ON THE COMPUTATION OF ABSORPTION IN THE VIBRATIONAL-ROTATIONAL SPECTRUM BAND

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Integral absorption in a spectrum band is represented as a series. Monotone growth of the coefficients in the series and their limits are established. The results are used to analyze known absorption formulas and to compare approximate formulas.

Heat exchange occurs mainly because of radiation and absorption of a medium with a vibrational-rotational spectrum in the combustion chambers of steam generators, gas turbines, and other aggregates. The characteristics of the spectrum band must be taken into account in computations of the heat exchange by radiation. The geometric optics quantity A, called the integrated absorption in the spectrum band,

$$A = \Delta\omega \int_0^\infty [1 - \exp(-\alpha_\omega(y)\, x)]\, dy \tag{1}$$

$$\alpha_\omega = \alpha_0 \psi(y), \quad \alpha_0 = S / \Delta\omega, \quad y = |\omega - \omega_0| / \Delta\omega$$

has acquired the central role.

Here ω is the wave number (cm^{-1}), ω_0 is the location of the center of the band, $\Delta\omega$ is a width parameter, S is the integrated intensity ($cm^{-1}/m \cdot atm$), x is the ray path ($m \cdot atm$), α_ω is the spectral coefficient of absorption $(m \cdot atm)^{-1}$, and ψ is a dimensionless function. A special section of the theory including a model of the bands is devoted to the quantity A.

Furthermore, in place of (1) let us examine the series for dimensionless absorption obtained by expanding the exponential term in (1).

$$\bar{A} = \frac{A}{\Delta\omega} = \alpha_1 x - \alpha_1\alpha_2 \frac{x^2}{2!} + \ldots + (-1)^{i+1} \frac{x^i}{i!} \prod_{j=1}^{i} \alpha_j \ldots \tag{2}$$

$$\prod_{j=1}^{i} \alpha_j = \int_0^\infty \alpha_\omega{}^i dy \tag{3}$$

THEOREM. The sequence of coefficients of the series (2) increases monotonely to the limit

$$\lim_{i\to\infty} \alpha_i = (\alpha_\omega)_{\max}, \quad i \geqslant 2\ . \tag{4}$$

Here $(\alpha_\omega)_{max}$ is the maximum spectrum absorption coefficient. Let us first note in the proof that the band can always be rearranged so that the spectrum coefficient α_ω would diminish monotonely from the maximum value at v = 0 to zero at infinity. Here $v = \nu/\Delta\omega$, ν is the value of the argument after rearrangement of the wave-number axis.

Let us replace the contour of the rearranged band by the line

$$\alpha_\omega = (\alpha_\omega)_{\max}(1 - \nu / \nu_0)$$

where v_0 is the abscissa at which the coefficient $\alpha_\omega(v)$ decreases to zero. The line contour covers the actual contour or touches it. The theorem is thereby proved under less favorable conditions. It follows from (3) that

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$$\alpha_i = (\alpha_\omega)_{\max} \frac{\int_0^{v_0} (1 - v/v_0)^i \, dv}{\int_0^{v_0} (1 - v/v_0)^{i-1} \, dv} = \frac{i}{i+1} (\alpha_\omega)_{\max} .$$

The theorem is proved.

A singularity originates as $v_0 \to \infty$. But in this case it is sufficient to examine a rectangular contour overlapping all the others. A simple result is obtained: all the α_j are equal and the series (2) is curtailed exactly.

$$\bar{A} = 1 - \exp(-\alpha_i x)$$

The theory is verified easily in examples of single lines with dispersion of Doppler contours. It can be proved phenomenologically if a physical meaning is ascribed to the coefficients α_j. Thus, the coefficient α_1 determines the absorption of the black flux in the band at the initial section (for x = 0). The coefficient α_2 determines the absorption of the reradiated flux in the initial section. The coefficient α_3 determines the reradiation of the described absorbed flux if there is no energy redistribution in the wave numbers in this as in the later stages of the interaction between the radiation and the gas. The coeffient α_4 determines the absorption of the described reradiated flux in the initial section, etc. In principle, the number of reradiations is infinite. The flux components with lower values of α_ω vanish with reradiation; there remains the last component with the maximum spectrum coefficient of absorption.

An investigation of the known functions $\bar{A}$ is possible after they have been differentiated and the sequence α_j has been determined on the basis of the equality

$$\prod_{j=1}^{i} \alpha_j = (-1)^{i+1} (\partial^i \bar{A} / \partial x^i)_{x=0} = (-1)^{i+1} \bar{A}_0^{(i)} . \tag{5}$$

Divergences from the theorem indicate the incorrectness of the formula for $\bar{A}$ being investigated. Here $(\alpha_\omega)_{\max}$ can be found by means of the theorem (4).

The determination of the derivatives $A_0^{(i)}$ will often be awkward. Only the first derivatives are found successfully. In that case, deductions can be made for low and medium thicknesses, when the first coefficients α_1, α_2,... play a fundamental part. As the gas layer thickens, their role is reduced, although not rapidly since the optical thickness on the bandheads remains small for very high layer thicknesses.

Let us examine the class of formulas obtained on the basis of the band models

$$\bar{A} = \int_0^\infty A_\omega dy . \tag{6}$$

Here A_ω is the mean absorption in a sufficiently narrow spectrum range. The quantities A_ω are described by narrowband models. It has been shown in [1] that

$$z = \frac{sx/d}{\sqrt{1 + axs/\beta d}}, \quad \beta = 2\pi \frac{b}{d}, \quad 2 \geqslant a \geqslant \frac{\pi}{2} \tag{7}$$

can be taken as the argument of A_ω in all models from the regular to the statistical.

Here s, b, and d are the integrated intensity, line halfwidth, and mean spacing between them. The number a depends on the model taken. It follows from (5) and (6) that

$$\prod_{j=1}^{i} \alpha_j = (-1)^{i+1} \int_0^\infty A_{\omega 0}^{(i)} dy, \quad A_{\omega 0}^{(i)} = (\partial^i A_\omega / \partial x^i)_{x=0} . \tag{8}$$

The derivative $A_{\omega 0}^{(i)}$ consists of a sum in whose terms diverse derivatives $z_0^{(k)} = (\partial^k z / \partial x^k)_{x=0}$ including the higher derivative $z_0^{(i)}$ enter. In conformity with (7)

$$z_0^{(k)} = (-1)^{k+1} \left(\frac{s}{d}\right)^k \left(\frac{a}{2\beta}\right)^{k-1} k \times 1 \times 3 \times 5 \times \ldots \times (2k-3) .$$

After substituting $z_0^{(k)}$ in (8), we obtain

$$\prod_{j=1}^{i} \alpha_j = F_i(\beta) \int_0^\infty \left(\frac{s}{d}\right)^i dy \tag{9}$$

if the parameter β is independent of the wave number.

The function F_i is a polynomial whose terms contain the factor $(1/\beta)^{k-1}$ for k = 1, 2, ..., i.

The dependence of the parameter s/d on the wave number is determined in the so-called wideband model [2]

$$s/d = \alpha_0 f(y), \quad \alpha_0 = S/\Delta\omega, \quad \int_0^\infty f(y)\,dy = 1. \tag{10}$$

The function $f(y)$ is the envelope of the band. From (9) and (10) follows

$$\prod_{j=1}^{i} (\alpha_j/\alpha_0) = C_i F_i, \qquad C_i = \int_0^\infty f^i(y)\,dy. \tag{11}$$

As is seen, the sequence of numbers C_i is determined only by the wideband model. The theorem is satisfied for any function $f(y)$ remotely similar to the envelope of the band. The sequence of numbers F_i is determined only by the narrowband model. It does not determine the pressure dependence of the absorption.

Let us turn to specific formulas of integrated absorption which are extensively used.

Wideband Model of Edwards [2]. The envelope of the band corresponds to the model of a rigid rotator

$$f(y) = y \exp(-y^2). \tag{12}$$

Here the Q-branch is discarded, and the P- and R- branches are assumed symmetric. The parameter β is independent of the wave number. The parameter $\Delta\omega$ characterizes one branch of the band, which alters part of (10) and (11) somewhat.

$$C_1 = 2\int_0^\infty f(y)\,dy = 1, \quad C_i = 2\int_0^\infty f^i(y)\,dy = \Gamma\left(\frac{i+1}{2}\right) \Big/ i^{(i+1)/2}, \qquad i \geqslant 2. \tag{13}$$

A simpler model $f(y) = \exp(-y)$ for which $C_i = 1/i$ is often used.

The Goode model

$$A_\omega = 1 - e^{-z}, \quad z = \frac{sx/d}{\sqrt{1 + 2sx/\beta d}} \qquad (\beta = 2\pi b/d) \tag{14}$$

is usually relied upon as narrowbanded.

Using (14), six quantities are represented below:

F_i:

i	F_i
1	1
2	$1 + \frac{2}{\beta}$
3	$1 + \frac{6}{\beta} + \frac{9}{\beta^2}$
4	$1 + \frac{12}{\beta} + \frac{48}{\beta^2} + \frac{60}{\beta^3}$
5	$1 + \frac{20}{\beta} + \frac{150}{\beta^2} + \frac{480}{\beta^3} + \frac{524.8}{\beta^4}$
6	$1 + \frac{30}{\beta} + \frac{360}{\beta^2} + \frac{2100}{\beta^3} + \frac{5760}{\beta^4} + \frac{5670.4}{\beta^5}$

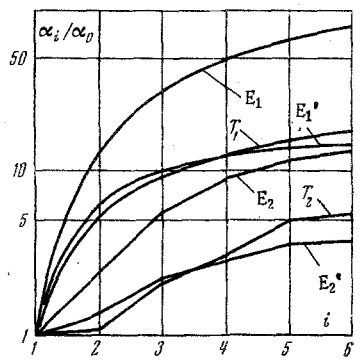

Fig. 1

A curious agreement of all the polynomials F_i is obtained for $A_\omega = 1 + \exp(z)$ and all positive derivatives $z_0^{(k)}$.

Shown in Fig. 1 are the coefficients α_i/α_0 corresponding to the series (2). The notation on the curves denotes: E_1, E_2 by means of (11)-(14), the polynomials $F_i(\beta)$ have been represented earlier; E_1', E_2' by means of (11), (12) and (15); T_1, T_2 by means of (5) and (16). The subscripts 1 and 2 in the notation on the curves correspond to β = 0.051266 and β = 0.29. As is seen, the theorem is satisfied (see the expression for α_i/α_0).

According to (14) the magnitude of $(\alpha_\omega)_{max}$ turns out to be infinite. This follows from the fact that the statistical model (14) includes lines with infinite intensity for a fixed width.

If lines with identical intensity are taken in the same model, then

$$z = \beta L\,(sx / \beta d) \tag{15}$$

where L is the Landenburg and Reiche function. Now $(\alpha_\omega)_{max}$ is some finite quantity. As $\beta \to 0$, when the lines do not overlap, the quantity $(\alpha_\omega)_{max} = s/\pi b$ as for a single line.

The quantities α_i/α_0 for the same β_1 and β_2 are shown in Fig. 1 for Eq. (15). The polynomials F_i differ from those represented earlier by just the numbers in the numerators.

Instead of (14) let us use an approximation within the scope of the Elsasser model:

$$A_\omega = \operatorname{erf}(z\sqrt{\pi}/2).$$

The argument z is written in (7) for $a = \pi/2$. According to [1], in the case of a weak line the approximation has the greatest error < 3% at $\beta = 1$. It increases to 7-7.5% as β diminishes. The maximum absolute deviation does not exceed 0.03-0.035. Let us use the simplification [1]

$$\operatorname{erf}(z\sqrt{\pi}/2) \approx \sqrt{1 - \exp(-z^2)}$$

with the additional error < 0.7%.

Then the fourth derivative $A^{(4)}_{\omega 0}$ becomes infinite. The theorem (4) is not satisfied because of the approximations introduced.

Let us examine the empirical formula proposed in [3] and still used extensively in the literature:

$$\bar{A} = \ln\left(1 + uf\,\frac{u+2}{u+2f}\right)$$
$$u = \alpha_0 x, \quad \alpha_0 = \frac{S}{\Delta\omega}, \quad f = 2.94\,[1 - \exp(-1.3\beta)], \quad \beta = 2\pi\frac{b}{d}. \tag{16}$$

The first ratios α_i/α_0 are represented in general form below:

i	$\prod_{j=1}^{i} (\alpha_i/\alpha_0)$
1	1
2	$1/f$
3	$\frac{3}{2f^2} + \frac{3}{2f} - 1$
4	$3\left(\frac{1}{f^3} + \frac{2}{f^2} - 1\right)$
5	$\frac{15}{2}\left(\frac{1}{f^4} + \frac{3}{f^3} + \frac{2}{f^2} - \frac{2}{f} - \frac{4}{5}\right)$
6	$\frac{45}{2}\left(\frac{1}{f^5} + \frac{4}{f^4} + \frac{44}{9f^3} + \frac{1}{3f^2} - \frac{16}{3f} + \frac{4}{9}\right)$

The ratios α_i/α_0 are presented in the figure for $\beta = \beta_1$ and $\beta = \beta_2$. For $\beta \leq \beta_1 = 0.051266$ it can be assumed that $f = 3.82\,\beta$ with < 3% error.

Under definite conditions, (16) simplifies:

$$\bar{A} = \ln(1 + uf), \quad \alpha_i/\alpha_0 = (i-1)f, \quad f \geqslant 2.$$

According to (2) we obtain

$$\bar{A} = uf - \frac{(uf)^2}{2} + \frac{(uf)^3}{3} - \ldots$$

The series diverges for $uf > 1$. Therefore, (16) is not fully correct. For example, it has a lower bound in the parameter β. For $u \gg 2f$ the coefficient α_1 obtained is incorrect since it depends on the pressure. The empirical formula $\bar{A} = \ln(2 - \beta + u\beta)$ is recommended in [4] for $\bar{A} > 2$. Very small values of $u\beta$ are thereby eliminated. Furthermore, the quantity $(\alpha_\omega)_{max}$ obtained, if it has meaning, is infinite according to (16). And finally, let us note that the contour $f(v)$ of the rearranged poles corresponding to (16) exists apparently only for $x \to 0$, $f(v) = v\exp(-v)$.

Actually, for low thicknesses in conformity with (16)

$$f(v) = ve^{-v} \approx -\frac{1}{u}\ln[1 - e^{-v}h(vu)]$$

$$A = \int_0^\infty [1 - \exp(-uf(v))]\,dv = \int_0^\infty e^{-v}h(uv)\,dv = \ln(1+u).$$

Here $h(vu) = \ln(\gamma vu) + E_1(vu)$, $\ln\gamma = 0.57722$, E_1 is the exponential integral, $h(vu) \approx vu$ for $vu \ll 1$.

A comparison of the expressions presented earlier for the polynomials shows the essential differences in the dependences of the coefficients α_j on the parameter β.

Let us turn to important examples of the approximate formulas which are produced by using the properties of the series (2). If at least the first coefficients α_j are known, the series (2) yields a formula suitable for small thicknesses. Its limit can be extended after an estimation of the remainder of the series. An approximate curtailment of the whole series is often successful.

Landenburg and Reiche Function. The function L(u) determines the absorption in a single line with a dispersion contour. The interest in the function grew after Goode had used it to describe absorption in a narrow band [see (15)]. In conformity with the series (2)

$$L(u) = \frac{A}{2\pi b} = u_1 - \frac{u_1u_2}{2!} + \ldots + (-1)^{i+1}\frac{1}{i!}\prod_{j=1}^{i} u_j + \ldots$$

$$u = \frac{sx}{2\pi b}, \quad u_j = \frac{sx}{2\pi b}m_j, \quad m_1 = 1, \quad m_j = 2 - \frac{1}{j-1}, \quad j \geqslant 2. \tag{17}$$

Here A is the integrated absorption in the line (cm^{-1}).

The sequence of numbers m_j permitted selection of a function suitable for all thicknesses:

$$L = \sqrt{\frac{2}{\pi}u}\,\mathrm{erf}\left(\frac{\pi}{2}\sqrt{\frac{u}{2}}\right)$$

Using the approximation of the probability integral presented above, we obtain

$$L_0 = \sqrt{\frac{2}{\pi}u\left[1 - \exp\left(-\frac{\pi}{2}u\right)\right]}$$

with a maximum error of 5.7% for u = 1.2-1.6.

The formula

$$L = u\left[1 + \left(\frac{\pi}{2}u\right)^{1.25}\right]^{-0.4} \tag{18}$$

is presented in [1] with $\leqslant$ 1% error. Its simplification yields

$$L_* = u/\sqrt{1 + \pi u/2}$$

with the greatest error of 7.5% at $u \approx 1$.

Because the deviations of L_0 and L_* are opposite, we obtain the interpolation formula

$$L = 0.57L_0 + 0.43L_* \tag{19}$$

with < 1% error (considerably less than 1% as a rule). Formula (19) is more convenient than (18).

Very exact approximations can be obtained for small thicknesses by taking account of the first terms of the series (17) separately. Because the sequence of numbers m_j converges rapidly, the remainder of the series can be curtailed by using the exponential function

$$L = 0.2u + 0.14u^2 - 0.065u^3 + [1 - \exp(-1.6u)]/2. \tag{20}$$

The u^3 coefficient is revised so that the function would be exact for u = 1.2. In this case, (20) describes the function well up to u = 1.4.

Constructions of the formulas for taking account of the first terms of the series separately can be different.

Let us also present an extrapolation formula suitable for large arguments:

$$L(u_*) = \sqrt{u_* / u}\, L(u).$$

For u = 5, $0.7 \leq u_*/u \leq 1.56$, the error in the formula is 1.2-1%. As u increases and the arguments u_*, u approach each other, the error diminishes rapidly.

Absorption in a Band according to the Model (12) with Overlapping Lines.

$$A_\omega = 1 - \exp(-sx/d), \quad \bar{A} = 2I(u_0)$$
$$2I = u_0 - C_2 \frac{u_0^2}{2!} + C_3 \frac{u_0^3}{3!} - \ldots \quad (u_0 = \alpha_0 x,\ \alpha_0 = S/\Delta\omega) \tag{21}$$

Here C_j is defined by (13), $C_2 = 0.3133$. Furthermore, C_j / C_{j-1} tends to the limit $1/\sqrt{2e} \approx 0.43$. Nearby values of the numbers C_j/C_{j-1} permitted the use of the exponential function

$$I = 1.6\,[1 - \exp(-0.625\, u_0/2)]$$

to curtail the series (21).

The maximum error of the formula in the interval $0 \leq u_0 \leq 4$ equals 1.7% for $u_0 = 4$. Furthermore, it increases rapidly. For $u_0 \geq 20$ [5]

$$I = 1.11 \sqrt{\ln(1.21 u_0)}$$

with < 3% error.

The formula

$$I = \sqrt{1.7\,[1 + \exp(-0.43 u_0)] \ln(u_0/2)}$$

is found for the intermediate values $4 \leq u_0 \leq 20$ with a maximum error of < 1.5% for $u_0 = 8$.

There are now sufficiently simple and exact formulas of I for all u_0. They are considerably more exact than the approximation in [6] for all u_0:

$$I = \sqrt{[1 - \exp(-u_0/2)]\,[0.5772 + \ln(u_0/2)] + E_1(u_0/2)}\,.$$

Finally, let us present another formula with the first terms of the series (21) taken separately into account:

$$I = \frac{u_0}{2}\left\{1 - \frac{C_2 u_0}{2}\left[1 - \frac{C_3^2}{C_2 C_4}\left(1 - \frac{2C_3\varphi}{C_4 u_0}\right)\right]\right\}$$
$$\varphi = 1 - \left[1 - \exp\left(-\frac{C_4 u_0}{C_3}\right)\right]\frac{C_3}{C_4 u_0}$$
$$(C_2 = 0.3133,\ C_3 = 0.1111,\ C_4 = 0.04158)\,.$$

The error in the formula is negligible to $u_0 = 6$. Furthermore, it increases and equals 0.25% for $u_0 = 10$. Graphs of the function $I(u_0)$ in [5], which are more detailed than in [6], were relied upon for the comparison.

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