ROTATIONAL SPECTRUM OF THE WATER-VAPOR DIMER

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ROTATIONAL SPECTRUM OF THE WATER-VAPOR DIMER

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In 1966 the authors published calculations of the rotational spectrum of the water-vapor dimer and showed that dimers of atmospheric water vapor make a substantial contribution to the absorption of microwaves by the Earth' s atmosphere ([1,2]).

The existence of water-vapor dimers was shown by an indirect experiment earlier by Ewing ([3]) and Sengers ([4]), and directly (with the aid of a mass spectrometer) by Leakey and Robbins ([5]). Since the publication of papers ([1,2]), a number of interesting works have also appeared ([6–14]), devoted to experimental verification and discussion of the results of ([1,2]). We add that in work ([15]), at pressures of $2 \div 10$ atm and temperatures of $400 \div 500$°K, in the spectral region $600 \div 1000$ cm^{-1}, excess absorption of water vapor was detected with such a temperature dependence as testifies to the dimer nature of this absorption (apparently, absorption due to the translational-vibrational spectrum of the H_2O dimer).

By the rotational spectrum of the dimer in the present work and in work ([20]) is meant the spectrum of the linear model of the dimer ([19]), composed of two rigid H_2O molecules, rigidly, if one does not speak of their relative (internal) rotation about the line of the hydrogen bond O—H…O, bound to each other by a hydrogen bond. Thus, in the rotational spectrum, along with "pure" rotational transitions $\Delta v = 0$ (v is the torsional quantum number for quantization of the hindered internal rotation), transitions with $\Delta v \neq 0$ are also included. The vibrations of both H_2O molecules relative to each other along the line of the hydrogen bond and the bending vibrations are not taken into account (rigid model); allowance for such vibrations with frequency $\lambda^{-1} \approx 200$ cm^{-1} would introduce a change in the absorption spectrum of the dimer outside the spectral interval considered here, $\lambda^{-1} \leq 30$ cm^{-1}.

In the present work and in work ([20]), in comparison with ([1,2]), the following refinements have been made.

1. Instead of the parabolic approximation for the shape of the potential barrier of internal rotation (the harmonic-oscillator approximation), a more

correct cosine approximation has been used. The wave functions obtained as a result, describing the internal rotation, differ noticeably from the wave functions of the harmonic oscillator ([16]), which led to a decrease of the matrix elements of the electric dipole moment averaged over torsional states by a factor of 3.25 for transitions $\Delta K = \pm 1$ and, as a consequence of this, to a decrease of the absorption coefficient of dimers by ~ 2.1 times. The energy of internal rotation became determined not only by the torsional quantum number v (the harmonic-oscillator approximation), but also by the quantum number K of the projection of the angular momentum of the dimer on the axis of internal rotation (the axis of an effective symmetric top). This considerably complicated the pattern of the rotational spectrum: for transitions $\Delta K = \pm 1$, the rotational spectra for different torsional levels turned out to be shifted relative to one another (rotational-vibrational interaction, as in works ([1,2]),

is not taken into account here), as a result of which the number of spectral lines increased greatly (in the calculations [1,2] in the frequency range $\lambda^{-1} = 0 \div 15$ cm^{-1} there were 252 spectral lines, whereas now there are 668). Allowing for the shift and splitting of spectral lines due to the dependence of the internal-rotation energy on the quantum number K under atmospheric conditions at sea level has the strongest effect in the frequency region $\lambda^{-1} < 7$ cm^{-1}. But even there it changes the dimer absorption coefficient γ_{dim} by no more than a few percent. The largest change consists in a slight spreading and, because of this, a decrease of the Q-peak of absorption at $\lambda^{-1} = 7.07$ cm^{-1} by $\sim 10\%$.

2. Transitions between energy terms $E_{J,K,v}$ with $\Delta v \neq 0$ were taken into account; however, the contribution from such transitions to the absorption coefficient γ_{dim} for the spectral region under consideration, $\lambda^{-1} < 30$ cm^{-1}, was less than 1%.

In the present work and in Ref. [20], as in Refs. [1,2], an assignment is made to the absorption line $(\lambda^{-1})_{ij} = 49.5$ cm^{-1}, visible on the spectrograms of Refs. [17,18] and identified in Refs. [1,2] with the dimer absorption peak caused by the Q-branch. For this purpose, in the present work and in Ref. [20], the following expression was used for the quantity $E_{J,K}$ (see Ref. [1]):

$$E_{J,K} = 0.23J(J+1) + 7.07K^2 \ \ (\text{cm}^{-1}) \, ,$$

in which the coefficient 7.07 was chosen so as to assign one of the peaks of the Q-branch to the frequency $\lambda^{-1} = 49.5$ cm^{-1}. Let us note that in the originally constructed model of the dimer [19], instead of the coefficient 7.07 the coefficient 6.75 was obtained. Replacing the coefficient at K^2, $6.75 \to 7.07$, has little effect on the absorption coefficient γ_{dim}; this effect reduces to an insignificant shift of the Q-branch peaks $K = 0, 1, 2, \ldots$, respectively by $0.32;\ 0.96;\ 1.60, \ldots$ cm^{-1} toward higher frequencies. We note that Gebbie and Burroughs [7] did not at all detect in the laboratory any water-vapor absorption peak near $\lambda^{-1} = 49.5$ cm^{-1}. However, in Refs. [21–23], in high-altitude observations of solar radiation, telluric lines $\lambda^{-1} = 21.20;\ 35.35;\ 49.70\ \text{cm}^{-1}$ were found; all of them satisfy the relation $\lambda^{-1} = 7.07(2K+1)\ \text{cm}^{-1}$, $K = 0, 1, 2, ...$, and therefore must be identified with the Q-peaks of the water-vapor dimer. Thus, the observations agree with the coefficient 7.07, and not with the coefficient 6.75.

Under the assumption that the effective collision cross section of the dimer with surrounding molecules does not depend on the relative velocity V, for the collision frequency ν_{ef} with surrounding molecules of concentration C we have

$$\nu_{ef} \sim CV \sim \frac{p}{T}\sqrt{T} = \frac{p}{\sqrt{T}}.$$

Then the half-width of a spectral line of the dimer is equal to

$$\left(\frac{\Delta\nu}{c}\right)_{ij} = \left(\frac{\Delta\nu}{c}\right)^{0}_{ij} \sqrt{\frac{293}{T}}\,\frac{p}{760},$$

where $(\Delta\nu/c)^{0}_{ij}$ is the value of the half-width at temperature $T = 293°\text{K}$, pressure $p = 760$ mm Hg.

The calculation of the dimer absorption coefficient, as in Ref. (2), was carried out by the formula*

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

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

* In Refs. (1,2), in this formula the factor $\sqrt{293/T}$ was incorrectly printed as $\sqrt{T/293}$.

Here $N = 10^{-6}\rho_{\text{dim}}N_0/\eta$ is the number of water-vapor dimer molecules in 1 cm^3, where $N_0 = 6.025 \cdot 10^{23}$ is Avogadro' s number, $\eta = 36$ is the molecular weight of the dimer, and ρ_{dim} is the concentration of dimers in g/m^3. The law of mass action, for a dimer binding energy ε in kcal/mol for model (^{19}) and for the vibrational statistical sum of the dimer $\prod(1 - e^{-h\nu_i/kT})^{-1}$, calculated under the assumption of the existence of two vibrations with frequencies $\lambda^{-1} = 215\ \text{cm}^{-1}$ and $500\ \text{cm}^{-1}$, gives

$$\rho_{\text{dim}}[\text{g/m}^3] = 0.00119T^{-1.7}e^{(502.9\varepsilon - 81.4)/T}(\rho[\text{g/m}^3])^{2}. \tag{2}$$

Fig. 1

Figure 1: Fig. 1

Figure 1 shows the absorption coefficient of dimers γ_{dim} at a dimer concentration $\rho_{\text{dim}} = 0.0122$ g/m^3 and with identical half-widths of the dimer spectral lines $(\Delta\nu/c)^0_{ij} = 0.2;\ 0.02$ cm^{-1} (for plots corresponding to the values $(\Delta\nu/c)^0_{ij} = 0.4;\ 0.8;\ 1.6$ cm^{-1}, see Fig. 1 of Ref. (^{20})). The calculations were carried out using formula (1) at $T = 293$°K, $p = 760$ mm Hg. The adopted dimer concentration $\rho_{\text{dim}} = 0.0122$ g/m^3 is obtained according to formula (2) at $T = 293$°K, dimer binding energy $\varepsilon = 4.8$ kcal/mol, and absolute humidity $\rho = 7.5$ g/m^3 (in (^{1,2}) the dimer binding energy was assumed equal to $\varepsilon = 5.2$ kcal/mol, which under the same conditions gave a larger dimer concentration, $\rho_{\text{dim}} = 0.022$ g/m^3).

Fig. 1. Dependence of γ_{dim} on λ^{-1}. $T = 293$°K, $p = 760$ mm Hg, $\rho = 7.5$ g/m^3, $\varepsilon = 4.8$ kcal/mol. 1–$(\Delta\nu/c)^0_{ij} = 0.02$ cm^{-1}; 2–$(\Delta\nu/c)^0_{ij} = 0.2$ cm^{-1}.

It is seen that at $(\Delta\nu/c)_{ij} = 0.2$ cm^{-1} the dimer spectrum begins to be resolved; at $(\Delta\nu/c)_{ij} = 0.02$ cm^{-1} the resolution reaches a high degree.

Let us note that at $T = 293$°K, $p = 760$ mm Hg, the widths of the dimer spectral lines in air are most likely of the order of 0.8 cm^{-1} (see (^{20})). Therefore, in actuality, the plots of Fig. 1 constructed for $(\Delta\nu/c)^0_{ij} = 0.2$ and 0.02 cm^{-1} correspond to low air pressures.

If it is assumed (by analogy with monomers) that the effective optical cross section of the dimer for collisions with an H_2O molecule is 5 times greater than that for collisions with air molecules (O_2 and N_2), then, after complete removal of the dry part of the air at fixed humidity $\rho = 7.5$ g/m^3 (corresponding to 1% of the partial pressure of water vapor for air at the usual pressure of 760 mm Hg), in the remaining pure water-

for vapor at a pressure of 7.6 mm Hg the half-width of the spectral line of the dimer will decrease by $100/5 = 20$ times. In this case it will become equal to $(\Delta\nu/c)^0_{ij} = 0.04$ cm^{-1}, and not 0.02 cm^{-1}, if in air at $T = 293$° K, $p = 760$ mm Hg it was $(\Delta\nu/c)^0_{ij} = 0.8$ cm^{-1}. This circumstance, of course, does not reduce the significance of the plots in Fig. 1, which make it possible to obtain the values of γ_{dim} after the appropriate conversion to the experimental conditions under consideration.

Let us note that the measurements of water-vapor absorption at a pressure of 4 mm Hg in White' s multipass vacuum cell with a resolution of ~ 0.5 cm^{-1}, carried out by Harries, Burroughs, and Gebbie $^{(13)}$, although they naturally did not make it possible to resolve the fine structure of the dimer absorption spectra (see Fig. 1), nevertheless revealed at $\lambda^{-1} \approx 7.2$ cm^{-1} a distinct absorption peak of width ~ 1 cm^{-1} (see Fig. 1 of Ref. $^{(13)}$) with a quadratic dependence of the magnitude of the absorption on pressure. The latter circumstance indicates the dimer nature of the absorption peak found; its position and width agree with the data of Fig. 1. The authors of (13) also found a second absorption peak, the Q-branch, at the frequency $\lambda^{-1} = 22$ cm^{-1}, but without certainty.

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