Int. J. Heat Mass Transfer. Vol. 17, pp. 793–795. Pergamon Press 1974. Printed in Great Britain

SHORTER COMMUNICATIONS

TOTAL BAND ABSORPTANCE OF CARBON DIOXIDE AND WATER VAPOR INCLUDING THE EFFECTS OF OVERLAPPING

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(*Received* 26 *October* 1973)

IN A PREVIOUS study the total band absorptance of the 4·7 μ band of carbon monoxide was obtained in terms of the basic spectroscopic variables [1]. These include the half-width of the spectral lines $b(\text{cm}^{-1})$, a band width parameter

$$F(\text{cm}^{-1}) = (kTB_e/hc)^{1/2} = 13{\cdot}8(B_eT/273)^{1/2},$$

and an intensity parameter,

$$S_0(\text{atm}^{-1}\,\text{cm}^{-2}) = (hcB_e/kT)^{1/2} = 0{\cdot}0741\alpha(273B_e/T)^{1/2},$$

where $T(^\circ\text{K})$ is the temperature, $B_e(\text{cm}^{-1})$ is the rotational constant, and $\alpha(\text{atm}^{-1}\,\text{cm}^{-2})$ is the integrated band intensity. With the specification of the spectroscopic variables, the total band absorptance [2, 3] was obtained as a function of pathlength and good agreement was obtained with experimental data for carbon monoxide. At high temperatures, the effect of additional bands, called "hot bands", also becomes important and this contribution may also be included in the basic formulation [4].

The form of the intensity distribution used (cf. [1], equation (5) [5, 6]) suggests that the previous results should also be applicable to triatomic gases.† In particular, we shall consider the 2·7 μ bands of carbon dioxide and water vapor and evaluate the total band absorptance *directly* from the spectroscopic results. For these bands $d = 2B_e(\text{cm}^{-1})$ is equal to 0·791 for CO_2 [8] and 34·45 for H_2O [6].‡ The 2·7 μ region of CO_2 is comprised of bands which have centers at 3609 and 3716 cm^{-1} for which $\alpha(\text{atm}^{-1}\,\text{cm}^{-2})$ equals 37 and 54, respectively [10]; for H_2O the value is 200 [11]. The values for α correspond to a temperature of 300°K.

The remaining quantity is the line half width which, for CO_2 is given by [12]

$$b_C(\text{cm}^{-1}) = 0{\cdot}07(273/T(^\circ\text{K}))P_e(\text{atm}). \tag{1}$$

Here P_e is the effective pressure given by [13]

$$P_e = [(1-C_c)P_T + 1{\cdot}3C_cP_T],$$

with C_c the mole fraction of carbon dioxide and P_T the total pressure. The mole fraction is necessary because many experiments are carried out with nitrogen gas as a diluent. Comparable expressions are available for H_2O [14].

The total band absorptance, $A(\text{cm}^{-1})$, may now be directly calculated and the results are presented in Table 1 for CO_2 and in Table 2 for H_2O. The agreement with the experimental data is seen to be quite good over a broad range of conditions. We recall that in our previous studies with carbon monoxide the approximate intensity distribution that was used resulted in an arbitrary constant, D_1, which was set equal to unity. The same value has also been used in this study so that the present calculation truly represents an a priori calculation.

We now consider the absorption of a mixture of radiating gases. The total band absorptance for a two component mixture of radiating gases I and II, is given by

$$A = \int_{\Delta\nu} [1 - e^{-(k_\text{I} X_\text{I} + k_\text{II} X_\text{II})}]\,d\nu \tag{4}$$

where k is the spectral absorption coefficient and X is the pathlength. Equation (4) may be rewritten in the following form:

$$A = A_\text{I} + A_\text{II} - \int_{\Delta\nu} (1 - e^{-k_\text{I} X_\text{I}})(1 - e^{-k_\text{II} X_\text{II}})\,d\nu \tag{5}$$

where A_I and A_II are the total band absorptances of the pure components, I and II, respectively which we have previously evaluated (e.g. for CO_2,* $A_C = \int_{\Delta\nu}(1 - e^{-k_C X_C})\,d\nu$). For CO_2–H_2O mixtures it has been shown [15, 13] that the third term may by approximated by

$$\sum_{\Delta\nu_i} (1 - e^{-\bar{k}_{W,i} X_W}) \int_{\Delta\nu_i} (1 - e^{-k_{C,i} X_C})\,d\nu \tag{6}$$

where the subscripts C and W refer to carbon dioxide and water vapor, respectively, and $\Delta\nu_i$ is a small spectral interval. Introducing the narrow band absorptance for CO_2 we have

$$\alpha_{C,i} \simeq \int_{\Delta\nu_i} (1 - e^{-k_{C,i} X_C})\,d\nu, \tag{7}$$

and making the approximation $1 - \exp(-\bar{k}_{W,i} X_W) \simeq \alpha_{W,i}\Delta\nu_i$ allows us to write equation (5) in the form

$$A = A_C + A_W + \sum_{\Delta\nu_i} \alpha_{C,i}\alpha_{W,i}\Delta\nu_i. \tag{8}$$

The evaluations of the total band absorptances A_C and A_W follow in the manner previously discussed. To evaluate $\alpha_{C,i}$

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†For an alternative application refer to [7].

‡For H_2O, B_e is taken to be the mean rotational constant; that is, $B_e = (A + B + C)/3 = 17{\cdot}225\,\text{cm}^{-1}$ [9].

*There is a change in the sense that the half-width changes for different mixtures. General expressions and values are given in reference [12].

Table 1. Results for absorption of CO_2 in the 2·7 μ region

CO_2 2·7 μ at 300°K					
Effective pressure Pe(atm)	Pressure pathlength PX(atm-cm)	Experimental data A(cm^{-1})	Reference for data	Present theoretical results	Correlation results (Edwards and Menard [5])
0·0763	0·081	4·0	9	3·89	4·4
0·549	0·081	6·5	9	6·31	6·5
2·05	0·081	6·9	9	5·65	6·9
0·078	0·685	14·3	9	13·72	14·8
0·569	0·685	27·9	9	31·46	26·0
2·06	0·685	39·9	9	36·69	36·8
0·676	6·205	98·2	9	101·17	89·7
2·33	6·205	127·4	9	112·61	115
2·72	24·898	179	9	168·19	171
0·25	0·484	18·5	16	18·55	17·2
0·26	0·862	24·8	16	26·56	23·9
0·225	13·876	92·5	16	92·99	95·3
1·3	132·042	214	16	242·60	220
0·33	9·903	112	17	91·53	91·2
1·30	132·042	261	17	242·6	220
12·9	1309·230	366	17	314·38	342

Table 2. Results for absorption of H_2O in the 2·7 μ region

H_2O 2·7 μ at 300°K					
Total pressure P_T(atm)	Pressure pathlength PX(atm-cm)	Experimental data A(cm^{-1})	Reference for data	Present theoretical results	Correlation results (Edwards *et al.* [20])
0·397	2871·92	1104	18	903·79	861
0·171	2871·92	1002	18	831·76	795
0·082	2871·92	940	18	785·51	747
0·966	2297·57	1158	18	967·82	913
0·966	1531·71	1064	18	919·23	869
0·397	1531·71	966	18	816·47	789
0·021	1531·71	781	18	660·05	625
0·973	880·73	931	18	845·64	801
0·184	880·73	721	18	661·23	640
0·007	880·73	486·8	18	462·08	532
0·966	382·93	809	18	753·09	712
0·397	382·93	723	18	662·32	633
0·021	382·93	562·3	18	493·91	473
0·966	191·46	699	18	632·59	634
0·397	191·46	623·2	18	579·26	556
0·083	191·46	507·1	18	544·73	442
0·066	88·07	339·8	18	293·6	353
0·010	88·07	259·6	18	233·69	218
0·033	23·52	141·8	18	119·84	106
0·003	23·52	83·5	18	71·90	58·9
1·00	3·26	155	18	197·74	186
0·525	3·26	125	18	143·81	133
0·066	3·26	59	18	69·51	57·9
775	138·13	664	9	719·04	605

and $\alpha_{W,i}$ we use the Goody result [16] for a narrow band of rotational lines:

$$\alpha_i = 1 - \exp \frac{-(S/d)_i X}{\left[1 + \frac{4(S/d)_i}{(b/d)_i}\right]^{1/2}}. \tag{9}$$

The values for S_i are obtained from Penner [8], p. 276.

The total band absorptance for mixtures of carbon dioxide, water vapor and nitrogen may now be calculated from equation (8). The results for the 2·7 μ bands are presented in Table 3 and are in good agreement with the experimental data and correlation of Hines and Edwards [13].

Table 3. Results for absorption of a mixture of CO_2 and H_2O in the 2·7 μ region

		2·7 μ Band H_2O and CO_2 mixture				
Pressure (atm)	Temperature (°R)	Concentration H_2O	Concentration CO_2	Total band absorptance (cm^{-1}) [experiment (13)]	Total band absorptance (cm^{-1}) [present result]	Correlation total band absorptance (cm^{-1}) [Hines and Edwards (13)
1·042	982	0·258	0·254	434	428·55	403
1·098	990	0·051	0·249	241	245·77	231
1·093	990	0·241	0·046	320	362·89	350
1·070	1475	0·250	0·249	324	331·31	298
1·162	990	0·101	0·099	256	249·04	260
1·178	1475	0·100	0·098	236	234·79	220
1·175	990	0·752	0·248	618	637·99	594

In summary the absorption of triatomic molecules and their mixtures may be determined directly from the basic spectroscopic variables. By having the results in the form of the useful approximate relations given in [1] it is also possible to directly extend the results to include high temperatures as well as nonisothermal effects. Future studies should determine whether the band constant, D_1, which was set equal to unity for carbon dioxide, water vapor, as well as for carbon monoxide, is truly a universal constant.

Acknowledgement—The authors gratefully acknowledge support of this study by the National Science Foundation.

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