $|\mu_{mn}|$ is a matrix element of the dipole moment of transition; c is the velocity of light; k is the Boltzmann constant; T is the absolute temperature; $\Delta\nu$ is the half-width of the collision line for the half-intensity. All the values are presented in the centimeter-gram-second system of units.

Table. Measured and theoretical frequencies (MHz) of water dimer transitions in $E_1^{\pm}$-states, $K = 0$

Transition	Experiment	Calculation
$R(0)$	12320.997	12321.00
$R(1)$	24640.807	24640.80
R(2)	36958.13	36958.20
$R(3)$	49271.94	49271.99
$R(4)$	61580.86	61580.97
$R(5)$	73884.03	73883.94
$R(6)$	86179.50	86179.71
$R(7)$	98467	98467.06
$R(8)$	110745	110744.79
$R(9)$	–	123011.71
$R(10)$	–	135266.60
$R(11)$	–	147508.28
$R(12)$	–	159735.53
$R(13)$	–	171947.16
$R(14)$	–	184141.97
$R(15)$	–	196318.74
$R(16)$	–	208476.28
$R(17)$	–	220613.40
$R(18)$	–	232728.87
$R(19)$	–	244821.52
$R(20)$	–	256890.12

Various experimental and theoretical estimates of the equilibrium constant for the dimerization reaction are presented in Ref. 5. For the temperature of 270 K, these estimates lay within 0.05–0.1 atm⁻¹. To calculate n_{D}, we take some mean value of the equilibrium constant $K_{\text{eq}} \cong 0.07$ atm⁻¹, which is close also to estimates from Ref. 14, and pressure of water monomers $P_{\text{m}} = 3$ Torr $\cong 4 \cdot 10^{-3}$ atm. Then, for pressure of dimers we obtain $P_{\text{D}} = K_p P_{\text{m}}^2 \cong 1 \cdot 10^{-6}$ atm. Correcting the Loschmidt number L to $T = 270$ K as $L' \cong 3 \cdot 10^{19}$ 1/cm³, we obtain $n_{\text{D}} \cong L' P_{\text{D}} \cong 3 \cdot 10^{13}$ 1/cm³.

Table 4 from Ref. 5 presents calculated vibration-rotational statistical sums of the water dimer for levels of different symmetries without regard to spin statistical weights. Statistical weights are also presented in Ref. 5, Table 1. Taking them into account, we obtain the value of the vibration-rotational statistical sum of the dimer $Q_{\text{VR}} \cong 3.2 \cdot 10^6$ at $T = 270$ K. The part of dimers in the lower state of transition $J = 16 \leftarrow 15$, $K = 0$, $E_1^{\pm}$ is

$$f_m \cong 6[(2J + 1)/Q_{\text{VR}}] \times$$
$$\times \exp[-hB_{\text{eff}} J(J + 1)/kT] \cong 5 \cdot 10^{-5}. \qquad (3)$$

Here we take into account the statistical weight of the states $E_1^{\pm}$, equal to 3, and their double degeneration.

The dipole moment of the water dimer $\mu_a \cong 2.6\,D = 2.6 \cdot 10^{-18}$ e.-s.u. [Ref. 2], and the squared matrix moment of the dipole transition moment averaged by quantum numbers M is approximately[13] $|\mu_{mn}|^2 \cong \mu_a^2/2$ for the transition of an elongated weakly asymmetric top $J + 1 \leftarrow J$, $K = 0$ at $J \gg 1$.

For calculations, we need also estimates of broadening of dimer lines by the water vapor pressure. We estimate it based on the following reasons. In collisions of strongly polar molecules, the dipole—dipole interaction plays the main part in the broadening. Assuming (roughly) that the broadening parameter is proportional to dipole moments of collided molecules, we obtain that the broadening parameter increases by ~ 1.4 times in collisions of the dimer with water monomers as compared to the broadening of monomer lines. It means that the broadening parameter of dimer lines is $\sim 22 - 28$ MHz/Torr. The largest of the known self-broadening parameters for the strongly polar CH_3CN molecule with a dipole moment of $\sim 3.9\,D$ is[15] ~ 50 MHz/Torr, which does not contradict to the above-mentioned estimate. Experimental observations in the equilibrium state of lines of the H_2O—HF complex,[16] which is the closest to the water dimer, also agree with this broadening value. For estimates, we took a larger of the obtained values $\Delta\nu_{dim} \sim 30$ MHz/Torr, and at a pressure of ~ 3 Torr the half-width of a line is about 100 MHz.

Substituting all the values into the formula for maximal absorption of a line, we obtain

$$\alpha_{max} \cong 4 \cdot 10^{-8}\ \text{cm}^{-1}. \qquad (4)$$

Since we do not know exactly what parameters define intensities of lines, we do not try to show many significant digits in this estimate. In addition to above-mentioned ambiguities, it is shown in Ref. 5 that, for instance, the error in the value of dissociation energy of 50 cm^{-1} (at the dissociation energy D_0 from calculations *ab initio* 1230 cm^{-1}) leads to a change of the equilibrium constant K_e by 26%. There is no exact experimental value of D_0, and all its present-day estimates contain uncertainties exceeding 50 cm^{-1}. Other sources of uncertainties are connected, for example, with account or neglect of metastable states of the dimer in statistical sums,[5] etc. However, the obtained estimates of the order of magnitude of lines' intensity already make it possible to appreciate possibilities of their observation.

The resonant spectrometer[9] was successfully used in observations of atmospheric spectral lines of water and oxygen molecules immediately under atmospheric pressure. Comparison of the calculated line absorption coefficient of about $4 \cdot 10^{-8}$ cm^{-1} and reached sensitivity of $4 \cdot 10^{-9}$ cm^{-1} of the new resonant spectrometer[9] demonstrates that it is possible in principal to observe an individual line of a dimer in the equilibrium conditions. Such a possibility was never mentioned earlier. However, for better elimination of the instrumental function and other disturbing factors (for instance, neighboring dimer lines that are not taken into account, continuous absorption, etc.), it is very desirable to increase the expected signal-to-noise ratio. The sensitivity demonstrated in Ref. 9 is referred to a single frequency point. To observe and measure some rather broad line, it is necessary to scan a range of frequencies. Fortunately, it is possible to improve the spectrometer sensitivity. In Ref. 9, a common SHF-detector was applied. Its replacing by the present-day InSb-bolometer at a temperature of liquid helium (or by a superheterodyne receiver) can give a considerable gain in the sensitivity. For example, comparing the detector and the helium bolometer, the gain in sensitivity of about two orders of magnitude can be expected.

It is difficult to foresee all problems that will be solved in this experiment. In our opinion, it is very important to apply already developed replacement technique to eliminate the instrumental function.[17] To observe the water dimer line, the experimental methodology proposed in Ref. 9 should be somewhat changed. To scan lines at the atmospheric pressure, a "jump" from one longitudinal mode of the Fabry—Perot resonator to the neighboring one and so on was used,[9] which gave a sufficiently small step to obtain the line profile "by points" without mechanical retuning of the resonator. The distance between modes was ~ 380 MHz. In the presumed experiment, the line width is expected to be much narrower as compared to the atmospheric, and the resonator frequency should be scanned with a smaller step within the limits of 200—300 MHz. In this case, the reproducibility of the scanning frequency of the Fabry—Perot resonator (for instance, by displacement of one of the mirrors by a piezotransformator or by heat expansion of the mirror holder) should be provided. It can be expected that the line will be observed against a rather rugged background. Both the replacement of the sample and variation of its pressure and temperature will be required. It is desirable to observe as many spectral lines of a series as possible for their reliable identification.

In the RAD spectrometer, a sensitivity of $\sim 6 \cdot 10^{-10}$ cm^{-1} has been earlier achieved within pressure range $\sim 0.1 - 5$ Torr [Ref. 18]. Such sensitivity was reached by application of sufficiently powerful lamps of reverse wave (RWL), because sensitivity in this type of spectrometers is proportional to the power of radiation sources and the resonator (non-adjustable) cells. At present, it seems to be difficult to obtain powerful RWL, but it is possible to use other powerful sources of radiation and amplifiers of millimeter and submillimeter ranges (see, for instance, Refs. 19—21). Power of radiation sources described in Refs. 19—21 varies from 1 W at frequencies of ~ 200 GHz to ~ 50 W at frequencies of ~ 100 GHz, at RWL power of about hundreds of milliwatts. Thus, the sensitivity increase is possible also in this case, which would permit to work with samples of a less pressure, i.e., at a higher spectral resolution. In case of using the RAD spectrometer, the mechanical scanning of the range is not necessary. The sample replacement technique for the RAD spectrometer is developed in Ref. 22.

Thus, comparison of estimates of dimer line intensity and spectrometer's sensitivity demonstrates a possibility of conducting experiments on observation of individual rotational lines of water dimers in the equilibrium gas phase at present. The measurement of their main parameters (intensity and line width) would solve one of the remaining important problems in studying spectroscopic parameters of the atmosphere. At present, this acquires an especial significance in connection with development of global remote sensing of the Earth's atmosphere from space for problems of weather forecast and climate monitoring.

Acknowledgements

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