

component; ω , frequency of normal oscillations; X , B_z , spectroscopic constants; ψ , wave function; R_{ij} , matrix elements; S_{ij} , integral intensity of vibrational transition.

LITERATURE CITED

1. D. M. Dennison, *Rev. Mod. Phys.*, 12, 175 (1940).
2. C. P. Courtoy, *Can. J. Phys.*, 35, 608 (1957).
3. H. R. Gordon and T. K. McCubbin, Jr., *J. Mol. Spectrosc.*, 19, 137 (1966).
4. G. Amat and M. Goldsmith, *J. Chem. Phys.*, 23, 1171 (1955).
5. I. F. Golovnev, *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 7 (1977).
6. N. I. Moskalenko, *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 2 (1975).
7. P. W. Anderson, *Phys. Rev.*, 76, 647 (1949).
8. C. J. Tsao and B. J. Curnutte, *J. Quant. Spectrosc. Radiat. Transfer*, 2, 41 (1962).
9. G. Yamamoto, M. Tanaka, and T. Aoki, *J. Quant. Spectrosc. Radiat. Transfer*, 9, 371 (1969).

METHODS OF CALCULATING MOLECULAR-GAS RADIATION ON THE BASIS OF SPECTRAL-COMPOSITION MODELING

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A method is proposed for the calculation of the radiation of inhomogeneous molecular gases at low pressures; the method is based on the summation of the equivalent widths of spectral lines and a quasiexponential model of the absorption band.

In many technological processes, the working medium is a molecular gas active in the IR region of the spectrum. At high temperatures of the medium, radiant energy transfer plays an important role as well as the convective mechanism of heat transfer, whereas carbon and metal-oxide particles emit and absorb radiation over the whole spectral region; the absorption of molecular-gas radiation occurs in vibrational-rotational bands, and beyond the limits of the bands the gas is practically transparent.

Each vibrational-rotational band consists of a more or less regular set of individual spectral lines whose characteristics can only be determined from a knowledge of the position, intensity, and contour shape. The bands with the simplest structure are the absorption bands of diatomic molecules, the wave function of which may be written in the first approximation as a superposition of a rigid rotator and a harmonic oscillator, although no difficulties are usually involved in taking account of anharmonic behavior [1]. The spectra of triatomic molecules — both linear (CO_2) and nonlinear (H_2O , SO_2) — are characterized by considerably greater complexity. At high temperatures, theoretical models of symmetric- or antisymmetric-gyro-scope type [1, 2] do not give the required accuracy and empirical data play a large role.

However, such detailed information on absorption spectra over a broad range of the parameters determining the thermodynamic state of the radiating medium is not only difficult to obtain but also excessive. At low pressures and temperatures $\geq 10^3$ °K, it is necessary to determine the two-parameter function $k_\nu(\rho T)$ — of the order of 10^7 - 10^8 — describing the spectrum of the gas mixture typical for the combustion products in the range 1-15 μm . It is practically impossible to obtain such a volume of data from experiment, and its use for direct calculations involves a huge consumption of machine time. Therefore, in practice, the calculation of radiant transfer in a selective medium is based on models of the band approximately describing the properties of the real spectrum averaged over a small spectral interval of 10-50 cm^{-1} . The models most often used are the isolated-line model, the regular model, and the statistical (or Goody) model [2-6]. A certain loss of accuracy is involved, but this is compensated by the simplicity and ease of review of the results. In consequence of the great

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success of model representations in describing the absorptive capacity of homogeneous molecular gases, experimental results have been analyzed to obtain the band parameters (see [7-10] and elsewhere). The parameters used are the ratio of the mean intensity of lines falling within a considered spectral interval to the mean distance between the lines, S/d , and the ratio of the mean half-width of the lines γ to d .

One of the assumptions on which use of the band model is based is that the spectral interval being considered is surrounded by regions with analogous spectral properties, which allows the contribution of the distant margins of lines not falling within the considered interval $\Delta\nu$ to be taken into account. However, by rejecting this assumption and taking into account sufficiently smooth dependences $S/d(\nu)$ and $\gamma/d(\nu)$ within the limits of an individual vibrational-rotational band, model representations have been successfully transferred to the calculation of the absorptive capacity of all bands for homogeneous gases [6, 11-13].

The importance of the results on the absorptive capacity of homogeneous gases is that they form the basis for methods of calculating the radiant transfer in inhomogeneous volumes.

When there is local thermodynamic equilibrium in the medium, with no scattering and no radiation from outside the medium, the formal solution of the equation of spectral-radiation transfer takes the form

$$J_\nu(R) = \int_R^0 B_\nu(r) k_\nu \exp \left\{ - \int_r^R k_\nu(x) dx \right\} dr, \quad (1)$$

and the spectral absorption coefficient is

$$k_\nu = \sum_i k_{\nu i}^0 p \frac{300}{T} c_i, \quad (2)$$

where $k_{\nu i}^0$ is the value of the absorption coefficient at the frequency ν of the i -th component of the mixture at STP.

It is expedient to introduce the spectral transmission of the layer (r, R)

$$\tau_\nu(r, R) = \exp \left\{ - \int_r^R k_\nu(x) dx \right\}. \quad (3)$$

Then Eq. (1) takes the form

$$I_\nu(R) = \int_R^0 B_\nu \frac{d}{dr} \tau_\nu(r, R) dr. \quad (4)$$

To eliminate the above-mentioned difficulties associated with direct integration in Eq. (4), this equation is integrated over the small spectral interval $\Delta\nu$, within which the Planck function may be regarded as independent of frequency at all values of the temperature realized in the given volume:

$$\bar{I}_\nu(R) \equiv \int_{\Delta\nu} I_\nu(R) d\nu = \Delta\nu \int_R^0 B_\nu(r) \frac{d}{dr} \bar{\tau}_\nu(r, R) dr, \quad (5)$$

where the mean transmission $\bar{\tau}_\nu$ is determined as follows:

$$\bar{\tau}_\nu(r, R) = \frac{1}{\Delta\nu} \int_{\Delta\nu} \tau_\nu d\nu. \quad (6)$$

Thus, the problem reduces to the calculation of the mean transmission along an inhomogeneous path.

If the spectral lines are sufficiently far apart for there to be no pronounced overlapping, the radiation of the volume will be equal to the sum of the radiation corresponding to the individual lines. In the case of collisional broadening of the spectral lines, the absorption coefficient of the line is

$$k_\nu(r) = \frac{S(r)}{\pi} \cdot \frac{\gamma(r)}{(\nu - \nu_0)^2 + \gamma^2(r)} \quad (7)$$

For the remaining calculations it is necessary to introduce a quantity called the equivalent line width W

$$W(r, R) = \int_{-\infty}^{\infty} \{1 - \tau_\nu(r, R)\} d\nu \quad (8)$$

The region of integration in Eq. (8) is taken to be infinite, since the lines are assumed to be isolated. Using W , Eq. (5) may be rewritten in the form

$$\bar{I}_\nu(R) = \int_0^R B_\nu(r) \frac{d}{dr} W(r, R) dr \quad (9)$$

Analytic calculation of the quantity W with the absorption coefficient in Eq. (7) is only possible in the limiting cases of "weak" and "strong" lines. The first approximation corresponds to an optically thin volume and the second to the case of large optical thickness, so that the fraction of the radiation transferred by the central part of the line in Eq. (7) with a width of order γ is negligibly small in comparison with the radiation coming from the margins of the line.

The approach based on the representation of the band as a set of nonoverlapping lines has a limited range of applicability [6, 14]. Taking overlapping of the lines into account must lead to some reduction in absorptive capacity. This effect becomes especially pronounced at pressures of the order of atmospheric, and for large absorbing masses.

Historically, the method first used for the calculation of atmospheric transmission was that proposed by Curtis [15] and Godson [16]. The Curtis-Godson method (CGM), having shown its effectiveness in problems of atmospheric optics, was extended by the efforts of many investigators [17-24] to nonisothermal volumes of molecular gases. The principle of the method is to replace transmission along an inhomogeneous path by transmission through a hypothetical homogeneous layer. In the limiting cases of strong and weak lines, the real layer and the hypothetical equivalent layer accurately coincide, while for parameter values at which this approximation does not hold such a substitution leads to errors, of course. However, numerous calculations made both by the CGM and by an accurate method, as well as comparisons with experiment [20, 25, 26], have shown that the Curtis-Godson approximation is in most cases also satisfactory in the intermediate region.

CGM is most often used in conjunction with the statistical model, which [2, 3] assumes the absence of a correlation between the position of a line and its intensity and also some distribution law of the line intensities in the frequency region considered. The statistical model provides a sufficiently good description of the vibrational-rotational bands of such molecules as H_2O , SO_2 , and CO_2 at high temperatures.

Usually two line-intensity distribution functions are used:

$$P(S) = \delta(S - S_0), \quad (10)$$

$$P(S) = \frac{1}{S_0} \exp\left(-\frac{S}{S_0}\right), \quad (11)$$

where S_0 is some characteristic value of the line strength for the given interval.

In the homogeneous case, the mean transmission in the frequency interval $\Delta\nu$ containing sufficiently many Lorentz lines of the same half-width is given by the formula

$$-\ln\bar{\tau}_\nu = \frac{2\pi\gamma}{d} f(z), \quad (12)$$

where $z = (S_0/d)R/2\pi(\gamma/d)$ and $f(z)$ takes the form of the Ladenburg-Reiche function in the case of a δ -like distribution law and $f(z) = z/\sqrt{1 + (\pi z/2)}$ in the case of an exponential law.

Although the assumptions made in deriving Eq. (12) — that the number of lines is conserved and the half-width of all the lines is the same — may not be satisfied in real conditions, an expression of the form in Eq. (12) for the transmission of an inhomogeneous layer is found to be very valuable in calculations of the radiation of nonisothermal volumes of molecular gases [17, 20, 25, 26]. In [17, 26], the traditional formulation of CGM was somewhat modified to take account of the possible appearance of new lines in the considered spectral interval. The merit of this method is that it is possible to use data on S/d and γ/D determined experimentally on isothermal radiation.

The standard procedure for extending results valid for homogeneous layers to the case of an inhomogeneous path is to use mean values over the optical path — $\bar{k} = (\bar{S}/d)$ and $\bar{\beta} = (\bar{\gamma}/d)$ — in the expressions for the mean transmission or the equivalent linewidth. The rules for the introduction of these mean values are as follows:

$$\begin{aligned} \omega &= \int_0^R \rho(x) dx, \quad \bar{k} = \frac{1}{\omega} \int_0^R \left(\frac{S}{d}\right) \rho(x) dx, \\ \bar{\beta} &= \frac{1}{\omega\bar{k}} \int_0^R \left(\frac{S}{d}\right) \left(\frac{\gamma}{d}\right) \rho(x) dx, \quad z = \bar{k}\omega/\bar{\beta}. \end{aligned} \quad (13)$$

In [20], an investigation of radiant transfer in a nonisothermal volume of water vapor in the 2.7- μm band, which is a combination of three basic bands, this version of CGM was called the equivalent-line method. However, in the given spectral range, with increase in temperature, a large number of so-called "hot" vibrational-rotational bands begins to appear; these bands correspond to a vibrational transition from an excited state. There is a rapid rise in the intensity of lines that are very weak at normal temperatures, and their contribution becomes significant. To take account of these new lines, it was suggested that transmission should be represented as the product of the transmission for individual vibrational-rotational bands

$$\bar{\tau} = \prod_{j=1}^3 \prod_{v_1=0}^{\infty} \prod_{v_2=0}^{\infty} \prod_{v_3=0}^{\infty} \bar{\tau}(v_i \rightarrow v_i + \delta_{ij}), \quad (14)$$

where $v_i \rightarrow v_i + \delta_{ij}$ denotes the transition from the quantum state defined by the triad of numbers v_1, v_2, v_3 to that defined by $v_1 + \delta_{1j}, v_2 + \delta_{2j}, v_3 + \delta_{3j}$; for the 2.7- μm band of the H_2O molecule, the values of δ_{ij} are given by the expression

$$\delta_{ij} = \begin{vmatrix} 0 & 2 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}. \quad (15)$$

The form of the transmission in Eq. (14) is valid when the individual bands are statistically independent. It was demonstrated in [1] that this independence prevails for overlapping bands of different absorbing components of a gas mixture. Comparison of calculations

for water vapor based on the assumption in Eq. (14) with experiment have shown that this assumption is sufficiently good [20].

In the nonisothermal case, the transmission for each vibrational-rotational band is given in a form analogous to Eq. (13). This method is called the hot-band model.

The accuracy of CGM calculations of the absorption of nonisothermal molecular-gas layers has been subjected to thorough experimental and theoretical verification. In [17], experimentally measured Goody-model fine-structure parameters were used to calculate the two-layer transmission of water vapor. At the same time, the transmission was measured experimentally. The layer temperatures took the two values 637 and 1273°K, and the water vapor pressure was varied in the range 50-150 mm Hg. The path length of the beam in each cell could be varied from 3 to 60.9 cm. The results for the transmission obtained by experiment and CGM calculation agree to a very high accuracy (~2%). Also in [17], experimental results are given for the transmission through the flames of three burners whose main absorbing component is CO₂. The flame temperature was regulated by controlled additions of cold carbon dioxide. The agreement between theory and experiment was also satisfactory in this case.

Numerous results obtained by experiment and CGM calculation for the transmission of inhomogeneous isothermal and nonisothermal two-layer regions of water vapor in the 2.7- μ m band were compared in [25, 21, 27]. The analytic expressions for the fine-structure parameters used in the calculations are also given. Calculation and experiment agree with an accuracy of $\leq 10\%$ for isothermal and nonisothermal layers.

In [26], the radiation of water vapor in the 2.7- μ m region with a known temperature distribution modeled by several isothermal cells was measured. The temperature was varied in the range 900-1200°K and the pressure in the range 200-500 mm Hg. The results for the radiation obtained by the equivalent-line model are found to be in good agreement with the experimental results.

In [20], experimental results on the absorption and radiation of the whole of the 2.7- μ m band of water vapor were compared with the results obtained using the equivalent-line model and the hot-band model. The gas was in a vertical cuvette of length 48 cm; the temperature difference reached 600°K; the pressure was atmospheric. It was shown that the equivalent-line model gives rather higher results than the hot-band model, and the agreement with experiment is not so good. (The mean error is ~15%.) But, on the whole, the results of the comparison must be regarded as good over the whole of the range investigated experimentally.

In [28] it was pointed out that one of the main sources of error in CGM is the inaccurate approximation of the spatial derivative of the mean transmission, and it was suggested that mean values should only be introduced in the expression for the derivative of the equivalent linewidth. This approach was developed in [29, 30]. In this method there appears a two-parameter function depending on the mean optical depth and the ratio of the local value of the parameter β to the mean value over the path. At the cost of some complication of the calculation procedure, it is possible to eliminate the appearance of nonphysical regions of transmission increase with increase in optical depth, as observed in CGM. The difficulty which arises in this method is that it is necessary to determine the distribution function of line strengths depending both on local values and on mean values over the path; this difficulty is overcome by assuming that it is possible to factorize this function and that the line strength of each line within the interval $\Delta\nu$ is proportional to its mean value. It follows from these assumptions that all the lines considered have the same temperature dependence. This means that "hot" lines are relatively poorly taken into account in this method. As a result, the mean derivative of the equivalent linewidth takes the form

$$\frac{1}{d} \frac{dW}{dr} = c(r) p(r) \bar{k}(r) y(z, \sigma), \quad (16)$$

where the two-parameter function $y(z, \sigma)$ is given in the form of a definite integral depending on the optical depth z and $\sigma = \gamma/\bar{\gamma}$. In [29] expressions are given for $y(z, \sigma)$ in the case of Lorentz and Doppler contours, and the analytic properties of these functions are analyzed.

There are definite objections to the simple extension of the above method for the calculation of the radiation of inhomogeneous gas volumes to the case of low pressures. Primarily, this is because all these methods use experimental data on homogeneous gases either

directly or by determining certain parameters appearing in the theory from empirical data. At present, it is very difficult to obtain the required experimental information at low temperatures, when the spectral-line contour is of composite or Doppler form. Systematic numerical calculations of layer transmission at low pressure have been made only for CO and CO₂ and not for water vapor. The method which has been developed is based on the approximate methods of describing the absorptive capacity of homogeneous layers at low pressure proposed in [31, 32], while the idea of the same approach was formulated in [19].

Detailed numerical calculations have shown that, with an accuracy of no worse than 10%, the absorptive capacity of a layer may be uniquely described if the sum of the equivalent linewidths within the spectral range $\Delta\nu$ considered is known:

$$u_\nu = \frac{1}{\Delta\nu} \sum_i \int_{-\infty}^{\infty} \left\{ 1 - \exp \left[- \int_0^r S_i(T) \varphi_i(p, T, \nu) dr \right] \right\} d\nu. \quad (17)$$

Here the frequency is measured from the center of each line. The mean absorption over $\Delta\nu$ of the layer is well described by a simple formula following from the statistical model

$$A_\nu = 1 - \exp(-u_\nu). \quad (18)$$

In the worst cases ($A_\nu \sim 0.6-0.8$), the error of the approximation in Eq. (18) reaches ~30%. It arises because the effects of line overlapping are not taken sufficiently accurately into account. It should be expected that this error would decrease with decrease in pressure, as a result of the fall in the role of the remote margins of the spectral lines.

The next approximation is to represent a spectral line with a composite contour as a superposition of two effective lines with a purely Lorentz and a purely Doppler contour, when

$$S_L = S \left(\frac{\gamma_L}{\gamma_\nu} \right)^2, \quad (19)$$

$$S_D = S \frac{\gamma_D}{\gamma_\nu} \left(1 - \frac{\gamma_L}{\gamma_\nu} \right), \quad (20)$$

$$\gamma_\nu = 0.5(\gamma_L + \sqrt{\gamma_L^2 + 4 \ln 2 \cdot \gamma_D^2}). \quad (21)$$

(The well-known relations of [2, 25] may be used to describe the dependence of the half-widths of the Lorentz γ_L and Doppler γ_D lines on temperature, pressure, and the composition of the mixture.)

By means of this approximation, which is no worse than the accuracy of the method, the problem may be reduced, for arbitrary pressure p , to separate calculations of the layer transmission for the case of Lorentz and Doppler mechanisms of line broadening:

$$u_\nu = u_{L\nu} + u_{D\nu}, \quad (22)$$

$$u_{j\nu} = \frac{1}{\Delta\nu} \sum_i \int_{-\infty}^{\infty} d\nu \left\{ 1 - \exp \left[- \int_0^r S_i \gamma_\nu^{-1} \varphi_j \left(\frac{\nu}{\gamma_\nu} \right) \varepsilon_j dr \right] \right\}. \quad (23)$$

Here

$$j = L \text{ or } D, \quad \varphi_L = \frac{1}{\pi} \frac{1}{1 + (\nu/\gamma_\nu)^2}, \quad \varphi_D = \frac{1}{\sqrt{\pi}} e^{-(\nu/\gamma_\nu)^2}, \\ \varepsilon_L = (\gamma_L/\gamma_\nu)^2, \quad \varepsilon_D = (\gamma_D/\gamma_\nu) (1 - \gamma_L/\gamma_\nu).$$

If a method of determining the line strength is available, the above approximation allows the mean absorption of the layer to be calculated using modern computers. For diatomic molecules, the line strengths may be calculated without great difficulty at any reasonable temperature, and for carbon dioxide and water vapor with sufficient accuracy at temperatures up to $T \leq 1500^\circ\text{K}$. However, it is necessary to develop simple models allowing the calculation

to proceed without unnecessarily cumbersome computations. Of the very many models investigated in the literature, two of the simplest and most often used are as follows:

1) the mean-line model, which assumes that in the interval $\Delta\nu$ there are n lines of equal intensity and line strength $S(T)$;

2) the quasiexponential model, which assumes that in the given spectral interval there are n series of lines, whose intensity is distributed according to an exponential law: $S_m = \kappa \cdot S e^{-\kappa m}$, where m is the number of the line series, and the parameter κ characterizes the width of the intensity distribution of the lines, i.e., determines the number of sufficiently strong lines in the series. As $\kappa \rightarrow \infty$, model 2 transforms to model 1, since the series degenerate to a single line. As $\kappa \rightarrow 0$, model 2 transforms in the limit to a weak line. Thus, the parameter κ may be used as a characteristic of the role of "hot" lines in considering inhomogeneous volumes.

In place of Eq. (17), models 1 and 2 have, respectively, the following expressions

$$u^1 = \frac{n}{\Delta\nu} \int_{-\infty}^{\infty} d\nu \left\{ 1 - \exp \left[- \int_0^r S \varphi dr \right] \right\}, \quad (24)$$

$$u^2 = \frac{n}{\Delta\nu} \int_0^{\infty} dm \int_{-\infty}^{\infty} d\nu \left\{ 1 - \exp \left[- \int_0^r S \kappa e^{-\kappa m} \varphi dr \right] \right\}. \quad (25)$$

To determine the parameters of models 1 and 2, consider a homogeneous layer of gas with Lorentz-broadened spectral lines. In this case, it follows from Eqs. (24) and (25) that

$$u_L^1 = \frac{n}{\Delta\nu} S \omega \Phi_L^1 \left(\frac{S \omega}{\pi \gamma} \right), \quad (26)$$

$$u_L^2 = \frac{n}{\Delta\nu} S \omega \Phi_L^2 \left(\frac{S \kappa \omega}{\pi \gamma} \right), \quad (27)$$

where the functions Φ_L^1 and Φ_L^2 are defined as follows

$$\Phi_L^1(z) = \frac{4}{\pi} \int_0^{\infty} \frac{x^2 dx}{(1+x^2)^2} \exp \left(- \frac{z}{1+x^2} \right), \quad (28)$$

$$\Phi_L^2(z) = \frac{4}{\pi z} \int_0^{\infty} \frac{x^2 dx}{(1+x^2)} \left\{ 1 - \exp \left(- \frac{z}{1+x^2} \right) \right\}. \quad (29)$$

These single-parameter functions, representing the growth curves for a characteristic line with a Lorentz profile, are easily tabulated. In addition, they may be represented by a sufficiently good (with an error no worse than 10%) analytic approximation

$$\Phi_L^1(z) = \left(1 + \frac{\pi}{4} z \right)^{-1/2}, \quad (30)$$

$$\Phi_L^2(z) = \left(1 + \frac{\pi}{16} z \right)^{-1/2}, \quad (31)$$

which allows the relationship between the parameters of models 1 and 2 and the experimentally measured quantities $(S/d)_e$ and d_e to be established:

$$n^1 = \frac{\Delta\nu}{d_e}, \quad S^1 = \left(\frac{S}{d} \right)_e d_e,$$

$$\left(\frac{n}{\Delta v} S\right)^2 = \left(\frac{S}{d}\right)_e, \quad \left(\frac{\kappa}{4} \frac{\Delta v}{n}\right)^2 = d_e.$$

Note that for a quasiexponential model containing three parameters (S , κ , and n), the unique determination of these parameters must involve additional considerations, e.g., the temperature dependence of $(S/d)_e$ and d_e .

For a purely Doppler line contour, analogous calculations give the following result:

$$u_D^1 = \frac{n}{\Delta v} S \omega \Phi_D^1 \left(\frac{S \omega}{\gamma \sqrt{\pi}} \right), \quad (32)$$

$$u_D^2 = \frac{n}{\Delta v} S \omega \Phi_D^2 \left(\frac{S \kappa \omega}{\gamma \sqrt{\pi}} \right), \quad (33)$$

where

$$\Phi_D^1 = \frac{4}{\sqrt{\pi}} \int_0^{\infty} x^2 \exp(-x^2 - z e^{-x^2}) dx, \quad (34)$$

$$\Phi_D^2 = \frac{4}{z \sqrt{\pi}} \int_0^{\infty} x^2 [1 - \exp(-z e^{-x^2})] dx. \quad (35)$$

The functions Φ_D^1 and Φ_D^2 , corresponding to equivalent growth curves, are approximated with 5% accuracy in the Doppler case by the expressions

$$\Phi_D^1(z) = \frac{[1 + \ln(1 + 1.49z)]^{1/2}}{1 + 0.9085z}, \quad (36)$$

$$\Phi_D^2(z) = \frac{[1 + \ln(1 + 0.7988z)]^{3/2}}{1 + 1.35/z}. \quad (37)$$

As is evident from Eqs. (30) and (31), the different models lead to practically the same expressions for the layer transmission in the case of Lorentz broadening of the lines [25]. This means that it is impossible to make a decisive choice of model on the basis of experimental data on the absorption of homogeneous layers at high pressure. However, in the case of Doppler broadening at large absorbing masses, the different models lead to qualitatively different results. It may be shown by comparison with direct numerical calculations that the quasiexponential model, effectively taking into account the presence of weak lines, always leads to the best results. Therefore, in investigating the transmission of inhomogeneous gases, attention will be restricted to the quasiexponential model.

The expression for the sum of the equivalent linewidths appearing in Δv takes the form (see Eq. (25))

$$u_j = \frac{n}{\Delta v} \int_0^{\infty} dm \int_{-\infty}^{\infty} dv \left\{ 1 - \exp \left[- \int_0^r S \kappa e^{-\kappa m} \varphi_j \left(\frac{v}{\gamma} \right) \gamma^{-1} \varepsilon_j dr \right] \right\}. \quad (38)$$

In the case of Lorentz lines, choosing the appropriate method of averaging κ and γ over the layer, it is not difficult to pass from Eq. (38) to a formula of Curtis-Godson type. However, for the Doppler case, this is not possible without cumbersome calculations. Therefore, integrating by parts with respect to the frequency in Eq. (38) and introducing the variables $y = v/\gamma$ and $t = \kappa m$, the following expression is obtained

$$u_j = \frac{2n}{\Delta v} \int_0^r S \varepsilon_j dr \int_0^{\infty} dt \int_0^{\infty} y^2 dy e^{-t} \left[- \frac{\partial \varphi_j(y)}{\partial y} \exp \left[- \int_0^t S' \kappa' e^{-\frac{\kappa'}{\gamma'} t} \varphi_i \left(\frac{\gamma'}{\gamma} y \right) \frac{\varepsilon_j'}{\gamma'} dr' \right] \right]. \quad (39)$$

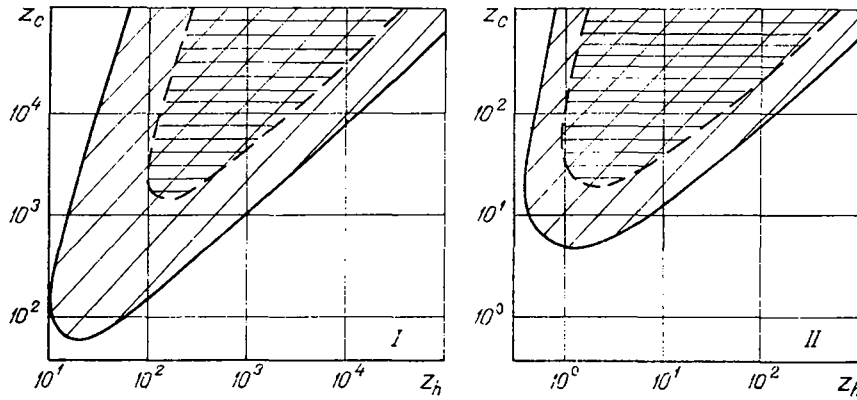


Fig. 1. Regions of the parameters z_h and z_c in which the relative error of Eq. (40) is more than 30% (light shading) and 50% (heavier shading): I) $\alpha = T_h/T_c = 3$; II) $\alpha = T_h/T_c = 9$.

To simplify the calculations, set $\kappa' = \kappa$ and $\gamma' = \gamma$ in the exponent of the integrand. Then Eq. (39) takes a very simple form:

$$u_j = \frac{n}{\Delta\nu} \int_0^r S \epsilon_j dr \Phi_j^2 \left(\frac{\kappa}{\gamma} \int_0^r S' \epsilon_j' dr' \right). \quad (40)$$

Calculations by Eq. (38) are comparable in bulk with CGM calculations.

The accuracy of the approximation in Eq. (40) was analyzed using a numerical calculation for a two-layer region according to Eq. (38). It was assumed that $\kappa \sim T^{-1}$ (this dependence is characteristic of most spectral intervals and most molecular gases). In this case, U_j depends on three parameters: the temperature ratio of the two layers $\alpha = T_h/T_c$, and the optical depths at the center of the effective line z_h and z_c . In Fig. 1, the regions of the parameters z_h and z_c in which the relative error of the approximation in Eq. (40) is more than 30% (light shading) and 50% (heavier shading) in the case of Doppler lines is shown. For Lorentz broadening with $\alpha \leq 10$, the error of Eq. (40) when $z < 10^5$ was no more than 30%. Thus, even for sufficiently strong nonisothermal behavior, the applicability of Eq. (40) is sufficiently broad, and covers practically all the cases of practical interest, with the possible exception of transmission through the atmosphere.

In recent attempts to improve methods of calculating the thermal radiation of molecular gases (e.g., [29]), the main attention was directed toward improving the accuracy of the spatial derivative of the equivalent width of the effective line in the nonisothermal case. There has been no discussion of the correct summation of equivalent linewidths over the given spectral interval $\Delta\nu$. However, it is no less important to take account of all the lines (including the weak lines) arising in transitions between excited levels, especially for radiation transfer in a strongly inhomogeneous medium. These shortcomings are avoided by a method based on the introduction of distribution functions depending only on the spectroscopic characteristics of the molecule. The line strength corresponding to a transition between an upper level of energy E' and a lower level of energy E'' may be written in the form

$$S(E', E'') = \frac{273}{T} \frac{P}{Q(T)} M(E', E'') \exp\left(-\frac{E''}{T}\right), \quad (41)$$

where $Q(T)$ is the statistical sum of the molecule; $M(E', E'')$ corresponds to the line strength for a transition from the level E'' with a population equal to the Loschmidt number.

The line-strength distribution function is now replaced by the function $f(\epsilon, m)$ determining the density of the number of spectral lines of strength m within the interval $\Delta\nu$ which are due to transitions from the low level ϵ . The sum of equivalent widths for the nonisothermal layer may then be written in the form

$$U_v = \int_0^{\infty} d\varepsilon \int_0^{\infty} dm f(\varepsilon, m) W(\varepsilon, m), \quad (42)$$

where

$$W(\varepsilon, m) = \int_{-\infty}^{\infty} \left\{ 1 - \exp \left[-m \int_0^r \frac{273}{T} \frac{P}{Q(T)} \right] \varphi(v, r) \exp \left(-\frac{\varepsilon}{T} \right) dr \right\} dv. \quad (43)$$

In deriving this expression, it was assumed that all the lines have the same contour $\varphi(v, r)$.

The function $f(\varepsilon, m)$ may in principle be determined theoretically. However, it is more reliable to find an approximate expression on the basis of experimental data for the transmission of homogeneous layers. Substituting Eq. (42) into the formula for the transmission, the following integral equation is obtained on the basis of the statistical model:

$$\ln \tau_e(R, T) = \int_0^{\infty} d\varepsilon \int_0^{\infty} dm W(\varepsilon, m; R, T) f(\varepsilon, m), \quad (44)$$

where $\tau_e(R, T)$ is the experimental value for the layer transmission of geometric dimension R at a temperature T .

Since the main bulk of the experimental data has been obtained for pressures close to normal, the line contour will be assumed to be Lorentzian. In the limiting cases of small and large optical depths, the experimental data on transmission are approximated by the expressions

$$-\ln \tau_e = k(T) \rho \frac{273}{T} R, \quad -\ln \tau_e = 2 \left\{ k(T) \rho \frac{273}{T} \frac{\gamma(T)}{d(T)} R \right\}^{1/2} \quad (45)$$

respectively. Then from Eq. (44), two integral equations may be obtained:

$$k(T) Q(T) = \int_0^{\infty} f(\varepsilon) \overline{m(\varepsilon)} \exp \left(-\frac{\varepsilon}{T} \right) d\varepsilon, \quad (46)$$

$$\left\{ k(T) \frac{Q(T)}{d(T)} \right\}^{1/2} = \int_0^{\infty} f(\varepsilon) \sqrt{\overline{m(\varepsilon)}} \exp \left(-\frac{\varepsilon}{2T} \right) d\varepsilon, \quad (47)$$

where

$$f(\varepsilon) = \frac{1}{\Delta v} \int_0^{\infty} f(\varepsilon, m) dm; \quad \overline{m(\varepsilon)} = \frac{1}{f(\varepsilon) \Delta v} \int_0^{\infty} f(\varepsilon, m) m dm; \quad \sqrt{\overline{m(\varepsilon)}} = \frac{1}{f(\varepsilon) \Delta v} \int_0^{\infty} f(\varepsilon, m) \sqrt{m} dm. \quad (48)$$

Equation (48) gives integral Laplace transforms for the functions $f(\varepsilon) \overline{m(\varepsilon)}$ and $f(\varepsilon) \sqrt{\overline{m(\varepsilon)}}$. These functions may be determined by means of the well-known numerical methods of inverse Laplace transformation, using experimental data on the dependences $k(T)$ and $d(T)$. If it is assumed that

$$\sqrt{\overline{m(\varepsilon)}} = \sqrt{\overline{m(\varepsilon)}}, \quad (49)$$

then

$$\int_0^{\infty} f(\varepsilon, m) W(\varepsilon, m; R, T) dm = f(\varepsilon) W(\varepsilon, \overline{m(\varepsilon)}; R, T), \quad (50)$$

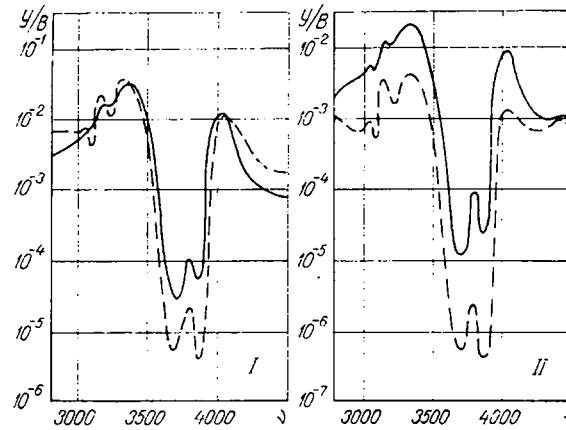


Fig. 2. Radiation intensity of a hot layer of water vapor in the 2.7- μ m band transmitted through the atmosphere ($T_h = 1800^\circ\text{K}$, $T_c = 300^\circ\text{K}$). The dashed curve corresponds to CGM calculation. I) $\gamma_h = \gamma_c = 0.1 \text{ cm}^{-1}$; II) $\gamma_h = 0.01 \text{ cm}^{-1}$, $\gamma_c = 0.1 \text{ cm}^{-1}$.

and to calculate the sum in Eq. (42) it is sufficient to know the functions $f(\epsilon)$ and $\overline{m(\epsilon)}$. By introducing the functions in this way, the satisfaction of the limiting relations in Eqs. (46) and (47) is ensured.

To determine the approximate form of the functions $f(\epsilon)$ and $\overline{m(\epsilon)}$ in the present work, the method of moments is used. The expressions taken as the trial functions were as follows:

$$f(\epsilon) = a(v) \exp[-c(v)(\epsilon - b(v))], \quad \overline{m(\epsilon)} = p(v) \exp[-h(v)(\epsilon - b(v))] \quad \text{for } \epsilon \geq b$$

and

$$f(\epsilon) = \overline{m(\epsilon)} = 0 \quad \text{for } \epsilon < b. \quad (51)$$

Depending on the frequency range, the constants a , c , p , h , and b are determined from the approximation of experimental data for $k(T)$ and $d(T)$ [33] by the least-squares method. When $c = h = 0$, Eq. (51) yields the line-strength distribution function $P(S) \sim S^{-1}$ cut off in the region of large lines, which was used in [30]. The spectral-line density d^{-1} in this case depends linearly on the temperature.

To illustrate the difference between the method here proposed and CGM, Fig. 2 compares the results obtained by the two methods for the spectral intensity of the radiation of a hot water-vapor layer in the 2.7- μ m band transmitted through the atmosphere; the temperature of the hot layer is 1800°K and that of the cold layer 300°K; the absorbing masses are 0.24 atm·cm and 1000 atm·cm for the hot and cold layers, respectively; the half-width of the lines in both the hot and cold layers is the same in case I, while in case II the half-width is 0.01 cm^{-1} in the hot layer and 0.1 cm^{-1} in the atmosphere. When the half-width of the lines in the hot and cold layers is the same, the method gives approximately the same results as CGM in the spectral regions corresponding to a maximum of transmitted radiation. The difference at the center of the band is insignificant, since the total level of radiation there is small. In case II, the transmitted radiation is considerably higher than that found in CGM. This is because the atmosphere absorbs only the lines corresponding to transitions between low energy levels, and transmits "hot" lines. Therefore, in the method here developed, the transmitted radiation is little affected by the half-width of the line in the hot layer, whereas in CGM it is reduced. This difference indicates that the method developed in the present work provides a better qualitative description of thermal-radiation transfer through a large absorbing layer of gas.

LITERATURE CITED

1. S. S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities, Addison-Wesley (1959).
2. R. M. Goody, Atmospheric Radiation, Oxford Univ. Press (1964).
3. R. M. Goody, Q. J. R. Met. Soc., 78, No. 536 (1952).
4. W. Malkmus and A. Thomson, J. Quant. Spectrosc. Radiat. Transfer, 2, 17 (1962).
5. G. N. Plass, Appl. Opt., 6, 1995 (1967).

6. C. L. Tien, "Radiation properties of gases," in: Progress in Heat Transfer [Russian translation], Mir, Moscow (1971), p. 280.
7. V. R. Stull, P. J. Wyatt, and G. N. Plass, Appl. Opt., 3, 243 (1964).
8. S. S. Ferriso, J. Chem. Phys., 37, 9 (1962).
9. D. E. Burch and D. Williams, Appl. Opt., 7, 587 (1962).
10. D. K. Edwards, J. Opt. Soc. Am., 50, 617 (1960).
11. D. K. Edwards and W. A. Menard, Appl. Opt., 3, 621, 847 (1964).
12. C. L. Tien and J. E. Lowder, Int. J. Heat Mass Transfer, 9, 698 (1966).
13. L. S. Wang, J. Quant. Spectrosc. Radiat. Transfer, 8, 851, 1233 (1968).
14. G. N. Plass, J. Opt. Soc. Am., 50, 9 (1960).
15. A. R. Curtis, Q. J. R. Met. Soc., 78, 638 (1952).
16. W. L. Godson, J. Meteorol., 12, 272 (1955).
17. B. Krakow, H. J. Babrow, I. J. McLay, and A. L. Shabott, Appl. Opt., 5, 1791 (1966).
18. L. Klein and L. I. Penzias, AIAA J., 5, 1690 (1967).
19. G. N. Plass, J. Opt. Soc. Am., 48, 10 (1958).
20. M. M. Weiner and D. K. Edwards, J. Quant. Spectrosc. Radiat. Transfer, 8, 1171 (1968).
21. S. H. Chan and C. L. Tien, J. Quant. Spectrosc. Radiat. Transfer, 9, 1261 (1969).
22. R. D. Cess and L. D. Wang, Int. J. Heat Mass Transfer, 13, 547 (1970).
23. D. K. Edwards and S. J. Morizumi, J. Quant. Spectrosc. Radiat. Transfer, 10, 175 (1970).
24. D. K. Edwards and A. Balakrishnan, Int. J. Heat Mass Transfer, 16, 25 (1973).
25. R. M. Huffaker, J. Quant. Spectrosc. Radiat. Transfer, 8, 87 (1968).
26. F. S. Simmons, Appl. Opt., 5, 1801 (1966).
27. K. Ya. Kondrat'ev and Yu. M. Timofeev, Izv. Akad. Nauk SSSR, Fiz. Atmos. Okeana, 5, No. 4 (1969).
28. C. H. Lindquist and F. S. Simmons, J. Quant. Spectrosc. Radiat. Transfer, 12, 807 (1972).
29. S. I. Young, J. Quant. Spectrosc. Radiat. Transfer, 15, 483, 1137 (1975).
30. S. I. Young, J. Quant. Spectrosc. Radiat. Transfer, 18, 1 (1977).
31. V. S. Matveev, Zh. Prikl. Spektrosk., 12, 486 (1970).
32. V. S. Matveev, Zh. Prikl. Spektrosk., 16, 228 (1972).
33. C. B. Ludwig, Appl. Opt., 10, 1057 (1971).