ON THE ROLE OF DETAILED BALANCE IN THE LINE MIXING TREATMENT

A.P. Galtsev and M.N. Kuznetsov

Institute of Atmospheric Physics, Academy of Sciences of the USSR, Moscow

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A theoretical study of spectral line mixing is carried out on the basis of the general expression for detailed balance, providing thermodynamic equilibrium in a gas phase. Results of calculations are compared with those obtained using the model of strong collisions and the model of weak line coupling. It is shown that the absorption in the wings of rovibrational bands calculated for these cases may differ from measured values by an order of magnitude.

A priori information about the fine structure of molecular spectra including the shape of individual spectral lines is needed for solving a number of problems of atmospheric optics. Numerous experimental studies of absorption in rovibrational bands of CO, CO_2, N_2O and some other molecules have shown inadequacy of the Lorentzian line shape for describing absorption in the transmission microwindows and band wings. Several mechanisms of formation of the absorption spectra of atmospheric gases have been proposed[1–3] to explain the experimentally observed regularities. In recent years many researchers concentrated on studying the line mixing effect (interference of spectral lines) and on the formation of rovibrational absorption bands of gases. The origin of the line mixing is associated with the presence of collision–induced transitions between the energy states of an absorbing molecule. This intermolecular interaction results in the intensity redistribution among the rotational absorption lines of molecules. Several simple models have been proposed in the literature[3–7] which enable one to calculate the line mixing contribution into the molecular rovibrational absorption bands within the limits of the impact approximation.

The present paper deals with analysis of the relations which must be satisfied in any theoretical model aimed at adequate description of the spectral line interference. In discussion of this problem we shall consider the line mixing effect alone within the impact approximation, i.e., under this restriction the influence of other factors on the shape of rovibrational bands is omitted.

The general expression for the dipole absorption coefficient of a molecular system within the framework of the impact theory of spectral line broadening is given in the form[7-8]

$$k(\omega) = \frac{4\pi^2 \omega n_a}{3\hbar\, c}\left[1 - \exp\left(-\frac{\hbar\,\omega}{kT}\right)\right] I(\omega)\ ,$$

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Im}\left\{\underset{jk}{d_j}\, d_k\, \rho_k \left(\frac{1}{\hat{\omega} - \hat{\omega}_0 - i\hat{\omega}}\right)_{jk}\right\}\ , \qquad (1)$$

where ω is the frequency, T is the gas temperature, and n_a is the number density of absorbing molecules. Subscript j denotes the transition between two energy states of an absorbing molecule. The quantity d_j is the reduced matrix element of the dipole moment operator of the absorbing molecule for the jth transition, ρ_k describes the population of the lower level for the kth transition, $\hat{\omega}$ and $\hat{\omega}_0$ are understood as operators, their matrix elements being defined by the rules, $<j|^{\wedge})|k> = \omega\delta_{jk}$, and $<j|^{\wedge})_0|k> = \omega_j\ \delta_{jk}$, where ωj is the frequency of the jth line center. The relaxation operator $^{\wedge})$ describes the collisional broadening of spectral lines. Its diagonal matrix elements ω_{kk} correspond to the line half–widths γ_k. The nondiagonal matrix elements ω_{jk} characterize the spectral exchange. In the absence of spectral exchange (i.e., $\omega_{jk} = 0$ ae $j \neq k$) Eq. (1) is equivalent to the additive sum of the Lorentzian lines.

For making calculations by Eq. (1) numerical values of d_k, ρ_k, and ω_{jk} are to be preset, and therefore they may be assumed as known. Moreover, they may be determined either experimentally or theoretically. Therefore the problem on calculating absorption coefficients is reduced to determining nondiagonal elements ω_{jk}.

Some auxiliary relations were proposed in the literature when theoretically modeling parameters ω_{jk} alone. The condition of detailed balance was introduced in Ref. 9 as

$$\omega_{jk}\, \rho_k = \omega_{jk}\, \rho_j\ . \qquad (2)$$

The sum rule for matrix elements ω_{jk}

$$\sum_j \omega_{jk} = 0 \qquad (3)$$

is being widely used in calculations as the second auxiliary relation.

When the perturbation of the levels of an absorbing molecule can be neglected the only result of collisions is the transitions between different states of the molecule under study and the matrix elements ω_{jk} can be simplified:[10–11]

$$\gamma_k = \omega_{kk} = (1 - P_{kk})\, n_0\ ,\ \omega_{jk} = -\,P_{jk}\, n_0\ ,\ j \neq k, \qquad (4)$$

where P_{jk} is the probability of the transition from the state k of the absorbing molecule to the state j induced by a single collision, and n_0 is the average number of collisions per unit time. For the parameters P_{jk} we have the evident relation

$$\sum_j P_{jk} = 1\ . \qquad (5)$$

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General expression for the detailed balance maintaining the thermodynamic equilibrium in a gas is given by a system of linear equations[10,11]

$$\sum_k P_{jk}\,\rho_k = \rho_j\,, \quad \sum_j \rho_j = 1\,. \tag{6}$$

For the case under study Eq. (3) is equivalent to Eq. (5), and formula (2) is reduced to the equality

$$P_{jk}\,\rho_k = P_{kj}\,\rho_j\,. \tag{7}$$

Condition (6) is the exact result of the theory of the Markovian processes.[12] Under this condition there occurs thermodynamically equilibrium distribution of populations over the rotational states of absorbing molecules. It should be noted that Eqs. (5) and (6) may be satisfied simultaneously at any ρ_k and γ_k, and these relations describe the thermodynamic equilibrium in a gas regardless of the spectroscopic problem under consideration. At the same time Eqs. (5) and (7) cannot be simultaneously fulfilled at an arbitrary choice of ρ_k and γ_k. This fact is specified by an approximate character of Eq. (7).

The main peculiarity of the present analysis of the spectral exchange between rotational lines is the use of general expression (6) as a condition of detailed balance. Relation (6) has the following advantages. First, it is compatible with Eq. (5) at any values of ρ_k and γ_k. Second, the general condition of detailed balance assumes more wide set of interference models than the approximate relation (7) does. Third, formula (6) gives a possibility of investigating the applicability limits of the approximate Eq. (7). Fourth, the general expression of detailed balance may be convenient for correction of the values of matrix elements of the relaxation operator, obtained by numerically solving the dynamic problem of interaction between the colliding molecules.

Based on Eqs. (2) and (3) two simplest interference models were proposed in the literature. In the weak spectral exchange model[4,5] it is assumed that every spectral line interferes only with two neighbor lines (i.e., $\omega_{jk} = 0$ for $|j - k| \geq 2$). In the model of strong collisions[3,6] an assumption is made that every collision yields an equilibrium distribution of molecules over the rotational states, i.e.,

$$P_{jk} = \rho_j\,.$$

To satisty condition (3) the strong collision model requires the spectral line half–width to be preset in a fixed form $\gamma_k = (1 - \rho_k)n_0$. The interference model proposed in Ref. 7 is analogous to the above–described model of strong collisions except for description of the half–widths, which in Ref. 7 agrees with the experimental data much better. Calculations of absorption coefficients according to the model from Ref. 7 give the results which quite well agree with the calculational data by model the of strong collisions.

Since the described interference models correspond to limiting situations the analysis of the intermediate cases in which the simplified condition of detailed balance (7) does not hold is of interest and it is necessary to use general expression (6) to be sure that the thermodynamically equilibrium distribution of populations ρ_k occurs. Therefore, in this paper we investigate the line mixing effect using the following model representation of the transition matrix P_{jk}:

$$P_{jk} = \begin{cases} C_k \exp[-(k-j)/m_0],\ j < k\,, \\ D_k \exp[-(k-j)/m_0],\ j > k\,, \end{cases} \tag{9}$$

Here the normalization parameters C_k and D_k are determined by Eq. (5), i.e.,

$$\sum_{j=1}^{k-1} P_{jk} = (1 - P_{kk})(1 - x_k), \quad \sum_{j=k+1}^{N} P_{jk} = (1 - P_{kk})\,x_k, \; x_k = \frac{N-k}{N-1}, \tag{10}$$

where N is the number of lines involved in the analysis. For the sake of simplicity of the analysis of obtained results we study alone the symmetric population distribution for which the dependence of the parameters x_k on the line number k is taken as in Eq. (10). The value m_0 characterizes the number of the coupled lines and in such a way accounts for the effect of the rotational relaxation rate in a gas. The limiting transition $m_0 \to 0$ leads to the weak spectral exchange model. As $m_0 \to \infty$ we obtain a simplified version of the model of strong collisions, when the transitions to all rotational states of the absorbing molecule are equally probable and the distribution of population ρ_k is uniform.

At the given values of parameters N and m_0 the solution of the system of linear equations (6) with P_{jk} from formula (9) allows one to obtain numerical values for the populations ρ_k. By taking, for simplicity, an equidistant spectrum with the line separation d_k = const and γ_k = const the calculation can be made of the correcting function

$$\kappa(\omega) = \frac{I(\omega)}{I_L(\omega)} = \frac{\left[\dfrac{1}{\pi}\sum\limits_{jk} \dfrac{\rho_k\, d_j\, d_k\, \omega_{jk}}{(\omega - \omega_j)(\omega - \omega_k)}\right]}{\left[\dfrac{1}{\pi}\sum\limits_{k} \dfrac{\rho_k\, d_j\, d_k^2\, g_k}{(\omega - \omega_k)^2}\right]}\,. \tag{11}$$

This representation of the correcting function $\kappa(\omega)$ is justified for a well resolved spectrum, when the condition $|\omega - \omega_k| \gg \gamma_k$ is fulfilled for all lines. Removal of the above restrictions imposed on the parameters d_k and γ_k does not introduce any peculiarities.

The results of calculations within the above model are presented in Fig. 1 for $N = 40$ and for four values of the parameters m_0. Also shown in Fig. 1 are the calculational results obtained using the weak spectral exchange model and the model of strong collisions. Vertical lines denote the population distribution ρ_k. For the frequencies $\omega < \omega_N$ the values $\kappa(\omega)$ are the centers of gaps between the lines. It can be seen from Fig. 1 that the weak spectral exchange model and the model of strong collisions can be considered as the lower and the upper boundaries for the absorption due to the effect of mixing the rotational lines in the absence of phase perturbations. With out additional information about the relaxation process in gases relations (5) and (6) imply the uncertainty in the band–wing absorption coefficients about two orders of magnitude. For not very broad population distributions of the absorbing molecule (for example for m_0 2) the strong collision model can overestimate the absorption coefficient in the band wing by more than one order of magnitude. The analysis of numerical values P_{jk} and ρ_k for the model (9) has shown that the simplified condition of detailed balance (7) is valid only for population distributions close to the uniform one. In other cases the use of the relation (7) is too problematic.

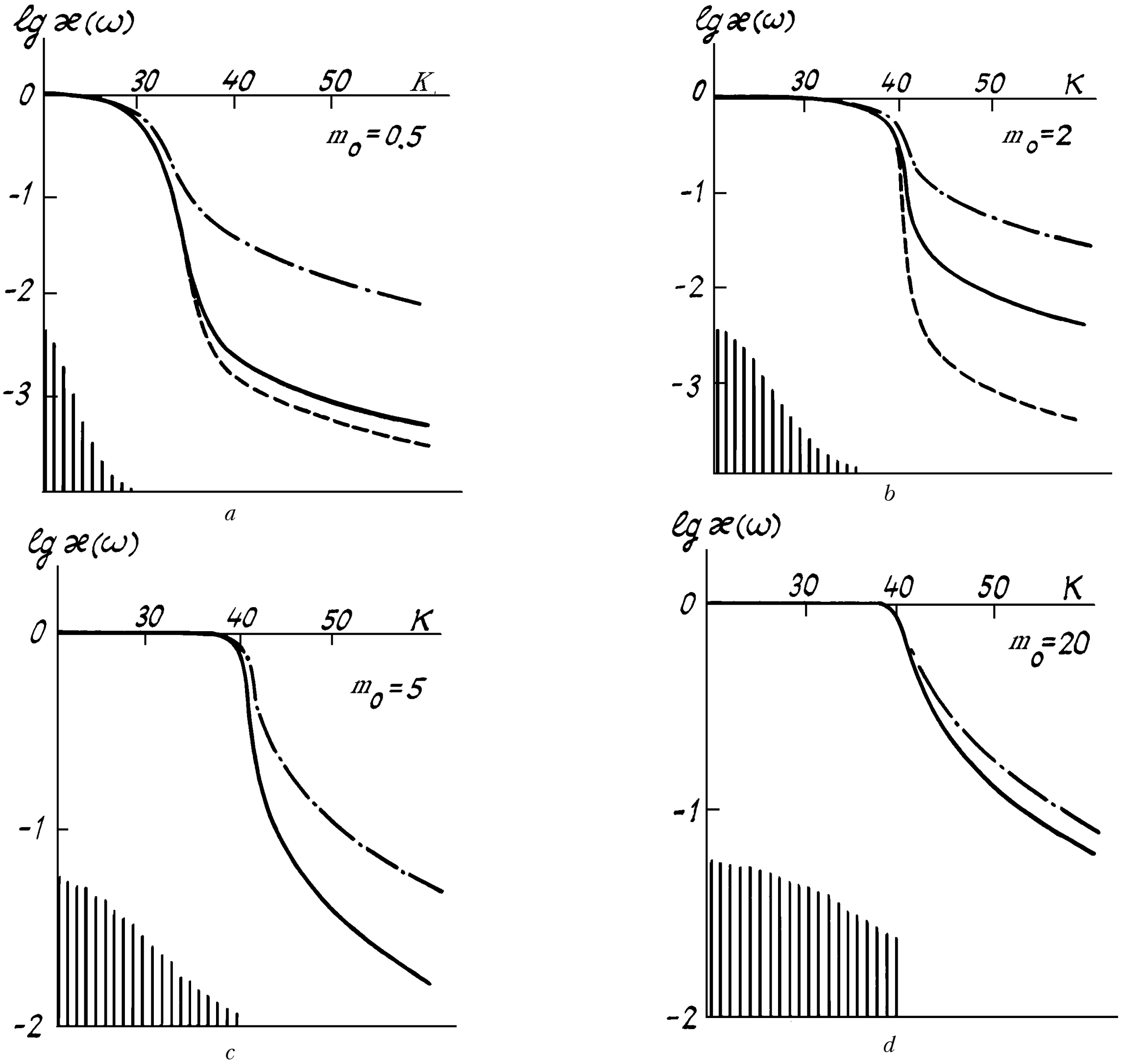

FIG. 1. Correcton function κ(ω) *for four values of the parameter* m_0*: solid curve denotes the present calculations, dashed curve stands for the calculations based on the weak spectral exchange model, and dot—dash curve presents the calculations of the model of strong collisions.*

Based on the above analysis of the line mixing effect we can arrive at two conclusions. First, when developing new interference models general expression (6) for detailed balance and additional information about the rotational relaxation in gases ought to be used. Second, the general condition of detailed balance can conveniently serve for testing the values of the relaxation operator matrix elements obtained as a result of solving the dynamic problem of the intermolecular interaction during collisions.

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