PHYSICAL REVIEW VOLUME 71, NUMBER 7 APRIL 1, 1947

The Absorption of Microwaves by Uncondensed Water Vapor*

J. H. Van Vleck
Harvard University, Cambridge, Massachusetts

(Received December 27, 1946)

The absorption due to uncondensed water vapor in the short microwave region is computed by means of quantum mechanics. The attenuation is attributed to two causes: (a) a single line $\lambda = 1.35$ cm, and (b) the combined residual effect of all the other lines, whose wave-lengths are too short for resonance. There is a sharp peak in the absorption due to (a) at 1.35 cm, amounting to about 0.2 db/km per gram of H_2O per cubic meter. The absorption caused by (b) is inversely proportional to the square of the wave-length. The theory is compared with existing microwave data on damp air, on pure water vapor at low pressures, and on steam. From these data one can determine the precise value of the resonance frequency in (a) and the line-breadth. Until recently these constants could only be roughly estimated from infra-red measurements. On the whole the theory and experiment agree satisfactorily, except that the attenuation due to the residual effect (b) is apparently about four times as large as predicted. Possible causes of this discrepancy are speculated upon—perhaps the Lorentz model of infinitely sharp collisions which we use is too simple. Finally a curve is included of the predicted absorption in the millimeter region, where water vapor is much more opaque than at centimeter wave-lengths, and new resonances come into play.

INTRODUCTION

In the present paper we consider only the absorption due to uncondensed water vapor. If any condensation is present, as in mists, rains, etc., there is also the absorption due to the drops of water, whose effect has been calculated by Stratton and others.[1] In heavy rains, the absorption due to the Stratton effect can be larger than that computed in the present article, but in any event the absorption due to the uncondensed vapor is always present in addition to any attenuation due to the formation of drops.

The absorption by the uncondensed vapor can only be treated by quantum mechanics, as it is necessary to know the rotational energy states of the water molecule in detail. A sharp contrast is thus presented to the absorption due to the condensed liquid. The latter can be handled entirely by classical theory if one knows the radius of the droplets and the empirical complex dielectric constant of water.

In order to have appreciable absorption by the water molecule, it is essential that there be very closely spaced energy levels which can combine with each other by means of electric dipole radiation. If the levels are not close together, the resonance region will be at frequencies far too high to give any appreciable attenuation of microwaves. It is also obviously necessary that transitions between the nearby states be permitted by the ordinary dipole selection rules of quantum mechanics, since quadrupole effects are of negligible intensity at long wave-lengths. The table of energy levels for the water molecule is honeycombed with pairs of nearly coincident levels, but in practically all cases they cannot combine with each other, owing to the selection rules resulting from symmetry classifications. According to quantum mechanics, the rotational energy levels of the water molecule are of four different symmetry types, which are usually designated as $++$, $--$, $+-$ and $-+$. (The origin of the notation is in the sign behavior of the wave functions under certain kinds of reflections, into whose details we need not enter here.[2]) The selection rules permit the rotational quantum number J to change only by not more than one unit, and allow $++$ to combine only with $--$, and $+-$ only with $-+$. Non-resonant absorption due to diagonal matrix

---

* The research basic to the present paper was performed mainly while the writer served as consultant for the M.I.T. Radiation Laboratory, NDRC Dv. 14, contract 262. See especially its reports 43-2 and 664.

[1] J. Stratton, Proc. Inst. Rad. Eng. **18**, 1064 (1930); for more recent literature see J. W. Ryde, and D. Ryde, Rep. Nos. 7831, 8516, and 8670 of the British General Electric Company; also article by H. Goldstein in Chap. VIII of Book 13 of the forthcoming M.I.T. Radiation Laboratory Series, *Microwave Propagation.*

[2] See D. M. Dennison, Rev. Mod. Phys. **12**, 189 (1940).

elements cannot exist in H_2O, for if the initial and final states are identical, they have the same symmetry classification, and hence diagonal matrix elements for the electric dipole moment are wanting. The reason that the non-resonant or diagonal effect is present in O_2, is that the absorption in O_2 is caused by the magnetic dipole moment, for which the rule is that $+$ combines with $+$ and $-$ with $-$.

Among the levels of the water molecule which are excited at ordinary temperatures, there is only one pair whose members can combine and at the same time are so closely spaced as to give resonance in the microwave region. This pair is formed by the so-called 5_{-1} and 6_{-5} states. According to infra-red measurements as interpreted by Dennison,[2] the energy values of these states, referred to the ground level as origin, are as follows

5_{-1}	446.39 cm^{-1}
6_{-5}	447.17 cm^{-1}

If these figures are accepted, the connecting transition should have a wave-length $1/0.78 = 1.28$ cm. It is, however, obvious that the small energy difference which is involved cannot be determined with precision from infra-red data. In an earlier paper, based on the same experimental work, Randall, Dennison, Ginsburg, and Weber[3] gave the energy levels at 446.52 and 447.20 cm, in which case the wave-length becomes $1/0.68 = 1.47$ cm. The discrepancy 0.19 cm between the two estimates of the wave-length is probably a rough measure of the accuracy of the infra-red data. The wave-length is now known with precision from measurements made with new microwave techniques. Becker and Autler[4] give the wave-length as 1.344 cm, with an estimated error of a little less than one percent. Very recently, by working at low pressures, Townes and Merritt[5] have achieved a still higher degree of accuracy, which they list as two parts in ten thousand, and find the wave-length to be 1.3481 cm.

It is the purpose of the present paper to calculate not only the absorption due to the 1.35 cm line, but also the influence of other lines, of much shorter wave-length, on the attenuation in the microwave region. We shall also see that other resonances come into play if the wave-length is reduced to the millimeter rather than centimeter region.

It is interesting to note now much the whole status of the subject has changed since the writer wrote his first report[6] some five years ago. At that time, no relevant measurements had been made on microwave absorption, and the attenuation could only be predicted. Furthermore the precise amount of absorption could not be calculated with much precision, since there was uncertainty not only in the resonance wave-length but also in the so-called line-breadth constant which tells how much the lines are broadened by collision. Now, however, the constants are quite well known, and correspondingly the emphasis has shifted from prediction of effects not yet observed to comparison of the details of the theory with experiment in the hopes of getting more insight into the mechanism of damping by collision. There are still no measurements for millimeter wave-lengths, but interesting experiments in this domain should be possible when techniques are developed to open it to observation.

FORMULAS FOR THE ABSORPTION

Effect of the 1.35 *cm line.* First we shall give the expression for the absorption due to the line at 1.35 cm. The relevant theory is that given in the preceding article on the absorption by oxygen,[7] but with, of course, the understanding that the dipole moment is now electric rather than magnetic. As we are dealing with but a single line, the expression (5) of our previous paper for the absorption

---

[3] Randall, Dennison, Ginsburg, and Weber, Phys. Rev. **52**, 160 (1937).
[4] G. E. Becker and S. H. Autler, Phys. Rev. **70**, 300 (1946).
[5] C. H. Townes and F. R. Merritt, Phys. Rev. **70**, 558 (1946).
[6] J. H. Van Vleck, report 43-2 of the M.I.T. Radiation Laboratory.
[7] J. H. Van Vleck, Phys. Rev. **71**, 413 (1947).

γ in db/km for microwaves of wave-length λ becomes

$$\gamma_{1.35}=\frac{\alpha}{\lambda^2}\left[\frac{\Delta\nu/c}{(1.348-1/\lambda)^2+(\Delta\nu/c)^2}+\frac{\Delta\nu/c}{(1.348+1/\lambda)^2+(\Delta\nu/c)^2}\right], \tag{1}$$

with[8]

$$\alpha=10^6(\log_{10}e)(8\pi^2cN/3GkT)\mu_{1.35}{}^2\exp[-E(5,\ -1)/kT], \tag{2}$$

$$G=\sum_{J=0}^{\infty}\sum_{\tau=-J}^{J}[2-(-1)^{|\tau|}](2J+1)\exp[-E(J,\ \tau)/kT]. \tag{3}$$

Here N is the number of water molecules per cc, $\Delta\nu$ is the line-breadth constant representing the effect of broadening by collision, and $E(J,\ \tau)$ denotes the energy of a state specified by quantum numbers J and τ in Dennison's notation. The factor which immediately follows the summation sign in (3) and which has alternately the values 1 and 3 is caused by nuclear spin. Since $E(5,\ -1)=447$ cm^{-1}, the Boltzmann factors for the states involved in the 1.35 cm line can be written as $10^{-278/T}$. The factor $\mu_{1.35}{}^2$ in (3) is the "line-strength" of the electric dipole moment for the transition $5_{-1}\rightarrow 6_{-5}$ inclusive of the augmentation of the statistical weight by a factor 3 due to nuclear spin. The value of $\mu_{1.35}{}^2$ can be calculated by means of the quantum mechanics of the asymmetrical top applied to the water molecule. We originally[6] computed $\mu_{1.35}{}^2$ to be $0.17\mu_0{}^2$, where $\mu_0=1.84\times10^{-18}$ e.s.u. is the permanent dipole moment of the H_2O molecule. The more exact calculations of King, Hainer, and Cross, given in the following article,[9] yield $\mu_{1.35}{}^2=0.165\mu_0{}^2$. The partition function G can be evaluated numerically since the energy levels of the water molecule are known from infra-red spectroscopic analysis. At 293°K, the value of G is 170.

When the numerical information given in the preceding paragraph is employed, the constant α defined in (2) acquires at 293°K the value

$$\alpha=0.00350\rho \quad\text{or}\quad \alpha=2.63q, \tag{4}$$

where ρ is the number of grams of water vapor per cubic meter. In the alternative form, q is the fraction of air molecules that are water ones, or, in other words, the ratio of the vapor pressure of water to atmospheric pressure.

Residual Effect of Other Lines. The 1.35 line just discussed is the only one that has a resonance at wave-lengths longer than 1 cm. However, the lines whose resonances are at shorter wave-lengths give a small contribution γ_{RES} to the attenuation in the centimeter region, which we shall term the residual absorption. It may be calculated, to a sufficient approximation, under the assumption that the incident frequency is small compared to the resonance frequency. In other words, the structure factor given in Eq. (2) of the preceding paper[7] may be replaced by $2\nu\cdot\Delta\nu/\pi\nu_{ij}{}^3$. The general formula (1) of that paper then becomes[10]

$$\gamma_{\text{RES}}=\lambda^{-2}\Delta\nu\cdot10^6(\log_{10}e)(16\pi^2Nc/3hG)\Sigma_{J,\tau,J',\tau'}(\mu_{J\tau,J'\tau'}{}^2/\nu_{J\tau,J'\tau'}{}^3)\exp[-E(J,\ \tau)/kT], \tag{5}$$

where $\mu_{J\tau,J'\tau'}{}^2$ means the line-strength, inclusive of nuclear spin, associated with the transition $J,\ \tau\rightarrow J',\ \tau'$. The numerical values of the line-strengths, which are computed by means of the quantum mechanics of the unsymmetrical top, are tabulated in the following paper by King, Hainer, and Cross up to $J=6$, inclusive. From the approximate estimates of Randall, Dennison, Ginsburg, and

---

[8] Equation (5) of the preceding paper involves all pairs of states symmetrically, so that at first sight it would seem as though our Eq. (2) should contain a Boltzmann factor for the 6, −5 as well as the 5, −1 state. However, this factor is very nearly the same for both states, so we have included a single factor and multiplied by 2.

[9] G. W. King, R. M. Hainer, and P. C. Cross, Phys. Rev. **71**, 433 (1947).

[10] For the transitions in which $|\nu_{J\tau,J'\tau}'|$ is small compared with kT/h we may follow a procedure explained in connection with Eq. (4) of the preceding article, and replace the factor $1/\nu_{J\tau,J'\tau'}{}^{-3}$ in (5) by $1/2kT\nu_{J\tau,J'\tau'}{}^2$. The need for distinguishing between positive and negative frequencies, and the difficulty of nearly compensating terms, which appears in (5) as it stands, is then avoided. Some of the transitions, however, involve too high frequencies to permit this simplification. It is instructive to examine the magnitude of the centroid frequency $\bar{\nu}$ defined by equating the quadruple sum in (5) to $G\mu_0{}^2/2kT\bar{\nu}^2$. The numerical value of the sum is such that $\bar{\nu}/c=47$ cm^{-1}.

Weber[3] on the intensities of water lines, or otherwise, it is found that the error involved in omitting the levels higher than $J=6$ is inconsequential, of the order of a percent or so. When the sum in (5) is computed with the aid of the results of King, Hainer, and Cross, Eq. (5) becomes at 293°K

$$\gamma_{\mathrm{RES}}=0.0116\rho\Delta\nu/\lambda^2 \quad \text{or} \quad \gamma_{\mathrm{RES}}=8.7q\Delta\nu/\lambda^2. \tag{6}$$

In a previous report,[11] we gave the constant as 9.65 instead of 8.7. The discrepancy of about 10 percent is presumably due to the fact that we previously calculated the intensities accurately only up to $J=3$, and thereafter used an approximate method due to Dennison.

VALUE OF THE LINE-BREADTH CONSTANT $\Delta\nu$

Before the absorption can be obtained numerically from (1)–(6), it is necessary to know the value of the constant $\Delta\nu$. In 1942, when the author began his study[6] of the water absorption he considered 0.3 cm^{-1} to be the best choice for $\Delta\nu/c$. This value was derived from experimental measurements by Cornell[12] on the infra-red spectrum of water vapor, which gave 0.20–0.28, and from somewhat higher estimates by Dennison (private communication). In view of the importance of the quantity $\Delta\nu/c$ for microwave physics and problems of radar propagation, improved measurements of the breadth of water-vapor lines in wet air were made by Adel[13] in the infra-red laboratory at the University of Michigan during 1944, and gave at first $\Delta\nu/c=0.17$, later 0.11 cm^{-1}. The error in the final value 0.11 cm^{-1} was estimated not to exceed 0.02 cm^{-1}. It has, however, subsequently proved possible to determine the breadth of the line more accurately with microwave than with infra-red technique, inasmuch as in the microwave region, the breadth is comparable with the frequency of the line itself. The experiments by Becker and Autler[4] at the Columbia Radiation Laboratory reveal the shape of the line in detail, and indicate that, for low densities of water vapor, the best choice of the parameter $\Delta\nu/c$ is 0.087 cm^{-1}, in agreement with the Michigan data to within the limits of accuracy of the latter. An interesting result of the Columbia experiments is that at atmospheric total pressure, the line breadth $\Delta\nu$ depends somewhat on the partial pressure of the water vapor. For instance, at a content of 50 grams/m^3, the value of $\Delta\nu/c$ is 0.107, instead of 0.087 cm^{-1}, the extrapolated value for air with an infinitesimal amount of moisture. As high a density as 50 grams per cubic meter cannot be obtained for water vapor at ordinary temperatures, and was possible in the experiments of Becker and Autler only because the temperature was raised to 45°C. The density of saturated water vapor at ordinary temperatures is about 18 grams/m^3, corresponding by interpolation to a $\Delta\nu/c$ approximately 0.094 cm^{-1}.

TABLE I. γ/ρ gives the absorption in db/km per g of water per cubic meter at 293°K for $\Delta\nu/c=0.1$ cm^{-1}. The contribution of the 1.35 cm line and the residual effect of other lines are denoted, respectively, by $\gamma_{1.35}$ and γ_{RES}.

λ	ν/c	$\gamma_{1.35}/\rho$	$\gamma_{\mathrm{RES}}/\rho$
10 cm	0.01 cm^{-1}	0.0000133	0.000013
3	0.333	0.000256	0.00013
2	0.50	0.00136	0.00029
1.5	0.667	0.0101	0.00052
1.428	0.700	0.0147	0.00057
1.350	0.740	0.0193	0.00064
1.250	0.800	0.0168	0.00074
1.111	0.900	0.0082	0.00095
1.00	1.000	0.0047	0.00116
0.667	1.500	0.00150	0.00262
0.500	2.000	0.00107	0.0047
0.333	3.000	0.00085	0.013

NUMERICAL VALUES OF THE ABSORPTION

In Table I we use the round value 0.1 cm^{-1} for $\Delta\nu/c$, for the sake of simplicity, since it reflects pretty closely the combined results of the Michigan and Columbia experiments. The third column gives the absorption due to the 1.35 cm line, obtained from Eq. (1), while the

---

[11] J. H. Van Vleck, report 664 of the M.I.T. Radiation Laboratory. A still earlier report gave the factor as 19.3 rather than 9.65 because the original Lorentz collision theory had not been properly modified to allow for thermal equilibrium at impact.

[12] S. D. Cornell, Phys. Rev. **51**, 739 (1937). We should mention that although the line-breadths reported by Cornell for water vapor in air are apparently too high, his values for steam are compatible with the results of Townes and Merritt and of Becker and Autler on H_2O-H_2O collision cross sections, which we discuss later.

[13] A. Adel, NDRC Div. 14, Rep. No. 320, and especially the supplement thereto. His "half-breadth" is twice our quantity $\Delta\nu/c$.

fourth column gives the residual effect, embodied in Eq. (6), which arises from lines of shorter wave-length. The actual absorption is, of course, the sum of that in the two columns.

COMPARISON WITH EXPERIMENT

The existence of the absorption due to the 1.35 cm line of water has been demonstrated by various investigators in a variety of ways. There is a very noticeable improvement with time in the refinement of method and resulting sensitivity.

Transmission Experiments. The simplest way to show that the absorption is present is merely to verify that if radar signals are propagated over long distances, the attenuation is greater on damp than on dry days. Experiments of this character were made by Bender[14] and collaborators of the M.I.T. Radiation laboratory in aeroplanes in southern climates of high humidity. Even with the best concomitant meteorological data to determine the water content of the atmosphere, the precision cannot be made high. Nevertheless, the experiments do demonstrate unequivocably the reality of the absorption, and show that within the limits of error its magnitude is compatible with the theoretical values calculated on the basis of $\Delta\nu/c = 0.10$ cm^{-1}.

Radiometer Method. A very ingenious method for detecting the absorption due to the column of water vapor in the earth's atmosphere has been developed by Dicke and collaborators.[15] It is based on the fact that the "effective temperature" or Johnson noise level of a microwave antenna is determined by the requirement of balance between the absorption and emission of the antenna. The exchange of radiation of radiation with the water vapor makes the temperature different from what it would be were the microwaves propagated through the air without attenuation. For a full account of the interesting theory involved, the reader is referred to the original paper.[15]

Dicke and his colleagues made measurements at wave-lengths of 1, $1\frac{1}{4}$, and $1\frac{1}{2}$ cm. They found at these wave-lengths absorptions amounting to respectively 0.011, 0.026, and 0.014 when expressed in db/km per gram of H_2O per cubic meter. The corresponding theoretical values given in our Table I, are 0.006, 0.018, and 0.011. The agreement would not be improved if a somewhat lower line breadth, say 0.009 rather than 0.010 cm^{-1}, were used.

Cavity Method. The most accurate existing determinations of the absorption due to water vapor at atmospheric total pressure are probably those of Becker and Autler.[4] By means of thermocouples, they studied how the "Q" of a cavity fed by microwaves was influenced by changing the moisture content of the air in the cavity. In a theoretical paper, Lamb[16] showed that the absorption coefficient can be deduced from their measurements.

The values of the attenuation yielded by the Columbia experiments are somewhat lower than those obtained by the radiometer method, but still are appreciably higher than predicted theoretically. Figure 1, which is reproduced from the paper of Becker and Autler, shows the experimental results, and also the theoretical curve calculated on the assumption $\Delta\nu/c = 0.087$. In Fig. 1, the ordinate is not the absorption coefficient, but rather the absorption divided by the square of the wave number. This kind of plot is advantageous, as then the residual effect, due to lines other than 1.35 cm, becomes independent of frequency. In fact, Fig. 1 shows pretty clearly

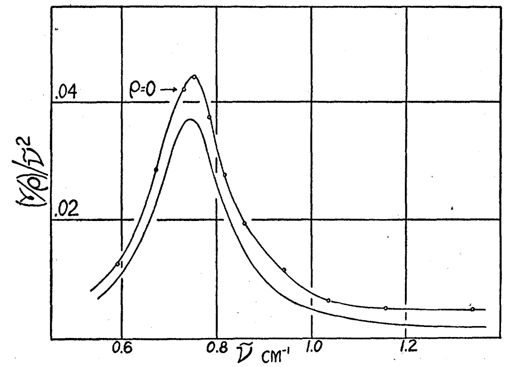

FIG. 1. Dependence of absorption on the wave number ν/c in the vicinity of the resonance at $\lambda = 1.35$ cm. The ordinates are the absorption in db/km per gram of H_2O/m^3, divided by the square of the wave number. The upper curve is an experimental one by Becker and Autler for very small water content. The lower curve is calculated from theory on the assumption $\Delta\nu/c = 0.087$ cm^{-1}.

---

[14] R. S. Bender, A. E. Bent and J. W. Miller, Report 729 of the M.I.T. Radiation Laboratory.

[15] R. H. Dicke, R. Beringer, R. L. Kyhl, and A. B. Vane, Phys. Rev. 70, 340 (1946).

[16] W. E. Lamb, Jr., Phys. Rev. 70, 308 (1946).

that the discrepancy between theory and experiment is caused by the residual absorption rather than to the 1.35 cm resonance. If the theoretical ordinate is raised by a uniform amount, then the theoretical curve can be made to coincide with the experimental one within the limits of error of the latter. Such an adjustment, however, involves use of a constant of proportionality in (6) which is between 4 and 5 times larger than the theoretical value 0.0116.

Observations in Water Vapor at Low Pressures. Townes and Merritt[5] have devised a wave-guide method to observe the absorption of pure water vapor at a pressure of only 0.1 mm, where the 1.35 cm line is exceedingly sharp. In their experiments, the resonance wave-length could be determined with high precision, but the attenuation is so weak that the absolute value of the absorption can only be found with an accuracy of 50 percent, or so. The experimentally estimated line-strength agrees with theory within 20 percent, or much less than the limits of error. Owing to the low pressure and resulting very small line-breadth, the residual absorption caused by lines other than 1.35 cm is completely negligible in the cm region. The line-breadth $\Delta\nu$ can be measured to within 20 percent. If it is assumed that $\Delta\nu$ is proportional to pressure, the magnitude of $\Delta\nu/c$ at 76 cm is found to be 0.36 cm^{-1}. This value of the parameter representing the effect of collision-broadening is one appropriate to H_2O-H_2O collisions. Hence we should not expect it to agree with the value 0.1 cm^{-1} which we used in Table I, as there we were interested in relatively low concentrations of water vapor in air, where the collisions are dominantly H_2O-N_2 or H_2O-O_2. By observing how much the line is broadened when the concentration of water is increased to 50 grams per cubic meter, Becker and Autler were able to estimate roughly the collision parameter for H_2O-H_2O collisions as a second-order effect. They concluded that $\Delta\nu$ was about 4.7 times as large for H_2O-H_2O as for H_2O-air collisions. Since they found $\Delta\nu/c$ to be 0.087 cm^{-1} for H_2O-air impacts, their value of $\Delta\nu/c$ for H_2O-H_2O is 0.42. The discrepancy of about 20 percent compared with the extrapolated value 0.36 of Townes and Merritt is well within the limits of error, which amounts perhaps to 50 percent since the H_2O-H_2O effects enter only weakly even in saturated air. Thus we can say that within the experimental error, $\Delta\nu$ is proportional to the pressure p even when the values of p are as diverse as 0.1 mm and 76 cm.

Observations on Steam. Saxton[17] has measured the absorption of steam at 1.6 cm. Here, of course, the relevant collision cross section is for H_2O-H_2O rather than H_2O-air impacts. Consequently, until recently, no information was available on the line-breadth constant. In a previous report,[11] the writer pointed out that the absorption reported by Saxton was larger than could be explained with any reasonable selection of $\Delta\nu/c$. In line with this remark, use of the subsequent value 0.36 of Townes and Merritt gives a theoretical absorption considerably smaller than found by Saxton, provided it is assumed that the residual effect is given correctly by Eq. (6) as it stands. However, if in the light of the Becker and Autler results shown in Fig. 1 it is assumed that the constant of proportionality should be approximately four times as large as that 0.116 given in (6), then the calculated absorption[18] agrees adequately with Saxton's results. It turns out, if anything, to be a little too high, but the discrepancy is doubtless no more than the experimental error. Thus Saxton's measurements which previously were an enigma to the author, can be now regarded

---

[17] J. A. Saxton, Paper No. RRBS 17.

[18] Since Saxton's measurements are at 373° rather than 293°K, one cannot apply Eqs. (4) and (6) to them without a temperature correction. At a given pressure the absorption γ/N per molecule varies with temperature according to theory in the following fashion. At resonance $\gamma_{1.35}/N$ is proportional to $T^{-2}10^{-278/T}$, and well away from resonance, to $T^{-3}10^{-278/T}$. On the other hand, γ_{RES}/N is proportional to $T^{-3/2}$. These statements follow from Eqs. (2) and (6) when allowance is made for the fact that $\Delta\nu$ is proportional to $T^{-\frac{1}{2}}$ at constant p. In (2), the partition function G may, for a rough approximation be considered proportional to $T^{3/2}$. (Explicit numerical calculations give the result that $G_{410}/G_{273}=1.70$ whereas $(410/273)^{3/2}=1.82$.) The temperature dependence of the sum in (5) may be regarded as the same as that of G/T since the centroid frequency defined at the end of footnote 10 varies but slowly with temperature.

The temperature corrections are not completely negligible even in the Columbia experiments, since they were made at 318° rather than 293°K. This explains why the ordinates of the theoretical curve in Fig. 1 are somewhat lower than would be calculated for 293°K as in Table I. The line-breadth $\Delta\nu/c=0.087$ cm^{-1} deduced from the Columbia experiments really applies to 318°. The corresponding value at 293°K is 0.091. This correction is smaller than the experimental error, and so we do not mention it elsewhere in the discussion.

as interesting additional evidence that the residual effect of other lines is greater than that given by (6). Because of the increased line breadth, this effect is relatively greater in steam than in damp air. In fact, at $\lambda = 1.6$ cm the influence of the 1.35 line is overshadowed by the combined residual contributions of other lines if the constant of proportionality in (6) is increased by a factor 4.

SPECULATION ON CAUSES FOR HIGHER RESIDUAL ABSORPTION

The problem for the theoretician is obviously to find a reason why the residual term, i.e., the attenuation due to lines of wave-length other than 1.35 cm, should be so much larger than we have calculated it to be. Any error in the estimation of the line-strengths by the quantum mechanics of the asymmetrical top is undoubtedly far too small to be relevant.[19] A conceivable explanation of the discrepancy, suggested to the writer by W. E. Lamb, is that different lines have different line-breadth constants. This might be the case, for instance, if due to resonance effects in energy exchange, the most effective collisions are those in which the colliding molecules merely exchange rotational states, and hence both have nearly the same Boltzmann factors, inasmuch as the energy transfer is small compared to kT. Then molecules in the populous states have larger line-breadths than those in less occupied ones, since they are more likely to collide with molecules of comparable energy. Thus the effective $\Delta\nu$ to be used in Eq. (6) might be larger than that involved in (1), since the important lines contributing to (5) involve more heavily populated states than the pair involved in the 1.35 cm line. The existing evidence, on the whole, seems to point against this effect being important enough to be the explanation of the trouble. For one thing, there is the fact that line-width measured by Adel[13] agrees fairly well with the value reported by Becker and Autler despite the Michigan and Columbia experiments being made on quite different spectral lines. Also no pronounced variation in line-breadth from line to line has come to light in the now extensive microwave measurements on the ammonia spectrum. Moreover, Townes and Merritt[5] find no great difference in line-breadth between two unrelated lines of H_2O and HDO, respectively.

The only alternative explanation that has occurred to us of why (6) could be wrong is that the collision theory of Lorentz, as slightly revised by Van Vleck and Weisskopf,[20] might be drastically incorrect in the wings of the lines. If the lines tail off much less rapidly away from resonance than predicted by the ordinary formulas, the effect of the lines of short wave-lengths might be stronger in the 1 cm region than (6) would indicate. As has been pointed out by Margenau, Lindholm, Foley, and others,[21] the Lorentz theory involves the idealization of treating the phase change at collision as infinitely sudden. More realistic models give complicated absorption curves which make the attenuation in the wings deviate from the Lorentz expression. It is not clear at present, however, whether the pressure at one atmosphere is high enough to make the modifications of the Lorentz formula really important. The fact that the quotient of line-breadth constant by pressure is the same at 0.1 mm and 76 cm within the limits of experimental error is presumptive but not conclusive evidence in favor of the Lorentz theory.

More study of the question, both experimentally and theoretically, is desirable. Lines should be observed further in the wings, and more measurements should be made on the pressure dependence of $\Delta\nu$. Studies should be made on how $\Delta\nu$ behaves from line to line when it becomes possible to extend the frequency range to embrace more lines. Thus microwave spectroscopy should furnish the clue to interesting theoretical questions connected with the mechanism of collision-damping.

---

[19] The calculations by means of the usual theory of the asymmetrical top do not include the corrections for centrifugal expansion, but this will, in all probability, increase the line-strength by not more than a percent or so,—very likely by only a few parts in a thousand.

[20] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).

[21] H. Margenau, Phys. Rev. **48**, 755 (1935); E. Lindholm, Arkiv Math., Astron. Fys. **32A**, No. 17 (1945); H. M. Foley, Phys. Rev. **69**, 616 (1946). It should be particularly mentioned that Lindholm's theory gives a less rapid drop of the absorption away from resonance on the low frequency side than does the Lorentz theory, at least if the pressure is sufficiently high to make the divergence between the two theories appreciable. A less rapid drop will make the ordinary infra-red rotational lines of water absorb more strongly in the microwave region than (6) would predict.

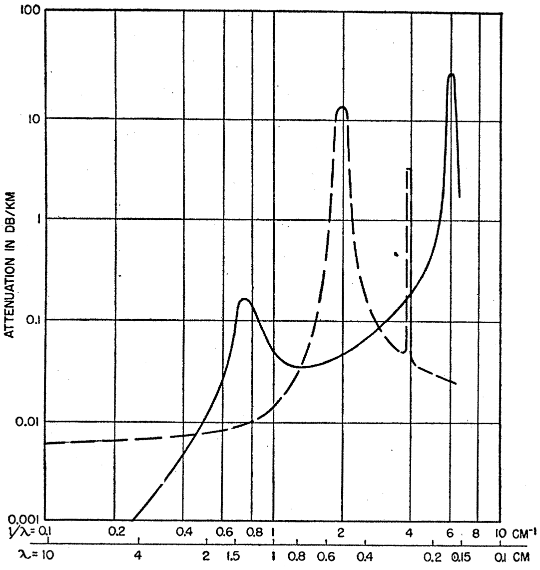

FIG. 2. Theoretical values of the atmospheric attenuation due to uncondensed water vapor and to oxygen at 293°K. The solid curve gives the absorption by water in an atmosphere containing 1.0 percent water molecules ($\rho = 7.5$ g/m^3), for $\Delta\nu/c = 0.1$ cm^{-1}. The dashed curve is the absorption by oxygen for $\Delta\nu/c = 0.02$ cm^{-1}.

COMPARISON OF THE ATTENUATION BY OXYGEN AND BY WATER VAPOR

It is interesting to plot in the same figure the absorption by both the oxygen and the water vapor in the atmosphere as a function of wave number. This is done in Fig. 2. In order to have a basis of comparison, it is assumed that one percent of the molecules in the atmosphere are H_2O. In a temperate climate approximately this amount of water is present in an average day. When there is saturation, the content can be two or three times higher, and in the tropics even greater. There is, of course, then a corresponding increase in the absorption by the uncondensed water vapor.

ABSORPTION BY WATER VAPOR IN THE MILLIMETER REGION

Figure 3 shows the theoretical absorption due to water vapor in the millimeter region. For such short wave-lengths, the attenuation due to oxygen is relatively unimportant, and so has been omitted. As in Fig. 2, it is supposed that the atmosphere has one percent of water molecules. In Fig. 3, it has been assumed that the line-breadth $\Delta\nu/c$ is 0.11 cm^{-1}, the Michigan value, inasmuch as the subsequent Columbia data which somewhat reduce $\Delta\nu$ were not available at the time the calculations for Fig. 3 were made. In view of the uncertainties connected with the constant in (6) it has not seemed worth while to recompute the curve for say 0.10 cm^{-1}. Obviously Fig. 3 loses some of its quantitative significance if $\Delta\nu$ varies from line to line, rather than retaining a constant value as supposed in the calculations, or if the line-structure is more complicated than envisaged by the Lorentz theory. In the latter event, the curve will be affected mainly in the valleys rather than at the peaks. In any case, the graph shows the location of the important resonance maxima. It is to be emphasized that in drawing Fig. 3 (and also in the last line of Table I) it is necessary to use the expression for the absorption given in Eq. (1) of the preceding paper, rather than Eq. (5) or (6) of the present article, in which the structure factor has been simplified by assuming that $|\nu_{J_\tau, J'_{\tau'}}| \gg c/\lambda$. In the millimeter region one is too close to resonance with many of the lines to warrant this assumption. In fact, here the in-

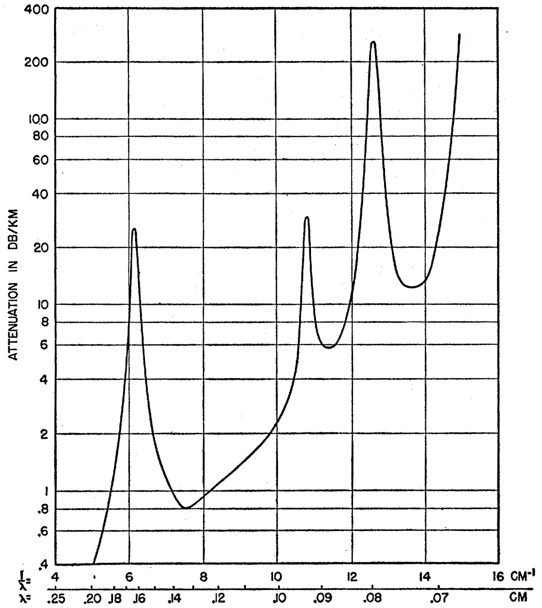

FIG. 3. Theoretical values of the absorption due to uncondensed water vapor in the millimeter region. The curve is for an atmosphere containing 1.0 percent water molecules ($\rho = 7.5$ g/m^3), for $\Delta\nu/c = 0.11$ cm^{-1}. There is no difficulty in adapting the results to other moisture contents, since short of saturation the absorption is directly proportional to ρ (neglecting the second-order effect of H_2O-H_2O collisions).

fluence of the 1.35 cm line is negligible, and the contributions of other lines are dominant rather than residual. Figure 3 shows that there are some very strong resonances in the millimeter region, and that even in the valleys the absorption due to water vapor is so high as to make wavelengths shorter than a millimeter or so useless for transmission except over exceedingly short distances. Incidentally, any modifications of the standard Lorentz theory such as we discussed previously will tend to make the absorption higher than shown in Fig. 3, especially in the valleys. Of course the opacity does not continue if the wave-length is reduced indefinitely. However, the opening up of the atmosphere to transmission occurs only when the frequency becomes high compared to the rotational frequencies of the water molecule, or in other words falls in the infra-red rather than microwave region.[22]

The writer wishes to express his thanks to Miss Mary Jane Farnsworth and Miss Eleanor Pressly for assistance in the calculations and curve-plotting for this and the preceding paper.

---

[22] For a calculation of the absorption of water vapor in the infra-red region, see W. M. Elsasser, Astrophys. J. **87**, 497 (1938).

PHYSICAL REVIEW VOLUME 71, NUMBER 7 APRIL 1, 1947

Expected Microwave Absorption Coefficients of Water and Related Molecules*

GILBERT W. KING
Arthur D. Little, Inc., and Massachusetts Institute of Technology, Cambridge, Massachusetts

R. M. HAINER
Arthur D. Little, Inc.

AND PAUL C. CROSS
Brown University, Providence, Rhode Island

(Received December 31, 1946)

The microwave absorption of water and related molecules is of interest for practical and theoretical reasons. Since these molecules are asymmetric rotors, the occurrence of lines is a matter of chance and the calculation of their intensities is rather difficult. The line strengths of all transitions of H_2O up to $J=6$ have been calculated exactly and the transformation matrices are given explicitly. Van Vleck has shown that the observed intensity of the $6_{16}-6_{23}$ radar line can be accounted for theoretically, by use of the calculated value of the line strength. The microwave absorption of HDO and D_2O is also predicted with the use of the dipole moment and half-width of H_2O which are presumably the same in the isotopic molecules. In addition, it is pointed out that HDO has components along both the least and intermediate axes of inertia. The selection rules for the former are quite different from the latter (obtaining in H_2O, D_2O), and give rise to transitions between levels which are components of doubly degenerate levels in the limiting case of the symmetric rotor. This splitting varies in magnitude so that lines of HDO should appear throughout the radio and microwave regions. One of these lines has been discovered at 0.7441 cm^{-1}, and is interpreted as the $5_{33}-5_{32}$ transition predicted at 0.79 cm^{-1}. The calculated absorption coefficient is 26×10^{-6} cm^{-1} which is in excellent agreement with the observed value of 30×10^{-6} cm^{-1}. The microwave absorption of H_2S and H_2Se is discussed, and it is pointed out that HDS and HDSe will also have many lines in this region.

INTRODUCTION

THE pure rotation spectra of gaseous molecules extend to the microwave region, where measurements are of value in determinations of molecular structure on account of the relatively great accuracy in which positions and absolute intensities of lines can be determined. The microwave absorption of asymmetric rotors is of particular interest because of the difficulties of analysis of their infra-red vibrational-rotational bands. The spectra of water and similar molecules are of primary interest because the small moments of inertia result in only a few

---

* Part of this work (on H_2O) was done in 1942 for a thesis presented by R. M. Hainer in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University. The calculation of the pure rotational spectra of the other molecules was done on a contract of Arthur D. Little, Inc., with the Office of Naval Research.