MULTILINE REPRESENTATION OF THE TOTAL ABSORPTION OF RADIATION IN MOLECULAR BANDS

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An asymptotic representation of the equivalent width of a band containing ,n spectral lines is obtained in the asymptotic approximation. The main term of the representation in the nonoverlapping lines approach is the equivalent bandwidth. A criterion for the validity of this representation within the required limits of accuracy is also derived.

Now that complete and exact information on spectral line parameters is available,[1] the "line-by-line" method for the calculation of the total absorption in the vibrational-rotational molecular bands has become the standard. In this approach the molecular bands are regarded in general as consisting of n overlapping lines, each of which is characterized by the intensity (S_1), the HMHW (γ_1), the line center frequency (ν^0), and the line profile $\alpha(\nu^0-\nu)$, $i = 1, 2, \ldots, n$. The equivalent band width $W(n)$, which describes the total absorption in a molecular band of an optically homogeneous medium, has the following representation:

$$W(n) = \int d\nu \left\{1 - \exp\left[-\sum_{i=1}^{n} \tau_i \alpha(\nu_i^0 - \nu)\right]\right\}. \quad (1)$$

where τ_1 is the optical thickness at the i-th line center. As can be seen, the line-by-line method implies the numerical integration of an oscillatory function (in general the number of oscillations is equal to the number of spectral lines in the band). The labor-intensiveness of the calculations increases with increasing sharpness of the absorption coefficient spikes at the line center frequencies. The latter, in turn. Is proportional to the decrease of the amount of line overlap. In the case of weak line overlap a new approach to the calculation of the total band absorption may be proposed. The following representation for $W(n)$ may serve as a basis for it:

$$W(n) = \sum_{i=1}^{n} W_i - \sum_{i_1, i_2, \; i_1 \neq i_2} \int d\nu \prod_{k=1}^{2} \left\{1 - \exp\left[-\tau_{i_k} \alpha\left(\nu_{i_k}^0 - \nu\right)\right]\right\} + \ldots$$

$$+ (-1)^{l+1} \sum_{i_1, \ldots, i_l, \; i_\alpha \neq i_\beta} \int d\nu \prod_{k=1}^{l} \left\{1 - \exp\left[-\tau_{i_k} \alpha\left(\nu_{i_k}^0 - \nu\right)\right]\right\}$$

$$+ \ldots + (-1)^{n+1} \int d\nu \prod_{i=1}^{n} \left\{1 - \exp\left[-\tau_i \alpha\left(\nu_i^0 - \nu\right)\right]\right\}, \quad (2)$$

where W_1 is the equivalent width of the i-th isolated line.

The first term on the right side of Eq. (2) represents the equivalent bandwidth $W_n(n)$ in the nonoverlapping lines approximation, when to each line corresponds its own photon ensemble and these ensembles do not mix with each other. The second term takes into account the overlapping of two lines, i.e., photon mixing from two different ensembles, and so on. We name the new formula (2) the multiline representation for the equivalent bandwidth. Its validity can be proved by mathematical induction, and despite its cumbersome form, it has been found to be useful in practice because of the following reasons.

First, formula (2) is an asymptotic expansion of $W(n)$, in which the principal term represents the equivalent bandwidth $W_n(n)$ the nonoverlapping lines approximation, since the ith term decreases with increase of the separation between the line centers, and with decrease of the optical thicknesses at the line centers (i.e., when the situation become closer to the case of nonoverlapping lines) $\int d\nu \prod_{k=1}^{1} \tau_{i_k} \alpha\left(\nu_{i_k}^0 - \nu\right)$. Consequently, taking only the first few terms in formula (2) into account will give more accurate values of $W(n)$, which are that much more justified, the more accurate the approximation of nonoverlapping lines is. Second, since the subsequent terms in formula (2) in this situation will be only a small addition to $W_n(n)$, their values cam be approximated by applying some physical ideas about the properties of the absorption of radiation in gases.

Let us rank the lines in the band in their order of decreasing optical thickness τ_1 ($\tau_1 \geq \tau_2 \geq \ldots \geq \tau_n$) and use the approximate relation

$$\int d\nu \prod_{i=1}^{1} \left\{1 - \exp\left[-\tau_i \alpha\left(\nu_i^0 - \nu\right)\right]\right\}$$

$$\approx W_1 \prod_{i=2}^{1} \left\{1 - \exp\left[-\tau_i \alpha\left(\nu_i^0 - \nu_1^0\right)\right]\right\}. \quad (3)$$

Then by mathematical induction over index n we obtain the following expression in place of formula (2):

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$$W(n) = \sum_{i=1}^{n} W_i + \Delta,$$

$$\Delta \approx \sum_{i=1}^{n-1} W_i \left\{1 - \exp\left[- \sum_{k=i+1}^{n} \tau_k \alpha \left(\nu_i^0 - \nu_k^0\right)\right]\right\}. \qquad (4)$$

The approximate relation (3) was obtained on the basis of the fact that in the case of weak line overlap radiation transfer is realized within a narrow spectral interval near the line center with the maximum $\tau = \tau_1$ against the background of the line wings of the rest of the lines in the integral (3) (for which $\tau \le \tau_1$). Evidently, other approximate representations for Δ in Eq. (4) are possible, but the one presented has the advantage that it involves in addition to elementary functions only the functions W_1, which describe the absorption of isolated lines whose values were calculated previously at the stage at which the principal term of the multiline representation (2) was determined.

The multiline representation (2) is exact. It is valid for any band, or combination of bands, including the case of optically inhomogeneous media. If the following substitution has been made:

$$\tau_1 \alpha\left(\nu_1^0 - \nu\right) \to \int_0^l dz S_1(z) \alpha\left(\nu_1^0 - \nu;\ z\right) N(z), \qquad (5)$$

where l is the geometrical length of the radiation path and $N(z)$ is the density of absorbing molecules at the point z.

The physical characteristics of light absorption and emission in a molecular medium were used at the stage of the approximate estimation of Δ. Their features are those that relation (3), all other conditions being equal, fulfills least well In the case when $\tau_I = \tau_1$ for all i. Since the line wings are described by the Lorentzian line shape, we can restrict ourselves to the Lorentzian line shape when testing the approximate relation (3). Also note that the half-widths γ_1 and separations $\left|\nu_{i+1}^0 - \nu_1^0\right|$ between neighboring lines in the vibrational-rotation bands vary slightly with i, in comparison with the variation of the intensities $S_1(\tau_1)$. Therefore it would seem to be expedient to illustrate the obtained results not by means of isolated examples of specific bands but by the most critical situation of a band consisting of n identical equidistant Lorentzian lines.

The numerical integration was carried out using the adaptive quadrature subroutine QUANC8 (Ref. 5), with the required relative error of the final result RELERR = $1 \cdot 10^{-7}$. The equivalent widths W_1 for the Lorentzian lines were calculated with the help of algorithms described in Ref. 6.

The isolines $\sigma_1 = \left|1 - W(n)(1) / W_n(n)\right|$, $\sigma_2 = \left|1 - W(n)(4) / W_n(n)\right|$, and $\sigma_3 = \left|\Delta(4) / W_n(n)\right|$ are presented in Fig. 1. It can be seen that in the scale of the figure the strict inequality $\sigma_3 > \sigma_2$ holds, which means that the representation (4) also gives a criterion for an exact estimation of its error. The curves in Fig. 1 were obtained with the help of the subroutine CONDEK,[7] the $\delta = \left|\nu_1^0 - \nu_2^0\right| / \gamma_1$ axis was divided into 60 equal intervals, and the lgτ axis — into 30.

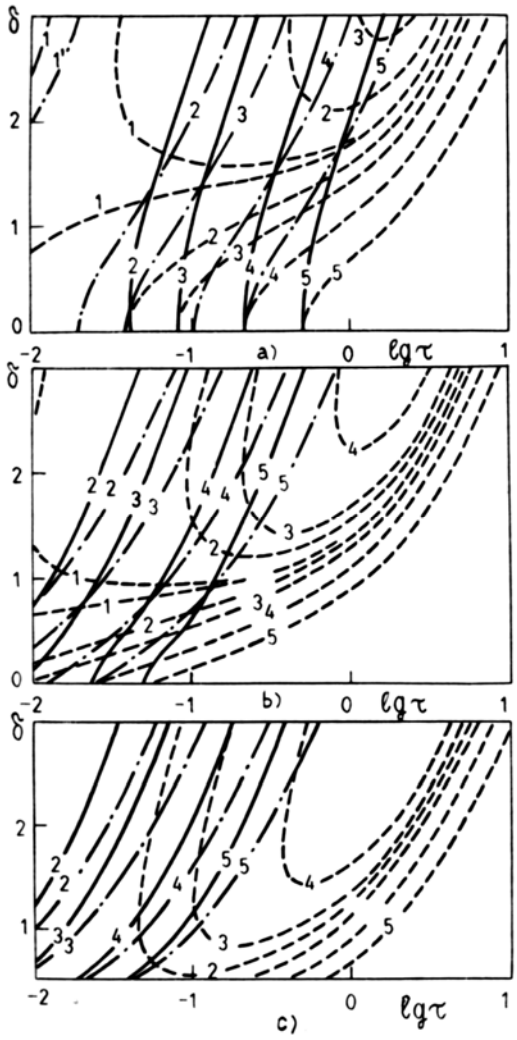

FIG. 1. Isolines of the relative error for different approaches to the calculations of the equivalent width of the bands consisting of n = 2 (a), 10 (b), and ∞ (c) (the Elsasser model)[3] lines. 1) 0.1%, 2) 1%, 3) 2%, 4) 5%, and 5) 10%. The solid lines correspond to σ_1, the dotted ones — to σ_2, and the dash-dot ones — to σ_3.

In this connection note the following. For the purpose of calculations of the total absorption in the molecular bands an effective method has been developed in the nonoverlapping lines approximation (see, for example. Ref. 4) that is based on the introduction and use of universal functions for each type of molecule. Nevertheless, its practical application is limited by the absence of analytical criteria for the validation of the indicated approximation. Such a criterion can be obtained by expressing all the sums In Ref. 4 in terms of the appropriate universal functions with the help of the well-known scheme given in Ref. 4.

In conclusion we note that the proposed approach can be realized also for other functions used in the description of radiative transfer in molecular bands, e.g., for the transmittance functions.

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