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COMPUTED TOTAL RADIATION PROPERTIES OF COMPRESSED OXYGEN BETWEEN 100 AND 1000 K[*]

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Abstract—The total emissivity, total band absorptance and Planck mean absorption coefficient of compressed oxygen have been computed in the temperature range 100–1000 K. Computations were based on published data for the spectral absorption coefficient and extrapolations above and below room temperature were performed in accordance with published theory. It was found possible to represent all of the total band absorptance results with a two-parameter correlation.

NOMENCLATURE

a,	empirical constant for line intensity [cm^5 g mole^{-2}];
A_i,	total band absorptance of the *i*th band defined in equation (9) [cm^{-1}];
$\bar{A}$,	dimensionless total band absorptance (defined in equation (16));
B,	normalization constant for a band profile [cm];
B_0,	rotational constant of a molecule in the ground vibrational state [cm^{-1}];
c,	velocity of light in a vacuum [cm s^{-1}];
C,	dimensionless constant used in band profile to join exponential tail to the Lorentzian line profile;
C_1,	integrated absorption coefficient of band [cm^{-2}];
C_3,	constant defined in equation (16) [cm^{-1}];
D,	dimensionless constant used in band profile to join exponential tail to the Lorentzian line profile;
f_2,	dimensionless constant defined by equation (18);
h,	Planck's constant [Js];
I_ν,	spectral radiation intensity [W cm^{-1} sr^{-1}];
$I_{b\nu}$,	spectral radiation intensity of a black-body [W cm^{-1} sr^{-1}];
I_{bc},	black-body spectral intensity at a band center [W cm^{-1} sr^{-1}];
$(\bar{I}_{b\nu})_i$,	average black-body spectral intensity for the *i*th band defined by equations (9), (11) and (12) [W cm^{-1} sr^{-1}];
$I(T)$,	tabulated integral for overlap contribution to the induced dipole moment;
$J(T)$,	tabulated integral for the quadrupole contribution to the induced dipole;
J,	rotational quantum number of a molecule;
k,	absorption coefficient [cm^{-1}];
k_B,	Boltzmann's constant [J K^{-1}];
$K_1(T)$,	factor incorporating the temperature dependence of the induced dipole for the pure rotational band [cm^5 g mole^{-2}];
$K_2(T)$,	factor incorporating the temperature dependence of the induced dipole for the fundamental and first overtone bands [cm^5 g mole^{-2}];

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K_p,	Planck mean absorption coefficient defined in equations (13) and (15) [cm^{-1}];
l,	path length of the radiation [cm];
$L(J)$,	J dependent factor of the transition moment matrix element defined in equation (7);
Q,	rotational partition function;
s_0,	line intensity [cm^{-2}];
T,	absolute temperature [K];
T^*	reduced temperature ($= Tk_B/\varepsilon$);
u,	dimensionless path length defined in equation (16);
V,	vibrational quantum number of a molecule;
W,	modified path length ($= (\rho/\rho_0)^2 l$) [cm];
x,	fractional contribution of the overlap induced dipole moment.

Greek symbols

α,	total absorptivity;
α_i,	absorptivity of the ith band;
δ,	line half-width at half intensity [cm^{-1}];
ε,	to conform with standard usage the energy parameter of the Leonard–Jones intermolecular potential function is denoted by this symbol. Equally well established is the use of this symbol for total emissivity. No confusion should result in the use of ε for both quantities since it is self evident from the text which meaning is intended;
ε_i,	band emissivity of the ith band;
ν,	frequency [cm^{-1}];
ν_0,	frequency at line center [cm^{-1}];
ρ,	density of gas [g cm^{-3}];
ρ_0,	density of gas at N.T.P. [g cm^{-3}];
σ,	the Stefan–Boltzmann constant [$\text{W cm}^{-2}\,\text{K}^{-4}$].

INTRODUCTION

INFRARED radiative transfer in the homonuclear diatomic gases O_2, N_2 and H_2 has generally been disregarded in the past since at atmospheric pressure other trace gases or combustion products, e.g. CO_2, H_2O, CH_4 and N_2O dominate radiation processes. The need to store large quantities of these fluids, however, has changed the picture somewhat. The homonuclear diatomic gases exhibit absorption varying as the square of the density in contrast to the linear dependence of the other named gases. The difference is due to the origin of the electric dipole moment, which in the case of the homonuclear diatomic gases, exists only during the course of a collision and is caused by induction, whereas the more usual case is that of a molecule possessing a permanent electric dipole moment, or a nonzero derivative with respect to vibrational coordinates. Now, in the cryogenic storage of oxygen gas, densities of the order of 1000 times NTP densities may occur. In this case the integrated intensity of the O_2 fundamental band, for example, is greater than the 15 μm CO_2, 6·3 μm H_2O or the 3·3 μm CH_4 bands at one atmosphere. Thus, it happens that radiation emission and absorption within the stored gas become an important consideration in energy transport, for example, whenever heating is to be applied [1] or when stratification takes place.

In this paper we present total radiative properties of oxygen gas computed from published absorption coefficients. These quantities are: (i) total band absorptances (sometimes known as equivalent black band widths), (ii) total emissivities, and (iii) Planck mean absorption coefficients. These quantities will be useful in making radiative transfer calculations. We stress here that the data above and below room temperature must be regarded as provisional, since we have had to extrapolate the absorption coefficients based upon theoretical considerations.

THE ABSORPTION BANDS OF O_2

Four bands are observed in the infrared. These are:

(i) The pure rotational band [2] centered at about 100 cm^{-1} (100 μm) at room temperature. This is a broad band with a half width of about 75 cm^{-1}.

(ii) The fundamental vibration–rotation band [3, 4]. This is centered at 1556 cm^{-1} (6·4 μm) and also has a half width of 75 cm^{-1}.

(iii) The first overtone band [4] centered at 3085 cm^{-1} (3·2 μm). This is a factor of over 100 less intense than the fundamental band and has a half width of 80 cm^{-1}.

(iv) The "atmospheric bands" [5]. These arise from electronic transitions. The longest wavelength band involving transitions from the ground vibrational state is centered at 7895 cm^{-1}.

For the temperature range of interest here, the "atmospheric bands" do not contribute significantly to thermal radiation and our calculations have therefore been based on (i), (ii) and (iii).

The nature of these bands is fairly well understood from both experimental results and the theoretical work of Van Kranendonk [6] and Van Kranendonk and Kiss [7]. Shapiro [3] and Shapiro and Gush [4] have shown how the experimental band profile of the fundamental band may be fitted by superposing the suitably broadened theoretical vibration–rotation lines. The line shape used was the modified Lorentz shape deduced from the pure rotational lines of hydrogen by Kiss and Welsh [3] and modified further by the addition of exponential tails by Bosomworth and Gush [2]. The band profiles so constructed by these authors were within experimental error, so we chose to follow essentially the same procedure in fitting all three bands and extending the calculations to both lower and higher temperatures. For the fundamental and first overtone bands the simpler, but no less successful, procedure of Shapiro [3] was used.

In order to illustrate the relative importance of bands (i), (ii) and (iii) the absorption coefficients are plotted in Fig. 1 vs. wave number at room temperature on a semi-lograrithmic scale. Also shown on this figure are lines for different temperatures within whose length lies 99 per cent of the black body radiation. The cross on each line marks the position of maximum radiation intensity. Thus, it is already clear that the fundamental band will dominate the emissivity at high temperatures, while at low temperatures the emissivity will be completely determined by the rotational band. The first overtone appears to be a minor contributor in the temperature range under consideration.

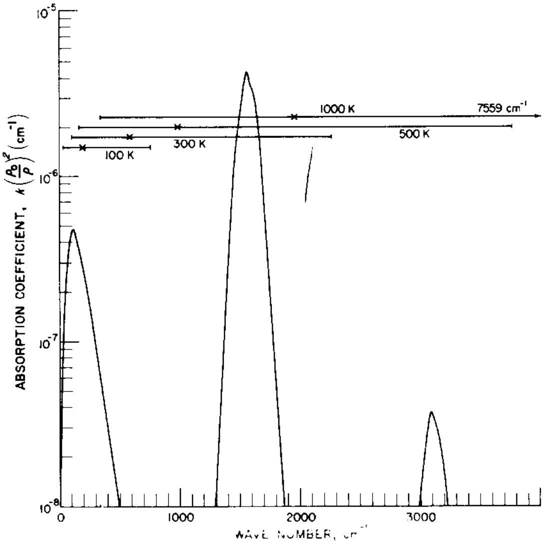

FIG. 1. Infrared absorption bands of compressed oxygen of importance in radiative transfer below 1000 K.

SYNTHETIC BAND PROFILES

The construction of the synthetic band profiles is achieved by summing, at a particular wave number, the contributions from individual lines. The line contributions are based on the following premises, all of which have been more or less verified in the references quoted.

(i) Individual lines have the following shape [3]

$$\frac{k(\nu, T)}{s_0(T)} = B/(1 + [(\nu - \nu_0)/\delta]^2), \nu_0 \leqslant \nu \leqslant \nu_0 + 1{\cdot}75\delta$$

$$= BC\exp(-D[\nu - \nu_0]), \nu > \nu_0$$

$$+ 1{\cdot}75\delta$$
$$= [B/(1 + [\nu - \nu_0)/\delta]^2] \exp(-[\nu_0 - \nu]\, hc/k_B T),\ \nu_0 - 1{\cdot}75\delta \leqslant \nu \leqslant \nu_0$$
$$= B\,[C \exp(-D\,[\nu - \nu_0])] \exp(-[\nu_0 - \nu]\, hc/k_B T),\ \nu < \nu_0 - 1{\cdot}75\delta. \quad (1)$$

$k(\nu, T)$ is the absorption coefficient at a frequency ν, s_0 is the integrated intensity of a given line, ν_0 is the line origin and δ is the width parameter. h and k_B are Planck's and Boltzmann's constants respectively. The dimensionless constants C and D are determined by the requirements of continuity of k and $(\mathrm{d}k/\mathrm{d}\nu)$ at the points $\nu = \nu_0 \pm 1{\cdot}75\delta$ and are, respectively, 1·1116 and 0·8615. B is a normalization constant, i.e.

$$B = \left[\delta \int_0^\infty \frac{k(\nu)}{s_0}\,\mathrm{d}\nu\right]^{-1}.$$

(ii) The line width parameter δ is independent of density and proportional to $\sqrt{T}$ [3].

(iii) For pure rotation, line frequencies are determined by the selection rule for the rotational quantum number J

$$\Delta J = +2,\ J = 1, 3, 5, 7 \ldots\ldots \quad (2)$$

Double transitions are neglected.

(iv) For the fundamental band, line frequencies are determined by the selection rules

$$\Delta J = 0, \pm 2,\ J = 1, 3, 5, 7 \ldots\ldots \quad (3)$$
$$\Delta V = +1$$

where V is the vibrational quantum number. Again, double transitions are neglected.

(v) For the first overtone band, line frequencies are governed by the selection rules

$$\Delta J = 0, \pm 2 \quad (4)$$
$$\Delta V = +2$$

for single transitions and

$$\Delta J = 0, \pm 2 \quad (5)$$
$$\Delta V = +1$$

for double transitions. The contributions from (4) and (5) are in the ratio 3 to 1 as approximately determined by Shapiro [3].

(vi) For the pure rotational band, the integrated intensity s_0 of each line at a density ρ is given by the expression [7]

$$\frac{s_0(T)}{\rho^2} = \frac{K_1(T)\,\nu_0}{Q(T)} \cdot \frac{3(J+1)(J+2)}{2(2J+3)} \times \{e^{-1{\cdot}4387 B_0 J(J+1)/T} - e^{-1{\cdot}4387 B_0 J'(J'+1)/T}\},$$
$$J' = J + 2. \quad (6)$$

In this expression the constant $K_1(T)$ incorporates the variation of the induced dipole arising from the temperature dependence of the pair distribution function, $Q(T)$ is the rotational partition function and B_0 is the rotational constant in the ground vibrational state in units of cm^{-1}.

(vii) For the fundamental and first overtone bands, the integrated intensity of each line is given by the expression [3]

$$\frac{s_0(T)}{\rho^2} = \frac{K_2(T)\,\nu_0}{Q(T)}\, L(J)\, e^{-1{\cdot}4387 B_0 J(J+1)/T} \quad (7)$$

where

$$L(J) = \frac{J(J+1)(2J+1)}{(2J-1)(2J+3)} \quad \text{for } \Delta J = 0$$
$$= \frac{3(J+1)(J+2)}{2(2J+3)} \quad \text{for } \Delta J = +2$$
$$= \frac{3(J-1)J}{2(2J-1)} \quad \text{for } \Delta J = -2$$

and $K_2(T)$ is similar in origin to $K_1(T)$.

The procedure for computation was to empirically determine $K_1(T)$ or $K_2(T)$ and δ for the pure rotational and fundamental bands at room temperature by requiring the best fit. which, in addition, gave the correct integrated band intensities [2, 4]. Then, it only remained to determine the temperature dependence of $K_1(T)$ and $K_2(T)$ for the band profile to be calculated at any temperature. The spectroscopic constants required for these calculations were all obtained from Herzberg [9].

The temperature dependence of $K_1(T)$ and

$K_2(T)$ is treated in the theory of Van Kranendonk [5] and Van Kranendonk and Kiss [7]. In this theory, the induced electric dipole moment is represented in the so-called (exp-4) model by the sum of two terms: a short range part due to the electron overlap and a long range part due to the quadrupole field of the inducing molecule. The two parts are proportional, respectively, to an exponential and reciprocal fourth power of the intermolecular distance, from which the model derives its name, and their relative strengths are given as a function of reduced temperature, T^*. ($T^* = T/(\varepsilon/k_B)$, where ε is the Leonard–Jones intermolecular potential parameter and k_B is Boltzmann's constant; for O_2, $\varepsilon/k_B = 118\,\mathrm{K}$ [10]). The appropriate integrals have been evaluated and tabulated by the authors, but their relative contributions must usually be determined empirically. Thus, according to Van Kranendonk [6], we may write for the fundamental band

$$K_2(T) = a[xI(T) + (1 - x)J(T)] \qquad (8)$$

where a is a constant and x is the fractional contribution of the overlap induced moment. $I(T)$ and $J(T)$ are the tabulated integrals referred to. From the band profile analysis of Shapiro and Gush [4], we find $x = 0{\cdot}11$, and we adjusted the constant, a, to give the correct integrated band intensity at room temperature. $K_2(T)$ is now determined for all temperatures. Although no extensive investigation of temperature dependence has been published, the results of Shapiro [3] show about a 7 per cent increase in the integrated intensity at 195 K over that at 298 K, but it was claimed that this is within experimental error. Our calculations, based on (7) and (8), confirm this finding. The same temperature dependence was also assumed for the first overtone band. For the pure rotational band, the relative contributions are not well known, but Bosomworth [11] concluded, from the width of the O_2 rotational band and its integrated intensity compared to that of N_2, that the overlap moment must be contributing about 80 per cent of the total. In our calculations, therefore, we have assumed that the temperature dependence of $K_1(T)$ is entirely due to this contribution.

In all cases the temperature dependence of the integrated band intensity is not great, since for O_2 at room temperature both the integrals I and J are close to a minimum.

In Fig. 2 we show a comparison between experimental and calculated band profiles for the fundamental band at room temperature, and we give calculated profiles for 100 K and 1000 K. The experimental curve of $k(\rho_0/\rho)^2$ vs. ν is the average of four spectra with density ratios (ρ/ρ_0) from 9·59 to 78·6. In the density ratio, ρ_0 is the density at NTP. The calculated points were adjusted to the published area of $7{\cdot}18 \times 10^{-4}\,\mathrm{cm}^{-2}$, the average of nine observations given by Shapiro and Gush [4]. The fit is within experimental error except in the region of the band center, but it is not likely that the total properties discussed below would be sensitive to such details.

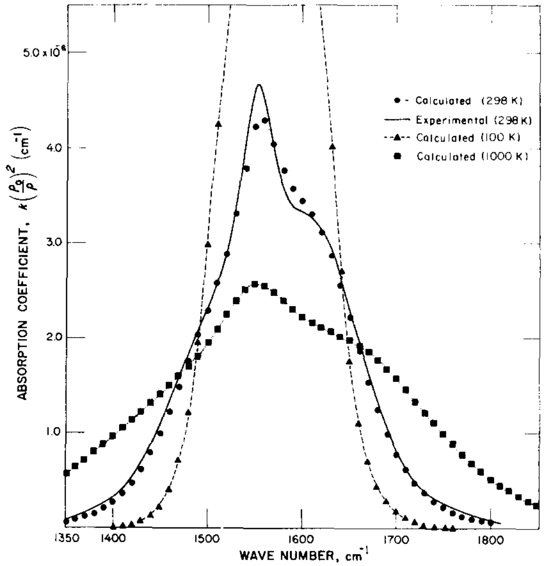

FIG. 2. Calculated and experimental absorption coefficients of oxygen—fundamental band.

THE TOTAL BAND ABSORPTANCE AND RELATED FUNCTIONS

Rigorous calculations of radiative transfer involving an absorbing medium are based on the equation of radiative transfer [12] and require a complete specification of the monochromatic absorption coefficient, $k(\nu, T)$. Because of the complexity of the calculations, however, approximations have been made in actual computations varying from the gray gas model to various band models. The band character of the absorption coefficient leads to the concept of the total band absorptance to which all other commonly used total radiation properties can be related. Further, recent work [13, 14] has demonstrated that a rigorous formulation can be made in terms of the total band absorptance and its derivatives with respect to optical path, even for non-homogeneous gases [15]. We have, therefore, computed this quantity for each band over a series of path lengths and have derived other band and total properties as follows.

The total band absorptance A_i for the ith band, when the path length is l and the fluid is at temperature T, is defined by

$$A_i(l, T) = \int_{\Delta\nu} (1 - e^{-k(\nu, T)l})\, d\nu \tag{9}$$

where $\Delta\nu$ is a frequency interval large enough for A_i to be independent of it. On the other hand, the band absorptivity α_i to radiation of spectral distribution of the intensity I_ν is defined by

$$\alpha_i(l, T) = \frac{\int_{\Delta\nu} \pi I_\nu (1 - e^{-k(\nu, T)l})\, d\nu}{\int_0^\infty \pi I_\nu\, d\nu}. \tag{10}$$

Now, if the fluid is in radiative equilibrium with the radiation, the absorptivity is equal to the emissivity ε and is now a property of the fluid alone, while I_ν becomes $I_{b\nu}(T)$, viz: the specific intensity of black body radiation of temperature T, or, simply, the Planck function. Thus,

$$\varepsilon_i(l, T) = \int_0^\infty \pi I_{b\nu}(T) (1 - e^{-k(\nu, T)l})\, d\nu / \sigma T^4 \tag{11}$$

where σ is the Stefan–Boltzmann constant. Equations (9) and (11) define an average band value $(\bar{I}_{b\nu})_i$ for $I_{b\nu}$ from which we can write

$$\varepsilon_i = \frac{\pi (\bar{I}_{b\nu})_i A_i}{\sigma T^4}. \tag{12}$$

In many cases $(\bar{I}_{b\nu})_i$ can be replaced without loss of accuracy by the value at the band center, i.e. I_{bc}. However, it should be noted that, because of the zero frequency origin of a rotational band, $(\bar{I}_{b\nu})_i$ is a function of path length for those bands.

In the gray gas approximation one can compute the band contribution to the Planck mean absorption coefficient defined as

$$(K_P)_i = \int_{\Delta\nu} k I_{b\nu}\, d\nu \Big/ \int_0^\infty I_{b\nu}\, d\nu. \tag{13}$$

It may be easily shown that

$$(K_P)_i = \lim_{l \to 0} \frac{\pi (I_{b\nu})_i}{\sigma T^4} \left(\frac{\partial A_i}{\partial l} \right). \tag{14}$$

Finally, the total quantities are obtained by summation over the index i

$$\varepsilon = \sum \varepsilon_i \text{ and } K_P = \sum (K_P)_i. \tag{15}$$

In Tables 1a, 1b and 1c we give selected values of A_i for various temperatures and the quantity $W = (\rho/\rho_0)^2 l$. Also given is the temperature dependent factor from equation (12) for converting A_i to ε_i. In view of the path length dependence of this factor for the rotational band, we have listed it separately for this case in Table 2. In Fig. 3 we give the total emissivity ε as a function of temperature for various values of W, and in Fig. 4 we show the band and total emissivities for two values of W. In Table 3 K_P is given for various temperatures.

CORRELATION OF TOTAL BAND ABSORPTANCES

One of the attractive features of the total band absorptance concept for permanent dipole gases has been the fact that experimental data correlate well as a function of path length [16, 17] and, as shown by Tien and Lowder [18], a simple expression may be used to

Table 1a. *Total band absorptance* (cm^{-1})—*rotational band*

T(K)	100	200	300	400	500	600	700	800	900	1000
W (cm)										
10^3	0·0947	0·0826	0·0864	0·0945	0·1037	0·1129	0·1222	0·1316	0·1407	0·1500
10^4	0·945	0·824	0·863	0·944	1·0355	1·1280	1·221	1·314	1·405	1·498
10^5	9·203	8·112	8·513	9·319	10·22	11·14	12·05	12·97	13·87	14·78
10^6	72·54	69·67	74·66	82·29	90·47	98·63	106·7	114·8	122·6	130·5
10^7	220·8	271·6	315·5	357·4	396·8	433·8	468·9	502·5	534·4	565·5
10^8	339·3	446·4	533	610	679·8	744	803·4	859·4	912·1	962·2
10^9	445	597·2	719	825	919·8					

Table 1b. *Total band absorptance* (cm^{-1})—*fundamental band*

T(K)	100	200	300	400	500	600	700	800	900	1000
W (cm)										
10^3	1·245	0·767	0·717	0·705	0·716	0·732	0·748	0·763	0·779	0·794
10^4	12·00	7·54	7·08	6·97	7·09	7·25	7·41	7·57	7·73	7·88
10^5	86·0	64·6	62·9	63·0	64·6	66·5	68·3	70·0	71·7	73·3
10^6	208·7	243·6	274·7	299·4	322·3	343·1	361·7	378·6	394·5	409·8
10^7	299·1	383·1	452	510	563	611	654	694	732	767
10^8	386·9	514	612	696	772	841	904	962	1017	1068
10^9	474	647	772	883	980	1069	1151	1226	1296	1361
$\frac{\pi I_{bc}}{\sigma T^4}$	4·701 $\times 10^{-9}$	2·137 $\times 10^{-5}$	1·762 $\times 10^{-4}$	3·615 $\times 10^{-4}$	4·571 $\times 10^{-4}$	4·710 $\times 10^{-4}$	4·408 $\times 10^{-4}$	3·937 $\times 10^{-4}$	3·435 $\times 10^{-4}$	2·966 $\times 10^{-4}$

Table 1c. *Total band absorptance* (cm^{-1})—*first overtone band*

T(K)	100	200	300	400	500	600	700	800	900	1000
W (cm)										
10^3	0·0112	0·00691	0·00646	0·00635	0·00645	0·00659	0·00674	0·00688	0·00702	0·00716
10^4	0·112	0·0691	0·0646	0·0635	0·0645	0·0659	0·0674	0·0688	0·0702	0·0716
10^5	1·119	0·690	0·645	0·634	0·644	0·659	0·633	0·687	0·702	0·716
10^6	10·83	6·80	6·38	6·28	6·39	6·53	6·68	6·82	6·97	7·11
10^7	80·7	59·3	57·4	57·4	58·8	60·5	62·1	63·6	65·1	66·6
10^8	208·9	238·4	266·2	288·5	310·4	328·7	345·9	361·6	376·4	390·1
10^9	300·3	298·3	447	504	556	603	645	685	722	757
$\dfrac{\pi I_{bc}}{\sigma T^4}$	1·03 $\times 10^{-17}$	2·79 $\times 10^{-9}$	8·98 $\times 10^{-7}$	1·148 $\times 10^{-5}$	4·328 $\times 10^{-5}$	9·167 $\times 10^{-5}$	1·425 $\times 10^{-4}$	1·850 $\times 10^{-4}$	2·146 $\times 10^{-4}$	2·316 $\times 10^{-4}$

Table 2. *Factor for converting total band absorptances of Table* 1a *to emissivities*

T(K)	100	200	300	400	500	600	700	800	900	1000
W (cm)										
10^3	1·743 $\times 10^{-3}$	6·107 $\times 10^{-4}$	3·164 $\times 10^{-4}$	1·950 $\times 10^{-4}$	1·328 $\times 10^{-4}$	9·663 $\times 10^{-5}$	7·358 $\times 10^{-5}$	5·794 $\times 10^{-5}$	4·688 $\times 10^{-5}$	3·867 $\times 10^{-5}$
10^4	1·743 $\times 10^{-3}$	6·113 $\times 10^{-4}$	3·163 $\times 10^{-4}$	1·950 $\times 10^{-4}$	1·329 $\times 10^{-4}$	9·663 $\times 10^{-5}$	7·358 $\times 10^{-5}$	5·798 $\times 10^{-5}$	4·690 $\times 10^{-5}$	3·868 $\times 10^{-5}$
10^5	1·749 $\times 10^{-3}$	6·127 $\times 10^{-4}$	3·174 $\times 10^{-4}$	1·957 $\times 10^{-4}$	1·334 $\times 10^{-4}$	9·695 $\times 10^{-5}$	7·389 $\times 10^{-5}$	5·821 $\times 10^{-5}$	4·709 $\times 10^{-5}$	3·886 $\times 10^{-5}$
10^6	1·800 $\times 10^{-3}$	6·327 $\times 10^{-4}$	3·279 $\times 10^{-4}$	2·024 $\times 10^{-4}$	1·381 $\times 10^{-4}$	1·0056 $\times 10^{-4}$	7·668 $\times 10^{-5}$	6·045 $\times 10^{-5}$	4·897 $\times 10^{-5}$	4·050 $\times 10^{-5}$
10^7	2·046 $\times 10^{-3}$	7·714 $\times 10^{-4}$	4·079 $\times 10^{-4}$	2·554 $\times 10^{-4}$	1·762 $\times 10^{-4}$	1·295 $\times 10^{-4}$	9·957 $\times 10^{-5}$	7·912 $\times 10^{-5}$	6·450 $\times 10^{-5}$	5·367 $\times 10^{-5}$
10^8	2·137 $\times 10^{-3}$	9·834 $\times 10^{-4}$	5·664 $\times 10^{-4}$	3·721 $\times 10^{-4}$	2·649 $\times 10^{-4}$	1·992 $\times 10^{-4}$	1·558 $\times 10^{-4}$	1·254 $\times 10^{-4}$	1·033 $\times 10^{-4}$	8·663 $\times 10^{-5}$
10^9	1·975 $\times 10^{-3}$	1·073 $\times 10^{-3}$	6·745 $\times 10^{-4}$	4·667 $\times 10^{-4}$	3·443 $\times 10^{-4}$					

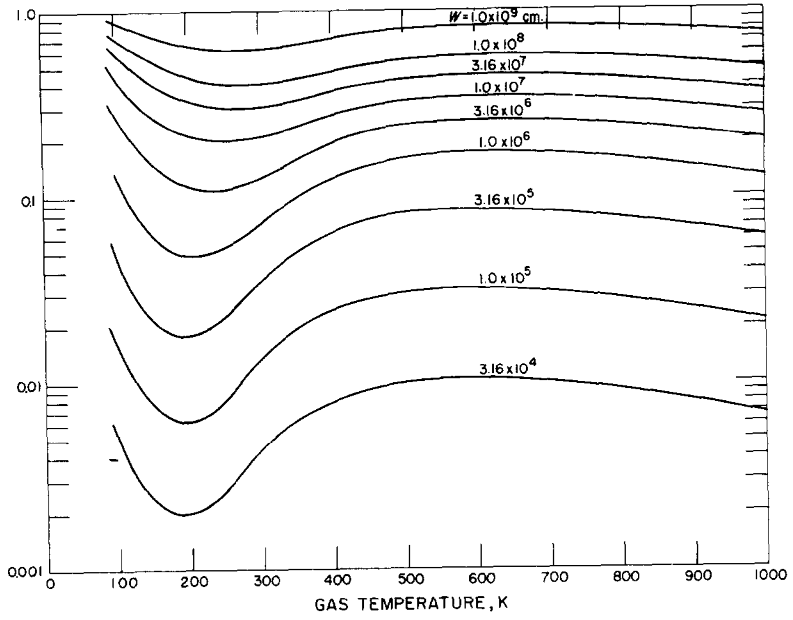

FIG. 3. The total emissivity of oxygen gas.

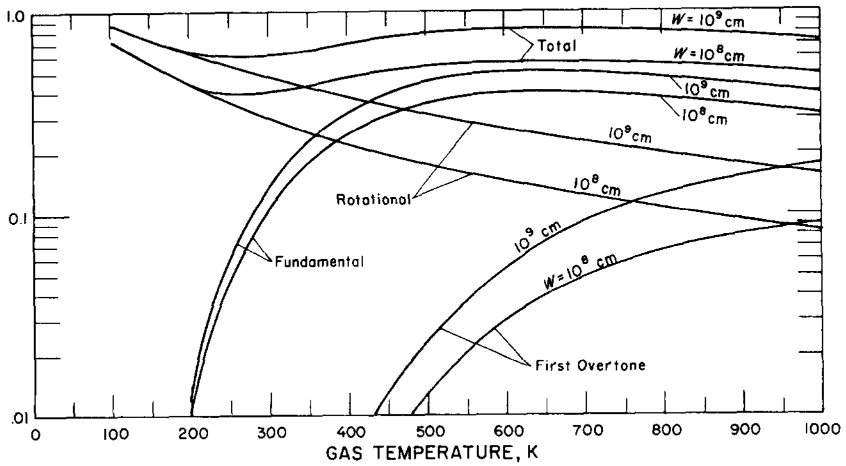

FIG. 4. Band contributions to the total emissivity.

Table 3. The Planck mean absorption coefficient

$T\,(K)$	100	200	300	400	500	600	700	800	900	1000
$K_p(\rho_0/\rho)^2$ (cm^{-1} × 10^{-7})	1.651	0.669	1.539	2.735	3.352	3.563	3.399	3.094	2.758	2.432

represent the path length dependence. It has also been possible to incorporate the pressure dependence, which, in permanent dipole gases, results from line broadening. In general, three parameters are required. These may be interpreted as a mean line intensity-to-line-spacing ratio, a mean line width-to-spacing ratio and an effective broadening pressure. Now, in the present case, line broadening results from a different mechanism; the width of a line depends upon the duration of collision in contrast to the time between collisions in permanent dipole radiation. Hence, pressure or density has little or no effect on line width, which, as stated above, is proportional to $\sqrt{T}$. Furthermore, the lines being extremely broad, one is for the most part dealing with the limit of heavily overlapping lines, and line width ceases to be a parameter. It has been found possible to correlate all of the calculated total band absorptances in this way with two parameters determined for each band at each temperature. Thus, we have the simple functional dependence in dimensionless form

$$\bar{A}_i = \bar{A}_i(u) \tag{16}$$

where $\bar{A}_i = A_i/C_3$ and $u = (C_1/C_3)\,W$. C_1 is the integrated absorption coefficient for the band and was readily determined from the small path length asymptote

$$\lim_{u\to 0} \bar{A}_i(u) = u \tag{17}$$

while C_3 was determined from the large path length asymptote

$$\lim_{u\to 0} \bar{A}_i(u) = \ln\,[uf_2]. \tag{18}$$

These asymptotes are necessary properties of any total band absorptance law. In the original form proposed for the correlation, f_2 is a function of broadening pressure, but, here, is a constant for which we find the value 10.59.

The correlation is given in Fig. 5, with points referring to various bands and various temperatures. The line drawn through the points is the equation

$$\bar{A}_i(u) = \ln\left\{10.59u\left[\frac{u+2}{u+21.18}\right]+1\right\} \tag{19}$$

which is the modified two-parameter version of the Tien and Lowder correlation. The constants C_1 and C_3 are listed for each band at various temperatures in Tables 4a, 4b and 4c.

Table 4. Constants for total band absorption correlation

$T\,(K)$	100	200	300	400	500	600	700	800	900	1000
(a) Rotational band										
$C_1 \times 10^5$ (cm^{-2})	9.47	8.26	8.64	9.46	10.37	11.23	12.17	13.04	14.00	14.89
C_3 (cm^{-1})	44.2	62.6	76.6	88.3	98.6	105.9	114.3	122.2	129.5	136.4
(b) Fundamental band										
$C_1 \times 10^5$ (cm^{-2})	124.9	76.8	71.8	70.6	71.6	73.2	74.8	76.3	77.9	79.5
C_3 (cm^{-1})	37.08	54.3	66.2	76.9	86.0	94.5	102.2	109.4	116.0	122.2
(c) First overtone band										
$C_1 \times 10^5$ (cm^{-2})	1.123	0.691	0.646	0.635	0.645	0.659	0.674	0.688	0.702	0.716
C_3 (cm^{-1})	37.6	55.3	67.1	77.6	87.1	95.7	103.5	110.6	117.0	122.4

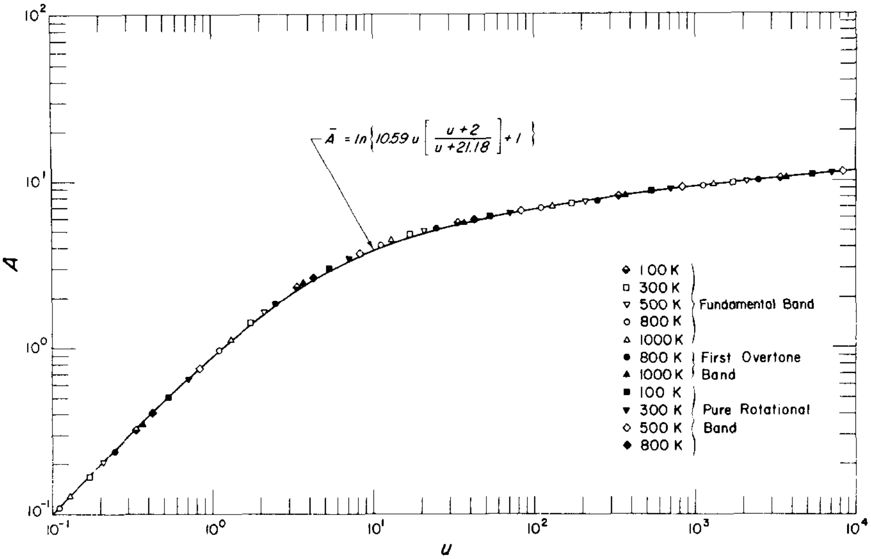

FIG. 5. Total band absorptance correlation.

DISCUSSION

As anticipated, it can be seen from Fig. 4 that the fundamental band is indeed the major contributor to the total emissivity for most of the temperature range, but, at low temperatures, emissivity is exclusively governed by the rotational band. On account of its width, the rotational band extends its influence over quite a temperature range, while the first overtone band only contributes significantly above about 700 K.

With regard to the total band absorptance correlation one can only be extremely gratified by the success indicated in Fig. 5. For, if the extrapolated absorption coefficients prove to be reasonably accurate, we can very efficiently represent the essential radiative properties of O_2 with one simple equation (equation (18)) and the constants listed in Tables 4a, b and c. One comment is in order with regard to the value of f_2 in equation (18).

In the original form of the correlation Tien and Lowder found a value of 2·94 for the limit of heavily overlapped lines. This was based on the work of Edwards and Menard for carbon monoxide, carbon dioxide, methane, and water vapor and is in no way to be regarded as unique. The most obvious qualitative difference between O_2 and these molecules is the much greater line width of the former, being several orders of magnitude greater at NTP and, in this connection, the precise shape chosen may well influence the value of f_2 required.

We wish now to discuss two points concerning the application of these results. The first refers to the accuracy or reliability of the computed quantities. Where the computed results do not involve an extrapolation of the absorption coefficient, the computed total band absorptances and derived quantities are reliable and quite accurate, say, to ± 2 per cent. That is, so long as the temperature is close to 300 K, the quantity $W = (\rho/\rho_0)^2 l$ is less than 10^6 cm, and the density ratio (ρ/ρ_0) itself is less than about 100, we are on fairly reliable ground, but beyond this the calculations rely heavily on extrapolation. Now, there is experimental evidence that our temperature extrapolation procedure is good down to 195 K, as noted above. Further, extensive evidence exists for the correctness of this approach for both the fundamental and rotational bands of hydrogen [19] to temperatures below 100 K. Thus, we have some confidence in the extrapolation, but the reader should be warned that, above room temperature, the theory has not been tested.

For $W > 10^6$ the calculations rely on the extrapolation of the absorption coefficients in the band wings and this is based on the assumed line shape, i.e. equation (1), and above room temperature the population of rotational states. Again, no experimental confirmation is available. Finally, the quadratic dependence of the absorption coefficient appears good up to about $\rho/\rho_0 = 100$. For denser fluids it is known that ternary and higher terms are required. For example, for the hydrogen fundamental band, the deviation from quadratic dependence has reached $+10$ per cent by $\rho/\rho_0 = 600$ [20].

In this connection, accurate data exist for the absorption coefficient of oxygen in the rotational band as a saturated liquid [21]. Here the density ratio is $\rho/\rho_0 = 800$ and the quadratic density dependence is certainly not valid. The observed band profile is, in fact, of somewhat smaller intensity and is broader than predicted by the present extrapolations using quadratic density dependence. It is not possible to say from this, however, whether it is the density or the temperature extrapolation which is inadequate. Data for the fundamental band of the saturated liquid [22] are in quite good agreement in the region of the band origin, but, again, appear to be broader than these extrapolations predict. From a practical point of view, the present results will certainly give the correct order of magnitude for the total radiation properties at saturated liquid conditions.

The second point we wish to discuss is the calculation of a gas absorptivity α from the total band absorptances. For example, one might wish to know the fraction of radiation from, say, a 500 K black or gray source absorbed in the fluid at 100 K. This quantity is not now a property of the fluid alone, but is a function of the source as well. However, the answer is quickly computed from equations (9) and (10) and Tables 4a, b and c, or Tables 1a, b, c and 2. For example, at $W = 10^6$ we get $\alpha = 0{\cdot}106$, while at $W = 10^8$ $\alpha = 0{\cdot}276$. In the latter case, the contributions from the rotational fundamental, and first overtone bands are, respectively 0·090, 0·177 and 0·009.

Finally, we should like to mention that considerable diversity is to be expected among the homonuclear diatomic fluids from the point of view of their total radiative properties, depending on the frequency distribution of the absorption bands. For example, the very broad rotational band of hydrogen [2, 23], reaching to some 1400 cm^{-1} makes this a very "black" fluid in the infrared. Total radiative properties of other fluids including hydrogen will be published at a later date. It is hoped that experimental work at higher and lower temperatures, especially in the band wings, will soon become available to buttress the computations we have made here.

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CALCUL DES PROPRIETES DE RADIATION TOTALE DE L'OXYGENE COMPRIME ENTRE 100 ET 1000 K

Résumé—L'émissivité totale, l'absorptance totale de bande et le coefficient d'absorption moyen de Planck pour l'oxygène comprimé ont été calculés dans le domaine de température compris entre 00 et 1 000°K. Les calculs basés sur des valeurs publiées pour le coefficient d'absorption spectrale et sur des extrapolations au-dessus et au-dessous de la température ambiante sont faits en accord avec la théorie publiée. On trouve qu'il est possible de représenter tous les résultats concernant l'absorptance totale de bande à l'aide d'une relation à deux paramètres.

BERECHNETE STRAHLUNGSEIGENSCHAFTEN VON KOMPRIMIERTEM SAUERSTOFF ZWISCHEN 100 UND 1000 K

Zusammenfassung—Das Gesamtemissionsvermögen, das Absorptionsvermögen über alle Banden und der mittlere Planck'sche Absorptionskoeffizient von komprimiertem Sauerstoff wurden für den Temperaturbereich zwischen 100 und 1000K berechnet. Die Berechnungen fussen auf publizierten Werten für den spektralen Absorptionskoeffizienten. Die Extrapolationen in die Bereiche unter und über Zimmertemperatur wurden entsprechend der vorhandenen Theorie ausgeführt. Es war möglich, alle Ergebnisse für das Absorptionsvermögen über alle Banden in einer zweiparametrigen Verknüpfung darzustellen.

РАСЧЕТ ИНТЕГРАЛЬНЫХ ХАРАКТЕРИСТИК ИЗЛУЧЕНИЯ СЖАТОГО КИСЛОРОДА В ДИАПАЗОНЕ ТЕМЕРАТУР 100–1000°К

Аннотация—Проведен расчет интегральной излучательной способности, интегрального коэффициента поглощения и среднего коэффициента поглощения Планка. Для расчета, проведенного в соответствии с уже опубликованной теорией, использовались имеющиеся данные по спектральному коэффициенту поглощения, которые экстраполировались для температур выше и ниже комнатной. Найдена возможность обобщения всех данных по интегральному коэффициенту поглощения с помощью выражения, включающего два параметра.