TECHNICAL REPORT ECOM-01378-5 October 1966

Calculation of Effective Absorption Coefficient and Spectral Density of Volumetric Power Production by Spontaneous Emission Near the Center of the 183.3GHz Line of Water Vapor.

Technical Report One

Contract No. DA 28-043 AMC-01378(E)

Prepared by
K. Nishina and M.L. Barasch
The University of Michigan
Department of Electrical Engineering
Radiation Laboratory
Ann Arbor

For

U. S. Army Electronics Research and Development Activity
White Sands Missile Range
New Mexico

TABLE OF CONTENTS

ABSTRACT

Expressions are obtained and presented for the effective absorption coefficient and the power per unit volume per unit frequency interval arising from spontaneous emission in a gas containing water molecules, both near the center of the line at 183.3 GHz of water. Since the molecule is an asymmetric rotor, and since the constants of the molecule, to which the calculations are sensitive, seem not to have been determined unambiguously, much re-investigation of the notation, numerical work and interpolation to apply approximations derived from symmetric rotor theory, and checking of previous calculations to select a satisfactory set of molecular constants, has been necessary. Finally, expressions for the two quantities first mentioned here are presented, in a form which permits application to many problems of practical interest. For example, the radiative intensity emerging from such a gas could be predicted only after computations such as those presented here.

I

INTRODUCTION

A microwave radiation line at 183.3 GHz has been attributed to the $3_{13} \rightarrow 2_{20}$ transition of water by King and Gordy (1954). They attributed the line to this transition on the basis of calculations made by King, et al, (1947). The latter publication calculates the frequency of this radiation and also the absorption coefficient associated with it. In this report an attempt will be made first to reproduce their calculations, both of the frequency (Chapter III) and of the absorption coefficient; the results are compared with their values. Because of the complicated notation in such calculations and the availability of various values for the constants involved such a checking procedure was felt necessary. After a good agreement is demonstrated, a general expression for the absorption coefficient will be given (see Eq. 5.34) with temperature and pressure as variables.

Another quantity calculated in this report is the source intensity, due to spontaneous emission (Chapter VI) resulting from the transition. Such a quantity, together with the absorption coefficient will furnish numerical data needed for radiative transfer calculations of the intensity emerging from a body of gas containing some water molecules. A general expression for the source intensity with temperature and pressure as variables will also be given.

The investigation will be formulated and computations presented in such a manner that calculations similar to the ones presented here can be performed easily with different parameters. This is necessary because new and improved values of molecular constants are published frequently, and because values of temperature and pressure other than those assumed by King et al may be of interest.

II

CONSTANTS OF A WATER MOLECULE

Before we embark on the calculations of various quantities, a discussion of values available for the constants describing water molecules seems in order. As for the rotational constants of the molecule, the values the authors could find are listed in Table II-1. Those various sets of values agree with each other (if some of them are rounded off to the proper number of decimal places), except for the value of C furnished by Townes and Schawlow (1955, p. 639). The latter group quote Herzberg, but apparently miscopied that value for C. Their value of C is expressed in MHz, and after a conversion it gives $C' = 9.96\ cm^{-1}$, whereas Herzberg's value is $C' = 9.28\ cm^{-1}$. The discrepancy is serious for the purpose of checking the transition assignment, since this much difference could result in a significant discrepancy in the value of the transition frequency. As for the rest of the table, if we adopt the values for the lowest vibrational level in Herzberg, the values are consistent, although A' by Randall, et al, (1937, p. 163) gives $27.81\ cm^{-1}$ when rounded off, while Herzberg gives $27.79\ cm^{-1}$, but this difference is unimportant for practical purpose. Penner does not mention how his values were obtained, incidentally.

For the above reasons, it does not make any difference which set of values we use, except Townes and Schawlow's. Here in our calculation we will use the values by Randall, et al, (1937). This has the advantage that these values were used by King, et al, (1947) and Randall, et al, (1937) in similar calculations to the present one, therefore using these values makes the comparison of our results with these groups easy. In energy value calculations King et al (1947) carried many significant figures in order to obtain some accuracy in

TABLE II-1: ROTATIONAL CONSTANTS OF A WATER MOLECULE

References	A (MHz)	A'(cm^{-1})	B (MHz)	B'(cm^{-1})	C (MHz)	C' (cm^{-1})	κ	Remarks
Herzberg (p. 488, 1945)								
Lowest Vibrational Level		27.79		14.50		9.28	-0436*	
Equilibrium Position		27.73		14.57		9.49		
Townes and Schawlow (p. 639, 1955)	8332×10^{2}	27.79*	4347×10^{2}	14.50*	2985×10^{2}	9.96*	-0.491*	Quotes Herzberg (1945)
Penner (p. 156, 1959)		27.8		14.5		9.28	-0.438*	
Randall, et al, (p. 163, 1937)		27.8055		14.499724		9.279276	-0.436431	
King, et al, (p. 437, 1947)							-0.436426	Quotes Randall, et al, (1937)
King, et al, (p. 39, 1943)							-0.436	

*These values were calculated by the writer for comparison.

Definitions

$$\kappa = \frac{2B - A - C}{A - C} \quad , \quad v_c = 2.9979 \times 10^{10} \text{ cm/sec} \quad , \quad h: \text{Planck's constant}$$

$$A = \frac{h}{8\pi^2 I_A} \quad , \quad A' = \frac{A}{v_c} \quad , \quad \text{similar definitions for } B, B', C \text{ and } C'.$$

frequencies resulting from energy differences, so at least for the purpose of checking the computational procedure and notation, the many digits in Randall, et al, (1937) are useful.

Therefore we will use

$$A' = 27.8055\ \mathrm{cm}^{-1} \qquad B' = 14.9997\ \mathrm{cm}^{-1}$$
$$C' = 9.2793\ \mathrm{cm}^{-1} \qquad \kappa = 0.43643 \tag{2.1}$$

These values give the following parameters:

$$b_p \equiv \frac{C - B}{2A - B - C} = -0.16400 \tag{2.2}$$

$$b_o \equiv \frac{A - B}{2C - B - A} = -0.56032 \tag{2.3}$$

b_p is a measure of deviation from a prolate symmetric top, and b_o from an oblate one (Townes and Schawlow, 1955).

The axes of symmetry for the H_20 molecule are shown in Fig. 2-1. I_A, I_B and I_C are the moments of inertia around the a, b and c axis respectively, where $I_A < I_B < I_C$, or $A > B > C$, for this molecule, in our notation.

As for its dipole moment, the radiation of H_20 is mainly associated with the electric dipole moment (Van Vleck, 1947a, p. 426) and this moment is parallel to the axis b (King, et al, 1947, p. 436). The latter statement can be justified by symmetry considerations. As for the magnitude of the moment, Townes and Schawlow (1955, p. 639) gives the value $\mu = 1.94 \times 10^{-18}$ (esu · cm) whereas Van Vleck (1947a, p. 427) uses $\mu = 1.84 \times 10^{-18}$ (esu·cm), which appears to have been used by King, et al, (1947) in their calculations. In the present report, the latter value will be used, again for the reasons of checking the procedures of computation. The values of absorption coefficients and source intensities, which are quadratic in the dipole moment, would be altered at most 10 per cent by the choice.

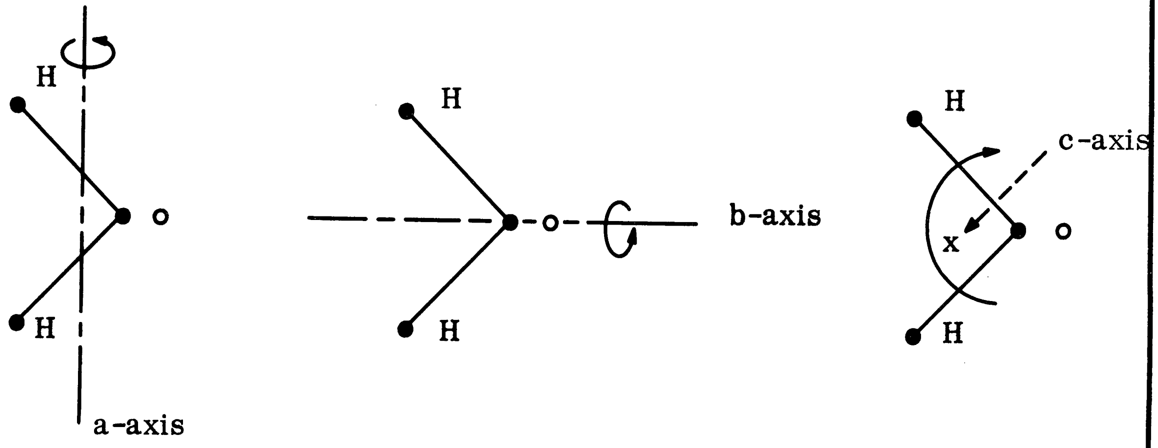


FIG. 2-1: THE AXES OF SYMMETRY FOR THE H_20 MOLECULE

III

ROTATIONAL ENERGY LEVELS AND THE FREQUENCY OF THE RADIATION

Since Ray's parameter of asymmetry is roughly $\kappa = 0.436$ for the water molecule, this rotor is closer to a prolate symmetry limit than to an oblate symmetry limit. To demonstrate such a condition together with other parameters which affect the energy levels, Fig. 3-1 and Fig. 3-2 are given. Figure 3-1 is the diagram shown in usual textbooks (for example, Townes and Schawlow, 1955, p. 86) with added numerical values for our specific problem. The notations are the same as those in the latter reference. Figure 3-1 shows where our transition takes place with an arrow. By calculating the energy associated with the levels 3_{13} and 2_{20} for our value of κ we will obtain the frequency of this radiation. There is no general analytical energy expressio which can be used for any value of (J, K_{-1}, K_1, κ). Hence we have to rely on available tabulations.

The simplest of the possible approaches is to use a formula (Townes and Schawlow, 1955, p. 89)

$$\frac{W}{h} = \frac{1}{2}(A + C)\,J(J + 1) + \frac{1}{2}(A - C)\,E_{J,\tau}(\kappa) \qquad (3.1)$$

where W is the energy of the level in energy units,

h is Planck's constant

$$\tau = K_{-1} - K_1 \qquad (3.2)$$

The quantities on the right hand side of the Eq. (3.1) must be expressed in units of frequency. If the result for W is wanted in terms of wave numbers the following formula may be used where v_c is the velocity of light:

$$\frac{W}{hv_c} = \frac{1}{2}(A' + C')J(J+1) + \frac{1}{2}(A' - C')E_{J,\tau}(\kappa) \qquad (3.3)$$

where

$$A' = \frac{A}{v_c} \qquad B' = \frac{B}{v_c} \qquad C' = \frac{C}{v_c} \quad .$$

The values of $E_{J,\tau}(\kappa)$ used in Eq. (3.1) or (3.3) are tabulated in various references (King, et al, (1943, p. 39); Townes and Schawlow, (1955, p. 527); Allen and Cross, (1963, p. 235)) as a function of J, τ and κ. For our transition, we find the following values of $E_{J,\tau}(\kappa)$, on employing interpolation and symmetric character.

For the 3_{13} level: $\tau = -2$

$$E_{J,\tau}(\kappa) = E_{3,-2}(-0.43643) = -E_{3,2}(0.43643)$$

tabulated values are $E_{3,2}(0.43) = 8.6535614$

$E_{3,2}(0.44) = 8.6757937$.

After the interpolation $E_{3,-2}(-0.43643) = -8.66786$

For the 2_{20} level: $\tau = 2$

$$E_{J,\tau}(\kappa) = E_{2,2}(-0.43643) = -E_{2,-2}(0.43643)$$

tabulations are $E_{2,-2}(0.43) = -2.7092576$

$E_{2,-2}(0.44) = -2.6941292$

after the interpolation $E_{2,0}(-0.43643) = 2.69953$.

These final values of $E_{J,\tau}(\kappa)$ are in good agreement with King, et al, (1947, p. 440). With these values, energy values are computed by Eq. (3.3)

$$\left(\frac{W}{hv_c}\right)_{3,1,3} = 142.2175\ \mathrm{cm}^{-1} \tag{3.4}$$

$$\left(\frac{W}{hv_c}\right)_{2,2,0} = 136.2604 \tag{3.5}$$

$$\Delta\left(\frac{W}{hv_c}\right) = \frac{1}{\lambda} = 5.9571\ \mathrm{cm}^{-1} \tag{3.6}$$

$$\nu = 178.59\ \mathrm{GHz} \tag{3.7}$$

The energy values are close to those of King, et al, (1947, p. 438), which are 142.30 cm^{-1} and 136.15 cm^{-1} while Randall, et al, (1937, p. 164) gave 142.17 cm^{-1} and 136.10 cm^{-1}. Although the final frequency value makes a 3 per cent difference from the 184.5 GHz quoted by King, et al, (1947), there is no other possible combination of levels that results in a frequency close to this value; therefore we can say that we are looking at the right transition, The discrepancy in ν is due to even smaller discrepancies in two energy values which alter the energy difference by the 3 per cent discrepancy found.

Another way of calculating energy levels will be mentioned briefly, to see how two methods compare. According to Townes and Schawlow (1955, p. 86) they can also be calculated by using the following relations:

$$\frac{W}{hv_c} = \frac{B' + C'}{2} J(J+1) + (A' - \frac{B' + C'}{2})\,\omega \tag{3.8}$$

where

$$\omega = K^2 + c_1 b_p + c_2 b_p^2 + c_3 b_p^3 + \ldots \tag{3.9}$$

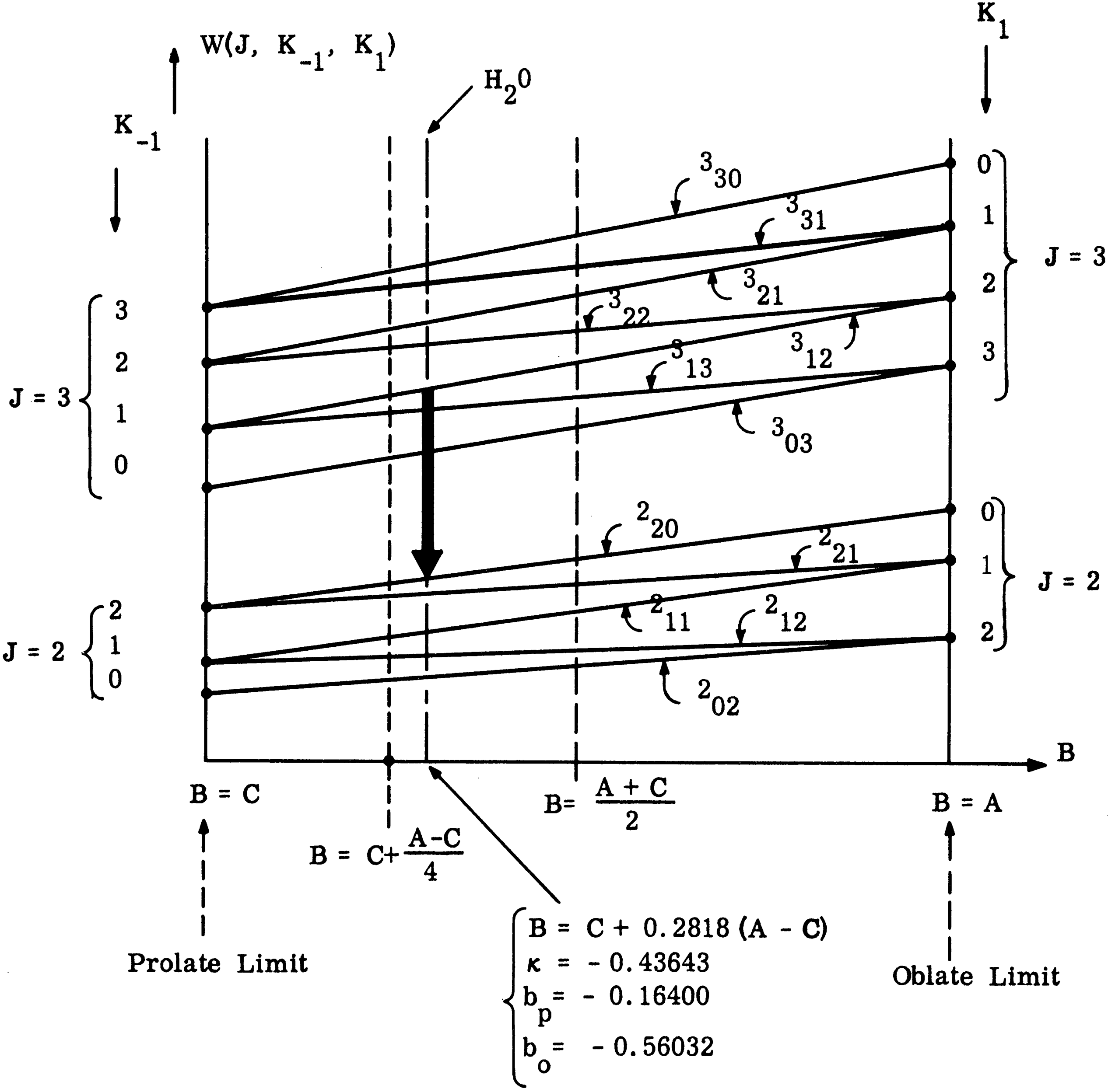
and c_n are tabulated in their Appendix III. After substitution of numerical values (b_p, A', B' and C'), the following results are obtained:

$\omega_{3,1,3} = -0.02869$ $\quad (\frac{W}{hv_c})_{3,1,3} = 142.2174\ \mathrm{cm}^{-1}$

$\omega_{2,2,0} = 4.07906$ $\quad (\frac{W}{hv_c})_{2,2,0} = 136.2593\ \mathrm{cm}^{-1}$

$\frac{1}{\lambda} = 5.9581\ \mathrm{cm}^{-1}$ $\quad \nu = \frac{c}{\lambda} = 178.62$ GHz

We notice they are quite close to those obtained by the first method (Eq. 3.4 through 3.7) in spite of the fact that Eq. (3.8) is supposed to be good only for an asymmetric rotor slightly deviated from a prolate limit. This means that for our $\kappa = -0.43643$, J = 2 and J = 3, Eq. (3.8) was essentially in agreement with Eq. (3.3), which on the other hand is said to be valid for any range of κ. For higher values of J, however, Eqs. (3.8) and (3.3) are expected to yield different results for the same κ, since our $\kappa = -0.43643$ is far from a slightly asymmetric top.



K_{-1}, K_1 are pseudo quantum numbers for an asymmetric top. The arrow indicates the transition we are interested in.

FIG. 3-1: ENERGY LEVELS AND THE TRANSITION IN OUR PROBLEM

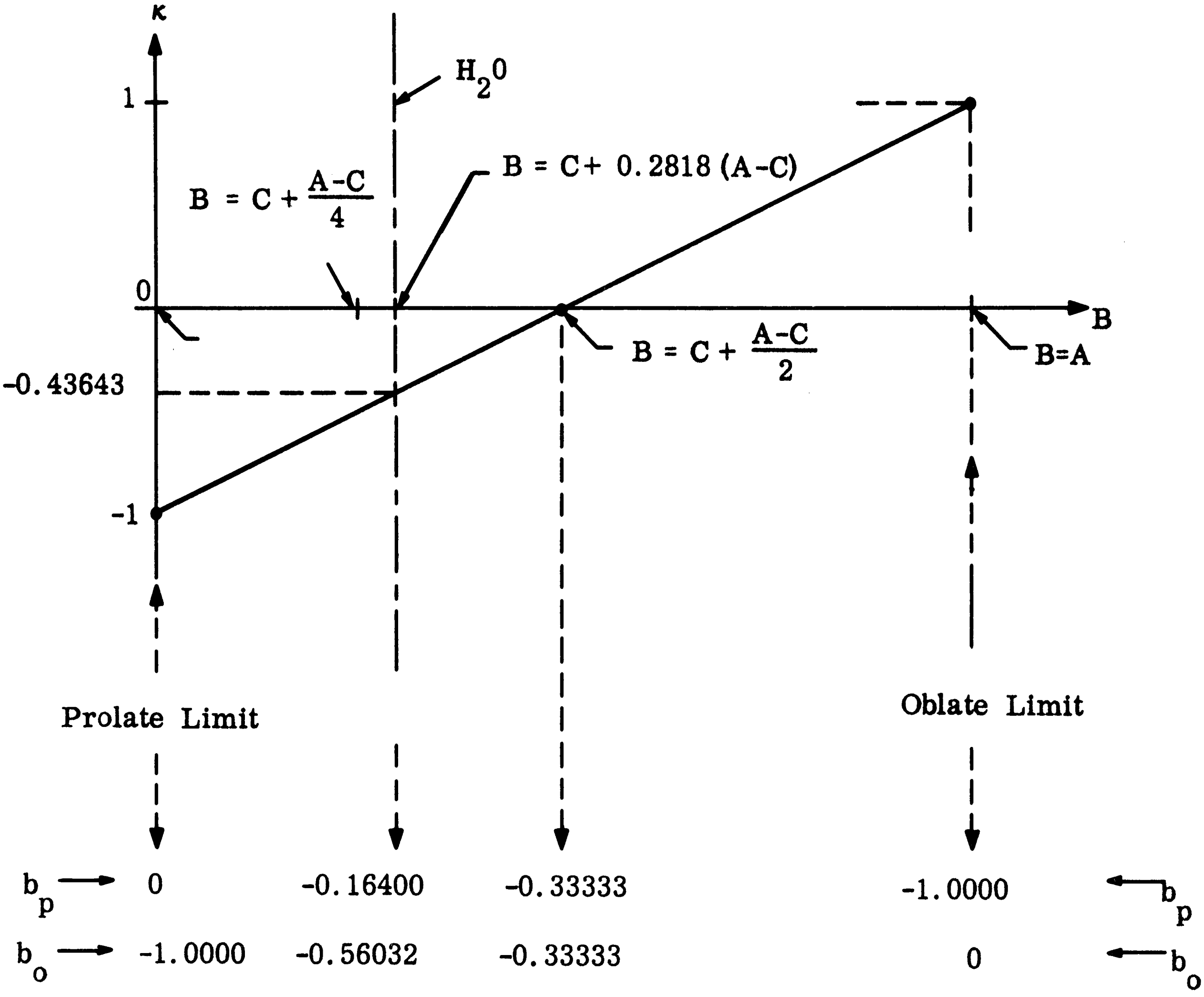


FIG. 3-2: THE RELATION BETWEEN ROTATIONAL CONSTANTS AND VARIOUS OTHER PARAMETERS FOR THE WATER MOLECULE

IV

THE VALUE OF THE DIPOLE MOMENT MATRIX ELEMENT

In the later chapters where we calculate the absorption coefficient and the source intensity we will need a value of the matrix element for our specific transition. The value of one of the factors in the matrix element is tabulated in many references and it is by interpreting the values from such tabulations that we will perform calculations later. Here in this section the theory behind such tabulations of matrix elements is briefly reviewed, inorder to facilitate the explanation of the calculating procedure later. No attempt will be made to give a full quantum-mechanical treatment which would reproduce and justify tabulated numerical values: the review is meant just to clarify notations which appear in formulae. For a full treatment, Allen and Cross (1963), King et al (1943), Cross et al, (1944) and Strandberg (1954) must be referred to.

What we will need in the later calculations is the following:

$$\left| e\,\underline{r}_{\beta\alpha} \right|^2 \equiv \left| eX_{\beta\alpha} \right|^2 + \left| eY_{\beta\alpha} \right|^2 + \left| eZ_{\beta\alpha} \right|^2 \quad . \tag{4.1}$$

Here X is the operator corresponding to the X component of the position vector $\underline{r}$ in space-fixed co-ordinates; Y and Z are defined in similar manners. $X_{\beta\alpha}$, $Y_{\beta\alpha}$ and $Z_{\beta\alpha}$ are corresponding matrix elements calculated between wave functions ψ_α and ψ_β. Here α and β stand for the intitial and final states specified by sets of quantum numbers respectively. What we need is the right hand side of Eq. (4.1), and we designate this summation by the left hand side. In other words Eq. (4.1) is the definition of $\left| e\,\underline{r}_{\beta\alpha} \right|^2$ (Schiff, 1955, p. 253). To write down the set of quantum indices that specify α and β,

$$\alpha = (R, V, E) \tag{4.2}$$

$$\beta = (R', V', E') \tag{4.3}$$

where primes indicate the final state. R and R' are rotational quantum states, namely,

$$R = (J, K_{-1}, K_1, M) \tag{4.4}$$

$$R' = (J', K'_{-1}, K'_1, M) \quad . \tag{4.5}$$

Similarly,

V, V' : vibrational quantum states

E, E' : electronic quantum states

Next we introduce a molecule-fixed co-ordinate system, the three axes being the principal axes a, b and c of the moment of inertia (Fig. (4-1)). In Fig. (4-1), the dipole moment vector $\underline{\mu}$ is drawn not to be parallel to the principal axes, in order to indicate a general case. $\underline{i}$, $\underline{j}$ and $\underline{k}$ are unit vectors along space-fixed axes X, Y and Z. If we denote the direction cosines of $\underline{i}$ with respect to a, b and c axes by cos (aX), cos (bX) and cos (cX),

$$eX = e\,a \cos(aX) + e\,b \cos(bX) + e\,c \cos(cX), \quad \text{and}$$

similarly, for eY and eZ.

To write them down in a compact form,

$$eF = \sum_g eg\cos(gF) \tag{4.6}$$

where

g = a, b and c

F = X, Y or Z

The wave function ψ_α can be approximated satisfactorily by a product of wave functions for rotational, vibrational and electronic states.

$$\psi_\alpha = \psi_R(Ⓗ) \cdot \psi_{V,E}(q) \tag{4.7}$$

$$\psi_\beta = \psi_{R'}(Ⓗ) \cdot \psi_{V',E'}(q) \tag{4.8}$$

Here Ⓗ represents three Eulerian angles that describe relative positions of the (a, b, c) axes with respect to (X, Y, Z) axes. q represents sets of co-ordinates which describe the electronic and vibrational states of the molecule. Then by Eq. (4.6),

$$eF_{\beta\alpha} \equiv \langle \beta | eF | \alpha \rangle$$

$$= \sum_g \langle \beta | eg\cos(gF) | \alpha \rangle$$

$$= \sum_g \int \psi^*_{R'} \cos(gF)\psi_R \, dv_{\textcircled{H}} \cdot \int \psi^*_{V'E'} \, eg \, \psi_{VE} \, dv_q \tag{4.9}$$

$\int dv_{\textcircled{H}}$ and $\int dv_q$ mean the integrations over all the co-ordinates represented by $\textcircled{H}$ and q respectively. In our problem, the transition is purely rotational, in the sense that no electronic or vibrational transition is involved. Therefore $V' = V$, $E' = E$ and the second factor in Eq. (4.9) becomes

$$\int \psi^*_{V,E} \, eg \, \psi_{V,E} \, dv_q = \langle eg \rangle_{V,E} = (\mu_g)_{V,E} \quad . \tag{4.10}$$

Here μ_g means the component of the electric dipole moment along the g-axis of the molecule. As mentioned in Chapter II, for a water molecule $\underline{\mu}$ is parallel to the b-axis. Then

$$\langle \mu_g \rangle_{V,E} = 0 \qquad \text{for } g = a, \text{ or } c$$

$$\langle \mu_g \rangle_{V,E} = \langle \mu_b \rangle = \mu_{V,E} \qquad \text{for } g = b \quad .$$

Consequently, Eq. (4.9) reduces to

$$e F_{\beta\alpha} = \langle \mu \rangle_{V,E} \cdot \int \psi^*_{R'} \cos(bF) \, \psi_R \, dv_{\textcircled{H}}$$

$$= \langle \mu \rangle_{V,E} \cdot \langle R' | \cos(bF) | R \rangle \quad . \tag{4.11}$$

In our case E is absolutely the ground electronic level E_o and V means predominantly the ground vibrational level: later in this investigation it is pointed out that the first and the second vibrational levels should be considered at high temperature. Since a different vibrational state means a different distribution of charges within the molecule, $<\mu>_{V_o, E_o}$, $<\mu>_{V_1, E_o}$ and $<\mu>_{V_2, E_o}$ may be all different. But in this calculation we assume

$$<\mu>_{V_o,E_o} \approx <\mu>_{V_1, E_o} \approx <\mu>_{V_2, E_o} = \mu \tag{4.12}$$

This is not a bad approximation, as indicated by the close agreement of A, B, and C in the ground and V_1 states. For the purpose of obtaining the numerical results required under this contract, the contribution of V_2 is negligible due to its small occupation probability at our temperatures, and it is therefore not important that this approximation is made.

With such assumptions, and from Eqs. (4.1) and (4.11), we have

$$\left| e \underline{r}_{\beta\alpha} \right|^2 = \mu^2 \sum_F \left| < R' \middle| \cos(bF) \middle| R > \right|^2 . \tag{4.13}$$

Following the notation of Cross, et al, (1944) we put

$$\Phi_{Fb} \equiv \cos(bF) \tag{4.14}$$

and write Eq. (4.13) as

$$\left| e \underline{r}_{\beta\alpha} \right|^2 = \mu^2 \sum_F \left| (\Phi^A_{Fb})_{R'R} \right|^2 . \tag{4.15}$$

Here A indicates that the calculation of the matrix element of $\bar{\phi}_{Fb}$ is carried out with wave functions of an asymmetric rotor. Writing R' and R in full expression

$$\left|e\underline{r}_{\beta\alpha}\right|^2 = \mu^2 \sum_F \left|(\bar{\phi}^A_{Fb})_{J', K'_{-1}, K'_1, M' : J, K_{-1}, K_1, M}\right|^2 \quad . \qquad (4.16)$$

This is the quantity we have to calculate, namely, the direction cosine matrices for the asymmetric rotor. In the case of symmetric rotors, corresponding matrix ments, $(\bar{\phi}^{s_o}_{Fg})_{R'_s, R_s}$ have been calculated and tabulated by Cross et al, (1944 p. 212). Here s_o stands for the calculation performed with symmetric rotor wave functions, and R'_s , R_s are rotational states of symmetric rotors, s being a suffix that stands for symmetric rotor. Just as before, F is either X, Y, or Z, g is either a, b, or c. Suppose

$$R_s = \left\{J_s, K_s, M_s\right\} \quad , \qquad R'_s = \left\{J'_s, K'_s, M'_s\right\} \quad ;$$

then the expression for $(\bar{\phi}^{s_o}_{Fg})_{R'_s, R_s}$ is given in Cross, et al, (1944) as a function of J_s, K_s and M_s, which are in turn related to J'_s, K'_s and M'_s, by selection rules. If we could relate $(\bar{\phi}^{s_o}_{Fg})_{R'_s, R_s}$ to $(\bar{\phi}^A_{Fb})_{R', R}$, then our problem would be solved: we would be able to calculate the latter as a linear combination of the former, for example. This is done by the transformation of the matrix $(\bar{\phi}^{s_o}_{Fg})$, but not directly. The reason comes from the different symmetry property of the symmetric rotor wave function $\psi^s(J_s, K_s, M_s)$ and the asymmetric rotor wave function $\psi^A(J, K_{-1}, K_1, M)$ (Cross, et al, (1944, p. 212); Allen and Cross, (1963, p. 105); King, et al, (1943, p. 32)). We have to first form a linear combination of ψ^s to construct the "Wang function" $S(J, K, M, \gamma)$, to which $\psi^A(J, K_{-1}, K_1, M)$ converges at a prolate or an oblate limit. In terms of such function S, the direction cosine matrices of asymmetric rotors can be correlated properly with those of the symmetric rotor as limiting cases.

We denote a matrix which represents such a transformation of ψ^s by U (Wang transformation).

$$\psi^s = U \cdot S \qquad . \tag{4.17}$$

Furthermore we denote by T a transformation which diagonalizes the energy matrix of the asymmetric rotor after U is applied. Then the quantity of interest here, Φ^A_{Fg}, is written (Schiff, 1955, p. 129)

$$\Phi^A_{Fg} = T_f^*(\kappa_f)\, U^* \, \Phi^{s_o}_{Fg} \, U \, T_i(\kappa_i) \tag{4.18}$$

Here the asterisk designates the Hermitian adjoint of matrices, T_i the transformation matrix T for the initial state with initial asymmetry κ_i, and T_f for the final state. In our problem no change of asymmetry parameter takes place, so $T_f = T_i$. However, apart from our problem, if a transition occurs with a great change of energy, it may accompany a change in moment of inertia and hence a change in κ.

Now by Eqs. (4.16) and (4.18) the value we need is written

$$\left| e\underline{r}_{\beta\alpha} \right|^2 = \mu^2 \sum_F \left| \left\{ T^*(\kappa)\, U^*\, \overset{s}{\Phi}{}^{o}_{Fb}\, U\, T(\kappa) \right\}_{\beta\alpha} \right|^2 \tag{4.19}$$

where

$F = X, Y \text{ and } Z$

$\beta = J', K'_{-1}, K'_1, M'$

$\alpha = J, K_{-1}, K_1, M$

Cross, et al, (1944, p. 211) called this quantity $\left| \mu_{n'', n'} \right|^2$.

The value tabulated in references is related to the quantity in Eq.(4.19), but not identical to it. The first modification is the summation of this quantity over the initial and the final quantum numbers M and M'. This is relevant because in the case of free rotation the energy levels involved are degenerate with respect to M and M'. Then by measurement we are observing the result of Eq.(4.19) summed over every possible combination of M and M'. Furthermore, this modification has another advantage, that the same tabulation could be used both for absorption and emission, as will become clear soon. The second modification is dividing Eq. (4.19) by μ^2 such that the tabulation could be used for any molecule. Hence the tabulated value is

$$L = \frac{1}{\mu^2} \sum_M \sum_{M'} \left| e\underline{r}_{\beta\alpha} \right|^2 = \sum_M \sum_{M'} \sum_F \left| \left\{ T^*\, U^*\, \overset{s}{\Phi}{}^{o}_{Fb}\, U\, T \right\}_{\beta\alpha} \right|^2 \tag{4.20}$$

King, et al, (1947, p. 434) denoted this quantity by $\sum|\bar{\phi}|^2$. In Eq. (4.20), M and M' are related by selection rules. After the summation over possible M' is carried out, $\sum_{M'}\left|e\underline{r}_{\beta\alpha}\right|^2$ (which is called $\left|\mu_{J'\leftarrow J}\right|^2$ in Townes and Schawlow (1955, p. 97)) proves to be independent of M. Then Eq. (4.20) can be written

$$L = \sum|\bar{\phi}|^2 = \frac{1}{\mu^2}\,(2J+1)\sum_{M'}\left|e\underline{r}_{\beta\alpha}\right|^2 \tag{4.21}$$

$$= \frac{1}{\mu^2}\,(2J+1)\left|\mu_{J'\leftarrow J}\right|^2 , \tag{4.22}$$

in which J' denotes K'_{-1} and K'_1, as J represents K_{-1} and K_1, and a summation over M' is understood To maintain thermal equilibrium it is necessary that

$$(2J+1)\sum_{M'}\left|e\underline{r}_{\beta\alpha}\right|^2 = (2J'+1)\sum_{M}\left|e\underline{r}_{\beta\alpha}\right|^2 \tag{4.23}$$

Therefore the value $\sum\bar{\phi}^2$ tabulated can be used directly for both absorption and emission. A more general form of Eq. (4.20) is

$$L_g = \frac{1}{\mu_g^2}\,(2J+1)\sum_{M'}\left|e\underline{r}_{\beta\alpha}\right|^2 = (2J+1)\sum_{M'}\sum_{F}\left|\left\{T^*U^*\phi^{\overset{s}{o}}_{Fg}\,U\,T\right\}_{\beta\alpha}\right|^2 \tag{4.24}$$

where b has been replaced by g to include other cases where μ is parallel to g(a, b, or c). These values for possible transitions with various κ, J, K_{-1}, K_1, J', K'_{-1}, and K'_1 are given in Townes and Schawlow (1955, Appendix V) or in Cross, et al, (1944, p. 222).

The quantity necessary for our calculation can be looked up as follows. If we are interested in the absorption, the transition is $2_{20} \longrightarrow 3_{13}$. Hence $\Delta J = +1$, which is classified as R branch. Also $\Delta K_{-1} = -1$ and $\Delta K_1 = 3$. Then our transition is written $R_{-1,3}$, the reverse process (absorption) of which is $P_{1,-3}$. This transition is possible only when $\mu \uparrow\uparrow b$, so in the listing it is tabulated under the entry ${}^{b}R_{-1,3}$ (Townes and Schawlow, 1955, p. 588). The tabulation is widely spaced in κ, and the closest value of κ to our $\kappa = -0.43643$ is $\kappa = -0.5$, for which the value is found

$$L = (2J+1) \frac{\left| \mu_{J' \leftarrow J} \right|^2}{\mu^2} = 0.1097 \quad . \qquad (4.25)$$

In principle, in order to get an exact value of L for our κ, we have to use Eq.(4.20), after calculating the elements of $T(\kappa)$. However, for our specific transition, i.e., for this branch with such a low value of J , the interpolation turns out to be accurate enough. This is in contrast to the $5_{2,3} \longrightarrow 6_{1,6}$ transition which is also designated by ${}^{b}R_{-1,3}$, but for which the interpolation gives a rather poor result. The statement has been verified by King et al, (1947, pp. 436-437). The present authors obtained by interpolation the value

$$L\,(\kappa = -0.436) = 0.1016 \;, \qquad \text{(Fig 4-2)}$$

whereas the exact value given by King et al, (1947) is 0.1015 . In the following calculation the latter will be used, since we feel we have confirmed it.

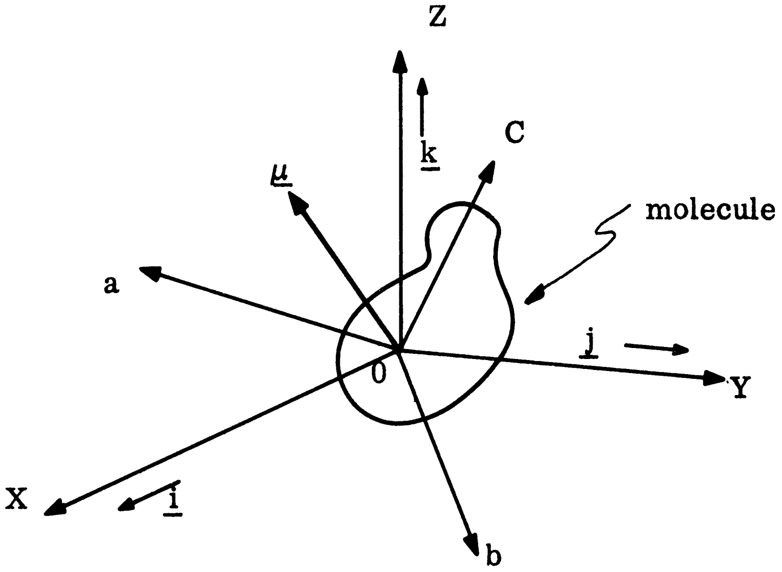


FIG. 4-1: TWO CO-ORDINATE SYSTEMS USED TO DESCRIBE THE WAVE FUNCTION OF A MOLECULE

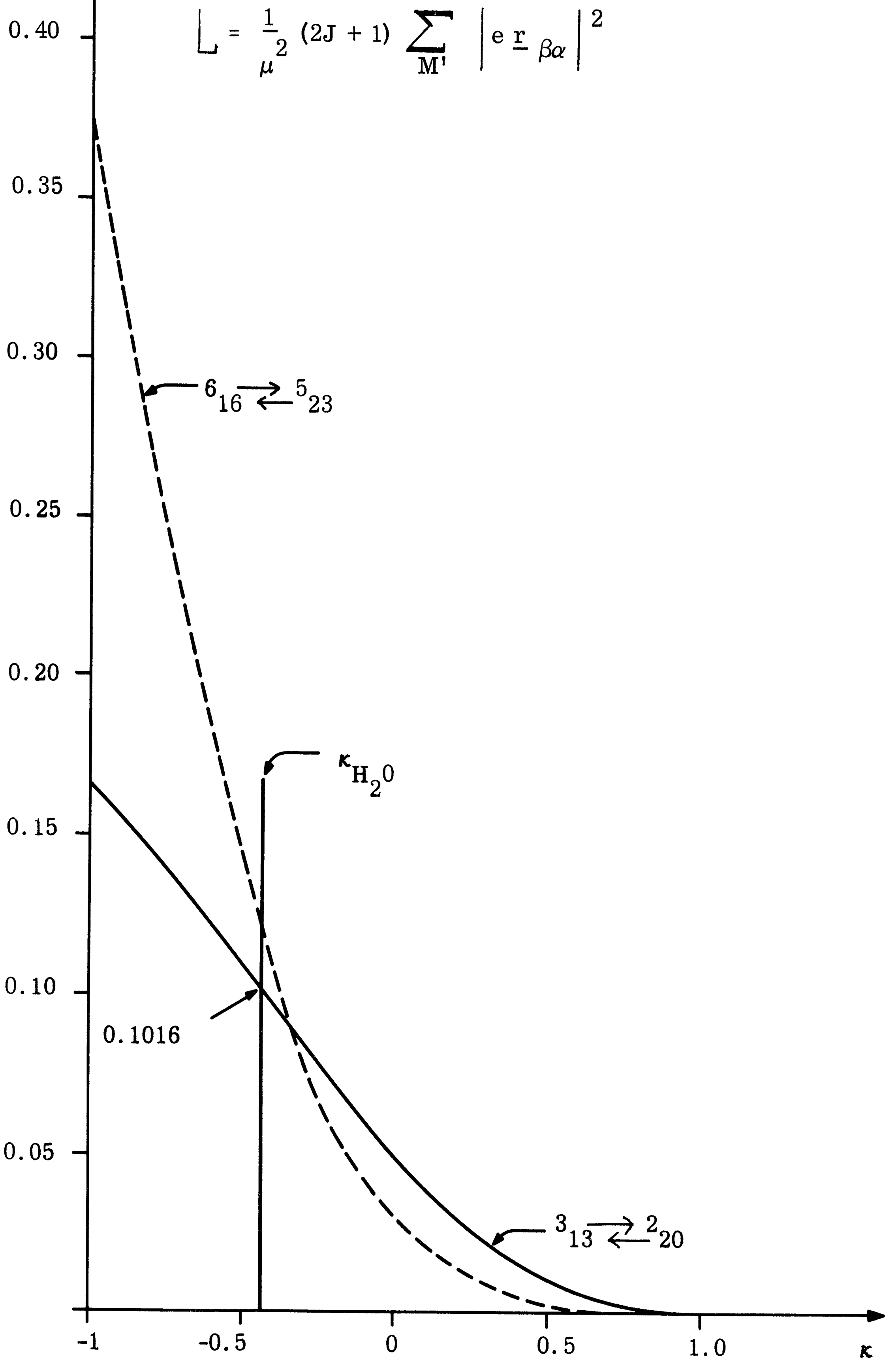


FIG. 4-2: THE LINE STRENGTH FOR ROTATIONAL TRANSITIONS AS A FUNCTION OF κ.

V

CALCULATION OF EFFECTIVE ABSORPTION COEFFICIENT

5.1 Derivation of Formula

If we take into account the broadening of the spectrum due to the collision of the emitting molecule (H_2O) with other molecules (H_2O, N_2 and O_2 in the air) the absorption coefficient at the peak of the broadened spectrum is given by King et. al., (1947)

$$\alpha(T,P_W) = \frac{8\pi^2 N(T)}{3kTQ(T)} \mu^2 (\nu')^2 g_\tau e^{-\frac{W_R}{kT}} \sum |\Phi|^2 \frac{P_W}{\Delta\nu'} \qquad (5.1)$$

(cm^{-1})

Primes in ν and $\Delta\nu$ indicate that they are in units of cm^{-1}. For $\Delta\nu$ and ν expressed in sec^{-1},

$$\alpha\ (T,P_W) = \frac{8\pi^2 N(T)}{3kTv_C Q(T)} \mu^2 \nu^2 g_\tau e^{-\frac{W_R}{kT}} \sum |\Phi|^2 \frac{P_W}{\Delta\nu} \qquad (5.2)$$

(cm^{-1})

Here,

P_W: partial pressure of water molecules in units of atmosphere

$N(T)$: number of water molecules per cm^3 at $T^o k$, one atmosphere

$N(T)P_W$: number of water molecules per cm^3 at $T^o k$ and at P_W atmosphere of water vapor.

$\sum|\Phi|^2$: Defined in (4.22).

g_τ: the factor which takes care of spin degeneracy of the initial state. For H_2O,

$$g_\tau = \left\{2 - (-1)^{|\tau|}\right\} \qquad (5.3)$$

$\Delta\nu$: half width at half maximum of the absorption curve, at temperature T and the total pressure P_t of the gas mixture.

ν: the frequency at the resonance, determined by

$$\nu = \frac{W_i - W_j}{h} , \tag{5.4}$$

in our case, 184 GHz.

Q(T): partition function, that is, the sum of all Boltzmann factors, including degeneracy due to quantum number M and spin. It is

$$Q(T) = \sum_{J=0}^{\infty} \sum_{\tau=-J}^{J} (2-(-1)^{|\tau|}) (2J+1) \exp \left\{ -W(J,\tau)/ kT \right\} \tag{5.5}$$

W_R: the rotational energy of the initial state.

$W(J,\tau)$: energy of the rotational level with J and τ

To derive Eq. (5.1) and (5.2), we have to consider first of all the various sources for broadening of spectral lines. Among them are (Townes and Schawlow, 1955, p. 336).

(1) natural line breadth

(2) Doppler effect

(3) pressure broadening (broadening due to collision)

but in our case the first two are negligible (VanVleck, 1947 b, p. 416); (Townes and Schawlow, 1955, pp. 336-338) and only the third is considered, on the basis of which equation (5.1) is derived (VanVleck and Weisskoff, 1945). After prodedures described by VanVleck and Weisskoff (1945), one obtains

$$\alpha = \frac{8\pi^3 \nu N}{hv_c} \frac{\sum_i \sum_j |\mu_{ij}|^2 \, f(\nu_{ij}, \nu) \, e^{-\frac{W_j}{kT}}}{\sum_j e^{-\frac{W_j}{kT}}} \tag{5.6}$$

Where

$$f(\nu_{ji},\nu) = -f(\nu_{ji},\nu)$$

$$= \frac{1}{\pi}\frac{\nu}{\nu_{ij}}\left\{\frac{\Delta\nu}{(\nu_{ij}-\nu)^2+\Delta\nu^2} + \frac{\Delta\nu}{(\nu_{ij}+\nu)^2+\Delta\nu^2}\right\} \tag{5.7}$$

i : the final state

j : the initial state

N : the number of atoms per cm^3

ν_{ij} : $\dfrac{W_i - W_j}{h}$

ν : the frequency of the incident radiation

$$\Delta\nu : \frac{1}{2\pi\tau} \tag{5.8}$$

τ : the mean interval between the collisions

For the simplicity of argument, let us assume that $\left|\mu_{ij}\right|^2$ is merely the matrix element squared, ignoring the degeneracy of the ith and jth level. The Eq. (5.6) gives the absorption coefficient for any incident frequency ν. To calculate this value of $\alpha(\nu)$, all pairs i and j must be taken. However, when we are interested only in the peak value of α at a certain resonant frequency $(\nu \approx \nu_{ij})$, only two terms in Eq. (5.6) are important, due to the nature of the function $f(\nu_{ij},\nu)$. In our case these are the terms for

$$i = 3_{13} \qquad j = 2_{20}$$

and

$$i' = 2_{20} \qquad j' = 3_{13}$$

The former is absorption and the latter, induced emission. What we usually observe as absorption is the net effect of those two terms. Therefore, taking the sum of two terms will give what we need. This is also in agreement with the purpose of the calculation of parameters such as "effective" absorption coefficient, which appear in radiative transfer considerations. In other words, we really want a result which corrects α for induced emission.

Then we put $\nu = \nu_{ij}$ in Eq. (5.6) and take only the two domimant terms mentioned in the summation. We employ the property

$$\nu_{ij} = -\nu_{ji} \; , \qquad f(\nu_{ij}, \nu) = -f(\nu_{ji}, \nu)$$

$$\left| \mu_{ij} \right|^2 = \left| \mu_{ji} \right|^2$$

and the following terms appear:

$$e^{-\frac{W_j}{kT}} - e^{-\frac{W_i}{kT}} = e^{-\frac{W_j}{kT}} \left(1 - e^{-\frac{h\nu_{ij}}{kT}}\right)$$

$$= e^{-\frac{W_j}{kT}} \frac{h\nu_{ij}}{kT} \; , \qquad (5.9)$$

where we have assumed the condition

$$h\nu_{ij}/kT << 1 \qquad (5.10)$$

By such an approximation in (5.6) one obtains an expression quite close to Eq. (5.2). The Eq. (5.2) contains additional considerations: the degeneracy of the initial and the final state with respect to M and M', and also that due to the spin of the initial state. The expression $g_T \sum' |\Phi|^2$ takes care of all of them. Moreover, the pressure dependence of N is explicity given by $N(T)P_w$.

For the range of validity of Eq. (5.6), one is advised to refer to Van-Vleck (1947 b); a brief discussion is given in chapter IX of this report.

5.2 Calculations

5.2.1 Check of Numerical Calculations for t = 14.5°C

Now we can calculate $\alpha(T)$. In this portion of the report we will use the same data as King et al. (1947) used and check their calculations, thus verifying our interpretations and procedures. If they do not provide the necessary data we will find it in other references and state the origin. Quantities used in Eq. (5.2) are:

$t = 14.5^{o}C$

$T = 287.7^{o}K \qquad T_N = 273.2^{o}K$

$$N(T) = \frac{N_{AV}}{22.4 \times 10^3} \cdot \frac{T_N}{T} \tag{5.11}$$

$$= 2.554 \times 10^{19} / \text{cm}^3 \text{atm}$$

N_{AV} = Avogadro's number = 6.025×10^{23} molecules/mol.

$\mu = 1.84 \times 10^{-18}$ (esu. cm) (VanVleck 1947a p. 427)

$\nu = 184.5 \times 10^9 \text{ sec}^{-1}$

$\frac{\nu}{v_c} = 6.15 \text{ cm-1} = \nu'$

τ for our initial state $= K_{-1} - K_1 = 2 - 0 = 2.$

$g_\tau = \left\{ 2 - (-1)^2 \right\} = 1$

As given in Eq. (4.22), et seq.

$$\sum |\Phi|^2 = \frac{1}{\mu^2}(2J+1)\left|\mu_{J' \leftarrow J}\right|^2$$

$$= 0.1015$$

As for Q, we would like to avoid calculating Eq. (5.5) exactly, since that would be quite tedious. If we define Q'(T) which represents a similar function to Q except for the spin factor, namely

$$Q' \equiv \sum_{J=0}^{\infty} \sum_{\tau=-J}^{J} (2J+1) \exp\left\{\frac{-W(J,\tau)}{kT}\right\} \tag{5.12}$$

then an approximation gives

$$Q' \approx \sqrt{\frac{\pi}{ABC}\left(\frac{kT}{h}\right)^3} = \sqrt{\frac{\pi}{\frac{A}{v_c}\,\frac{B}{v_c}\,\frac{C}{v_c}}\left(\frac{kT}{hv_c}\right)^3} \tag{5.13}$$

(Townes and Schawlow, 1955 , p. 101). This approximation is said to be good when

$$\frac{kT}{h} >> A \tag{5.14}$$

In our case $kT/hv_c = 200.0^{cm-1}$ for $t = 14.5^oC$ i.e., $T = 287.7^oK$.

$$\frac{A}{v_c} = 27.8 \text{ cm-1}$$

Therefore Eq. (5.14) is moderately well satisfied. Assuming that we use Eq. (5.13), we still have to relate Q' to Q. For this purpose we consider a factor F and relate them as

$$Q = FQ'$$

In other words F is an average weighting factor due to spin of the two hydrogen atoms within a water molecule. In a full expression

$$Q = \sum_{J,\tau} g_\tau (2J + 1)\, e^{-\frac{W(J\tau)}{kT}} = F \sum_{J,\tau} (2J + 1)\, e^{-\frac{W(J,\tau)}{kT}} \qquad (5.15)$$

For H_2O,

$g_\tau = 3$ when τ is odd

$g_\tau = 1$ when τ is even.

As an approximation we here simply put F = 2. This is justified by the discussion in Gordon (1934, p. 72), and furthermore considered appropriate by the following reason: with the expression Eq. (5.13) and F = 2, we obtain from the previously given data

$$\left.\begin{aligned} Q' \quad (t = 14.5^\circ\ C) &= 81.8 \\ Q \quad (t = 14.5^\circ\ C) &= 163.6 \end{aligned}\right\} \qquad (5.16)$$

This result, which will be used in the following calculations, compares fairly well with

$$Q \quad (t = 20^\circ\ C) = 170$$

calculated numerically by VanVleck (1947a), considering that Q is an increasing function of temperature. In fact if we use the approximation Eq. (5.13) for $t = 20^\circ$ C, we realize the difference with the above Q = 170 is 1 percent.

$\Delta\nu$: This is given by

$$\Delta\nu = P_t \cdot \Delta\nu_o(T) \qquad (5.17)$$

where P_t is the total pressure of the gas mixture, and $\Delta\nu_o$ is the value of $\Delta\nu = \frac{1}{2\pi\tau}$ at $P_t = 1$ atmosphere at a certain temperature. $\Delta\nu_o$ must be chosen carefully depending on the physical phase of the absorbing material (King et al., 1947, p. 435; VanVleck, 1947a, p. 428), but has been determined so far by experiments. For H_2O in air

$$\frac{\Delta\nu_o(T)}{v_c} = (0.1 \pm 0.02)\ \mathrm{cm}^{-1} \text{ per atmosphere} \qquad (5.18)$$

is fairly well established. King et al. (1947) used this value for 14.5°C whereas VanVleck (1947a) used it for 20°C. Since its temperature dependence is (King, et al., 1947, p. 435.)

$$\Delta\nu_o(T) = d\,T^{-1/2} \quad , \qquad (5.19)$$

where d is a constant, this choice makes a 4 percent difference. The reason why they did not consider this variation with T seems due to the roughness in the value of Eq. (5.18). In our calculation we follow King et al., (1947).

$$\frac{\Delta\nu_o(T)}{v_c} = 0.1\ \mathrm{cm}^{-1} \text{ per atmosphere for } 14.5^{\circ}\mathrm{C}$$

Other numerical values for a checking calculation are $P_t = P_W$. (This means that gas is pure water vapor), and

$$\frac{W_{2_{20}}}{kT} = \frac{\frac{W_{2_{20}}}{hv_c}}{\frac{kT}{hv_c}} = \frac{136.15^{\mathrm{cm}-1}}{200.0^{\mathrm{cm}-1}} = 0.6808 \cdot$$

The energy value of King et al., (1947) mentioned in Chapter III was used.

$$e^{-\frac{W_{2_{20}}}{kT}} = 0.5061$$

$$kT = 3.962 \times 10^{-14} \text{ erg}$$

After the substitution of all these numbers into Eq. (5.2) the value of

$$\alpha(14.5^{\circ}\text{C}, \ P_t = P_W) = 6799 \times 10^{-6} \text{ cm}^{-1} \tag{5.20}$$

was obtained, which differs by less than 1 percent from

$$\alpha(14.5^{\circ}\text{C}, \ P_t = P_W) = 6838 \times 10^{-6} \text{ cm}^{-1} \tag{5.21}$$

of King et al., (1947). A similar calculation for $5_{2_3} \longrightarrow 6_{16}$ transition also gives a good agreement with King et al., (1947): the writer obtained 37.42 x 10^{-6} cm-1 whereas their value is 37.83 x 10^{-6} cm -1.

5.2.2. A general Expression $\alpha(T, P_W, P_t)$ and a Test Calculation for $T = 1000^{\circ}$ K.

The dependence of α on pressure comes through the factor $\frac{P_W}{\Delta\nu(P_t, T)}$ in Eq. (5.2). This is written as

$$\frac{P_W}{\Delta\nu_o(T) \cdot P_t} = \frac{P_f}{\Delta\nu_o(T)} , \tag{5.22}$$

where P_f is the fractional pressure of water vapor in the gas mixture. On the other hand the dependence on temperature is due to the quantities N, Q, ν_o, and 1/kT in Eq. (5.2). They result in the following functional form:

Where T_o is any reference temperature and T is the temperature where $\alpha(T)$ is sought as a whole factor,

$$\frac{N(T)}{kTQ(T)\Delta\nu_o(T)} = \left(\frac{T_o}{T}\right)^3 \frac{N(T_o)}{kT_oQ(T_o)\Delta\nu_o(T_o)} . \tag{5.23}$$

In addition, the Boltzmann factor $e^{-\frac{W_R}{kT}}$ is temperature dependent.

Another important factor about temperature dependence is that at high temperature, appreciable fraction of molecules could be in higher vibrational state. Herzberg (1945, p. 281) gives frequencies for three modes of vibration of water molecules The energy levels can be computed in terms of the frequencies (ν_1, ν_2, ν_3), the lowest three of which are stated to be

$$\frac{\nu_2}{v_c} = 1595 \text{ cm-1} \quad , \quad e^{-\frac{h\nu_2}{kT}} = 0.1008 \text{ at } T = 1000^o \text{ K}$$

$$\frac{2\nu_2}{v_c} = 3151 \text{ cm-1} \quad , \quad e^{-\frac{2h\nu_2}{kT}} = 0.0107 \text{ at } T = 1000^o \text{ K}$$

$$\frac{\nu_1}{c} = 3650 \text{ cm-1} \quad , \quad e^{-\frac{h\nu_1}{kT}} = 0.0052 \text{ at } T = 1000^o \text{ K.}$$

The Boltzmann factors calculated on the preceeding page for $T = 1000^{o}K$ indicated that we can not ignore the fration (11.7 percent) of molecules excited to these levels, at this temperature. In order to include such a situation in the calculation of $\alpha(T)$ in Eq. (5.2), we make the following assumption, although it may be crude: there is no interaction between rotational and vibrational levels, therefore the $2_{20} \longrightarrow 3_{13}$ transition at the ground vibrational level ($n_1=0$, $n_2=0$, $n_3=0$) and $2_{20} \longrightarrow 3_{13}$ transition with ($n_1 \neq 0$, $n_2 \neq 0$, $n_3 \neq 0$) give the same transitional frequency (Fig. 5-1). Here (n_1, n_2, n_3) are the vibrational quantum numbers. This means at least that we assume rotational constants A, B, and C and the dipole moment μ do not change even if the molecule is excited to higher vibrational levels. The tabulation of Herzberg (1945, p. 488) given in Chapter II of this report on rotational constants suggests A, B, and C do change due to vibration. The dependence of μ on vibrational state was discussed in Chapter IV. These contradict our above assumption, therefore our result should be used at high temperature with such a limitation of accuracy in mind.

By virtue of such assumptions, the only modification that should be made in Eq. (5.1) and (5.2) due to vibrational excitation is the form of the Baltzmann factor, but this makes no difference in our final result for the following reason. In Eq. (5.1) or (5.2) the factor

$$\frac{g_\tau (2J+1)\, e^{-\frac{W_R}{kT}}}{Q(T)} = f \qquad (5.24)$$

is the fraction of molecules which are in the 2_{20} rotational level. We wrote in Eq. (5.24) the factor (2J + 1) explicitly, which is included in $\sum |\Phi|^2$ of the Eq. (5.2). This was correct when we completely ignored the vibrational excitation. As discribed in Townes and Schawlow (1955, p. 101) the fraction f must be written in general as

$$f = g_\tau \cdot f_{rot} \cdot f_{vib} \quad , \tag{5.25}$$

where

$$f_{rot} = \frac{(2J+1)\, e^{-\frac{W_R}{kT}}}{\sum_{J'} g'(2J'+1)\, e^{-\frac{W_{R'}}{kT}}} = \frac{(2J+1)\, e^{-\frac{W_R}{kT}}}{Q(T)} \tag{5.26}$$

$$f_{vib} = e^{-\frac{W_v}{kT}} \prod_n \left(1 - e^{-\frac{h\nu_n}{kT}}\right)^{d_n} \tag{5.27}$$

and where W_v is the vibrational energy of the initial level, d_n is the degeneracy of a vibrational mode n. In H_2O, $n = 1, 2, 3$ and $d_1 = d_2 = d_3 = 1$. At low temperature as in the previous calculation ($t = 14.5^oC$) $f_{vib} = 1$ and only the factor $g_\tau f_{rot}$ appeared in Eq. (5.2). At high temperature, if we are interested only in a particular vibrational mode f_{vib} has to be calculated by Eq. (5.27) and substituted into Eq. (5.25). But here we do not care which vibrational state the molecules are in, and by virtue of the assumptions previously stated, we can modify Eq. (5.25) in the following manner to include all possible vibrational states.

$$\begin{aligned} f(T) &= \sum_v g_\tau f_{rot} \cdot f_{vib} \\ &= g_\tau f_{rot} \sum_v f_{vib} = g_\tau f_{rot} \end{aligned} \tag{5.28}$$

The notation $\sum_v$ means the summation over various vibrational states and $\sum_v f_{vib}$ must add up to unity. Then, Eq. (5.28) is exactly the same as the previous one, Eq. (5.24). After such discussions we conclude that the temperature dependence of α comes about through Eq. (5.23) and the Boltzmann factor for the rotational level.

Then

$$\alpha\left(T, \frac{P_W}{P_t}\right) = \alpha\left(T_o, \frac{P_W}{P_t} = 1\right) \cdot \left(\frac{T_o}{T}\right)^3 \frac{e^{-\frac{W_{2_{20}}}{kT}}}{e^{-\frac{W_{2_{20}}}{kT_o}}} \cdot \frac{P_W}{P_t} \qquad (5.29)$$

Taking the value we already calculated as a reference

$$T_o = 287.7^oK \qquad W_{2_{20}} = 136.15^{cm-1}$$

$$\alpha\left(T_o, \frac{P_W}{P_t} = 1\right) = 6838 \times 10^{-6} \text{ cm-1}$$

$$e^{-\frac{W_{2_{20}}}{kT}} = e^{-0.6808} = 0.5064$$

$$\alpha\left(T, \frac{P_W}{P_t}\right) = 6838 \times 10^{-6} \cdot \left(\frac{287.7}{T}\right)^3 \frac{\left(\exp -\frac{136.15}{kT/hv_c}\right)}{0.5061} \frac{P_W}{P_t} \qquad (5.30)$$

(cm^{-1}),

where

$$\frac{k}{hv_c} = 0.6950 \frac{cm^{-1}}{deg.} \qquad (5.31)$$

For $$T = 1000^{o}K\ , \qquad \frac{136.15}{\frac{kT}{hv_c}} = 0.1959\ ,$$

$$\exp\left(\frac{-\ 136.15}{\frac{kT}{hv_c}}\right) = 0.8221\ .$$

Assuming

$$\frac{P_W}{P_t} = 1,$$

$$\alpha\ (1000^{o}K,\ \frac{P_W}{P_t} = 1)\ =\ 6838 \times 10^{-6} \times 3.865 \times 10^{-2}$$

$$= 264.3 \times 10^{-6}\ (cm^{-1}) \qquad (5.32)$$

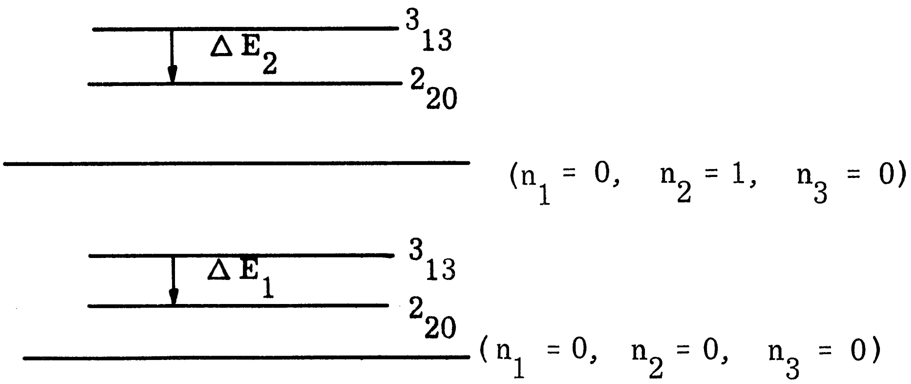


FIG. 5-1: THE ASSUMPTION $\Delta E_1 = \Delta E_2$.

VI

VOLUMETRIC POWER PRODUCTION OF SPONTANEOUS EMISSION

The power intensity, S, sought here is the amount of energy emitted per sec. per unit volume of water vapor pressure P_W. In the present calculation we will not take into account any broadening (as will be discussed in section VII, the quantity actually required for calculation of emergent intensity is the spectral density of S. This will be obtained by simply multiplying the value obtained here for S by a factor. The result derived in this section is thus a necessary intermediate step, with line-broadening considerations to be incorperated in section VII).

The transition probability for a molecule per unit time is given by quantum mechanics to be (Schiff, 1955, p. 400)

$$\theta = \frac{4\omega^3 \left| e\underline{r}_{\beta\alpha} \right|^2}{3\hbar v_c^3} . \tag{6.1}$$

Then the source intensity $S(T, P_W)$ is given by

$$S(T,P_W) = \sum_{M'} \theta \cdot h\nu \cdot G(T, P_W) , \tag{6.2}$$

where $G(T, P_W)$ is the number of water molecules in the initial 3_{13} level, summed over the quantum number M, per unit volume at the temperature T and the water vapor pressure P_W. It is given by

$$G(T\ P_W) = N_N \cdot \frac{T_N}{T} P_W \cdot f , \tag{6.3}$$

where

N_N = Loschmedt's number = 2.687×10^{19} molecules/cm^3 at S.T.P

$T_N = 273.2^{\circ}K$

P_W: expressed in the unit of atmospheres

f : fraction of molecules in the upper state, i.e., 3_{13} state.

$$f = \sum g_\tau f_{rot} \cdot f_{vib} \cong g_\tau f_{rot}$$

$$= \frac{g_\tau (2J+1)\, e^{-\frac{W_{3_{13}}}{kT}}}{Q(T)} \tag{6.4}$$

After substitution of Eq. (6.1), (6.3) and (6.4) into (6.2), we can use the relation

$$\frac{(2J+1)}{\mu^2} \sum_{M'} \left| e\, \underline{r}_{\beta\alpha} \right|^2 \equiv \sum \left| \Phi \right|^2 \tag{6.5}$$

as before, and Eq. (6.2) becomes

$$S(T, P_W) = \frac{64\, \pi^4 \nu^4}{3\, v_c^3}\, \mu^2 \sum \left| \Phi \right|^2 \cdot N_N \frac{T_N}{T} P_W \frac{g_\tau\, e^{-\frac{W_{3_{13}}}{kT}}}{Q(T)} \tag{6.6}$$

As an example we will calculate this quantity with the following data:

$$\begin{cases} T = 287.7^{\circ}K \qquad (t = 14.5^{\circ}C) \\ P_W = 1 \text{ atmosphere} \end{cases}$$

Other values are the same as before:

$$\nu' = 6.15\ \text{cm}^{-1}\ \text{(the line frequency in wave-number units)}$$

$$\mu = 1.84 \times 10^{-18} (\text{esu}\cdot\text{cm})$$

$$Q(T) = 163.6$$

$$e^{-\frac{W_{3_{13}}}{kT}} = e^{-\frac{142.30}{199.95}} = 0.4908$$

$$\sum |\Phi|^2 = 0.1015$$

$$v_c = 2.998 \times 10^{10}\ \text{cm/sec}$$

The result is

$$S_S\ (T = 287.7^oK,\ P_W = 1\ \text{atm}) = 5.870 \times 10^{-4}\ \text{erg/sec-cm}^3 \qquad (6.7)$$

The temperature-dependent expression will be derived next. The temperature dependence of Eq. (6.6) comes from

$$e^{-\frac{W}{kT}},\ \text{and from}\ \ Q(T)\ ,$$

which is proportional to $T^{3/2}$, and T in the denominator of Eq. (6.6). Then

$$S(T, P_W) = S(T_o, P_W = 1) \left(\frac{T_o}{T}\right)^{5/2} \frac{e^{-\frac{W_{3_{13}}}{kT}}}{e^{-\frac{W_{3_{13}}}{kT_o}}} \cdot P_W\ . \qquad (6.8)$$

where T_o is any reference temperature and T is the temperature at which S is sought. If we take T_o as 287.7°K, then with the aid of Eqs. (6.7) and (6.8)

$$S(T, P_W) = 5.870 \times 10^{-4} \left(\frac{287.7}{T}\right)^{5/2} \frac{e^{\frac{142.30}{\frac{kT}{hvc}}}}{0.4908} \cdot P_W \qquad (6.9)$$

$\left(erg/\,sec\cdot cm^3\right)$

VII

LINE-SHAPE AND SPECTRAL DENSITY FOR VOLUMETRIC POWER PRODUCTION

The quantities calculated in this report are obtained for use in evaluating a solution to the radiative transfer equation. However, it is not really the volumetric power production which appears in that equation and its solution, but rather the spectral density of this quantity, evaluated near the line center. Therefore, we will state in this section the relation between the spectral density and volumetric power production. This relation, of course, is based on considerations of line-broadening or line-shape. It is necessary first, then, to establish what cause of line-broadening predominates, in order to deduce the line-shape associated with the volumetric power production by spontaneous emission.

For this purpose, we shall assume a pressure of 1 atmosphere and temperature of 1000°K. The line-width due to pressure broadening as discussed in Eq. (5.17) through Eq. (5.19), will be roughly 1.6 GHz. On the other, the contribution from Doppler broadening is given (see Aller, 1963, p. 111) by

$$\frac{\Delta\nu}{\nu} \sim 7.16 \times 10^{-7} \left[\frac{T}{\mu}\right]^{1/2} \qquad (7.1)$$

in which μ is the molecular weight, or $\mu = 18$ for H'_2O^{16}. The computed Doppler half-width for a line at 183 GHz, at 1000°K temperature, is thus

$$\Delta\nu \sim 1 \text{ MHz} \quad .$$

and we conclude that pressure broadening alone need be considered for the conditions chosen and this particular line of water. The desired spectral density may then be obtained by dividing the volumetric power production due to spontaneous emission Eq. (6.9) by $\pi\Delta\nu$, as may easily be demonstrated.* Clearly, this factor is of correct dimensionality to convert from power per unit volume to power per unit frequency interval and per unit volume, and the corresponding solution for radiative intensity, which has the dimensions of power per unit volume per unit frequency interval divided by absorption coefficient, is of dimensions power per unit area per unit frequency interval, or radiative intensity. The conversion discussed in this section is thus at least dimensionally consistent.

---

* This proof has been given in the quarterly report ECOM-01378-6 on this contract.

VIII

POPULATION OF STATES -ADDITIONAL COMMENTS

As given in Eq.(6.3), the population of state can be calculated immediately if the fractional number of molecules, f, is calculated. Suppose we look for the fraction of molecules at (J, K_{-1}, K_1) rotational level and (n_1, n_2, n_3) vibrational level. Then f is given by

$$f = g_\tau \cdot f_{vib} \cdot f_{rot} \tag{8.1}$$

$$f_{rot} = \frac{(2J+1)\, e^{-\frac{W(J, K_{-1}, K_1)}{kT}}}{\sum g_\tau' \cdot (2J'+1)\, e^{-\frac{W_{R'}}{kT}}} \tag{8.2}$$

$$f_{vib} = e^{-\frac{W_v(n_1, n_2, n_3)}{kT}} \prod_n \left(1 - e^{-\frac{h\nu_c}{kT}}\right) \tag{8.3}$$

In the case of water molecules there is no degeneracy of vibrational mode. ν_1, ν_2 and ν_3 are given by Herzberg (1945, p. 281). They are

$$\frac{\nu_1}{v_c} = 3650 \text{ cm-1} \quad , \quad \frac{\nu_2}{v_c} = 1595 \text{ cm -1}$$

$$\frac{\nu_3}{v_c} = 3756 \text{ cm-1} \quad .$$

From these data and Eq. (8.3), f_{vib} can be calculated for various temperatures. A convenient set of numbers to remember is

$$\left\{\begin{array}{ll} \frac{kT}{hv_c} = 199.95 \ \text{cm-1} \approx 200.0 \ \text{cm-1} & \text{at } t = 14.5^{\circ}\ \text{C.} \\ \frac{kT}{hv_c} = 695.0 \ \text{cm-1} & \text{at } T = 1000^{\circ}\text{K.} \end{array}\right.$$

As for the factor f_{rot}, the partition function in the denominator of Eq. (8.2) is given by

$$Q(T) \equiv \sum_{J'\tau'} g_{\tau'} \cdot (2J' + 1)\, e^{-\frac{W(J',\, K'_{-1},\, K'_{1})}{kT}}$$

$$\approx 2 \sqrt{\frac{\pi}{ABC}\left(\frac{kT}{h}\right)^{3}} = 2 \sqrt{\frac{\pi}{A'B'C'} \left(\frac{kT}{hv_c}\right)^{3}} \qquad (8.4)$$

The energy $W(J, K_{-1}, K_1)$ in the numerator of Eq. (8.2) is calculated by Eq. (3.1) or (3.8). g_τ in Eq. (8.1) has already been given in Eq. (5.3). Hence f in Eq. (8.1) can be completely determined.

In our previous calculations of α, the factor (2J + 1) in Eq. (8.2) was put together with

$$\frac{1}{\mu^2} \sum_{M'} \left| e\, \underline{r}_{\beta\alpha} \right|^2$$

and appeared as

$$\sum \left| \Phi \right|^2 = \frac{1}{\mu^2} (2J + 1) \sum_{M'} \left| e\, \underline{r}_{\beta\alpha} \right|^2 \qquad (8.5)$$

in Eq. (5.1) and (5.2). $\sum |\Phi|^2$ in Eq. (8.5) is the value looked up in a table.

IX

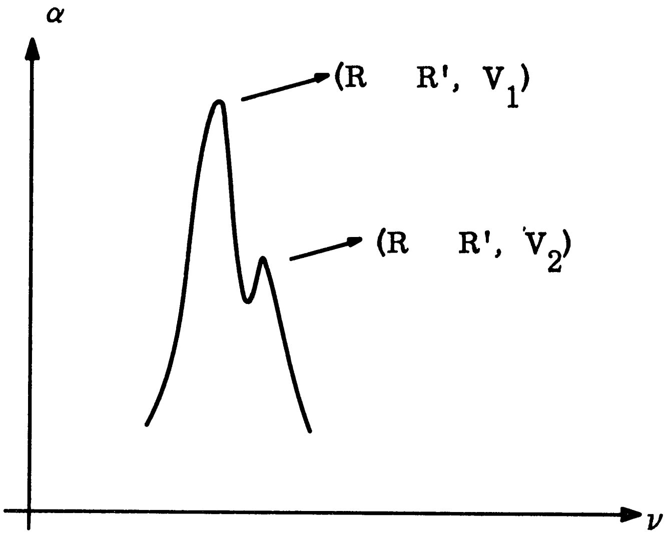
APPROXIMATIONS MADE AND POSSIBLE IMPROVEMENT ON THE PRESENT CALCULATIONS

As pointed out already, the vibrational excitation is non-negligible at high temperatures and this is the point where the improvement should be made. The assumption that rotational constants A, B, C and the dipole moment μ stay the same in spite of vibrational excitation is apparently slightly wrong. In addition, it appears to the writer that a certain interaction between vibrational and rotational motion should exist for asymmetric rotors, just as that described in Townes and Schawlow (1955, p. 80) for symmetric rotors. Then the spectrum would be something like Fig. (9.1). Naturally, the line for the ground vibrational state would be the strongest. If we would like to obtain α for this strongest line, it can be calculated in similar manner to the previous calculations in Chapter V, with the factor f_{vib} of Eq. (8.3) in addition. In that case all the constants such as A, B, C, and μ should be all known for the ground vibrational level specifically.

Another point of possible improvement is the derivation of Eq. (5.1). This depends on whether $\nu_{ij} \ll \frac{kT}{h}$ is satisfied or not. since this inequality was assumed in expanding the exponential.

The approximation on Q(T) made by Eq. (5.13) and by putting $F = 2$ in Eq. (5.15) seems reasonable in our temperature range, i. e., T greater than 100^{o}K (Gordon, 1933; Townes and Schawlow, 1955).

The last thing that should be mentioned is the centrifugal stretching of the rotor. However this should be of rather small effect since our transition takes place between small J(2 and 3), and at the same time the change in J is small. As a conclusion, unless one wishes to obtain the accuracy within several percent, the approximations mentioned above seem to have no consequence in our result, except at extremely high temperature, say $T >> 1000^{o}$K. One should keep in mind that constants A, B, C and μ should be examined on their accuracy to see if those refinements are worth doing. In addition the present ambignity in $\Delta\nu$ alone could nullify the meaning of the refinements, since it is of the order of 10 ~ 20 percent.



Frequency dependence of α

R,R': the initial and the final rotational levels
V_1, V_2: the vibrational levels

FIG. 9-1:

X

SUMMARY OF NUMERICAL RESULTS

The quantities needed for construction of a numerical solution to the radiative transfer equation in cylindrical geometry are, as discussed in a previous report on this contract (Barasch, Chu, and LaRue, 1966), and in section VII of the present report, the spectral density S_ν of volumetric power production originating in spontaneous emission and the effective absorption coefficient α. With these, evaluated near the line center, the specific intensity radiated near the peak frequency which would be encountered outside a gas body containing water molecules can be computed as a function of the gas temperature, partial pressure of water, and total pressure of the gas. The relations from which S_ν and ν may be evaluated have been developed earlier in this report; we collect them here for improved convenience in using them.

10.1 Expressions for S_ν

Combination of equation (6.9) and the discussion of section VII determines this quantity. That is, in cgs units of erg $\mathrm{cm}^{-3}\,\mathrm{sec}^{-1}/\Delta\nu$

$$S_\nu(T, P_W) = \frac{1}{\pi\Delta\nu}\; 5.87 \cdot 10^{-4} \left(\frac{287.7}{T}\right)^{5/2} \frac{\exp\left(\dfrac{-142.30}{kT/h\nu_c}\right)}{0.4908}\; P_W\,, \qquad (10.1)$$

wherein T is the absolute temperature and P_W the partial pressure of water vapor, in units of atmospheres. The line-width parameter $\Delta\nu$ has been defined in equations (5.17) through (5.19). The result of combining them is

$$\Delta\nu = 3\left(\frac{288}{T}\right)^{1/2} P_t \ \mathrm{GHz} \qquad (10.2)$$

in which P_t is the total gas pressure, measured in atmospheres, and T as always the absolute temperature.

10.2 The Effective Absorption Coefficient, α

This has been given in equation (5.30), which we reproduce here

$$\alpha(T, P_W/P_t) = 6.838 \times 10^{-3} \text{ cm}^{-1} \left(\frac{287.7}{T}\right)^3 \frac{\exp\left[-\frac{136.15}{kT/h\nu_c}\right]}{0.5061} \frac{P_W}{P_t} \qquad (10.3)$$

ACKNOWLEDGMENTS

The authors would like to express their thanks to Dr. R.K. Osborn and Dr. A.Z. Akcasu of The University of Michigan Nuclear Engineering Department for their clarifying discussions on many points in this work.

REFERENCES

Allen, H. C. Jr., and P. C. Cross (1963), Molecular Vib-Rotors, John Wiley and Sons, Inc. New York.

Aller, L. H. (1963) "Astrophysics - The Atmospheres of The Sun and Stars", Ronald Press Co. New York.

Barasch, M. L., C-M Chu, and J. J. LaRue, (1966) "Missile Plume Radiation Characteristics" (U), Technical Report ECOM-01378-2, January, 1966, SECRET. (Brief designation U. of M. Radiation Laboratory Report 7455-2-Q).

Cross, P. C., R. M. Hainer and G. W. King (1944), "The Asymmetric Rotor, II, Calculation of Dipole Intensities and Line Classification," Journ. of Chemical Physics 12, 210-243.

Gordon, A. R. (1934), "The Calculation of Thermodynamic Quantities from Spectroscopic Data for Polyatomic Molecules; the Free Energy, Entropy and Heat Capacity of Steam," Journ. of Chemical Physics 2, 65-72.

Herzberg, G. (1945), Infrared and Raman Spectra, D. Van Nostrand Company Inc., New York.

King, G. W., R. M. Hainer and P. C. Cross (1943), "The Asymmetric Rotor, I, Calculation and Symmetry Classification of Energy Levels," Journ. of Chemical Physics 11, 27-42,

King, G. W., R. M. Hainer and P. C. Cross (1947), "Expected Microwave Absorption Coefficients of Water and Related Molecules," Phys. Rev. 71 433-443.

King, W. C. and W. Gordy (1954), " One-to-Two Millimeter Spectroscopy," Phys. Rev. 93, 407-412.

Penner, S. S. (1959), Quantitative Molecular Spectroscopy and Gas Emissivities, Addison - Wesley Publishing Company, Inc., Reading Massachussetts.

Randall, H. M., D. M. Dennison, N. Ginsburg and L. R. Weber (1937), "The Far Infrared Spectrum of Water Vapor", Phys. Rev. 52, 160-174.

Schiff, L. I. (1955), Quantum Mechanics 2nd Ed., McGraw-Hill Book Company, Inc., New York.

Strandberg, M. W. P. (1954), Microwave Spectroscopy, Methuen and Co. Ltd., London.

Townes, C. H. and A. L Schawlow (1955), Microwave Spectroscopy, McGraw-Hill Book Company, Inc., New York.

VanVleck, J. H. (1947a), "The Absorption of Microwaves by Uncondensed Water Vapor," Phys. Rev. 71, 425-433.

VanVleck, J. H. (1947b), " The Absorption of Microwaves by Oxygen," Phys. Rev. 71, 413-424.

VanVleck, J. H. and V. R. Weisskoff (1945), "On the Shape of Collision-Broadened Lines", Revs. Mod. Phys. 17, 227-236.