

# THEORETICAL EXPRESSION OF WATER VAPOR SPECTRAL EMISSIVITY WITH ALLOWANCE FOR LINE STRUCTURE

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**Abstract**—Theoretical relations of Penner and Varanasi and Gray for overlapped lines are extended to account for line structure. Spectral emissivity expressions for the 2.7 and 6.3  $\mu$  regions of the water vapor spectrum are derived and compared with experimental measurements. Account is taken of the temperature-dependencies of line intensity and line width in the many superposed vibration-rotation bands active in each region of the spectrum.

## NOMENCLATURE

$A_T$ , band absorption, wave numbers, equation (36);  
 $A$ , rotational constant, wave numbers;  
 $b$ , self-broadening to foreign gas broadening ratio, equation (15);  
 $B$ , rotational constant, wave numbers;  
 $c$ , velocity of light;  
 $C$ , rotational constant, wave numbers;  
 $d$ , line spacing, wave numbers;  
 $f$ , initial state quantum number dependence of the square of the electric dipole moment;  
 $h$ , Planck constant;  
 $k$ , Boltzmann constant;  
 $L$ , path length or beam length;  
 $P$ , pressure;  
 $S$ , integrated intensity of an absorption line, wave numbers;  
 $T$ , absolute temperature;  
 $u$ , equation (4);  
 $v$ , integer vibrational quantum number;  
 $X$ , density-path-length product.

numbers per unit of density-path-length product;  
 $\beta$ , rotational parameter; see equation (10);  
 $\gamma$ , line width, wave numbers;  
 $\delta$ , integer change in vibrational quantum number;  
 $\epsilon$ , emissivity;  
 $\nu$ , wave number or reciprocal wavelength [ $\text{cm}^{-1}$ ];  
 $\rho$ , density;  
 $\tau$ , transmissivity;  
 $\phi$ , line-width-to-spacing parameter, equation (26);  
 $\Phi$ , line-width-to-spacing parameter, equation (24).

## Subscripts

$e$ , equivalent value;  
 $i$ , principal quantum number subscript,  $i = 1, 2, 3$ ;  
 $j$ , transition subscript;  
 $0$ , reference state value.

## DEDICATION

DEAN MYRON TRIBUS has rightly said that students in the next century studying heat transfer will unknowingly be influenced by L. M. K. Boelter. The present authors are second and third generation students of L. M.

## Greek symbols

$\alpha$ , integrated intensity of a band, wave

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K. Boelter, but we are not unknowing of the Boelter influence, both because of the awe and reverence in the voices of his first generation students when they mentioned "Professor Boelter" and because we were fortunate enough to have come into direct contact with him, even if all too briefly. Professor Boelter instilled a desire in his students to do work which was not just elegant but which was useful to the engineer and therefore to society. He consistently urged that problems be viewed not narrowly but in their true breadth. He liked to see engineering relations based not on speculation but on data. The present authors realize that the present paper cannot be compared to the pioneer work in two-phase flow done by Dean Boelter's first generation students but we nevertheless offer the present paper as one of a series of investigations which we believe fills a niche in the grand scheme of heat transfer which Boelter envisioned and which can be glimpsed, for example, in the *Heat Transfer Notes*. We dedicate it to the memory of the great engineering educator.

### INTRODUCTION

Spectral values of gas emissivity at elevated temperatures are often desired for making detailed radiation transfer calculations, because receivers, either heat-transfer surfaces or detectors, are frequently spectrally sensitive. Using molecular concepts and spectroscopic data, Penner and Varanasi [1] have developed approximate analytical expressions for the spectral emissivity, which apply for the case of complete overlapping of spectral lines in water vapor infrared vibration-rotation bands. A more exact theoretical treatment for overlapped H<sub>2</sub>O lines was developed by Gray [2]. Ferriso, Ludwig and Thompson [3] obtained empirical spectral absorption coefficients for H<sub>2</sub>O at elevated temperatures by fitting laboratory data. Corrections for line structure effects were made by correlating spectral absorption with the Goody [4] line structure model, assuming a band-averaged, mean line-width-to-spacing ratio.

Edwards and coworkers [5] used a simple variation of the mean absorption coefficient with wavelength and a band-averaged, mean line-width-to-spacing-ratio to obtain band absorption correlations for H<sub>2</sub>O.

It is the purpose of this paper to develop an analytical expression for the spectral emissivity of high temperature water vapor which will account for incompletely overlapped lines and to compare the results with experimental measurements. Two models will be used: (1) a locally-random superposition of spectral lines belonging to disordered vibration-rotation bands (e.g. see Plass [6, 7]), and (2) a simpler, equivalent-line model derived from the first. The second model gives an analytical prediction of a spectrally-varying line-width-to-spacing ratio to accompany the average intensity predictions given previously by Penner and Varanasi [1] and Gray [2].

### THEORY

#### *Effect of line structure on the 2.7-μ bands*

Absorption in the 2.7-μ region is contributed by three types of transitions [8] between vibrational states specified by the principal quantum numbers,  $v_1$ ,  $v_2$ , and  $v_3$ :

$$v_1, v_2, v_3 \rightarrow v_1, v_2 + 2, v_3$$

$$v_1, v_2, v_3 \rightarrow v_1 + 1, v_2, v_3$$

$$v_1, v_2, v_3 \rightarrow v_1, v_2, v_3 + 1,$$

which we abbreviate as

$$v_i \rightarrow v_i + \delta_{ij},$$

where

$$\begin{vmatrix} \delta_{11} & \delta_{21} & \delta_{31} \\ \delta_{12} & \delta_{22} & \delta_{32} \\ \delta_{13} & \delta_{23} & \delta_{33} \end{vmatrix} = \begin{vmatrix} 0 & 2 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}. \quad (1)$$

The integrated intensity of a single band we denote as

$$\alpha(v_1, v_2, v_3 \rightarrow v_1 + \delta_{1j}, v_2 + \delta_{2j}, v_3 + \delta_{3j}) = \alpha_j(v_i). \quad (2)$$

The intensity  $\alpha_j(v_i)$  of a "hot" band, one whose lower state is above the ground state ( $v_1 = 0$ ,  $v_2 = 0$ ,  $v_3 = 0$ ), is for nondegenerate vibrations [9]

$$\alpha_j(v_i) = \alpha_j(0, 0, 0) \prod_{i=1}^3 \frac{(v_i + \delta_{ij})!}{\delta_{ij}! v_i!} \exp(-u_i v_i) \quad (3)$$

where [8]

$$\left. \begin{aligned} u_i &= hc v_i / kT, & v_1 &= 3651.7 \text{ cm}^{-1}, \\ v_2 &= 1595.0 \text{ cm}^{-1}, & v_3 &= 3755.8 \text{ cm}^{-1} \end{aligned} \right\} \quad (4)$$

$$\alpha_j(0, 0, 0) = \alpha_{0j} \frac{1 - \exp(-\sum_{i=1}^3 u_i \delta_{ij})}{\prod_{i=1}^3 [1 - \exp(-u_i)]^{-1}} \quad (5)$$

In the above expressions the harmonic-oscillator approximation has been employed. With this simplification, and the appropriate values of  $\delta_{ij}$ , inserted into equation (3), there results

$$\alpha_j(v_i) = \alpha_{0j} \frac{1 - \exp(-\sum_{i=1}^3 u_i \delta_{ij})}{\prod_{i=1}^3 [1 - \exp(-u_i)]^{-1}} f_j(v_i) \times \exp(-\sum_{i=1}^3 u_i v_i) \quad (6)$$

where

$$|f_j| = \begin{vmatrix} f_1 \\ f_2 \\ f_3 \end{vmatrix} = \begin{vmatrix} (v_1 + 1) \\ (v_2 + 1)(v_2 + 2)/2 \\ (v_3 + 1) \end{vmatrix} \quad (7)$$

The three values of  $\alpha_{0j}$  must be found from experiment. The temperature dependence of the total integrated intensity is then found to be [10]

$$\alpha_j = \sum_{v_3=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_1=0}^{\infty} \alpha_j(v_i) = \alpha_{0j} \frac{1 - \exp(-\sum_{i=1}^3 u_i \delta_{ij})}{\prod_{i=1}^3 [1 - \exp(-u_i)]^{\delta_{ij}}} \quad (8)$$

Total integrated intensities  $\alpha_j$  at 300°K were chosen as follows based upon data from Gates *et al.* [11], Ferriso and Ludwig [12] and Goldstein [13, 14].

$$\alpha_1 = 0.19 \text{ cm}^{-1}/\text{gm m}^{-2}$$

$$\alpha_2 = 2.3 \text{ cm}^{-1}/\text{gm m}^{-2}$$

$$\alpha_3 = 22.4 \text{ cm}^{-1}/\text{gm m}^{-2}.$$

These values then fix the values of  $\alpha_{0j}$ .

Two analytical expressions have been used to approximate the spectral variation of the average line-intensity, that for the rigid rotator used by Penner and Varanasi [1] and that for the symmetric top used by Gray [2]. They are, respectively,

$$S/d = \alpha \frac{hc|v - v_0|}{4kTB_e} \exp\left(-\frac{hc(v - v_0)^2}{4kTB_e}\right) \quad (9)$$

$$S/d = \alpha \frac{hc|v - v_0|}{4kTB_e} \times \left(\frac{1 + \beta}{\beta}\right)^{\frac{1}{2}} \operatorname{erf}\left(\frac{\beta hc(v - v_0)^2}{4kT}\right)^{\frac{1}{2}}, \quad (10)$$

where

$$\beta = \frac{A}{B_2} - 1, \quad B_2 = (BC)^{\frac{1}{2}},$$

$$B_e = (A + B + C)/3$$

$$A = 28.8778 \text{ cm}^{-1}, \quad B = 14.5092 \text{ cm}^{-1},$$

$$C = 9.2869 \text{ cm}^{-1}.$$

The rotational constants  $A$ ,  $B$  and  $C$  for HHO<sup>16</sup> were taken from Benedict *et al.* [15] by Gray [2]. Very little difference is found when the two envelopes are compared, so that the simpler of the two, equation (9), is used. The spectral mean line intensity of a particular band,  $S_{ij}/d$ , is thus obtained by replacing  $\alpha_0$  with  $\alpha_j(v_i)$  and  $v_0$  with  $v_{ij}$  in equation (9). For accurate calculations at high temperatures the band origins  $v_{ij}$  should be calculated by taking into account anharmonicity in vibrational energy levels [16]. However, if only moderate temperatures are encountered, as in the present correlations, the

origins of "hot" bands may be assumed coincident and equal to the change in vibrational energy associated with the corresponding ground state transition  $0, 0, 0 \rightarrow \delta_{1j}, \delta_{2j}, \delta_{3j}$ .

To account for line structure, the Goody model [4] for a disordered array of spectral lines is selected. The spectral emissivity is then

$$\epsilon(\nu) = 1 - \prod_{j=1}^3 \tau_j \quad (11)$$

where

$$\tau_j = \prod_{v_3=0}^{\infty} \prod_{v_2=0}^{\infty} \prod_{v_1=0}^{\infty} \exp \frac{-(S_{ij}/d)X}{\left[1 + \frac{(S_{ij}/d)X}{\pi(\gamma_{ij}/d)}\right]^{\frac{1}{2}}}. \quad (12)$$

In the above expression  $\gamma_{ij}/d$  is the mean line width to spacing ratio for the  $ij$ th band (designated by  $j$  and the accompanying set of three values of  $\delta_{ij}$ ), and  $X$  is the density path-length product, which for convenience is expressed in grams per square meter,

$$X = \rho L \text{ g/m}^2. \quad (13)$$

Spectral measurements have not been sufficiently detailed to give  $\gamma_{ij}/d$  vs.  $\nu - \nu_j$ , and a detailed theoretical model cannot therefore be critically tested. For this reason, a value of  $\gamma_{ij}/d$  independent of  $\nu$ , the set of  $\nu_j$ , or the set of  $\delta_{ij}$  is chosen. Allowance for line broadening due to  $\text{N}_2\text{-H}_2\text{O}$  and  $\text{H}_2\text{O-H}_2\text{O}$  collisions is made by taking

$$\gamma_{ij}/d = (\gamma_0/d) (T_0/T)^{\frac{1}{2}} (P_e/P_0) \quad (14)$$

$$P_e/P_0 = (P_{\text{N}_2}/P_0) + b(P_{\text{H}_2\text{O}}/P_0), \quad P_0 = 1 \text{ atm}. \quad (15)$$

From Ferriso *et al.* [3], and the value of  $b = 5.5$  at  $300^\circ\text{K}$  taken from Benedict and Kaplan [17, 18], there results

$$b(T) = 5.0 (T_0/T)^{\frac{1}{2}} + 0.5, \quad T_0 = 300^\circ\text{K}. \quad (16)$$

The quantity  $\gamma_0/d$  above is the only adjustable parameter introduced here to account for line structure. It is chosen to be 0.046 to give the best agreement with the selected total band absorption data points in Table 3 of [5].

It should be observed that, although a spectrally independent value of  $\gamma_{ij}/d$  has been chosen for each vibration-rotation band, an effective value for the entire absorption band has not been defined as was done by Ferriso *et al.* [4]. As will be seen in the next section, an effective value does result when absorption in each vibration-rotation band is due to completely non-overlapped strong lines. This effective value of  $\gamma/d$  will be wave-number dependent in the  $2.7\text{-}\mu$  band.

#### Equivalent line structure for the $2.7\text{-}\mu$ band

An expression of the equivalent line-width-to-spacing ratio may be derived by defining an equivalent band which gives the correct spectral emissivity in two limiting cases. In one case, the multitude of ground-state and hot bands superposed on top of each other could have completely overlapped lines, so that the equivalent ratio of mean line-intensity to mean line-spacing is merely the sum of that ratio for each band

$$\langle S/d \rangle = \sum_{j=1}^3 \sum_{v_3=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_1=0}^{\infty} (S_{ij}/d). \quad (17)$$

In another case, the multitude of bands could have completely non-overlapped strong lines, so that equations (11) and (12) reduce to

$$\epsilon(\nu) = 1 - \exp \left\{ - \sum_{j=1}^3 \sum_{v_3=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_1=0}^{\infty} \left[ \pi (S_{ij}/d) (\gamma_{ij}/d) X \right]^{\frac{1}{2}} \right\}. \quad (18)$$

We define an equivalent band as one with the same emissivity in this limit but consisting of only one set of lines.

$$\epsilon(\nu) = 1 - \exp - [\pi \langle S/d \rangle \langle \gamma/d \rangle X]^{\frac{1}{2}}. \quad (19)$$

Equations (17), (18), and (19) therefore define the two equivalent band parameters varying with wavenumber, pressure, composition, and temperature,  $\langle S/d \rangle$  and  $\langle \gamma/d \rangle$ .

The multitude of overlapped bands can be considered as three overlapped equivalent bands rather than a single band, and some algebraic

simplification introduced. In this case

$$\langle S/d \rangle_j = \sum_{v_3=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_1=0}^{\infty} (S_{ij}/d) \quad (20)$$

and

$$\begin{aligned} & [\langle S/d \rangle_j \langle \gamma/d \rangle_j]^{\ddagger} \\ &= \sum_{v_3=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_1=0}^{\infty} [\langle S_{ij}/d \rangle \langle \gamma_{ij}/d \rangle]^{\ddagger}. \end{aligned} \quad (21)$$

By definition of  $\alpha_j$ , equation (8), and equation (9), there results for the spectral intensity

$$\begin{aligned} \langle S/d \rangle_j &= \alpha_{0j} \frac{1 - \exp(-\sum_{i=1}^3 u_i \delta_{ij})}{\prod_{i=1}^3 [1 - \exp(-u_i)]^{\delta_{ij}}} \\ &\times \frac{hc|v - v_j|}{4kTB_e} \exp\left(-\frac{hc|v - v_j|^2}{4kTB_e}\right). \end{aligned} \quad (22)$$

Equation (21) together with equation (14) becomes

$$\begin{aligned} \langle \gamma/d \rangle_j &= (\gamma_0/d) (T_0/T)^{\ddagger} [(P_{N_2}/P_0) \\ &+ b(P_{H_2O}/P_0)] \Phi_j \end{aligned} \quad (23)$$

where

$$\Phi_j = \frac{\left\{ \sum_{v_3=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_1=0}^{\infty} [f_j(v_i) \exp(-\sum_{i=1}^3 u_i \delta_{ij})]^{\ddagger} \right\}^2}{\sum_{v_1=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_3=0}^{\infty} f_j(v_i) \exp(-\sum_{i=1}^3 u_i \delta_{ij})} \quad (24)$$

Substitution of  $f_j(v_i)$  gives

$$\Phi_j = \prod_{i=1}^3 \phi_i^2(u_i, \delta_{ij}) [1 - \exp(-u_i)]^{\delta_{ij}+1} \quad (25)$$

where

$$\phi(u, \delta) = \sum_{n=0}^{\infty} \left[ \frac{(n + \delta)!}{n! \delta!} \exp(-nu) \right]^{\ddagger}. \quad (26)$$

The quantity  $\phi(u, 0)$  is seen to be

$$\phi(u, 0) = [1 - \exp(-u/2)]^{-1}. \quad (27)$$

When  $\delta \neq 0$  in equation (26) the function approaches unity as  $u \rightarrow \infty$ , and a function of  $\delta$  as  $u \rightarrow 0$ . The latter is found by replacing the summation by an integral. These asymptotic

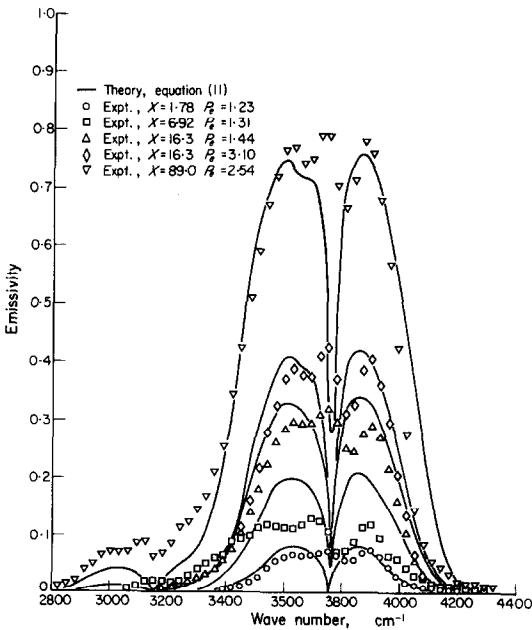


FIG. 1. Spectral emissivity of the 2.7- $\mu$  band at 555°K.

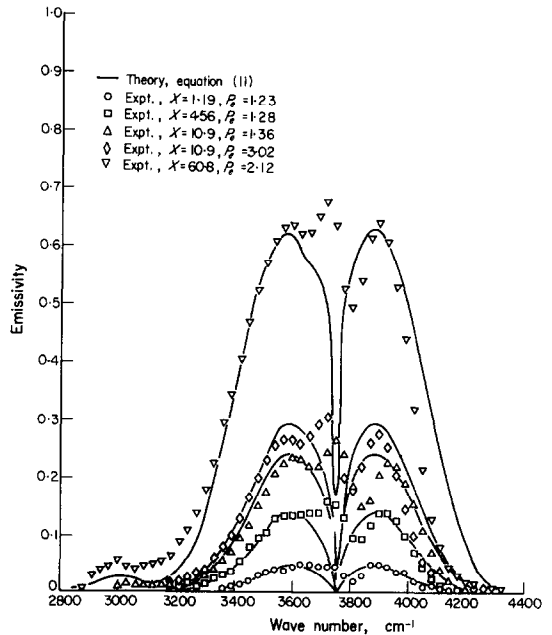
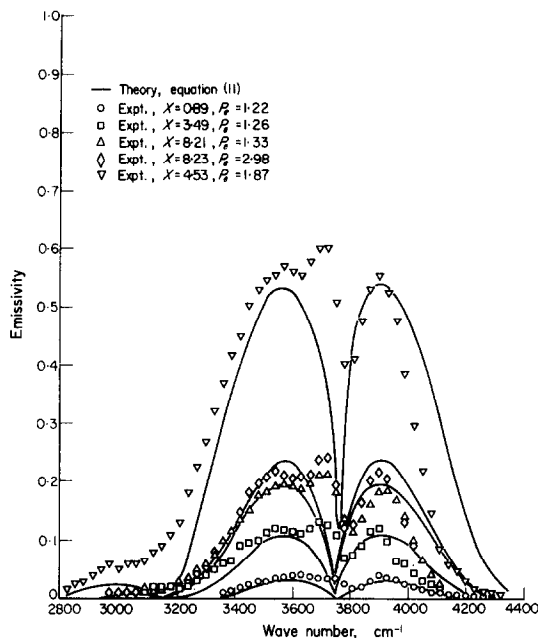


FIG. 2. Spectral emissivity of the 2.7- $\mu$  band at 833°K.

FIG. 3. Spectral emissivity of the 2.7- $\mu$  band at 1110°K.

limits can be patched together, as was done for the case of CO [19]. There results

$$\phi(u, \delta) = \{1 + [(2/u)^{\delta/2+1} \Gamma(\delta/2 + 1)/(\delta!)^{\frac{1}{2}}]\}. \quad (28)$$

Equations (22) and (23) are thus quite convenient for introduction into

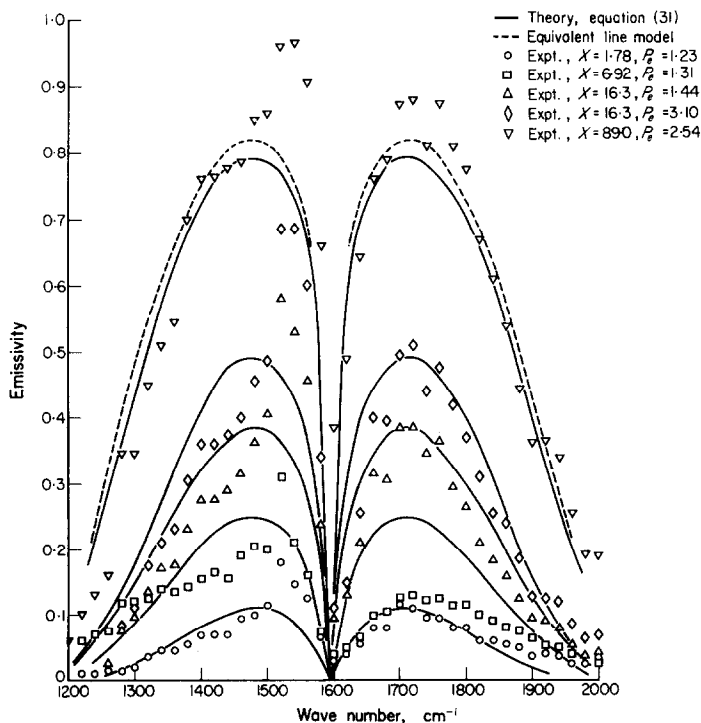
$$\langle \tau_j \rangle = \exp \frac{-\langle S/d \rangle_j X}{[1 + \langle S/d \rangle_j X / (\pi \langle \gamma/d \rangle_j)]^{\frac{1}{2}}} \quad (29)$$

which in turn may be substituted into equation (11) to obtain the emissivity. Even hand calculation is seen to be readily accomplishable.

#### Effect of line structure on the 6.3- $\mu$ band

The 6.3- $\mu$  fundamental band arises from transitions [8]

$$v_1, v_2, v_3 \rightarrow v_1, v_2 + 1, v_3$$

FIG. 4. Spectral emissivity of the 6.3- $\mu$  band at 555°K.

so that equation (6) becomes

$$\alpha(v_i) = \alpha_0 \frac{1 - \exp(-u_2)}{\prod_{i=1}^3 [1 - \exp(-u_i)]^{-1}} \times (v_2 + 1) \exp\left(-\sum_{i=1}^3 u_i v_i\right) \quad (30)$$

where  $\alpha_0 = \alpha = 41.2 \text{ cm}^{-1}/\text{gm}^{-2}$  [20] is used.

The spectral emissivity is then

$$\epsilon = 1 - \exp\left\{-\sum_{v_1=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_3=0}^{\infty} \frac{(S_i/d) X}{[1 + (S_i/d) X/\pi(\gamma_i/d)]^{\frac{1}{2}}}\right\} \quad (31)$$

where

$$\langle S_i/d \rangle = \alpha(v_i) \frac{hc|v - v_2|}{4kTB_e} \exp\left(-\frac{hc|v - v_2|^2}{4kTB_e}\right) \quad (32)$$

Again, the equivalent line structure can be

represented by

$$\langle S/d \rangle = \alpha \frac{hc|v - v_2|}{4kTB_e} \exp\left(-\frac{hc|v - v_2|^2}{4kTB_e}\right) \quad (33)$$

and

$$\langle \gamma/d \rangle = (\gamma_0/d) (T_0/T)^{\frac{1}{2}} (P_e/P_0) \Phi \quad (34)$$

where  $P_e$  is given by equation (15),  $\gamma_0/d = 0.040$  for  $T_0 = 300^\circ\text{K}$  and  $P_0 = 1 \text{ atm}$ , and

$$\begin{aligned} \Phi &= \phi^2(u_1, 0) \phi^2(u_3, 0) \phi^2(u_2, 1) \\ &\times [1 - \exp(-u_1)] [1 - \exp(-u_3)] \\ &\times [1 - \exp(-u_2)]. \end{aligned} \quad (35)$$

#### COMPARISON OF THEORY WITH EXPERIMENT

Comparison between the calculated spectral emissivity and experimental data is of interest for a range of parameters wherein substantial effects of line structure can be expected. This range occurs at rather low values of  $P_e$ , so that

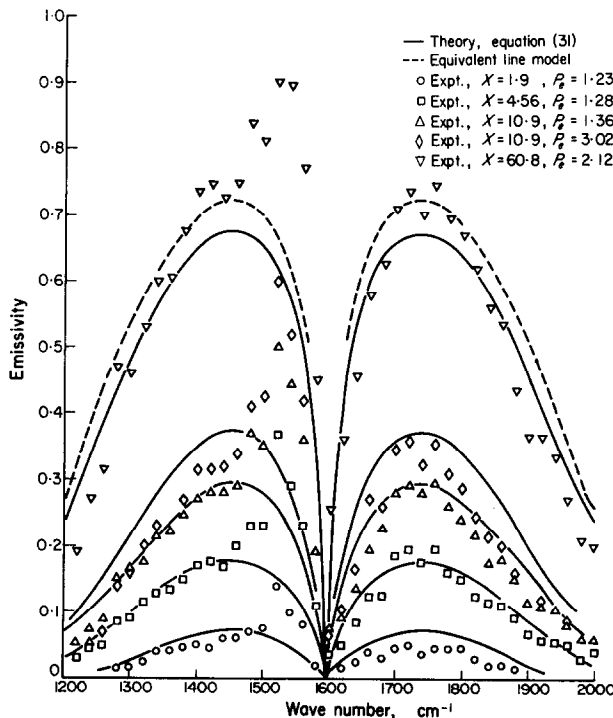


FIG. 5. Spectral emissivity of the 6.3- $\mu$  band at 833°K.

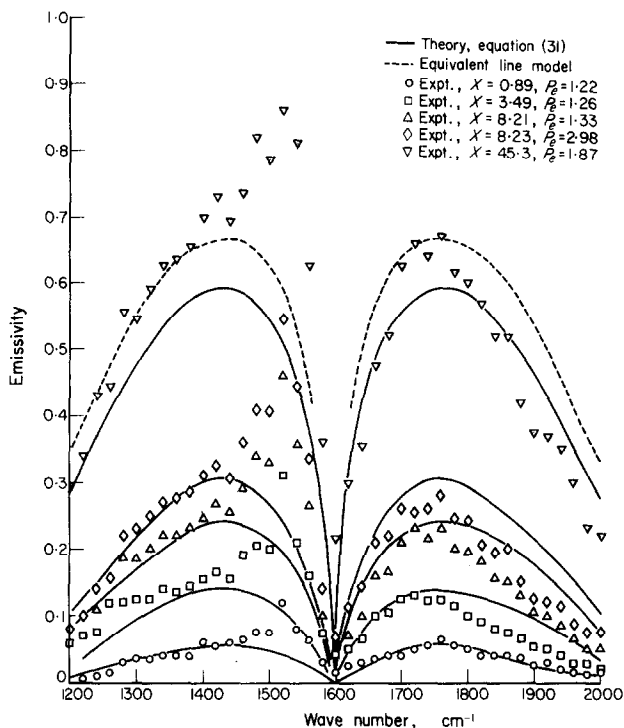


FIG. 6. Spectral emissivity of the 6.3- $\mu$  band at 1110°K.

the collision broadened lines are narrow, and at moderate values of temperature. The temperature should be sufficiently high that the first few "hot" bands are a significant factor, but not so high that a large number of hot bands contribute to complete line overlapping. For this reason, the data of Flornes [21] are chosen. Figures 1-6 show comparisons of calculations made according to equation (11) *et seq.* and equations (31) and (32). While the simple calculation technique presented does not take into account the obvious asymmetry in the band branches (particularly for the 6.3- $\mu$  band) it does yield reasonable agreement.

The calculated curves shown in full in the figures are obtained using randomly superposed lines. Calculations made with the equivalent line structure model yield results only slightly higher as shown by the broken lines in Figs. 4, 5 and 6. Since this latter model is more

convenient, because of the simple closed form expressions for the  $\phi$  functions, it is preferred for engineering calculations.

Comparison of total band absorption, defined as

$$A = \int_0^{+\infty} \epsilon(\nu) d\nu \quad (36)$$

where  $\epsilon$  is the emissivity (absorptivity) for a particular absorption band, is shown in Table 1. Agreement between experiment [21-24] and prediction is somewhat better than that obtained with the empirical correlations given in [5]. There, three arbitrary parameters were chosen in addition to values of  $\alpha_0$  taken from [12] and [20].

#### SUMMARY AND CONCLUSIONS

An expression for spectral emissivity which accounts for line structure has been derived and



Table 1. Total band absorption of water vapor

Band	Temp. (°K)	Mass path length (g/m <sup>2</sup> )	Pressure (atm)	Mol. Fraction	Total band absorption			Discr. (%)
					Measured (cm <sup>-1</sup> )	Ref.	Calculated (cm <sup>-1</sup> )	
2-7	300	21000	0.397	0.054	1104	[22]	949	-14
		21000	0.082	0.263	940	[22]	830	-12
		11200	0.021	1.000	781	[22]	700	-10
		6440	0.184	0.036	721	[22]	704	-2
		2800	0.397	0.054	723	[22]	694	-4
		1400	0.083	0.259	507	[22]	487	-4
		1010	0.305	0.072	582	[23]	540	-7
		688	0.0329	0.080	236	[23]	245	+4
		172	0.033	0.080	141.8	[23]	136.2	-4
		23.8	0.525	0.015	125.0	[23]	145.4	+16
		307	2.00	1.00	740.0	[24]	752.0	+2
		153	1.00	1.00	559.0	[24]	593.0	+6
		89.0	0.604	1.00	470.7	[21]	451.16	-4
		16.3	2.75	0.04	197.4	[21]	206.4	+5
	16.3	1.09	0.10	156.0	[21]	171.0	+10	
	16.3	0.274	0.40	116.3	[21]	132.8	+14	
	15.3	1.09	0.10	151.2	[21]	164.9	+9	
	6.92	1.16	0.04	96.4	[21]	97.7	+1	
	1.78	1.19	0.01	32.6	[21]	35.0	+7	
	833	2.00	1.00	741.0	[24]	783.0	+6	
	102.0	1.00	1.00	576.0	[21]	575.0	0	
	60.8	0.606	1.00	425.0	[21]	417.0	-2	
	10.9	2.75	0.04	159.6	[21]	169.0	+6	
	10.9	1.09	0.10	140.4	[21]	141.9	+1	
	10.9	0.276	0.40	99.4	[21]	110.2	+11	
	4.56	1.16	0.04	81.3	[21]	76.2	-6	
	1.19	1.20	0.01	24.5	[21]	25.5	+4	
1110	2.00	1.00	785	[24]	798	+2		
76.6	1.00	1.00	560	[24]	557	0		
45.3	0.603	1.00	406	[21]	389	-4		
45.0	0.603	1.00	416	[21]	389	-7		
8.23	2.75	0.04	135	[21]	145	+8		
8.21	1.10	0.10	126	[21]	125	-1		
8.18	0.273	0.40	101	[21]	98	-3		
3.49	1.16	0.04	77	[21]	65	-16		
0.887	1.19	0.01	22	[21]	20	-9		
6.3	300	14900	0.016	1.00	564	[22]	532.6	-6
		12000	0.969	0.014	745	[22]	642.4	-14
		6870	0.083	0.159	560	[22]	512.4	-9
		1720	0.382	0.0172	513	[22]	485.9	-5
		213	0.162	0.0203	247	[22]	225.5	-9
		95	0.526	0.6025	287	[22]	265.0	-8
		36	1.00	0.004	216	[23]	211.3	-2
		34	0.004	1.0	31.8	[23]	41.0	+29
		17	0.101	0.0366	60.3	[23]	63.6	+5
		17	0.004	1.0	25.0	[23]	29.2	+17
		307	2.0	1.0	764	[24]	688.5	-10
		153	1.0	1.0	621	[24]	566.9	-9
		89	0.604	1.0	503	[21]	444.4	-12
		16.3	2.746	0.04	235	[21]	237.2	+1
	16.3	1.091	0.10	178.7	[21]	187.7	+5	
	16.3	0.274	0.40	147.2	[21]	138.9	-6	
	15.3	1.094	0.10	182	[21]	182.0	0	

Table 1—continued

Band	Temp. (°K)	Mass path length (g/m <sup>2</sup> )	Pressure (atm)	Mol. Fraction	Total band absorption			Discr. (%)
					Measured (cm <sup>-1</sup> )	Ref.	Calculated (cm <sup>-1</sup> )	
833		6.92	1.157	0.04	108.9	[21]	115.3	+6
		1.78	1.189	0.01	53.0	[21]	47.7	-10
		204	2.00	1.00	766	[24]	763.3	0
		108	1.09	1.00	542	[24]	602.8	+11
		102	1.00	1.00	594	[21]	582.9	0
		60.8	0.606	1.00	479	[21]	433.4	-10
		10.9	2.75	0.04	194.7	[21]	208.4	+7
		10.9	1.09	0.10	174.5	[21]	165.8	-5
		10.9	0.276	0.40	112.9	[21]	121.7	+8
		4.56	1.16	0.04	106.3	[21]	96.3	9
1110		1.19	1.20	0.01	26.8	[21]	36.6	+36
		153	2.00	1.00	779	[24]	813.1	+4
		76.7	1.00	1.00	654	[24]	592.6	9
		45.3	0.60	1.00	467	[21]	423.9	9
		45.0	0.60	1.00	479	[21]	422.6	-12
		8.23	2.75	0.04	193.2	[21]	189.3	-2
		8.21	1.10	0.10	153.2	[21]	154.2	+1
		8.18	0.273	0.40	98.5	[21]	113.4	+15
		3.49	1.16	0.04	95.2	[21]	86.4	-9
		0.887	1.19	0.01	34.6	[21]	29.8	14

compared with experimental data. Agreement with measured spectral emissivity values was good, although asymmetry in the 6.3- $\mu$  band structure was not accommodated. Total band absorption (or emission) was found to agree well ( $\pm 10$  per cent RMS) with experimental data.

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**Résumé**—Les relations théoriques de Penner et Varanasi et de Gray pour les lignes qui se chevauchent sont étendues pour tenir compte de la structure des lignes. On obtient des expressions d'émissivité spectrale pour les régions de 2,7 et 6,3 microns du spectre de la vapeur d'eau qui sont comparées avec des mesures expérimentales.

On tient compte de la dépendance de l'intensité et de la largeur des lignes en fonction de la température dans les nombreuses bandes de vibration–rotation superposées qui sont actives dans chaque région du spectre.

**Zusammenfassung**—Die theoretischen Beziehungen von Penner und Varanasi und Gray für einander überdeckende Linien werden erweitert, um die Linienstruktur zu berücksichtigen. Spektrale Emissionsausdrücke für den 2,7 und 6,3 Mikronbereich des Wasserdampfspektrums werden abgeleitet und mit experimentellen Messungen verglichen. Berücksichtigung finden die Temperaturabhängigkeit der Linien, Intensität und Linienbreite in den vielen überlagerten Vibrations–Rotationsbanden, die in jedem Bereich des Spektrums aktiv sind.

**Аннотация**—Теоретические соотношения Пеннера и Варанаси, а также Грея для перекрывающихся спектральных линий обобщаются для учета структуры спектральной линии. Выводятся выражения для спектрального лучеиспускания водяного пара в области 2,7 и 6,3 микрон, которые сравниваются с экспериментальными измерениями. Учитываются температурные зависимости интенсивности спектральных линий и их ширины для многих налагающихся вибрационно–вращательных полос, имеющих в каждой области спектра.