TABLE 1. Relative Fraction of Photon Heat Conduction, m, %

T, K	$m_{\max}$	m	T, K	$m_{\max}$	m
300	1,5	0,12	500	7,0	0,32/0,35
400	3,6	0,21	600	11,5	0,39/0,58

Thus, it has been established both analytically and experimentally that heat transfer by electromagnetic radiation is negligibly small in polyethylene. From a comparison of the absorption spectra for polyethylene, polystyrene, polymethyl methacrylate, and Teflon given in [4] in the wavelength range 2.6-15 μm, it appears that this conclusion is true also for other polymer samples a millimeter or more thick.

NOTATION

λ_T, overall thermal conductivity, W/m·K; λ_p, photon thermal conductivity, W/m·K; λ, wavelength, m; ε, emissivity; Q, total heat flux, W/m^2; δ, sample thickness, m; $\tau(\lambda)$, spectral transmission coefficient; E, radiative heat transfer, W/m^2; $I(\lambda)$, spectral density of blackbody radiation; T, temperature, K; l_i, relative fraction of total blackbody radiant energy in the range 0 to λ_i; σ_o, Stefan–Boltzmann constant, W/m^2K^4; φ, irradiance coefficient; D, diameter of sample, m; m, relative fraction of photon heat conduction; K_λ, absorption coefficient, cm^{-1}.

LITERATURE CITED

1. A. G. Romashin, "Thermal conductivity of transparent materials," Teplofiz. Vys. Temp., 7, 659-665 (1969).
2. W. H. McAdams, Heat Transmission, McGraw-Hill, New York (1954).
3. M. A. Bramson, Infrared Radiation: A Handbook for Applications, Plenum, New York (1968).
4. V. M. Chulanovskii (ed.), Infrared Absorption Spectra of Polymers and Accessory Materials [in Russian], Khimiya, Leningrad (1969).
5. S. S. Kutateladze and V. M. Borishanskii, A Concise Encyclopedia of Heat Transfer, Pergamon, New York (1966).
6. T. R. Fuller and A. L. Fricke, "Thermal conductivity of polymer melts," J. Appl. Polym. Sci., 15, 1729-1736 (1971).

APPROXIMATE CALCULATION OF THE ULTRAVIOLET RADIATION OF DIATOMIC MOLECULES AT LOW PRESSURE

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UDC 535.231.4

A method is given of calculating the emission bands of isolated lines for a rigid rotator based on summation of equivalent linewidths. A comparison of this method with the method based on the rotational structure-averaged absorption coefficient is carried out.

The conventional method of calculating the radiation of diatomic molecules in gases at temperatures of 2000-10,000°K in the visible and ultraviolet spectral regions is based on rotational structure averaging of the emission and absorption coefficients [1, 2]. It is assumed in this approach that the rotational lines of the electronic–vibrational bands of the molecule are distributed densely and are broadened sufficiently so that the lines overlap. This basic simplifying assumption is normally not valid at temperatures less than 2000°K and pressures lower than 1 atm. Estimates of the mean distance between lines in the UV region of the spectrum are shown in Table 1 for some molecular systems at temperature 2000°K. The estimates were made by computing the number of electronic–vibrational bands n with the emis-

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sion coefficient within 1% of the maximum, and thus the range of wavelengths λ_1-λ_2 defining the most intense bands of the molecular system was determined. In similar fashion, the number of lines n_1 in the band branch with the emission coefficient within 1% of the maximum was determined. Dividing the wavelength range of the molecular system by n, n_1, and by the number of principal branches in the band gives an estimate of the mean distance between lines. The data given in Table 1 shows that the ratio of the mean distance between lines to the Doppler halfwidth, equal to 0.002 nm* for T = 2000°K, μ = 20 kg/kmole, λ = 300 nm, exceeds this figure by an order of magnitude for certain molecules. Even if we take into account that near the edges of the bands, the distance between lines can be several times less than the mean distance, it is obvious that the most unfavorable situation occurs in the case of hydroxyl molecule. The large mean distance between lines in the spectrum of this molecule is connected with the large value of its rotational constant.

Thus arises the problem of calculating the radiation of bands of isolated lines and an estimate of the error due to averaging of the absorption coefficient over the rotational structure. In practice, one seeks a method of calculating the radiation of the entire band without having to calculate the radiation of each line, even if this causes some loss in accuracy.

The solution of the radiative transfer equation along the radiation beam in the case of no external sources and no scattering of radiation can be written in the form

$$I_\nu = \int_0^L B_\nu \frac{dR_\nu}{dX} dX, \quad R_\nu = \exp\left[-\sum_k \int_X^L K_{\nu k} dx\right]. \tag{1}$$

Integrating (1) over the width $\Delta\nu_1$ of the rotational line band, we obtain

$$\overline{I}_\nu = \int_0^{\Delta\nu_1} I_\nu d\nu = \int_0^L \overline{B_\nu \frac{dR_\nu}{dX}} dX. \tag{2}$$

First we ignore the dependence of B_ν on frequency over the range of the lines. Next we decompose the Planck function into two factors, the first of which B_{ev} depends only on the electronic—vibrational transition frequency ν_{ev}, and the second of which b_{js} involves the frequency of the center of the rotational line $\Delta\nu_{js}$, calculated from the beginning of the band ν_{ev}:

$$B_\nu \approx B_{ev} b_{js}, \tag{3}$$

$$b_{js} = \left(1 + \frac{\Delta\nu_{js}}{\nu_{ev}}\right)^3 \exp(-\alpha\Delta\nu_{js}) = \left(1 + \frac{\Delta\nu_{js}}{\nu_{ev}}\right)^3 \sum_{n=0}^{\infty} \frac{(-\alpha\Delta\nu_{js})^n}{n!}. \tag{4}$$

Because $\alpha \ll 1$, if we are not interested in ultralow temperatures, we can cut off the series in (4) after the first few terms.

$$\Delta\nu_{js} = \frac{1}{B}(F'_{js} - F''_{js}), \tag{5}$$

$$\nu_{ev} = \frac{1}{B}(E' + G'_v - E'' - G''_v). \tag{6}$$

Since the lines are taken to be isolated, we split up the interval $\Delta\nu_1$ into subintervals $\Delta\nu$ such that each subinterval contains only a single line. Substituting (3) for the Planck function into (2), the latter now becomes a double summation over branches and lines of integrals over the range $\Delta\nu$. Bringing B_{ev} outside of the integral and double summation signs, and b_{js} outside of the integral sign, and then changing the order of integration over frequency and differentiation with respect to coordinate, we find

$$\overline{B_\nu \frac{dR_\nu}{dX}} = B_{ev} \sum_s \sum_j b_{js} \frac{d}{dX}\left(\int_{\nu_{js}-\frac{\Delta\nu}{2}}^{\nu_{js}+\frac{\Delta\nu}{2}} R_\nu d\nu\right), \tag{7}$$

$$R_\nu = \exp\left(-\sum_{s^*}\sum_{j^*}\int_X^L K_{\nu j^* s^*} dx\right). \tag{8}$$

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*The Lorentz halfwidth of the line at pressure 1 atm is about an order of magnitude smaller.

TABLE 1. Mean Distance between Lines for Some Molecular Band Systems at 2000°K

Band system	Region of spectrum λ_1-λ_2, nm	$\Delta\lambda$, nm	Band system	Region of spectrum λ_1-λ_2, nm	$\Delta\lambda$, nm
OH (violet)	283—347	0,1	NO (δ)	175—262	0,01
O_2 (Schumann–Runge)	210—465	0,008	CO (4th positive)	145—205	0,009
NO (β)	214—600	0,009			
NO (ε)	173—256	0,01	N_2 (2nd positive)	298—467	0,025
NO (γ)	205—334	0,016			

Since the interval $\Delta\nu$ contains only a single line, the largest term in the sum in (8) is that involving $K_{\nu js}$. The other terms in the sum are small and can be ignored. Substituting the resulting expression for the transmission into (7), transforming the integral to one over frequency measured from the center of the line and introducing the equivalent linewidth W_{js}, we obtain

$$\overline{B_\nu \frac{dR_\nu}{dX}} = -B_{ev} \sum_s \sum_j b_{js} \frac{dW_{js}}{dX}, \tag{9}$$

$$W_{js} = \int_{-\infty}^{+\infty} d\nu \left[1 - \exp\left(-\int_X^L K_{\nu js} dx\right)\right], \tag{10}$$

$$K_{\nu js} = \frac{S_{js}}{\gamma_{js}} f_k\left(\frac{\nu}{\gamma_{js}}\right), \quad k = D,\ L,$$
$$f_D(x) = \frac{1}{\sqrt{\pi}} \exp(-x^2), \quad f_L(x) = \frac{1}{\pi} \frac{1}{1+x^2}. \tag{11}$$

The limits of integration in (10) have been taken over all frequencies. This is justified because the absorption coefficient falls sharply even within the range $\Delta\nu$. Substituting (4) into (9), changing the order of summation over n and that over j and s, and bringing under the derivative factors which are dependent on $\Delta\nu_{js}$ we find

$$\overline{B_\nu \frac{dR_\nu}{dX}} = -B_{ev} \sum_{n=0}^{\infty} \frac{(-\alpha)^n}{n!} \frac{dF_n(X)}{dX}, \tag{12}$$

$$F_n(X) = \sum_s \sum_j \left(1 + \frac{\Delta\nu_{js}}{\nu_{ev}}\right)^3 (\Delta\nu_{js})^n W_{js}. \tag{13}$$

Here F_0 is the total absorption of the band; F_n for $n \neq 0$ does not have such an obvious physical interpretation. The advantage of (12) over (9) is that the operations of summation over lines and branches are decoupled from the operation of differentiation with respect to coordinate.

Approximation formulas have been obtained [3] for the equivalent linewidth for lines with Doppler and Lorentz profiles in which integration over frequency and coordinate are decoupled:

$$W_{js} \approx \int_X^L dx S_{js} \Phi_k(Z_{js}), \quad Z_{js} = \frac{1}{\sigma_k \gamma_{js}} \int_X^L S'_{js} dx', \tag{14}$$

$$\Phi_D(x) = \frac{4}{\sqrt{\pi}} \int_0^\infty dy y^2 \exp[-y^2 - x\exp(-y^2)],$$
$$\Phi_L(x) = \frac{4}{\pi} \int_0^\infty dy \frac{y^2}{(1+y^2)^2} \exp\left(-\frac{x}{1+y^2}\right), \quad \sigma_D = \sqrt{\pi},\ \sigma_L = \pi. \tag{15}$$

In [3] the following two approximation formulas for these functions are given which are valid for all positive values of x, and are correct to within 5% and 10%, respectively. If, however, we restrict the maximum value of x to 10^4, the accuracy increases to within 2.5 and 3.5%, respectively:

$$\Phi_D(x) = \frac{\sqrt{1 + \ln(1 + 1.65\,x)}}{1 + 0.941\,x},$$
$$\Phi_L(x) = \sqrt{\frac{1 - \exp(-0.837\,x)}{0.837\,x}}. \tag{16}$$

TABLE 2. Coefficients of the Approximation Formulas

Doppler profile

branch	i	$c_i\ (\alpha)$	a_i	b_i
R	0	$2{,}332 \exp(-\alpha)$	1,237	1,242
	1	$2{,}332 \left\{\frac{\sqrt{\pi}}{2} - \sqrt{\alpha}[1 - \exp(-\alpha)]\right\}$	1,700	2,390
	2	$2{,}332 (1+\alpha) \exp(-\alpha)$	2,260	4,540
P	0	$2{,}200 \exp(-3{,}14\,\alpha)$	0,998	1,110
	1	$1{,}998 \exp(-1{,}20\,\alpha)$	1,430	2,160
	2	$2{,}322 \exp(-0{,}423\,\alpha)$	2,260	4,540

Lorentz profile, m = 1 for R-branch, m = 2 for P-branch

i	$a_i\ (\alpha)$	$b_i\ (\alpha)$
0	$2{,}332 \exp(-m^2\alpha);$	$0{,}4198 + 0{,}1819\, m\sqrt{\alpha} - 0{,}3315\, m^2\alpha$
1	$2{,}332 \left\{\frac{\sqrt{\pi}}{2} - m\sqrt{\alpha} \times \left[1 - \frac{m^2\alpha}{3} - \exp(-m^2\alpha)\right]\right\};$	$0{,}3380 + 0{,}04741\, m\sqrt{\alpha} - 0{,}1168\, m^2\alpha$
2	$2{,}332 (1 + m^2\alpha) \exp(-m^2\alpha);$	$0{,}2286 + 0{,}02002\, m\sqrt{\alpha} - 0{,}06580\, m^2\alpha$

Substituting now (14) for the equivalent width into (13), replacing the summation over j by an integral and introducing the new variable $p = \sqrt{\alpha}/2(2j + 1)$, we obtain

$$F_n(X) = \int_X^L dx \sum_s \int_{p_{\min}}^{\infty} \frac{dp}{\sqrt{\alpha}} \left(1 + \frac{\Delta\nu_{ps}}{\nu_{ev}}\right)^3 (\Delta\nu_{ps})^n S_{ps} \Phi_k(Z_{ps}). \tag{17}$$

Below we present some simple approximation formulas for the functions appearing in the first integral for the case of a rigid rotator. These formulas contain the optical thickness and the parameter α (dimensionless inverse temperature) as independent variables. With their help it is possible to calculate $F_n(X)$ without doing the sum over lines. It is not difficult to obtain similar expressions not only for the rigid rotator model, but also for actual molecules, such as those given in Table 1. These formulas can be used as an alternative to the method of averaging the absorption coefficient over the rotational structure in the case of low pressures and not too high temperatures, when the approximation of isolated lines is valid.

The bands of a rigid rotator split up into two branches, R and P. Formulas for the rotational terms have the same form for the upper and lower electronic states:

$$F' = B'j'(j' + 1), \quad F'' = B''j''(j'' + 1). \tag{18}$$

Introduicng the variable p and using the fact that j' = j" + 1 for the R-branch and j' = j" − 1 for the P-branch, after several transformations, we find from (5)

$$\Delta\nu_{ps} = (\beta - 1)(y - y_m)^2 + f_m,$$

$$y = \frac{p}{\sqrt{\alpha}}, \quad y_m = \pm\frac{\beta}{1-\beta}, \tag{19}$$

$$f_m = \pm\beta y_m + \frac{3\beta + 1}{4}. \tag{20}$$

Since (20) is independent of both p and α, and depends only on β (this characterizes the electronic–vibrational transition), we redefine $\Delta\nu_{ps}$, absorbing f_m into ν_{ev}.

The integral index of line absorption can be expressed as

$$S_{js} = S_0 \nu_{js} \Sigma_{js} \exp\left(-\frac{hc}{kT} F''_{js}\right), \tag{21}$$

TABLE 3. Ranges of θ_k for the Sample Calculations. $\theta_1 = 0\text{-}10^2$, for a Rigid Rotator T = 200-3000°K

System	β	ν_{ev}	B (cm^{-1})	Profile	θ_k
OH (v)	0,916	1750	18,5	D L	1—4 1—10^3
NO (β)	0,661	19500	1,69	D L	1—4 1—10
O_2 (S-R)	0,640	25800	1,25	D L	1—4 1—10
Line				D L	1—10^3 1—10^4

where we include in S_0 all factors depending only on electronic and vibrational terms, the electronic transition strength, the Franck—Condon factor, concentration of molecules, etc.; Σ_{js} is the Hunnel—London factor, equal to j + 1 and j for the R and P-branches:

$$\Sigma_{js} = \frac{p}{\sqrt{\alpha}} \pm \frac{1}{2} \approx \frac{p}{\sqrt{\alpha}}, \tag{22}$$

since $\alpha \ll 1$.

Substituting formulas for the rotational terms and the Hunnel—London factor in (21), we obtain after some transformations

$$S_{ps} = S_m \frac{\varkappa}{\varkappa_m} \nu_{ps}, \quad \varkappa = p \exp(-p^2),$$
$$\varkappa_m = \max_p \{\varkappa(p)\} = \frac{1}{\sqrt{2}} \exp\left(-\frac{1}{2}\right), \quad S_m = S_0 \frac{\varkappa_m}{\sqrt{\alpha}} \exp\left(\frac{\alpha}{4}\right). \tag{23}$$

With the help of (23) we find that (14) for the optical thickness takes the form

$$Z_{ps} = \frac{1}{\sigma_k \gamma_{ps}} \int_X^L S'_m \frac{\varkappa'}{\varkappa_m} \nu_{p's} dx'. \tag{24}$$

In order to do the integration with respect to p in (17), it is necessary to decouple the variables p and x' in (24). To do this, we introduce an approximation for the integral index of line absorption:

$$S'_{ps} = S'_m \frac{\varkappa'}{\varkappa_m} \nu_{p's} \approx S'_m \frac{\varkappa}{\varkappa_m} \nu_{ps} \frac{d(\alpha')}{d(\alpha)}, \tag{25}$$

$$d(\alpha') = \frac{2}{\sqrt{\alpha'}} \int_{p_{\min}}^{\infty} \frac{\varkappa'}{\varkappa_m} \left(1 + \frac{\Delta\nu_{p's}}{\nu_{ev}}\right) dp', \tag{26}$$

which is constructed such that an integration with respect to j of both sides of (25) converts the expression into an exact equality. In (26) the factor inside the brackets can, to a good approximation, be set equal to unity because the branch width is much smaller than the electronic—vibrational transition frequency. The integral can now be performed and for $\alpha \ll 1$ the result is

$$d(\alpha') \approx \frac{1}{\varkappa_m \sqrt{\alpha'}}. \tag{27}$$

The value of $p_{\min}$ is $\sqrt{\alpha}$ or $2\sqrt{\alpha}$ for the R and P branches, respectively, if we model a molecule with half-integral j by a rigid rotator. However, for small α, the integral in (26) depends only very weakly on its lower limit.

Using (23) and (25), $F_n(X)$ can be written in the following form, valid for either branch:

$$F_n(X) = \frac{B\nu_{ev}}{2} \int_X^L dx \frac{S_m}{\sqrt{\alpha}} H_n(Z_*, \alpha), \tag{28}$$

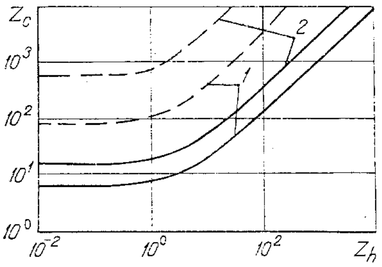

Fig. 1. Range of parameters Z_h and Z_c where the error in isolated line intensity due to approximation (14) is less than 30% (area below curves 1) and 50% (area below curves 2). The solid curves refer to a Doppler profile; the dashed curves to a Lorentz profile.

$$H_n(Z_*, \alpha) = 2 \int\limits_{p_{\min}}^{\infty} dp \left(1 + \frac{\Delta\nu_{ps}}{\nu_{ev}}\right)^4 (\Delta\nu_{ps})^n \frac{\varkappa}{\varkappa_m} \Phi_h\left(Z_* \frac{\varkappa}{\varkappa_m}\right), \tag{29}$$

$$Z_* = \frac{\nu_{ev}}{\sigma_h \gamma_{ev}} \int\limits_X^L S'_m \sqrt{\frac{\alpha}{\alpha'}}\, dx'. \tag{30}$$

The ratio ν_{ps}/γ_{ps} in the last expression is replaced by ν_{ev}/γ_{ev}; this is valid for the Doppler profile and also approximately correct for the Lorentz profile.

We now turn to the question of how many terms must be kept in the expansion of the Planck function (4) in powers of α. The answer depends on how significantly b_{ps} changes within the band. The comparison between our method and the exact results discussed below shows that it is sufficient to keep the first two terms in the series (zeroth and first order) if b_{ps} is normalized such that when $p_* = 1/\sqrt{2}$ (this value of p corresponds to the maximum value of the integrand for G_0 in (35)) we have b_{ps} equal to unity. We write b_{ps} in series form with new coefficients:

$$b_{ps} = \left(1 + \frac{\Delta\nu_{ps}}{\nu_{ev}}\right)^3 \exp(-\alpha\Delta\nu_{ps} + \alpha\Delta\nu_* - \alpha\Delta\nu_*) \approx \exp(-\alpha\Delta\nu_*) \left(1 + \frac{\Delta\nu_{ps}}{\nu_{ev}}\right)^3 \sum_{n=0}^{1} \frac{(-1)^n}{n!} f_n [\alpha(\Delta\nu_{ps} - \Delta\nu_*)]^n, \tag{31}$$

where $\Delta\nu_{ps} = (\beta - 1)(y - y_m)^2$; $\Delta\nu_* = \Delta\nu_{ps}(y = p_*/\sqrt{\alpha})$, and $f_0 = 1.064$, $f_1 = 0.9182$ for the R-branch and $f_0 = 0.9966$, $f_1 = 1.514$ for the P-branch. These values of f_0 and f_1 lead to accuracy within 15% for the expansion (31) when $|\alpha(\Delta\nu_{ps} - \Delta\nu_*)| \leqslant 0.7$ for the R-branch and also to within 15% when $-0.2 \leqslant -\alpha(\Delta\nu_{ps} - \Delta\nu_*) \leqslant 1.2$ for the P-branch. Then (12) takes the form

$$\overline{B_\nu \frac{dR_\nu}{dX}} \approx -B_{ev} \sum_{n=0}^{1} \frac{(-\alpha)^n}{n!} \varphi_n \frac{dF_n}{dX} \exp(-\alpha\Delta\nu_*), \tag{32}$$

$$\varphi_0 = f_0 + f_1 \Delta\nu_* \alpha, \quad \varphi_1 = f_1.$$

Substituting $\Delta\nu_{ps}$ in (29) and putting

$$\left(1 + \frac{\Delta\nu_{ps}}{\nu_{ev}}\right)^4 \approx 1 + 4\frac{\Delta\nu_{ps}}{\nu_{ev}}, \tag{33}$$

since $\Delta\nu_{ps}/\nu_{ev}$ is small, we obtain

$$H_0(Z_*, \alpha) \approx G_{0k} + \frac{4}{\nu_{ev}} \left[(\beta - 1)\left(\frac{G_{2k}}{\alpha} - \frac{2y_m}{\sqrt{\alpha}} G_{1k} + y_m^2 G_{0k}\right)\right], \tag{34}$$

$$G_{ik}(Z_*, \alpha) = 2 \int\limits_{p_{\min}}^{\infty} dp p^i \frac{\varkappa}{\varkappa_m} \Phi_h\left(Z_* \frac{\varkappa}{\varkappa_m}\right), \; i = 0, 1, 2. \tag{35}$$

Ignoring the term $4(\Delta\nu_{ps})^2/\nu_{ev}$ we find that $H_1(Z_*, \alpha)$ is exactly equal to the expression within the square brackets of (34). The functions G_{ik} can be written to good approximation by the following:

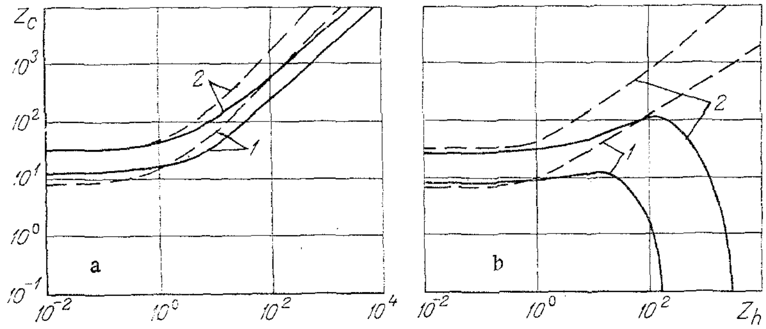

Fig. 2. Region of the parameters Z_h and Z_c in which the error in the rigid rotator radiation intensity for (a) OH and (b) O_2 is less than 30% (area below curves 1) and 50% (area below curves 2). The solid curves refer to a Doppler profile, the dashed curves to a Lorentz profile.

$$G_{iD}(Z_*,\ \alpha) \approx c_i(\alpha)\frac{[1+\ln(1+a_iZ_*)]^{1+\frac{i}{2}}}{1+b_iZ_*}, \qquad (36)$$

$$G_{iL}(Z_*,\ \alpha) \approx a_i(\alpha)\,[1+b_i(\alpha)\,Z_*]^{-\frac{1}{2}}.$$

The coefficients of these expressions are found by the method of least squares and are given in Table 2. For $\sqrt{\alpha} = 0.030\text{-}0.365$ and $Z_* = 10^{-4}\text{-}10^{4}$ these formulas yield an accuracy of within 10% or better for both branches.

The accuracy of our approximate results was tested using a double layer problem in which we calculate the radiation of a layer of gas consisting of two zones with different temperatures and concentrations of radiating gas. All parameters were taken to be constant within each of the two zones. The radiation was recorded as viewed from the zone with lower temperature.

For isolated lines, the problem is parametrized by the four quantities θ_k, θ_1, Z_h and Z_c:

$$\theta_D = \sqrt{a}, \quad \theta_L = \rho/\sqrt{a}, \quad \theta_1 = \alpha(a-1)\,\nu_{ev}. \qquad (37)$$

For a rigid rotator the number of parameters increases to six with the addition of β and ν_{ev}.

The accuracy of our approximation formulas was tested by calculating a large number (~200) of samples (Table 3). The values given for β and ν_{ev} refer to the most intense bands of the corresponding molecular band system. It is necessary to point out that certain combinations of θ_k and θ_1 in (37) lead to values of α such that the corresponding temperature T lies outside the range 200-3000°K. In these cases θ_k and θ_1 were restricted such that the resulting temperature was within the above limits. Obviously the rejected cases are not those with maximum error.

Figure 1 shows the accuracy of approximation (14) for the equivalent linewidth. The graph was constructed by taking the worst cases, i.e., those yielding minimum sizes of the regions 1 and 2. For the Lorentz profile this situation occurs for $\theta_L = 10$, $\theta_1 \geqslant 10$; for the Doppler profile we have $\theta_D = 2.5$, $\theta_1 \geqslant 10$. Further increase in θ_k leads to a decrease in the error because the narrower the line in the cold zone, the less it contributes, and the more closely the problem becomes uniform. For the Lorentz profile with $\theta_L < 1$, approximation (14) leads to negative values of the intensity, hence these values of θ_L were not considered.

We consider now a series of calculations for the R and P-branches of the rigid rotator (Figs. 2a, b). The results for NO(β) practically coincide with those for O_2, therefore we give the results only for the latter, in which the error turns out to be larger. As an exact solution we use calculations of the radiation of branches consisting of isolated Lorentz or Doppler lines for the rigid rotator. The results of those sample calculations showing the largest error are shown in Fig. 2. For the Lorentz profile this occurs for $\theta_L = 1$, for the Doppler profile $\theta_D = 1.5\text{-}2$. For both cases, the accuracy of our method improves with increasing θ_k; the value $\theta_L = 10$ was chosen as the maximum for NO(β) and O_2. Calculations were also done with $\theta_D = 10$ for Doppler lines in the violet OH system; the resulting errors were smaller than those shown in Fig. 2a. Transition for OH to NO(β) and O_2 leads to increasing error;

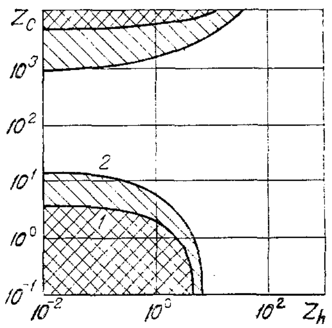

Fig. 3. Region of parameters Z_h and Z_c in which the error in radiation intensity of the (0, 0) band of Doppler lines of violet OH due to averaging of the absorption coefficient over the rotational structure is less than 30% (cross-hatched area) and 50% (diagonally shaded area).

this is due principally to approximation (31), since the change in the exponential of b_{js} within the band branch is larger for the latter two systems than for hydroxyl.

Figure 3 shows a comparison between the exact value of the radiation intensity of the (0, 0) band of hydroxyl (consisting of isolated Doppler lines), calculated using the Hunnel–London factor [4] and the rotational terms of [5], and the value of the radiation intensity of this band obtained by averaging the absorption coefficient [2]. Calculations were performed with T_h = 3000°K and a = 1-15. A curious feature of the results is the appearance of an "oasis" at large optical thicknesses in the cold zone. The regions 1 and 2 are at least three times smaller with respect to the Z_c axis than the corresponding regions in Fig. 2a.

Thus we see that our approximation formulas for the rigid rotator allow study calculations on the radiation of hydroxyl, nitric oxide, oxygen, and other molecular systems, confined in layers with temperature gradients in the range 200-3000°K. The amount of calculation with our approximation formulas is reduced by at least two orders of magnitude in comparison to the amount of calculation necessary to obtain the exact solution. Comparison with the method of absorption coefficient averaging shows that our approximation method leads to better results under the conditions considered. We point out that there is a significant difference between our method and that of [6], where an expression for the total absorption of a set of isolated Lorentzian lines is developed within the framework of various statistical models of band spectra. In our method, the molecule is modelled (by a rigid rotator or more exact model), then the summation over lines is done.

In the case when the line profile is complex, our formulas can still be used with the help of an approximate expression for the equivalent linewidth in the form of a linear combination of Lorentz and Doppler equivalent widths [3, 7, 8]. Then $F_n(X)$ in (13) becomes a corresponding linear combination of the F_n for the Lorentz and Doppler profiles. Our method is also applicable for the visible and IR spectral regions under the obvious condition that the lines can be taken as isolated, since in (37) θ_1 ranges from 0 to 100.

NOTATION

I_ν, spectral radiation intensity, $W/m^2 \cdot sec \cdot st \cdot m^{-1}$; B_ν, spectral equilibrium-radiation intensity, $W/m^2 \cdot sec \cdot st \cdot m^{-1}$; R, transmission; $K_{\nu k}$, spectral absorptivity of the k-th line, m^{-1}; L, beam path, m; X and x, current coordinates, m; E, G_v, F_{js}, electronic, vibrational, and rotational terms of a diatomic molecule, m^{-1}; B, rotational constant of lower electronic state, m^{-1}; T, temperature, °K; W_{js}, equivalent linewidth, m^{-1}; S_{js}, integral index of line absorption, m^{-2}; Z_{js}, optical thickness at center of the line; j, rotational quantum number; a, hot-to-cold temperature ratio; a_i, b_i, c_i, dimensionless coefficients in approximation formulas; ρ, hot-to-cold zone pressure ratio; $\alpha = hcB/kT$, dimensionless inverse temperature; β, ratio of rotational constants of higher and lower electronic levels; γ_{js}, line halfwidth, m^{-1}; ν_{ev}, dimensionless wavenumber in the beginning of band; $\Delta\nu_{js}$, dimensionless wave number of rotational line, calculated from the beginning of the band; ν_{js}, wave number of the center of rotational line, m^{-1}; θ_k (k = D, L), ratio of line halfwidths in hot and cold zones; θ_1, absolute logarithm of ratio of the Planck functions B_{ev} in cold and hot zones; $\sigma_D = \sqrt{\pi}$; $\sigma_L = \pi$. Subscripts: ev refers to electronic–vibrational transition; s, j, n, i correspond to band branch, line branch, terms in the expansion of the Planck function in a Taylor series, and approximation formula for G_{ik}, respectively; h, c stand for quantities pertaining to hot and cold layers; ' refers to upper level; " refers to lower level; D, Doppler profile; L, Lorentz profile.

LITERATURE CITED

1. L. M. Biberman (ed.), Optical Properties of Heated Air [in Russian], Nauka, Moscow (1970).
2. V. A. Kamenshchikov, Yu. A. Plastinin, V. M. Nikolaev, and L. A. Novitskii, Radiative Properties of Gases at High Temperature [in Russian], Mashinostroenie, Moscow (1971).
3. Yu. V. Khodyko, E. I. Vitkin, and V. P. Kabashnikov, "Calculation of radiation in molecular gases by modeling of the spectral structure," Inzh.-Fiz. Zh., 36, No. 2, 204 (1979).
4. G. H. Dieke and H. M. Crosswhite, "The ultraviolet bands of OH," J. Quant. Spectrosc. Rad. Transfer, 2, 97 (1962).
5. V. P. Glushko (ed.), Thermodynamical Properties of Materials [in Russian], Izd. Akad. Nauk SSSR, Moscow (1962).
6. G. N. Plass, "Useful representations for measurements of spectral band absorption," J. Opt. Soc. Am., 50, 868 (1960).
7. V. S. Matveev, "Approximate representation of absorption coefficient and equivalent linewidth for the Voight contour," Zh. Prikl. Spektrosk., 16, 228 (1972).
8. H. Y. Yamada, "Total radiances and equivalent widths of isolated lines with combined Doppler and collision broadened profiles," J. Quant. Spectrosc. Rad. Transfer, 8, 1463 (1968).

APPROXIMATE CALCULATION OF TRANSPORT COEFFICIENTS IN MULTICOMPONENT MIXTURES

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An efficient method is developed for calculating transport coefficients in dissociated gas mixtures with a large number of components.

For solution of problems of heat and mass exchange in the presence of hypersonic streamline flow around obstacles [1], data on the various transport coefficients in mixtures of reacting gases is necessary. Application of the expressions for the coefficients of viscosity, thermal conductivity, thermal diffusion, and multicomponent mass diffusion derived from the kinetic theory of gases [2-4] can often be unwieldy because of the large amount of computer time used in the calculation. Significantly simpler expressions can be obtained with the help of the bifurcation approximation to the binary diffusion coefficient [5-7]. This approximation is used in the present paper to obtain a relation for the diffusion current and expressions for the coefficients of viscosity, thermal conductivity, and thermal diffusion.

Specifically, calculations were done for stably dissociated air at temperatures ranging from 2000 to 8000°K and pressures between $0.1 \cdot 10^5$ and 10^5 Pa. Comparison of the results of our calculations for the transport coefficients with those of numerical calculations based on the kinetic theory of gases [2-3] indicates acceptable accuracy for our method.

1. The Chapman–Enskog method for a quasineutral mixture gives the following expressions for the mass diffusion current, heat current and viscous stress tensor [4]:

$$\mathbf{j}_i = \rho_i \mathbf{V}_i = \frac{n^2}{\rho} \sum_{k=1}^{N} m_i m_k D_{ik} \mathbf{d}_k - D_i^T \nabla \ln T,$$

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