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Abstract

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PHYSICS

A. A. VIKTOROVA, S. A. ZHEVAKIN

ABSORPTION OF MICRORADIO WAVES IN AIR BY WATER-VAPOR DIMERS

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Until now it has been assumed that the principal contribution to the molecular absorption of centimeter, millimeter, and submillimeter radio waves by the Earth's atmosphere is made by molecular oxygen and by monomer molecules of water vapor. Meanwhile, the very first quantitative measurements of the absorption coefficient of water vapor ⁽¹⁾ led to values which, for the frequency region outside resonances, exceeded the data of theoretical calculation ⁽²⁾. The latest measurements of the absorption coefficient in relative transparency windows of water vapor, carried out in ⁽³⁻¹⁰⁾, have shown that at present, for the centimeter, millimeter, and near submillimeter ranges, one may confidently speak of an excess of the measured absorption coefficient of water vapor over the absorption coefficient calculated for monomers H₂O ⁽¹¹⁾ in the transparency windows by approximately a factor of 2. The existing excess absorption was called an anomaly by the authors of ⁽⁴⁾. In all cases it turns out ⁽³⁻¹⁰⁾ that the excess absorption (in comparison with the calculated absorption by monomers ⁽¹¹⁾) increases with increasing air humidity, i.e., it is caused by atmospheric water vapor.

An explanation of this circumstance could tentatively be sought in the following:

1. In the calculation of absorption by H₂O monomers ⁽¹¹⁾, the parameters determining the rotational spectrum of water-vapor monomers were taken incorrectly.
2. The excess absorption is caused by water-vapor molecules composed of isotopes of oxygen and hydrogen.
3. The anomalous absorption is caused by some factor not taken into account up to the present time and related to water vapor.

Let us consider the indicated points in order.

1. As follows from ⁽¹¹⁾, the only parameter whose inaccurate knowledge could lead to a change in the calculated results for the absorption coefficient of water-vapor monomers by $\sim 100\%$ is the half-widths $(\Delta\nu/c)_{ij}$ of the spectral lines of H₂O monomers. These half-widths were taken from calculations ⁽¹²⁾ with a correction factor of 0.9 ⁽¹¹⁾. However, experiments ^(1,13,14),

in which the widths of three spectral lines were measured, $(1/\lambda)_{ij} = 0.74 \text{ cm}^{-1}$ ⁽¹⁾, $(1/\lambda)_{ij} = 6.12 \text{ cm}^{-1}$ ⁽¹³⁾, and $(1/\lambda)_{ij} = 18.58 \text{ cm}^{-1}$ ⁽¹⁴⁾, showed that the calculated values of the spectral-line widths adopted in ⁽¹¹⁾ are close to the true ones. Therefore at present it does not appear possible to reconcile the theoretical values of the absorption coefficient with the experimental values by increasing the widths of the spectral lines by a factor of ~ 2 . Moreover, although increasing the widths of the spectral lines does lead to an increase of absorption in the transparency windows, thereby making it possible to reconcile the calculation with experiment for the windows, nevertheless in the resonance peaks an excess of the experimental values over the theoretical ones is obtained by approximately the same factor of 2,

which does not improve the situation as a whole (an example of an unsuccessful attempt of this kind is the work ^(14a)).

2. Along with the isotope of the water molecule H_2O^{16} , the isotopes H_2O^{18} , H_2O^{17} , and H^1DO^{16} are most often encountered. Their influence on the absorption of radio waves by water vapor is small; they make the largest contribution for $1/\lambda$ equal to 1.82, 2.7, and $< 0.5 \text{ cm}^{-1}$, but even at these frequencies their absorption amounts to no more than 5-10% of the absorption coefficient of the principal isotope H_2O^{16} ⁽¹⁵⁾.

Thus, we see that the first and second of the possible explanations of the discrepancy between calculation and experiment are untenable.

3. There remains the third possibility—to introduce into the theory a factor not previously taken into account. We shall show that this factor is absorption by dimer molecules of water vapor (the percentage content of the other H_2O polymers in the atmosphere is negligibly small).

Using formula (3) of work ⁽¹⁶⁾ (we use the notation of that work),

$$\gamma \left[\frac{\partial \delta}{kM} \right] = 10^6 \log_{10} e \frac{32\pi^2 N}{3hcG(T)\lambda^2} \sum_{ij} |\mu_{ij}|^2 \frac{1}{\lambda_{ij}} \times$$

$$\times \left| e^{-E_i/kT} - e^{-E_j/kT} \right| \frac{(\Delta\nu/c)_{ij}^0 \sqrt{T/293}(P/760)}{[(1/\lambda_{ij})^2 - (1/\lambda)^2]^2 + 4 [(\Delta\nu/c)_{ij}^0 \sqrt{T/293}(P/760)]^2 (1/\lambda)^2} \quad (1)$$

we calculated the absorption coefficient of radio waves γ by water-vapor dimers in the atmosphere in the range $0 \div 300 \text{ cm}^{-1}$. As in the case of the H_2O monomer, the frequency dependence of the intensity of the rotational spectrum of the dimer has a “dome-like” character, i.e., there is a collapse of the rotational absorption spectrum both at low and at high frequencies (for the monomer “dome,” see Fig. 17 of work ⁽¹¹⁾; corrections to it are given in Fig. 3 of work ⁽¹⁷⁾).

The collapse toward low frequencies is due to the dipole character of the radiation, and also to the circumstance that there are always more weak spectral absorption lines than strong ones, and therefore it is “more probable” that the first (on the low-frequency side of the spectrum) absorption lines will be weak. The collapse toward high frequencies is due to the circumstance that these frequencies arise from transitions between states with high energy (large values of the quantum numbers J, K), whose population decreases exponentially as the energy of the states increases. In contrast to the monomer, the rotational absorption spectrum of the dimer, owing to the larger moments of inertia of the dimer, extends considerably farther into the low-frequency region of the spectrum, so that the absorption “dome” of the dimers is shifted relative to the “dome” of the water-vapor monomers into the low-frequency region, where the monomers make only a small contribution. Owing to this circumstance, despite the fact that the concentration of water-vapor dimers under normal atmospheric conditions ($T = 293^\circ$, $P = 760$ mm Hg, absolute humidity $\rho_{\text{H}_2\text{O}} = 7.5$ g/m³) and the energy of the hydrogen bond, equal to 5.2 kcal/mol⁽¹⁸⁾, are approximately three orders of magnitude smaller than the concentration of monomers, in the transparency windows of the monomers in the centimeter, millimeter, and near-submillimeter ranges the dimers contribute approximately as much to the atmospheric absorption coefficient as do the monomers (see Fig. 1).

In the present note we shall consider absorption by H₂O dimers only in the range $0 \div 30$ cm⁻¹ ($\lambda > 0.33$ mm). In this range the absorption is due to transitions $\Delta\nu = 0$ (ν is the quantum number describing the torsional oscillations corresponding to internal rotation in the dimer; see⁽¹⁶⁾).

In Fig. 1, 1 presents the absorption coefficient γ of H₂O dimers in the range $0 \div 30$ cm⁻¹, calculated by formula (3) according to the data of work⁽¹⁶⁾ at absolute temperature $T = 293^\circ$, atmospheric pressure $P = 760$ mm, absolute humidity of the air $\rho_{\text{H}_2\text{O}} = 7.5$ g/m³ (which corresponds to a dimer concentration $\rho_{\text{d}} = 0.022$ g/m³ at $T = 293^\circ$ and energy

of the hydrogen bond, 5.2 kcal/mole) and identical half-widths of the spectral lines $(\Delta\nu/c)_{ij} = 0.4$ cm⁻¹.

The real values of the half-width $(\Delta\nu/c)_{ij}$ of the dimer spectral lines are at present unknown. However, there is no doubt that, because of the large dimensions of the dimer in comparison with the monomer, the half-widths of the dimer spectral lines must exceed the half-widths of the monomer spectral lines. The theoretical values of the latter under atmospheric conditions at sea level are about 0.1 cm⁻¹⁽¹²⁾; these values are confirmed by experiment^(1,13,14). Therefore one should expect that the half-widths of the dimer spectral lines under atmospheric conditions at sea level will lie in the interval

$$(\Delta\nu/c)_{ij} = 0.2 \div 0.4 \text{ cm}^{-1}.$$

Fortunately, the absence of accurate data on the half-widths of the dimer spectral lines has little effect on the calculated value of the absorption coefficient γ

due to them. Since the intensity of the spectral lines of the P - and R -branches of the dimer varies very smoothly with their frequency, and the distance between them (at the same value of ν) is 0.46 cm^{-1} , i.e., of the order of the line half-widths $(\Delta\nu/c)_{ij}$ just indicated, under atmospheric conditions at sea level the spectral lines are smeared out (see Fig. 1).

Fig. 1. 1 –absorption coefficient of dimers of atmospheric water vapor for spectral-line half-widths $(\Delta\nu/c)_{ij} = 0.4 \text{ cm}^{-1}$; 2 –absorption coefficient of monomers of atmospheric water vapor. $T = 293^\circ \text{ K}$, $P = 760 \text{ mm Hg}$, $\rho_{\text{H}_2\text{O}} = 7.5 \text{ g/m}^3$.

Therefore, for values $(\Delta\nu/c)_{ij} > 0.4 \text{ cm}^{-1}$, the change in the absorption curve of Fig. 1 amounts only to the fact that the magnitudes of the peaks of the absorption coefficient γ at 7.07 and 21.2 cm^{-1} (the Q -branch) decrease and broaden by approximately the same factor by which $(\Delta\nu/c)_{ij}$ is increased in comparison with the value 0.4 cm^{-1} ; the absorption curve outside the peaks of the Q -branch remains practically unchanged. When the half-widths of the spectral lines are decreased, the peaks of the absorption coefficient γ due to the Q -branch increase and narrow in comparison with those shown in Fig. 1 by the same factor by which the half-widths are decreased in comparison with $(\Delta\nu/c)_{ij} = 0.4 \text{ cm}^{-1}$. In addition, at values $(\Delta\nu/c)_{ij} \approx 0.2 \text{ cm}^{-1}$, a weak “ripple” will appear on the absorption-coefficient curve, caused by the fact that at such half-widths the spectral lines of the P - and R -branches begin to be resolved. At $(\Delta\nu/c)_{ij} \approx 0.1 \text{ cm}^{-1}$ and less, the lines in the dimer absorption spectrum are well resolved. Such resolution should be observed experimentally under certain conditions, for example at low air pressures.

Curve 2 in Fig. 1 corresponds to the absorption coefficient of water-vapor monomers calculated for the same values of temperature, pressure, and absolute humidity of the air ⁽¹¹⁾. It is seen that absorption of radio waves by dimers in the range $0 \div 22 \text{ cm}^{-1}$ is of the same order as the absorption

electromagnetic waves by H_2O monomers in the frequency region outside the resonances. We note that, since the concentration of H_2O dimers is proportional to $(\rho_{\text{H}_2\text{O}})^2$ (at constant temperature) ¹⁸, the total absorption will no longer be proportional to $\rho_{\text{H}_2\text{O}}$, as it is for monomer absorption.

The calculations presented above show that the “anomalous” absorption (4a) is due to dimer molecules of atmospheric water vapor. Dimer absorption also explains the existence of the absorption line $(1/\lambda)_{ij} = 49.5 \text{ cm}^{-1}$, which is visible in spectrograms of water vapor recorded by N. G. Yaroslavskii and A. E. Stanevich ¹⁹ and by N. I. Furashov ⁶, and which cannot belong to the absorption spectrum of the water-vapor monomer. This line in the absorption spectrum of the H_2O dimer corresponds to transitions of the Q -branch from levels for which the quantum number $K = 3$ (see ¹⁶). The frequency of this line, $(1/\lambda)_{ij} = 49.5 \text{ cm}^{-1}$ ^{6,19}, was used by us to refine, in the expression for E_{JK} of Ref. ¹⁶, the value of the coefficient of K^2 (instead of the calculated value 6.75 cm^{-1} , the value 7.07 cm^{-1} was taken).

The contribution of dimers to the dielectric permittivity of air is negligibly small in comparison with the contribution $(\varepsilon_{vr}-1)_{\text{mon}}$ produced by monomers. Indeed, since the dipole moment of the dimer is ~ 2 times larger than the dipole moment of the monomer, while the concentration of the dimer is approximately 10^{-3} of the monomer concentration, the contribution of dimers will be $\sim 2^2 \cdot 10^{-3}$ of the contribution of monomers to the dielectric permittivity of air.

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Scientific-Research Radiophysical
Institute
at Gorky State University
named after N. I. Lobachevsky

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