final point of a visible region; G_{p_i,q_τ}, final point of a visible region; $t'_{p_i,k}$, relative distance of boundaries of the visible region from the beginning of the side; Δ, maximum relative error.

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RADIATION OF SULFUR DIOXIDE

Yu. A. Popov

UDC 536.3

Using spectral-analysis data and the statistical model of Goody, the emissivity and absorption coefficient of sulfur dioxide are calculated.

In many furnaces of nonferrous metallurgy and the chemical industry it is required to make allowance for the radiation of sulfur dioxide, SO_2. The nomograms of the integrated emissivity ε_{SO_2} presented in [1] were based on the Bouger law, which is not satisfied for the vibrational–rotational absorption bands of a gas when the frequency-averaging interval exceeds the width of the spectral lines. The calculation presented in [2] was based on the Edwards band contour model, which fails to describe the contour of the vibrational–rotational bands accurately enough. Reliable results for the integrated emissivity of SO_2 were obtained experimentally by Golitsin and Berlin [3, 4]. These results lay roughly 40% below those of [1] and were approximately double the theoretical data of Chan and Tien [2]. However, the volume of experimental material in [3, 4] was insufficient for practical application, and the empirical formulas proposed in [3] are insufficiently accurate even in the region covered by the experiments (Fig. 2).

In this paper we shall calculate the integrated emissivity and absorption coefficient of SO_2 using the statistical model of the absorption bands of gases developed by Goody [8]. In order to choose the parameters of the model and the shape of the band contour we used the spectral results obtained at room temperature by Chan and Tien [2]. An analogous method was employed for calculating the emissivity and absorption coefficient of CO_2 and water vapor [5].

The SO_2 molecule is nonlinear; its rotational constants are well known [6]:

$$A=2.027\ \text{cm}^{-1};\quad B=0.3442\ \text{cm}^{-1};\quad C=0.2935\ \text{cm}^{-1}.$$

The smoothed absorption coefficient of the band i of a nonlinear molecule takes the form [5]

$$\tilde{k}_{\nu i} = k_{0i} P_0 \frac{x_i (1-e^{-x})}{\sqrt{T}\, Q_i(T)} |y_i| \exp[-\gamma T y_i^2 f_i(y_i T)]. \tag{1}$$

Here $x_i = hc\nu_i/kT$, $x = hc\nu/kT$, $y_i = x_i - x$. The constant γ is determined by the expression

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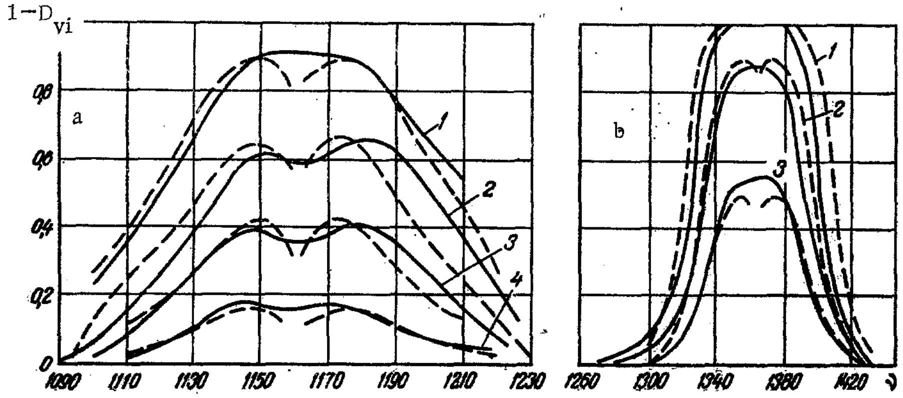

Fig. 1. Spectral absorption coefficients of the bands 1151 cm^{-1} (a) and 1366 cm^{-1} (b) of SO_2. Solid curves, experiment [2]; broken curves, calculation; l = 5 cm: for a) 1) P_0 = 0.699 atm, P = 3.992 atm; 2) P_0 = 0.3464, P = 1.732; 3) P_0 = 0.1732, P = 0.866; 4) P_0 = 0.0575, P = 0.2875; for b) 1) P_0 = 0.3 atm, P = 4.0 atm; 2) P_0 = 0.0801, P = 1.07; 3) P_0 = 0.024, P = 0.32; ν, cm^{-1}.

TABLE 1. Principal Constants for SO_2

Bands	Wave number of band center, cm^{-1}	a_i	b_i	S_{0i}, deg/cm · atm^2	Q_i
ν_1	1151	14,6	87	650	$1-e-x_1$
ν_2	524,5	14,6	87	1730	$1-e-x_2$
ν_3	1366	4,3	5,7	17000	$1-e-x_3$
$2\nu_1$	2340	15	70	75	$(1-e-x_1)^2$
$\nu_1+\nu_3$	2517	15	70	45	$(1-e-x_1)(1-e-x_3)$

TABLE 2. Emissivity of SO_2 with the Parameters $P_0 l$ = 50 cm·atom, P_0 = 1 atm in Relation to Temperature and Total Pressure.

T, °K	P, atm						
	1	1,5	2	3	5	10	20
	ε						
600	0,247	0,283	0,291	0,302	0,313	0,323	0,328
800	0,193	0,223	0,231	0,241	0,252	0,265	0,273
1000	0,141	0,165	0,171	0,179	0,190	0,202	0,210
1200	0,102	0,120	0,125	0,132	0,140	0,151	0,158
1400	0,0742	0,0885	0,0921	0,0974	0,104	0,113	0,120
1600	0,0549	0,0660	0,0687	0,0728	0,0781	0,0850	0,0907
1800	0,0413	0,0500	0,0521	0,0553	0,0595	0,0650	0,0696
2000	0,0316	0,0385	0,0402	0,0427	0,0460	0,0503	0,0541
2200	0,0245	0,0301	0,0314	0,0334	0,0360	0,0395	0,0426
2400	0,0193	0,0238	0,0249	0,0265	0,0286	0,0314	0,0339
2600	0,0154	0,0191	0,0200	0,0213	0,0230	0,0253	0,0274
2800	0,0124	0,0155	0,0162	0,0173	0,0187	0,0206	0,0223

$$\gamma = k/4hc\sqrt{BC}. \tag{2}$$

For SO_2 this equals 0.556 deg^{-1}. The functions Q_i are determined in the approximation of the harmonic oscillator. The spectral emissivity averaged over a narrow spectral range Δν for the band i has the form

$$D_{\nu i} = e^{-\tau_{\nu i}}, \tag{3}$$

where

$$\tau_{\nu i} = S_{\nu i}/\sqrt{S_{\nu i} + (\pi\alpha/\delta)^2}. \tag{4}$$

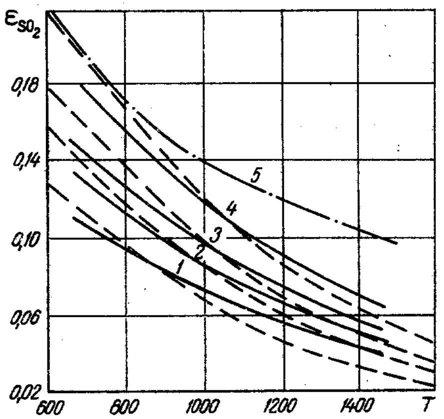

Fig. 2. Emissivity of SO_2. Solid curves, experiment [4]; broken curves, calculation: l = 15.5, P = 1 atm. 1) P_0l = 2.9 cm·atom; 2) 5.8; 3) 8.5; 4) P_0l = 14.0 cm·atom; 5) calculation based on the empirical formula of [3] for P_0l = 14.0 cm·atom; T in °K.

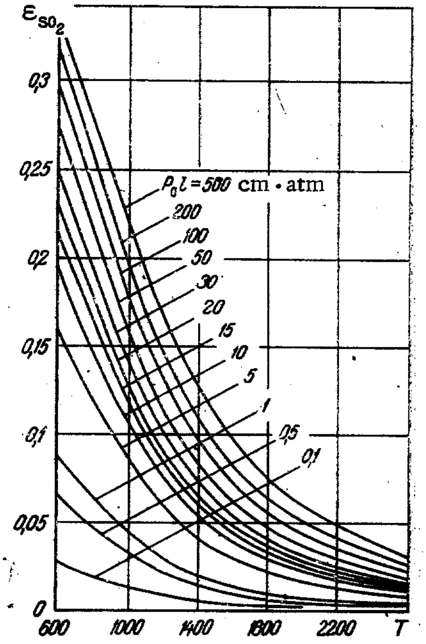

Fig. 3. Nomograms for the integrated emissivity of pure SO_2 at atmospheric pressure; T in °K.

TABLE 3. Integrated Absorption Coefficient of Pure SO_2 (P = 1 atm, P_0l = 10 cm·atom) at Various Temperatures and for Various Ratios of the Temperature of the Black Wall to the Gas Temperature R

R	T, °K				
	600	800	1000	1200	1400
1	0,192	0,148	0,106	0,075	0,054
1,2	0,166	0,117	0,079	0,054	0,037
1,5	0,130	0,082	0,052	0,034	0,023
2,0	0,084	0,048	0,028	0,017	0,011

Here α is the linewidth. We take the latter as equal to the sum of the Lorentz and Doppler widths and regard the line as having a Lorentz contour. The averaging interval $\Delta\nu$ is much smaller than the bandwidth but much greater than the average distance between the lines δ. We estimated δ from the spectral results of [7], δ = 0.46 cm^{-1}. The function $S_{\nu i}$ is related to $\tilde{k}_{\nu i}$ by the equation

$$S_{\nu i} = \tilde{k}_{\nu i} l \frac{\pi\alpha}{\delta}. \tag{5}$$

The coefficients k_{0i} or S_{0i} are to be determined from experimental data. These coefficients are related by

$$S_{0i} = k_{0i} \frac{\pi\alpha_{0L}}{\delta}. \tag{6}$$

The width of the lines depends on the temperature and pressure:

$$\alpha_L = \alpha_{0L} P^* / \sqrt{T}. \tag{7}$$

Allowance for the Doppler broadening has little effect on the result for $P^* \gtrsim 1$ atm. Averaging the results given in [2] we find $\pi \alpha_0 L/\delta = 2.6$ $\mathrm{deg}^{1/2} \cdot \mathrm{atm}^{-1}$. The effective pressure P^* is related to the total pressure P and the partial pressure P_0 by

$$P^* = P + (b - 1) P_0, \tag{8}$$

where b is the self-broadening coefficient, found in [2] as $b_{SO_2} = 1.28$. The function $f_i(y_i T)$ take the form [5]

$$f_i(y_i T) = 1 - a_i \left(\frac{y_i T}{300} \right)^2 + b_i \left(\frac{y_i T}{300} \right)^4 . \tag{9}$$

The coefficients a_i, b_i, S_{0i} were determined by matching the calculated transmission curves to the results of the spectral measurements [2]. An exception was the ν_2 band with its center at 524.5 cm^{-1}, for which the coefficient S_{0i} was determined from the integrated intensity of the band given in [2]. The main coefficients are given in Table 1. The coefficients a_i and b_i for the ν_2 band were taken the same as for ν_1. A comparison between the calculated results obtained for the quantity $1 - D_{\nu i}$ and the experimental values is presented in Fig. 1a, b. The contribution of the bands $2\nu_1$ and $\nu_1 + \nu_3$ to the integrated emissivity was also taken into account, although it was not very great [2].

The integrated emissivity and absorption coefficient of SO_2 were calculated on the Minsk-32 computer using the equation given in [5]. The integral with respect to frequency was calculated by the Simpson method. A comparison between the calculated emissivities of SO_2 and the experimental values of [4] is given in Fig. 2. The maximum deviation between theory and experiment is 25%. Figure 3 presents a computing nomogram for the emissivity of pure SO_2 for various temperatures and pressures, with $P_0 l$ = 50 cm•atm. Table 3 gives the calculated data for the integrated absorbing power of SO_2 corresponding to various ratios of the temperature of the black wall to the gas temperature R and different gas temperatures, with $P_0 l$ = 10 cm•atm. It follows from Table 2 that the emissivity increases considerably with rising gas pressure.

NOTATION

ε_{SO_2}, emissivity of SO_2; T, gas temperature; $\bar{k}$, smoothed absorption coefficient; h, Planck's constant; ν_i, wave number of the center of band i; k, Boltzmann's constant; A, B, C, rotational constants of the molecule; $D_{\nu i}$, spectral transmission for band i, averaged over a narrow frequency range; δ, mean distance between the lines; P, total pressure; P_0, partial SO_2 pressure; P^*, effective pressure; b, self-broadening coefficient; α, linewidth; α_L, linewidth due to the shock mechanism of broadening; l, path length of the beam in the gas; c, velocity of light in a vacuum; R, ratio of the temperature of the black wall to the gas temperature; ν, wave number.

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