

EMISSIVITIES AND SPECTRAL ABSORPTIVITIES OF COMBUSTION PRODUCTS

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This paper is concerned with the determination of the spectral absorptivities K_ω and emissivities ε of a thermodynamic-equilibrium mixture of combustion products consisting of CO_2 , H_2O , CO , OH , HCl , HF , H_2 , and NO molecules on the temperature interval $2000-5000^\circ\text{K}$. The proposed calculation method, based on the use of a graph of the molecular absorptivities reduced to atmospheric pressure, enables K_ω and ε to be calculated for any gas mixture composed of the above-mentioned molecules.

1. The emissivity of a unit area on the surface of a uniformly heated gas volume V is

$$\varepsilon = \frac{1}{\sigma T^4} \int_0^\infty S_\omega(V) d\omega. \tag{1.1}$$

Here, S_ω is the spectral flux density, ω is the wave number, σ is the Stefan-Boltzmann constant, and T is temperature in $^\circ\text{K}$. Engineers frequently use the value of ε for an area element located at the center of the base of a hemispherical volume of radius R :

$$\varepsilon = \frac{\pi}{\sigma T^4} \int_0^\infty [1 - \exp(-K_\omega R)] B_\omega d\omega. \tag{1.2}$$

Here, B_ω is Planck's function and K_ω is the spectral absorptivity. In what follows the quantities have the following dimensions: ω [cm^{-1}], K_ω [cm^{-1}], R [cm], $\sigma = 5.66 \cdot 10^{-12} \text{ W/cm}^2$. Obviously, for a gas volume of arbitrary configuration it is possible to find an effective radius such that the ε calculated from (1.1) and (1.2) coincide. The results of calculations of the effective radii for various configurations are presented in [1].

The spectral absorptivity K_ω depends on the concentration of absorbing particles N_i and the molecular absorptivities $\sigma'_{\omega i}$:

$$K_\omega = \sum_i \sigma'_{\omega i} N_i = \sum_i \sigma_{\omega i} p_i. \tag{1.3}$$

Here, p_i is the partial pressure of the i -th component and $\sigma_{\omega i}$ has been written with allowance for induced emission.

In the range of temperatures considered ($T = 2000-5000^\circ\text{K}$, the range characteristic of combustion products) the principal absorption processes are vibrational-rotational dipole transitions in diatomic and triatomic molecules. The absorption spectrum of these molecules consists of rotational lines grouped around the centers of the vibrational bands. In the general case in order to determine σ_ω it is necessary to know the absorptivities integrated over the rotational lines and also the location and width of each of the latter. The exact solution of this problem with allowance for all the factors is very complicated. In most cases it is made difficult, in particular, by a lack of information on the line widths. Frequently, however, in problems connected with radiative transfer in combustion products owing to the high temperatures and pressures the absorption spectrum consists of completely overlapping lines belonging to the vibrational bands, which partially or completely overlap each other. Thus, at temperatures $T \sim 3000^\circ\text{K}$ for a series of molecules, overlapping of the lines is observed at the following pressures: $\text{H}_2\text{O} \sim 1 \text{ atm}$, $\text{CO}_2 \sim 1 \text{ atm}$, $\text{CO} \sim 10 \text{ atm}$, $\text{HCl} \sim 18 \text{ atm}$, $\text{NO} \sim 13 \text{ atm}$, $\text{OH} \sim 20$ and $\text{HF} \sim 40 \text{ atm}$.*

*The values of the limiting pressures characteristic of the temperature range in question were estimated from the condition of overlapping of the rotational lines, starting from the experimentally measured values of the line half-widths, the gaskinetic collision diameters, and the measured dependence of the integral absorption of the vibrational bands on the total pressure in the gas mixture.

If we consider that for these molecules the band lines partially overlap, the above-mentioned pressure limits can be shifted by a factor of about 1.5 in the direction of smaller values. As a result, in computing K_ω the determination of the half-width of the lines is not a necessary procedure, and the shapes of the vibrational bands can be determined by an approximate, relatively simple method.

We will consider the integrated absorptivity of a group of vibrational bands, for which the change in the vibrational quantum number $\Delta v = n$:

$$\alpha^{(n)} = \sum_{v''=0} \alpha(v'', v'' + n), \quad \alpha(v'', v'' + n) = \sum_{J''} \sigma_\omega(v'', v'' + n, J'') d\omega. \quad (1.4)$$

Here, J'' is the rotational quantum number of the lower state of the molecule. The value of $\sigma_\omega(J'')$ is proportional to [2]

$$f(J'') = J'' \exp \left[-\frac{hc}{kT} B_{v''} J'' (J'' + 1) \right], \quad (1.5)$$

$$B_{v''} = B_e - \alpha_e (v'' + 1/2). \quad (1.6)$$

Here, $B_{v''}$ is the rotational constant of level v'' ; B_e is the rotational constant corresponding to the equilibrium internuclear distance; α_e is a spectroscopic constant. Data on B_e and α_e can be found for various molecules, for example, in [3]. We seek the mean value $\langle K_\omega \rangle$, calculated for a unit pressure of 1 atm, for a group of vibrational bands $\Delta v = n$:

$$\langle K_\omega^{(n)} \rangle = \alpha^{(n)} / \Delta\omega^{(n)}, \quad (1.7)$$

where $\Delta\omega^{(n)}$ is the equivalent width of the band group.

Then the emissivity ε for a system of vibrational bands with allowance for overlap is expressed as the sum over the i components of the gas mixture and j averaging intervals:

$$\varepsilon = \frac{1}{\sigma T^4} \sum_j \sum_i [1 - \exp(-\langle K_{ji} \rangle P_i R)] B_{\omega_{ji}} \Delta\omega_{ji}. \quad (1.8)$$

Here, $\langle K_{ji} \rangle$ is the absorptivity of the i -th molecule averaged over the wave number interval $\Delta\omega_{ji}$. The method of determining $\langle K_{ij} \rangle$ and $\Delta\omega_{ji}$ is illustrated in Fig. 1. Thus, each group of vibrational bands is associated with an effective width satisfying the condition

$$\int_{\Delta\omega^{(n)}} K_\omega^{(n)} d\omega = K_\omega^{(n)} \Delta\omega^{(n)} = \sum_{v''=0} \alpha(v'', v'' + n). \quad (1.9)$$

The choice of effective bandwidth can be quite arbitrary, since in accordance with (1.8) a change in K_ω is to a considerable extent compensated by an opposite change in $\Delta\omega$.

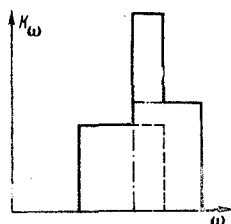


Fig. 1

Determination of the total absorptivity (solid curve) by means of the absorptivities of the effective bands (dashed and dash-dot curves).

2. One of the simplest methods of determining the effective bandwidth involves use of the factor $f(J)$ from Eq. (1.5), which is proportional to the intensity of the rotational line. From the equation of the rotational term

$$E(J) = B_v J(J+1) = [B_e - \alpha_e(v + 1/2)] J(J+1), \quad (2.1)$$

it follows that the distance between the rotational lines of the P and R branches of the band $v \rightarrow v'' + n$, which have the same starting value of J , is equal to

$$\Delta\omega_{v''}^{(n)} = \frac{hcB_e}{kT} \left[1 - \left(v'' + \frac{n+1}{2} \right) \frac{\alpha_e}{B_e} \right] J(J+1), \quad (2.2)$$

where a double prime denotes quantities relating to the lower vibrational state. Here and in what follows $hc/k = 1.438 \text{ cm}^{-1}$, and α_e and B_e are expressed in cm^{-1} .

As the effective bandwidth, in accordance with [2], we take the difference of the wave numbers of the lines of the P and R branches, for which the value of the function $f(J)$ from Eq. (1.5) is 10^{-3} of the maximum value of $f(J)$ for a given temperature. The maximum of J is reached at

$$J_{\max} = 2.48T^{1/2} \left\{ B_e \left[1 - \left(v + \frac{1}{2} \right) \frac{\alpha_e}{B_e} \right] \right\}^{-1/2}. \quad (2.3)$$

Solving the equation

$$f(J_{\max}) = 10^{-3} f(J), \quad (2.4)$$

we obtain

$$J^* = 2.47T \left\{ 1 - \frac{B_e}{T} \left[1 - \left(v + \frac{1}{2} \right) \frac{\alpha_e}{B_e} \right]^{-1} \right\}. \quad (2.5)$$

Substituting (2.5) into (2.2) and calculating the constant coefficient, we have

$$\Delta\omega_{v''}^{(n)} = 9.93 \left[1 - \left(v'' + \frac{n+1}{2} \right) \frac{\alpha_e}{B_e} \right] \left\{ TB_e \left[1 - \left(v'' + \frac{1}{2} \right) \frac{\alpha_e}{B_e} \right] \right\}^{1/2}, \text{ cm}^{-1}. \quad (2.6)$$

It follows from Eq. (2.6) that the effective bandwidth decreases with increase in the vibrational quantum number. Finding the upper limit of the effective width and assuming that in most cases $\alpha_e/B_e \leq 5 \cdot 10^{-2}$, we reduce (2.6) to the form:

$$\Delta\omega_{v''}^{(n)} = 9.93 \left[1 - \left(\frac{n+1}{2} \right) \frac{\alpha_e}{B_e} \right] (TB_e)^{1/2}, \text{ cm}^{-1}. \quad (2.7)$$

Expression (2.7) does not take into account the band edges that may limit the effective bandwidth on the short-wave side of the spectrum.

Obviously, the condition that the band is limited by an edge on the longwave side is given by the inequality

$$J_{\max} > J^*. \quad (2.8)$$

Using Eq. (2.3) and (2.5) and inequality (2.8), we obtain the edge criterion:

$$Y = 6.15 \alpha_e^2 n^2 B_e^{-3} \left[1 - \left(3v'' + \frac{2n+3}{2} \right) \frac{\alpha_e}{B_e} \right]^{-1} > 1. \quad (2.9)$$

For purposes of illustration we present below values of the criteria $Y = Y_1$ for the fundamental band ($n = 1$) and $Y = Y_2$ for the first overtone ($n = 2$):

$T^\circ K$	OH		HCl		NO		CO		CO ₂
	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1
2000	0.94	3.7	0.94	3.8	0.76	3.1	0.52	2.1	1.9
3000	1.4	5.6	1.4	5.6	1.2	4.2	0.78	3.1	2.9
4000	1.9	7.5	1.6	7.5	1.6	5.7	1.05	4.2	3.9

The wave number of the edge limiting the effective bandwidth on the shortwave side can be found from the equation [4]

$$\omega_k = \omega_0 - \frac{(B_{v'} + B_{v''})^2}{4(B_{v'} - B_{v''})}, \quad (2.10)$$

where ω_0 is the wave number of the center of the band.

After substituting (1.6) into (2.10) and transforming the expression obtained, we have

$$\Delta\omega_k^{(n)} = \omega_k - \omega_0 = [B_e - \alpha_e (v' + 1/2 (n+1))]^2 (\alpha_e n)^{-1}. \quad (2.11)$$

We use the following abbreviated notation for the effective width of the band corresponding to a transition with a change in the vibrational quantum number by n :

$$\Delta\omega^{(n)} = \Delta\omega_k^{(n)} (1 - \delta) + a (1 + \delta) (0.001 T)^{1/2} \quad (2.12)$$

$$\delta = 0 \text{ at } Y \geq 1; \quad \delta = 1 \text{ at } Y < 1$$

$$a = 1.57 \cdot 10^2 \left[1 - 0.5 (n+1) \frac{\alpha_e}{B_e} \right] B_e^{1/2}. \quad (2.13)$$

For diatomic and linear triatomic molecules we use as B_e the rotational constant for the equilibrium internuclear distance; for nonlinear triatomic molecules of the asymmetric-top type (for example, H_2O) the constant B_e is equal to \sqrt{BC} , where B and C are the rotational constants of the asymmetric top. The results of a determination of the coefficients required in calculating the effective width for the bands making the chief contribution to emission and absorption in the temperature range in question are presented in Table 1.

In this case for all the molecules except H_2 we have used the molecular constants given in [3]. For the H_2 molecule the constants for the effective bandwidth in the infrared region of the spectrum were obtained on the basis of an analysis of theoretical study [5].

3. The method of determining the integrated absorptivity (1.4) of the band group $\Delta v = n$ is based on the equation expressing the dependence of $\alpha^{(n)}$ on temperature:

$$\alpha^{(n)}(T) = \frac{T_0}{T} \alpha^{(n)}(T_0) \Phi^{(n)}(T). \quad (3.1)$$

Table 1

n	CO		HCl		OH		NO		HF	
	1	2	1	2	1	2	1	2	1	2
ω_{0n}	2143	4258	2885	5765	3569	6953	1876	3700	3959	7747
$\Delta\omega_k$	208	105	350	172	461	230	160	80	467	207
a	219	218	510	487	673	570	204	200	713	679
	H ₂		CO ₂			H ₂ O				
n	1	1	2	3	1	2	3	4	5	
ω_{0n}	4500	2349	3716	5109	1594	3700	5340	7240	9100	
$\Delta\omega_k$	0	49	41	36	0	0	0	0	0	
a	466	396	407	472	502	502	504	502	502	

Here, T_0 is a fixed temperature, for example, 300° K; $\alpha^{(n)}(T_0)$ is the integrated absorptivity at that temperature. For a diatomic molecule the function $\Phi(T)$ has the form [6]:

$$\Phi^{(n)}(T) = \frac{1 - \exp(-\eta\omega_{0n})}{1 - \exp(-\eta\omega_{01})^n}, \quad (3.2)$$

$$\eta = \frac{hc}{kT}$$

Here, ω_{01} is the wave number of the fundamental band, and ω_{0n} is the wave number of the n -th overtone.

For a linear triatomic molecule we have [27]

$$\Phi^{(n)} = \prod_{i=1}^3 \frac{[1 - \exp(-\eta n_i \omega_{0i})]}{[1 - \exp(-\eta \omega_{0i})]^{n_i}}. \quad (3.3)$$

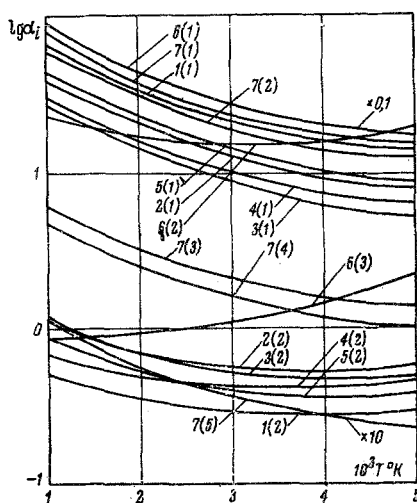


Fig. 2

Integrated absorptivities of the molecules: 1 - CO, 2 - HCl, 3 - OH, 4 - NO, 5 - HF, 6 - CO₂, 7 - H₂O. The numbers in parentheses denote the numbers of the band system.

Here the superscript *n* denotes the set of transitions $\nu_1 \rightarrow \nu_1 + n_1$, $\nu_2 \rightarrow \nu_2 + n_2$, $\nu_3 \rightarrow \nu_3 + n_3$, and ω_{01} , ω_{02} , and ω_{03} are the principal vibration frequencies of the molecule.

The results of determining α at 300° K with account for recent experimental data are presented in Table 2. For the infrared band of the H₂ molecule we have [5]

$$\alpha \{H_2\} = 629 P^2 \{H_2\} T^{-1} \text{ cm}^{-2} \cdot \text{atm}^{-1}. \quad (3.4)$$

The results of determining the integrated absorption coefficients of certain molecules determined from Eqs. (3.2) and (3.3) and the data of Table 2, together with spectroscopic constants taken from [3], are presented in Fig. 2.

Table 2

Integrated Absorptivities * (α) cm⁻² · atm⁻¹ at 300°K

<i>n</i>	H ₂ O [6-12]	CO ₂ [13-20]	CO [2,21,22]	OH [2,21]	HCl [2,21,23,24]	HF [25]	NO [26]
1	262	2700	237	100	450	150†	111
2	195	195	1.67	4.0	3.68	3.2	2.7
3	21.9	15	0.183	0.098	0.091	—	0.0119
4	16.2	—	—	—	—	—	—
5	0.405	—	—	—	—	—	—

*All the results were obtained by averaging the data of the indicated references.

† Mean value of α_{01} obtained from an analysis of the data of [25].

4. The data on $\Delta\omega$ and α presented above can be used to compute the spectral absorptivities of any gas mixture consisting of the components most frequently encountered in practical calculations: CO₂, H₂O, CO, OH, HCl, HF, NO, and H₂. Considering that both $\Delta\omega$ and α vary only slightly with temperature (see (2.7) and Fig. 2), the following method of determining the mean values $\langle K_\omega \rangle$ is proposed. To determine the spectral $\langle K_\omega \rangle$ curve of a gas mixture we first determine the values of $\langle K'_\omega \rangle$ by means of the $\langle K_{\omega i} \rangle$ data in Fig. 3 for the individual components, whose partial pressure is equal to 1 atm. These values are obtained by multiplying $\langle K_{\omega i} \rangle$ by the partial pressures of the components and then adding. In the second stage of the calculations the $\langle K'_\omega \rangle$ graph is corrected with allowance for the temperature of the gas mixture in accordance with the formula

$$\langle K_\omega \rangle = \langle K'_\omega \rangle 3000 \cdot T^{-1}. \quad (3.5)$$

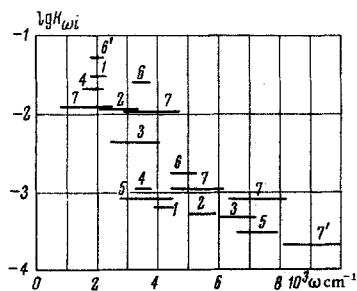


Fig. 3

Graph of molecular spectral absorptivities reduced to 1 atm: 1 - CO, 2 - HCl, 3 - OH, 4 - NO, 5 - HF, 6 - CO₂, 7 - H₂O, 6' - 0.1 $\langle K'_{\omega} \rangle$ CO₂, 7' - 10 $\langle K'_{\omega} \rangle$ H₂O.

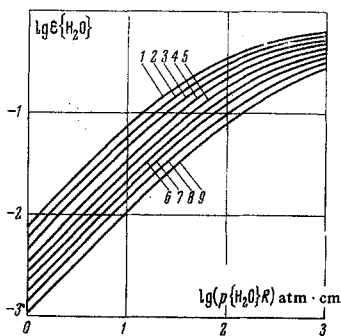


Fig. 4

Emissivity of H₂O molecules: H₂O. 1) T = 2000° K, 2) 2250° K, 3) 2500° K, 4) 2750° K, 5) 3000° K, 6) 3250° K, 7) 3500° K, 8) 3750° K, 9) 4000° K.

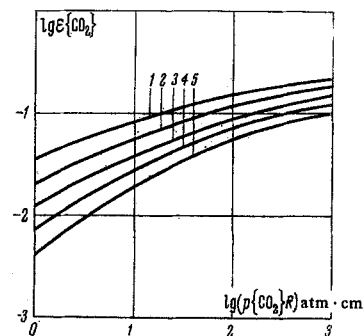


Fig. 5

Emissivity of CO₂ molecules: 1) T = 2000° K, 2) 2500° K, 3) 3000° K, 4) 3500° K, 5) 4000° K.

In many practical problems it is necessary to determine ϵ for combustion products consisting of CO₂ and H₂O. At a temperature $T \leq 2000^\circ \text{K}$ values of ϵ are usually determined from the data of [1], which were obtained by generalizing the known experimental results. Using the data on α and $\Delta\omega$ presented above it is easy to obtain values of $\epsilon \{H_2O\}$ and $\epsilon \{CO_2\}$ at temperatures $T = 2000 - 5000^\circ \text{K}$.

The results of such calculations are presented in Figs. 4 and 5.

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