

# Collisional interference of vibrational bands in the molecular spectra

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It is shown that collisional interference of vibrational bands can occur in the colliding molecules as a result of isotropic interaction. The equations for relaxation parameters are derived for the case of two colliding molecules, and spectral manifestation of this effect is discussed. A physical interpretation is given to the mechanism of collisional interference of lines.

## Introduction

Recently, much interest has been shown in theoretical and experimental studies of the collisional interference (spectral exchange) between spectral lines. Theoretical papers are devoted to the development of theory and calculation techniques for relaxation parameters and spectral shape, as well as analysis of spectral manifestation in the model and actual quantum systems.<sup>1-18</sup> For the first time, this phenomenon was noticed in the ammonia inversion spectrum at self-broadening (although, it was initially interpreted in a quite different manner, see, for example, Refs. 3 and 19). Then it was observed in NMR<sup>22</sup> and Raman spectra. In recent years this effect has been observed in infrared rotational-vibrational spectra of some molecules.<sup>20-25</sup>

However, analysis of the literature on this topic shows that until so far the mechanism of collisional interference of spectral lines is not clearly understood, and the systematic methods for calculation of relaxation (especially, cross-relaxation) parameters, which would allow consideration and analysis of the corresponding effects in molecular rotational-vibrational spectra, are insufficiently developed. Filling in, to a certain degree, of the above gaps is one of the goals of this paper. Another one goal is to consider the principle basis for appearance of collisional interference between vibrational bands because of the presence of an isotropic component in the interaction potential.

In the first section, we give some general results of the theory of collisional broadening of interfering spectral lines in the impact approximation for a convenience. But the main attention is paid to the technique of calculation of relaxation parameters, which will be used below. In the second section, based on Ref. 26, we consider the physical mechanism of collisional interference of spectral lines. Then the relations between relaxation parameters are discussed. (These relations are derived in a not entirely rigorous

way.) In the third section, the technique for calculation of relaxation parameters is modified and adapted for calculations in a specific case of collisional interference of molecular vibrational bands. In the fourth section, the equation for absorption coefficient is derived in the model of two interfering vibrational bands. In the final section, a possible spectral manifestation of the effect is qualitatively discussed.

## 1. Some findings from the theory of collisional broadening of interfering spectral lines

In the formalism of the space of lines<sup>1,27</sup> and in the collisional approximation, the coefficient of absorption of unpolarized  $2K$ -pole radiation of parity  $\pi$  ( $K = 1$  and  $\pi = -1$  for the dipole electric radiation) by an isotropic gas medium has the following form:

$$\alpha(\omega) = -\frac{4\pi\omega\eta_s}{c\hbar} \tanh\frac{\hbar\omega\beta}{2} (2K+1)^{-1} \times \\ \times \text{Im} \sum_Q (-1)^Q \text{Tr}^s \left\{ P_Q^{(\pi K)}(0) [\hat{\omega} - \hat{L}_s - \hat{\Lambda}]^{-1} [P_{-Q}^{(\pi K)}, \rho^s]_+ \right\}, \quad (1)$$

where  $P_Q^{(\pi K)}$  is the  $Q$ -component of an irreducible tensor operator of  $2K$ -pole moment of the absorbing molecule;  $\hat{L}_s$  and  $\rho^s$  are its unperturbed Liouville superoperator (Liouvillian) and density matrix (in contrast to ordinary operators, Liouville operators are denoted by a cap);  $\eta_s$  is the density of an optically active gas;  $\hat{\Lambda}$  is the impact relaxation superoperator; and  $[\dots, \dots]_+$  denotes the anticommutator. All other designations correspond to the generally accepted ones.

The superoperator  $\hat{\Lambda}$  acts in the space of lines of an absorbing molecule; its diagonal matrix elements determine half-widths and shifts of spectral lines, and the off-diagonal elements, which are hereinafter called the cross-relaxation parameters, are responsible for the

collisional interference. In terms of the scattering superoperator  $\hat{U}(-\infty, \infty)$  in the direct product of the Liouville spaces of an absorbing molecule and a thermostat particle, this operator has the following form:

$$\hat{\Lambda} = -i\eta_b \int dv P(v) \text{Tr}^b \{ [\hat{1} - \hat{U}(-\infty, \infty)] \rho^b \}, \quad (2)$$

where  $\eta_b$  is the density of thermostat particles;

$\int dv P(v)$  is the operator of averaging over classical collisional parameters. Its matrix elements in the basis invariant relative to the transformed rotational-inversion group<sup>5,9</sup> are determined by the equation

$$\hat{\Lambda}_{\hat{n}\hat{m}}^{(\pi K)} = -i\eta_b \int dv P(v) \times \left\{ \delta_{\hat{n}\hat{m}} - \sum_{(\beta l)} \rho_{\beta l}^b \left( \frac{2l'+1}{2l+1} \right)^{1/2} \langle \hat{n}(\hat{\gamma}) \| \hat{U}^{(\pi K)}(-\infty, \infty) \| (\hat{\beta})\hat{m} \rangle \right\}. \quad (3)$$

The parentheses below the summation sign indicate summation over both primed and unprimed subscripts shown in the parentheses.

For brevity, we use the following designations for the vectors of the invariant basis:

$$\begin{aligned} |\hat{m}\rangle &= |\alpha_f j_f (\alpha_i j_i)^+; \pi K Q\rangle, \\ |\hat{n}\rangle &= |\alpha_{f'} j_{f'} (\alpha_{i'} j_{i'})^+; \pi K Q\rangle, \end{aligned} \quad (4)$$

$$|\hat{\beta}\rangle = |\beta l (\beta l)^+; 00\rangle, \quad |\hat{\gamma}\rangle = |\beta' l' (\beta' l')^+; 00\rangle, \quad (5)$$

$$|(\hat{\beta}) \hat{m}\rangle = |\hat{\beta}\rangle |\hat{m}\rangle, \quad |(\hat{\gamma}) \hat{n}\rangle = |\hat{\gamma}\rangle |\hat{n}\rangle. \quad (6)$$

Note that the vectors  $|(\hat{\beta}) \hat{m}\rangle$  are a particular case of the vectors  $|\alpha_f j_f (\alpha_i j_i)^+; K_s |\beta_f l_f (\beta_i l_i)^+; K_b |KQ\rangle$  corresponding to the following scheme of relations among the moments:

$$\mathbf{j}_f - \mathbf{j}_i = \mathbf{K}_s, \quad \mathbf{l}_f - \mathbf{l}_i = \mathbf{K}_b, \quad \mathbf{K}_s + \mathbf{K}_b = \mathbf{K} \quad (7)$$

and forming a complete set. In these equations  $j(l)$  is the quantum number of the total angular momentum operator of the absorbing molecule (thermostat particle), and  $\alpha(\beta)$  denotes all other quantum numbers.

According to Eq. (3), calculation of the matrix elements of the superoperator  $\hat{\Lambda}$  is closely related to calculation of the matrix elements of the scattering superoperator  $\hat{U}(-\infty, \infty)$ . The latter, naturally, can be calculated by applying any known methods for calculation of scattering matrices in the superoperator form. Let us follow Ref. 10, which uses for this purpose a slightly modified method for solution of the evolution equation in the matrix form.<sup>31</sup> Application of this method leads to a solution in the exponential form. Since this method is used to determine the diagonal

matrix element of the evolution matrix, let us write Eq. (3) in the following form:

$$\begin{aligned} \hat{\Lambda}_{\hat{n}\hat{m}}^{(\pi K)} &= -i\eta_b \int dv P(v) \left\{ \delta_{\hat{n}\hat{m}} - \sum_{(\beta l)} \rho_{\beta l}^b \left( \frac{2l'+1}{2l+1} \right)^{1/2} \times \right. \\ &\times \sum_{\hat{k}, \hat{\alpha}} \langle \hat{n}(\hat{\gamma}) \| D \| (\hat{\alpha})\hat{k} \rangle \langle \hat{k}(\hat{\alpha}) \| D^{-1} \| (\hat{\beta})\hat{m} \rangle \times \\ &\times \langle \hat{\sigma}_u \| \hat{U}^{(\pi K)}(-\infty, \infty) \| \hat{\sigma}_u \rangle \left. \right\}, \end{aligned} \quad (8)$$

where  $|\hat{\sigma}_u\rangle$  are the eigenvectors of the superoperator  $\hat{U}^{(\pi K)}(-\infty, \infty)$  related to the vectors of the initial basis by the transformation

$$|\hat{\sigma}_u\rangle = D |\hat{k}(\hat{\alpha})\rangle. \quad (9)$$

Presenting the interaction Liouvillian  $\hat{L}_c(t)$  as a sum of the isotropic  $\hat{V}(t)$  and anisotropic  $\hat{R}(t)$  parts and taking into account the isotropic part already in the first order of the perturbation theory and the anisotropic part starting from the second order, we have

$$\langle \hat{\sigma}_u \| \hat{U}^{(\pi K)}(-\infty, \infty) \| \hat{\sigma}_u \rangle = \exp \{ -\langle \hat{\sigma}_u \| \hat{A}^{(\pi K)} \| \hat{\sigma}_u \rangle \}, \quad (10)$$

where  $\hat{A}^{(\pi K)}$  is the matrix of the reduced matrix elements of the superoperator  $\hat{A}$ . This matrix is diagonal in the basis of the vectors  $|\hat{\sigma}_u\rangle$ . The superoperator  $\hat{A}$  is determined by the series

$$\hat{A} = i \int_{-\infty}^{+\infty} \tilde{V}(t) dt + \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \tilde{L}'_c(t_1) \tilde{L}'_c(t_2) + \dots, \quad (11)$$

where the tilde means that an operator is taken in the interaction representation, and the prime indicates that the isotropic part of the interaction Liouvillian has no diagonal matrix elements. Substitution of Eq. (10) in Eq. (8) gives the sought exponential form for the matrix element of the collisional relaxation superoperator:

$$\begin{aligned} \hat{\Lambda}_{\hat{n}\hat{m}}^{(\pi K)} &= -i\eta_b \int dv P(v) \left\{ \delta_{\hat{n}\hat{m}} - \sum_{(\beta l)} \rho_{\beta l}^b \left( \frac{2l'+1}{2l+1} \right)^{1/2} \times \right. \\ &\times \sum_{\hat{k}, \hat{\alpha}} \langle \hat{n}(\hat{\gamma}) \| D \| (\hat{\alpha})\hat{k} \rangle \langle \hat{k}(\hat{\alpha}) \| D^{-1} \| (\hat{\beta})\hat{m} \rangle \times \\ &\times \exp \left[ -\langle \hat{\sigma}_u \| \hat{A}^{(\pi K)} \| \hat{\sigma}_u \rangle \right] \left. \right\}. \end{aligned} \quad (12)$$

In the basis of vectors (4)–(6), whose explicit form can be found in Refs. 4 and 9, the matrix elements of the superoperator  $\hat{A}^{(\pi K)}$  have the form

$$\begin{aligned} \langle \hat{n}(\hat{\beta}) \| \hat{A}^{(\pi K)} \| (\hat{\gamma}) \hat{m} \rangle &= iS_1(\hat{n}, \hat{m} | v) \delta_{\hat{\beta}\hat{\gamma}} + \\ &+ S_2(\hat{n}, \hat{m} | v)_{\text{outer}} \delta_{\hat{\beta}\hat{\gamma}} + \Theta_2(\hat{n}, \hat{m} | v)_{\text{middle}} + \dots \end{aligned} \quad (13)$$

and the parameters  $S_1(\hat{n}, \hat{m} | v)$ ,  $S_2(\hat{n}, \hat{m} | v)_{\text{outer}}$ ,  $\Theta_2(\hat{n}, \hat{m} | v)_{\text{middle}}$  are defined by the equations:

$$S_1(\hat{n}, \hat{m} | \nu) = \hbar^{-1} \{ \varepsilon_{f'f}(\beta l) \delta_{\alpha_i \alpha_i'} - (f \rightarrow i') \} \delta_{j_i j_i'} \delta_{j_f j_f'}, \quad (14)$$

where  $(f \rightarrow i')$  means that the term similar to the previous one should be added with  $f$  replaced by  $i'$  and  $f'$  replaced by  $i$ ,

$$\varepsilon_{f'f}(\beta l) = a_{00}^{00} \frac{(\alpha_{f'} j_f \| T^0(s) \| \alpha_f j_f) (\beta l \| T^0(b) \| \beta l)}{[(2j_f + 1)(2l + 1)]^{1/2}}; \quad (15)$$

$$a_{00}^{00} = \int_{-\infty}^{+\infty} dt \exp(-i\omega_{mn} t) C_{00}^{00}(t); \quad (16)$$

$$\omega_{mn} = \hbar^{-1} (E_{\alpha_f j_f} - E_{\alpha_f j_f'}). \quad (17)$$

(We use a series expansion of the interaction Hamiltonian over irreducible tensor operators of multipole moments of the colliding molecules in the following form<sup>10</sup>:  $H_c(t) = \sum_{q_1, q_2} C_{q_1, q_2}^{k_1, k_2}(t) T_{q_1}^{k_1}(s) T_{q_2}^{k_2}(b)$ .) It is seen from these equations that the first-order term is caused exclusively by the isotropic part of the interaction potential:

$$S_2(\hat{n}, \hat{m} | \nu)_{\text{outer}} = \sum_{k_1 k_2} \frac{C_{k_1 k_2}}{2\hbar^2} \sum_{\beta'' l''} \left\{ \sum_{\alpha_f'' j_f''} D(\alpha_f'' j_f''; \alpha_f'' j_f'' | k_1) \times \overline{D(\alpha_f j_f; \alpha_f'' j_f'' | k_1)} \tilde{f}_{k_1 k_2}(f'f) \delta_{\alpha_i \alpha_i'} \delta_{j_i j_i'} \delta_{j_f j_f'} + \overline{(f \rightarrow i')} \right\} |D(\beta l; \beta'' l'' | k_2)|^2 \delta_{\beta \beta'} \delta_{l l'}, \quad (18)$$

the bar here means complex conjugation. It is designated

$$D(\alpha j; \alpha' j' | k) = \frac{(\alpha j \| T^k \| \alpha' j')}{[(2k + 1)(2j + 1)]^{1/2}}, \quad (19)$$

and the function of non-adiabaticity  $\tilde{f}_{k_1 k_2}(f'f)$  is introduced by the equation

$$C_{k_1 k_2} \tilde{f}_{k_1 k_2}(f'f) = \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \times \exp\{i(\omega_{nm} t_1 - \omega_{\tilde{nm}} t_2)\} \sum_{q_1 q_2} C_{q_1, q_2}^{k_1, k_2}(t_1) C_{q_1, q_2}^{k_1, k_2}(t_2), \quad (20)$$

with the frequencies  $\omega_{nm}$  and  $\omega_{\tilde{nm}}$ , which are described as

$$\omega_{nm} = \hbar^{-1} \{ E_{\alpha_f'' j_f''} - E_{\alpha_f'' j_f'''} + E_{\beta l} - E_{\beta'' l''} \}, \quad (21)$$

$$\omega_{\tilde{nm}} = \hbar^{-1} \{ E_{\alpha_f j_f} - E_{\alpha_f'' j_f''} + E_{\beta l} - E_{\beta'' l''} \}. \quad (22)$$

Note that the coefficient  $C_{k_1 k_2}$  in Eq. (20), which determines the function of non-adiabaticity  $\tilde{f}_{k_1 k_2}(f'f)$ ,

can always be chosen so that for the diagonal matrix element, when  $f' = f$  and  $\omega_{\tilde{nm}} = \omega_{nm}$ , its real and imaginary parts coincide with the corresponding functions of the theory presented in Refs. 29, 30, and 32. The function  $\tilde{f}_{k_1 k_2}(f'f)$  in Bessel terms for a number of the multipole interactions is presented in Ref. 9.

$$\Theta_2(\hat{n}, \hat{m} | \nu)_{\text{middle}} = \sum_{k_1 k_2} (-1)^{j_i' + j_f' + K + k_1 + 1} \times [(2j_i' + 1)(2j_f' + 1)]^{1/2} \frac{C_{k_1 k_2}}{2\hbar^2} \times D(\alpha_i j_i'; \alpha_i j_i | k_1) D(\alpha_f j_f'; \alpha_f j_f | k_1) \left( \frac{2l + 1}{2l' + 1} \right)^{1/2} \times W(j_f' j_i' j_f j_i; K k_1) |D(\beta l; \beta' l' | k_2)|^2 \text{Re} \tilde{f}_{k_1 k_2}(i'f'), \quad (23)$$

where  $W(j_f' j_i' j_f j_i; K k_1)$  is the Racah coefficient and

$$C_{k_1 k_2} \tilde{f}_{k_1 k_2}(i'f') = \sum_{q_1 q_2} (-1)^{q_1 + q_2} a_{q_1, q_2}^{k_1, k_2}(\omega_{nm}) a_{-q_1, -q_2}^{k_1, k_2}(\omega_{\tilde{nm}}) \quad (24)$$

with the frequencies

$$\omega_{nm} = \hbar^{-1} \{ E_{\alpha_f'' j_f''} - E_{\alpha_f j_f} + E_{\beta l} - E_{\beta' l'} \}, \quad (25)$$

$$\omega_{\tilde{nm}} = \hbar^{-1} \{ E_{\alpha_i j_i} - E_{\alpha_i' j_i'} + E_{\beta l} - E_{\beta' l'} \}. \quad (26)$$

The coefficients  $a_{q_1, q_2}^{k_1, k_2}$  are the result of integration of the coefficients  $c_{q_1, q_2}^{k_1, k_2}(t)$  over time in the equation similar to Eq. (15). In terms of Bessel functions, Eq. (24) coincides with the real part of the function from Eq. (20).

After calculating, by Eqs. (13)–(26), the matrix  $A$  we should reduce it to the diagonal form, what gives the sets of its eigenvalues and eigenvectors. The procedure should be repeated for every step of averaging over classical collisional parameters and over quantum states of the thermostat particle. Then the reduced matrix element of the impact relaxation operator  $\hat{A}$  is calculated by Eq. (12).

## 2. Physical mechanism of collisional interference of spectral lines in the impact approximation

To reveal the physical mechanism of collisional interference of spectral lines, let us present the scattering superoperator  $\hat{U}(-\infty, \infty)$  in the form of direct product of the direct and inverse scattering matrices acting respectively in the spaces of the ket and bra wave vectors

$$\hat{U}^{(\pi K)}(-\infty, \infty) = S \otimes S^+, \quad (27)$$

and consider its typical matrix element:

$$\begin{aligned}
& \langle\langle \hat{n}(\hat{\gamma}) | \hat{U}^{(\pi K)}(-\infty, \infty) | (\hat{\beta}) \hat{m} \rangle\rangle = \\
& = \langle\langle f' i^+ (\gamma \gamma^+) | S \otimes S^+ | (\beta \beta^+) f i^+ \rangle\rangle = \\
& = \langle f'(\gamma) | S | (\beta) f \rangle \overline{\langle i^+(\gamma) | S | (\beta) i \rangle}. \quad (28)
\end{aligned}$$

The matrix elements of the relaxation superoperator  $\hat{\Lambda}$  are determined in terms of the similar matrix elements in Eq. (3). Upon its multiplication by the conjugate one, we have

$$\begin{aligned}
& |\langle\langle \hat{n}(\hat{\gamma}) | \hat{U}^{(\pi K)}(-\infty, \infty) | (\hat{\beta}) \hat{m} \rangle\rangle|^2 = \\
& = |\langle i^+(\gamma) | S | (\beta) i \rangle|^2 |\langle f'(\gamma) | S | (\beta) f \rangle|^2. \quad (29)
\end{aligned}$$

As known, the squared absolute value of the scattering matrix element determines the probability that two colliding particles being, for example, in the states  $|i\rangle$  and  $|\beta\rangle$  after collision are, respectively, in the states  $|i'\rangle$  and  $|\gamma\rangle$ . We are only interested in the states  $|i\rangle$  and  $|f\rangle$ , and  $|i'\rangle$  and  $|f'\rangle$ , which are connected by the selection rules for a  $2K$ -pole radiation of the parity  $\pi$ , what follows directly from Eq. (1). So

$$w_{\hat{n}\hat{m}}^{\hat{\alpha}(\beta, \gamma | \nu)} = |\langle\langle \hat{n}(\hat{\gamma}) | \hat{U}^{(\pi K)}(-\infty, \infty) | (\hat{\beta}) \hat{m} \rangle\rangle|^2 \quad (30)$$

can be interpreted as the probability that the molecule having absorbed radiation at the transition  $\hat{m} = f \leftarrow i$  after collision with the thermostat particle in the state  $|\beta\rangle$  arising at the set  $\nu$  of classical parameters experiences a radiative transition (that is, absorbs or emits – the latter is also not improbable)  $\hat{n} = f' \leftarrow i'$  of the same parity and the same multipolarity, and the thermostat particle experiences transition to the state  $|\gamma\rangle$ . Having averaged this probability over all the initial states  $|\beta\rangle$  of the thermostat particles, summed over all its final states  $|\gamma\rangle$  and over all “classical transitions”  $\hat{n} \neq \hat{m}$ , and averaged over the classical collisional parameters, we obtain the overall probability that the molecule absorbing radiation due to the transition  $\hat{m} = f \leftarrow i$  after collision with the thermostat particle experiences some other transition (but having the same multipolarity and parity). From this it follows, in particular, the rigorous criterion of whether or not a spectral line is isolated. Namely, the spectral line  $\hat{m} = f \leftarrow i$  broadens in the spectrum irrespective of all other lines, if

$$\sum_{\hat{n} \neq \hat{m}} \sum_{\beta} \rho_{\beta}^b \sum_{\gamma} \int d\nu |\langle\langle \hat{n}(\hat{\gamma}) | \hat{U}^{(\pi K)}(-\infty, \infty) | (\hat{\beta}) \hat{m} \rangle\rangle|^2 \ll 1. \quad (31)$$

Thus, in the theory of impact broadening of spectral lines, the mechanism of collisional interference of spectral lines can be interpreted as the phenomenon of collisional transfer of the radiative process (with its possible inversion) from one transition to another, but having the same multipolarity and parity. Consequently, this process has a purely non-adiabatic character. It is essential that this process proceeds without a

disturbance of the coherence of the radiative process.<sup>10</sup> As a result, the mean time of coherence increases, thus leading to a decrease in the half-width of the lines taking part in the spectral exchange as compared with the half-width of isolated lines under broadening. We explain a significant excess of the line half-widths in the ammonia inversion spectrum, calculated in the approximation of isolated line with the allowance made for only the dipole-dipole interaction, over the experimental values just in this manner.<sup>16</sup>

It should be emphasized here that the relaxation parameters themselves depend only on the probability amplitudes of the corresponding transitions. For this reason, all the attempts to interpret those from the probability point of view are inconsistent (except for the model case of a two-level system and some other particular cases). At the same time, such attempts are still being undertaken, and for reducing the bulk of calculations the equations are often used, which have the following form in our designations:

$$\sum_{\hat{n}} \hat{\Lambda}_{\hat{n}\hat{m}}^{(\pi K)} = \sum_{\hat{m}} \hat{\Lambda}_{\hat{n}\hat{m}}^{(\pi K)} = 0; \quad (32)$$

$$\hat{\Lambda}_{\hat{n}\hat{m}}^{(\pi K)} \rho_i^s = \hat{\Lambda}_{\hat{n}\hat{m}}^{(\pi K)} \rho_i^s. \quad (33)$$

The former can be obtained from Eq. (3), if in this equality the second term is interpreted as the probability of the corresponding transition. However, this is not the case, and, as was shown in Ref. 13, this equation is valid only for isotropic Raman scattering.

The latter equation was derived in Ref. 5 and is interpreted in the literature as the condition of detailed balance.<sup>13</sup> The central role in derivation of this equation belongs to the identity  $\rho_i^s \rho_{\beta}^b = \rho_{i'}^s \rho_{\beta'}^b$ , where  $|i\rangle$ ,  $|\beta\rangle$  and  $|i'\rangle$ ,  $|\beta'\rangle$  are, respectively, the states of the absorbing molecule and the thermostat particle before and after a collision. This identity is, in essence, the consequence of the following three assumptions:

(1) The sum energy is conserved at the collision and, consequently,  $E_{\beta} + E_i = E_{\beta'} + E_{i'}$ .

(2) Initial correlations are negligibly small, and the density matrix is factored, that is,  $\rho = \rho^s \rho^b$ .

(3) The states of the colliding particles are nondegenerate, so  $\rho_i^s = Z_s^{-1} e^{-E_i/(k_B T)}$ ,  $\rho_{\beta}^b = Z_b^{-1} e^{-E_{\beta}/(k_B T)}$  ( $k_B$  is the Boltzmann constant and  $T$  is the temperature), etc.

The first two assumptions are undoubted in the impact approximation, but the third one is, generally speaking, wrong. Actually, the number of molecules, from the entire statistical ensemble, that are in the state  $|i\rangle$  with the energy  $E_i$  is proportional not only to the factor  $e^{-E_i/(k_B T)}$ , but also to the statistical weight  $g_i^s$  of this level, i.e.,  $\rho_i^s = Z_s^{-1} g_i^s e^{-E_i/(k_B T)}$ ,  $\rho_{\beta}^b = Z_b^{-1} g_{\beta}^b e^{-E_{\beta}/(k_B T)}$ , etc. In this case, for the discussed identity to be valid, the condition  $g_i^s g_{\beta}^b = g_{i'}^s g_{\beta'}^b$  should hold under the assumptions (1) and (2), that is, the

product of statistical weights of colliding molecules must be invariant at collision, what, of course, does not hold in the general case. For this reason, the practical significance of Eq. (33) seems uncertain, especially, at small values of the total angular momentum.

In conclusion, let us consider one more equation, which was introduced in Ref. 6 and has gained some acceptance.<sup>28</sup> This equation relates the off-diagonal and diagonal matrix elements of the relaxation superoperator, and it can be written as:

$$\sum_{\hat{n} \neq \hat{m}} \rho_i^{1/2} P_{\hat{m}} \hat{\Gamma}_{\hat{n}\hat{m}} = - \rho_i^{1/2} P_{\hat{n}} \hat{\Gamma}_{\hat{n}\hat{m}}. \quad (34)$$

However, one should keep in mind that in Ref. 6 the scalar product of the form  $(A, B) = \text{Tr}\{\rho A^+ B\}$  in the Liouville space was used, and therefore the matrix elements of the relaxation superoperator in this equation cannot be identified with the matrix elements based on the scalar product  $(A, B) = \text{Tr}\{A^+ B\}$ , in particular, those used in this paper, which, in fact, are the parameters of the spectral shape. (Derivation of this equation is given in Appendix and, in particular, it is shown that the dependence on  $\rho_i$  in it is fictitious).

Moreover, at such a definition of the scalar product the equation of the type (34) is simply impossible. Actually, in our designations it would have the form

$$\sum_{\hat{n} \neq \hat{m}} \rho_i^{1/2} P_{\hat{m}} \hat{\Lambda}_{\hat{n}\hat{m}} = - \rho_i^{1/2} P_{\hat{n}} \hat{\Lambda}_{\hat{n}\hat{m}}. \quad (35)$$

This equation can be derived in the only way, if we assume

$$|M\rangle\rangle = \sum_{\hat{m}} \rho_i^{1/2} P_{\hat{m}} |\hat{m}\rangle\rangle \quad (36)$$

and take  $\hat{L}_c |M\rangle\rangle \equiv 0$  and, as a consequence,  $\hat{\Lambda} |M\rangle\rangle \equiv 0$ . In this case

$$\hat{\Lambda} |M\rangle\rangle = \sum_{\hat{n}\hat{m}} |\hat{n}\rangle\rangle \hat{\Lambda}_{\hat{n}\hat{m}} \rho_i^{1/2} P_{\hat{m}} \equiv 0, \quad (37)$$

and, in view of the linear independence of vectors of the space of lines

$$\sum_{\hat{m}} \rho_i^{1/2} P_{\hat{m}} \hat{\Lambda}_{\hat{n}\hat{m}} = 0, \quad (38)$$

what directly leads to Eq. (35). However, it is easy to see that as the vector  $|M\rangle\rangle$  is defined by Eq. (36),

$\hat{L}_c |M\rangle\rangle \neq 0$  since

$$\begin{aligned} \hat{L}_c |M\rangle\rangle &= \hat{L}_c (\rho^{1/2} P) = \\ &= \frac{1}{\hbar} (H_c (\rho^{1/2} P) - (\rho^{1/2} P) H_c) \neq 0, \end{aligned} \quad (39)$$

because  $[H_c, \rho] \neq 0$  and  $[P, \rho] \neq 0$ , what proves the statement.

### 3. Collisional interference of vibrational bands. Relaxation parameters

From here on, for some simplification, the states of the absorbing molecule are designated by indices  $v$

and  $j$ , and by  $\nu$  we mean the set of vibrational quantum numbers, all other quantum numbers omitted.

From Eqs. (13)–(26) it can be seen that the roles of the isotropic and anisotropic parts of the interaction potential in the processes of collisional interference are different: the isotropic part is responsible for interference of vibrational bands, whereas the anisotropic part is responsible for interference of lines within the same band. According to Eqs. (13)–(26), the isotropic part of the potential gives a nonzero contribution already in the first order of the perturbation theory, and terms of the second order are simply small perturbations. In this paper we ignore these.

According to Eq. (14), the structure of the first-order term  $S_1(\hat{n}, \hat{m} | \nu)$  is such that at  $\hat{n} \neq \hat{m}$  it can be nonzero only for the transitions  $\hat{m}$  and  $\hat{n}$ , having either the initial or final level as a common level. Besides, because of the presence of  $\delta$ -functions of angular momentum quantum numbers, rotational-vibrational lines in bands are not mixed. For certainty we assume that the transitions  $\hat{m}$  and  $\hat{n}$  have a common initial level, and, correspondingly, we have  $\hat{m} = v_f j_f \leftarrow v_i j_i$ ,  $\hat{n} = v_f' j_f' \leftarrow v_i j_i$ . For this case  $S_1(\hat{n}, \hat{m} | \nu)$  takes the form:

$$S_1(\hat{n}, \hat{m} | \nu) = \hbar^{-1} \varepsilon_{f'f}(\beta, l), \quad (40)$$

where  $\varepsilon_{f'f}(\beta l)$  is determined by the equations

$$\varepsilon_{f'f}(\beta l) = a_{00}^{00} \langle v_f' j_f' | T_0^0(s) | v_f j_f \rangle \langle \beta l | T_0^0(b) | \beta l \rangle; \quad (41)$$

$$a_{00}^{00} = \int_{-\infty}^{+\infty} dt \exp(-i\omega_{v_f' v_f} t) C_{00}^{00}(t); \quad (42)$$

$$\omega_{v_f' v_f} = \hbar^{-1} (E_{v_f'} - E_{v_f}). \quad (43)$$

We made use of the Wigner–Eckart theorem and expressed the reduced matrix elements in terms of the ordinary ones.

Note that in Eq. (41) the law of conservation of energy at collision is obviously violated. This is a direct consequence of the approximation of classical trajectories used. In the rigorous approach, the excess of energy is compensated for by the change in the energy of translation motion. For this reason, this consideration has a sense only at  $\hbar \omega_{v_f' v_f} \ll k_B T$ , what gives  $\omega \sim 250 \text{ cm}^{-1}$  under standard conditions. However, these conditions are not a strong restriction, since the presence of the exponential factor in Eq. (42) also imposes some restriction on the frequencies  $\omega_{v_f' v_f}$  namely,  $\omega_{v_f' v_f} \tau < 1$ , where  $\tau$  is the mean duration of a collision. This gives the estimate  $\omega_{v_f' v_f} < \sim 30 \text{ cm}^{-1}$ , i.e., vibrational bands spaced by about  $30 \text{ cm}^{-1}$  and more, for analysis of whose interference the model should be refined by not using the approximation of classical trajectories, interfere weakly under standard thermodynamic conditions.

For the potential of the form  $V(t) \sim 1/R^n$ , where  $R = (b^2 + v^2 t^2)^{1/2}$  is the distance between the colliding molecules,  $b$  is the impact parameter, and  $v$  is the

relative speed, the integral in Eq. (42) can be taken analytically and reduced to the form

$$a_{00}^{00} = \frac{C_{00}(n)}{b^{n-1}v} f_{00}(k|n). \quad (44)$$

Here the nonadiabaticity  $k = b\omega_{v_f'} v_f/v$  and the function of nonadiabaticity

$$C_{00}(n) f_{00}(k|n) = \sqrt{\frac{\pi}{2^{n-3}} \frac{1}{\Gamma(n/2)}} \times \\ \times k^{(n-1)/2} K_{(n-1)/2}(k) \quad (45)$$

are introduced,  $K_\nu(z)$  is the modified Bessel function (McDonald function).<sup>33</sup> The coefficient  $C_{00}$  can be chosen so that  $f_{00}(0|n) = 1$ .

The diagonal matrix elements are calculated directly by Eqs. (14)–(16) without any peculiarities. They determine, to a significant degree, line shifts in rotational-vibrational bands. Finally, let us note that with the real potential and proper choice of the phase of wave functions the matrix of  $S_1(\hat{n}, \hat{m}|v)$  is real and symmetric.

As was already mentioned, broadening and possible interference of lines within a vibrational band is determined by the anisotropic part of the interaction potential. In this paper our attention is focused on collisional interference of vibrational bands, therefore we omit detailed consideration of the line interference within a band. Moreover, we restrict our consideration to the case of two vibrational bands. This allows us to represent the matrix of the superoperator  $\hat{A}^{(\pi K)}$  in the form of a partitioned matrix

$$\hat{A}^{(\pi K)} = i \begin{pmatrix} p_1 - iq_1 & a \\ a & p_2 - iq_2 \end{pmatrix}, \quad (46)$$

where  $p_1$ ,  $p_2$ , and  $a$  are the diagonal  $r \times r$  matrices ( $r$  is the number of rotational-vibrational lines in a band) of  $S_1(\hat{n}, \hat{m}|v)$ , whereas  $q_1$  and  $q_2$  in the general case are non-diagonal  $r \times r$  matrices formed by parameters of the second order and caused by the anisotropic part of the interaction potential.

Hereinafter, for simplicity, we ignore the effects of rotational-vibrational interaction, believing the closeness of the states  $v_f$  and  $v_f'$  to be a convincing argument. This allows us to identify the matrices  $q_1$  and  $q_2$  and present the matrix  $\hat{A}^{(\pi K)}$  in the form

$$\hat{A}^{(\pi K)} = i \begin{pmatrix} p_1 - iq & a \\ a & p_2 - iq \end{pmatrix}. \quad (47)$$

Taking into account that matrices  $p_1$ ,  $p_2$ , and  $a$  are diagonal, this partitioned matrix can be reduced to a block-diagonal form

$$D^{-1} \hat{A}^{(\pi K)} D = i \begin{pmatrix} \tilde{c}_{11} & 0 \\ 0 & \tilde{c}_{22} \end{pmatrix} \quad (48)$$

by the transformation

$$D = \begin{pmatrix} c & -s \\ s & c \end{pmatrix}, \quad D^{-1} = \begin{pmatrix} c & s \\ -s & c \end{pmatrix}, \quad (49)$$

where it is denoted that

$$c = \cos\Theta; \quad s = \sin\Theta; \quad (50)$$

$$\Theta = \frac{1}{2} \arctan \frac{2a}{p_1 - p_2}, \quad |\Theta| < \frac{\pi}{4}. \quad (51)$$

The diagonal matrix elements in Eq. (48) are

$$\tilde{c}_{11} = c^2 p_1 + 2csa + s^2 p_2 - iq \equiv c_{11} - iq; \quad (52)$$

$$\tilde{c}_{22} = s^2 p_1 - 2csa + c^2 p_2 - iq \equiv c_{22} - iq. \quad (53)$$

The use of Eqs. (48) and (49) in Eq. (12) gives the following equations for the reduced matrix elements of the relaxation superoperator  $\hat{\Lambda}$ :

$$\hat{\Lambda}_{\hat{1}\hat{1}}^{(\pi K)} = -i\eta_b \int dv P(v) \sum_{\beta l} \rho_{\beta l}^b \{c^2(1 - e^{-i\tilde{c}_{11}}) + \\ + s^2(1 - e^{-i\tilde{c}_{22}})\}, \quad (54)$$

$$\hat{\Lambda}_{\hat{2}\hat{2}}^{(\pi K)} = -i\eta_b \int dv P(v) \sum_{\beta l} \rho_{\beta l}^b \{s^2(1 - e^{-i\tilde{c}_{11}}) + \\ + c^2(1 - e^{-i\tilde{c}_{22}})\}, \quad (55)$$

$$\hat{\Lambda}_{\hat{1}\hat{2}}^{(\pi K)} = -i\eta_b \int dv P(v) \sum_{\beta l} \rho_{\beta l}^b cs \{(1 - e^{-i\tilde{c}_{11}}) - \\ - (1 - e^{-i\tilde{c}_{22}})\} = \hat{\Lambda}_{\hat{2}\hat{1}}^{(\pi K)}, \quad (56)$$

where we have neglected the nondiagonal character of the matrix  $q$  in terms of the thermostat states, since it is insignificant for our calculation.

As is seen from these equations, the matrix of reduced matrix elements of the relaxation superoperator is block-symmetric. Recall also that  $c$ ,  $s$  and (if the nondiagonal character of the matrix  $q$  is neglected)  $\tilde{c}_{11}$  and  $\tilde{c}_{22}$  are diagonal  $r \times r$  matrices. Therefore, by setting vibrational quantum numbers, we can obtain relaxation parameters, including cross-relaxation ones, for individual lines in a band. These parameters depend on rotational quantum numbers regardless that the interference is caused by the isotropic part of the interaction potential. The problem becomes far more complicated, if we take into account the nondiagonal character of the matrix  $q$ . Then to obtain the relaxation parameters for individual lines, the matrix  $q$  should be reduced to the diagonal form by some transformation  $R$ , exponents in Eqs. (54)–(56) should be replaced by the expression of the form  $R e^{-R^{-1}\tilde{c}_{11}R} R^{-1}$ , where  $R^{-1}\tilde{c}_{22}R$  is a diagonal matrix, and the corresponding matrix element in terms

of rotational-vibrational transitions in a band should be taken.

#### 4. Collisional interference of vibrational bands. Spectral shape

By expanding the spur in Eq. (1) and passing to the reduced matrix elements by separating summation over magnetic quantum numbers, we have the following equation for the absorption coefficient  $\alpha(\omega)$ :

$$\alpha(\omega) = -\frac{4\pi\omega\eta_s}{c\hbar} \tanh \frac{\hbar\omega\beta}{2} (2K+1)^{-1} \times \\ \times \text{Im} \sum_{i \leq f} \sum_{i', f'} (\rho_i^s + \rho_f^s) P_{f' i'}^{(\pi K)} P_{f i}^{(\pi K)} \{R_{i' f'; i f}^{(\pi K)} + R_{f' i'; f i}^{(\pi K)}\}. \quad (57)$$

The first sum is taken over the states for which  $E_i \leq E_f$ , the reduced matrix elements of the irreducible tensor operator of the  $2K$ -pole moment of the molecule are assumed to be real, and  $R$  denotes the resolvent operator in Eq. (1). Its reduced matrix elements are determined by the equation

$$R_{f' i'; f i}^{(\pi K)} = \sum_{\substack{(m_i, m_f) \\ Q}} \frac{(j_i' K m_i' Q | j_f' m_f') (j_i K m_i Q | j_f m_f)}{[(2j_f + 1)(2j_f' + 1)]^{1/2}} \times \\ \times \langle\langle \alpha_{f' j_f' m_f'} (\alpha_{i' j_i' m_i'})^+ | \hat{R} | \alpha_{f j_f m_f} (\alpha_{i j_i m_i})^+ \rangle\rangle. \quad (58)$$

Taking into account that the Liouville operator  $L_s$  is spherically symmetric and the relaxation superoperator  $\hat{\Lambda}$  is diagonal relative to  $\pi$ ,  $K$ , and independent of  $Q$  in the case of an isotropic gas medium,<sup>4</sup> the reduced matrix element of the resolvent can be presented as follows:

$$R_{f' i'; f i}^{(\pi K)} = \left( \frac{1}{\hat{\omega} - \hat{L}_s^{(\pi K)} - \hat{\Lambda}^{(\pi K)}} \right)_{f' i'; f i}, \quad (59)$$

where the operators in the right-hand side are the matrices of the reduced matrix elements of the corresponding operators.

Neglecting the contribution of antiresonance terms (this is always allowed in the infrared and higher frequency spectral regions) in Eq. (57), we rewrite the equation for the absorption coefficient  $\alpha(\omega)$  in the following form:

$$\alpha(\omega) = -\frac{4\pi\omega\eta_s}{c\hbar} \tanh \frac{\hbar\omega\beta}{2} (2K+1)^{-1} \times \\ \times \text{Im} \sum_{\hat{n}, \hat{m}} (\rho_i^s + \rho_f^s) P_{\hat{n}}^{(\pi K)} P_{\hat{m}}^{(\pi K)} \hat{R}_{\hat{n}\hat{m}}^{(\pi K)}. \quad (60)$$

The sum here is taken over  $2K$ -pole absorption lines included into the consideration.

Let us come back to the problem of interference of two vibrational bands and assume the matrix  $q$  in Eqs. (47), (52), and (53) to be diagonal. This makes diagonal the blocks in the matrix of the relaxation superoperator and, consequently, in the matrix of the resolvent superoperator. Thus we can see that Eq. (60)

for the absorption coefficient should be somewhat modified:

$$\alpha(\omega) = -\frac{4\pi\omega\eta_s}{c\hbar} \tanh \frac{\hbar\omega\beta}{2} (2K+1)^{-1} \times \\ \times \text{Im} \sum_{\hat{n}, \hat{m}} P_{\hat{n}}^{(\pi K)+} \hat{R}_{\hat{n}\hat{m}}^{(\pi K)} ([P^{(\pi K)}, \rho^s]_{+})_{\hat{m}}, \quad (61)$$

since  $\hat{m}$  and  $\hat{n}$  now take the values  $\hat{1}$  and  $\hat{2}$  corresponding to the vibrational bands. Now all significant matrices have the block structure of the type:

$$\hat{P}^{(\pi K)} = \begin{pmatrix} \hat{P}_{\hat{1}}^{(\pi K)} \\ \hat{P}_{\hat{2}}^{(\pi K)} \end{pmatrix}; \hat{L}_s^{(\pi K)} = \begin{pmatrix} \omega_1 & 0 \\ 0 & \omega_2 \end{pmatrix}; \\ \hat{\Lambda}^{(\pi K)} = \begin{pmatrix} \delta_1 + i\gamma_1 & \xi + i\zeta \\ \xi + i\zeta & \delta_2 + i\gamma_2 \end{pmatrix} \dots \quad (62)$$

The matrix of the resolvent operator in Eq. (59) can be readily calculated. However, the equation for the absorption coefficient is rather cumbersome, and we do not present it here.

By setting the rotational quantum numbers, from Eq. (61) we can obtain the coefficients for individual lines in the spectrum. Although in this model these lines are not mixed by collisions, the shape of every line differs from the dispersion contour because of the collisional interference of vibrational bands and becomes the dispersion one in the  $|\xi + i\zeta| \rightarrow 0$  limit.

If bands have the same strengths and are identically broadened, then the line shape is described by the equation, similar to the well-known Ben-Reuven equation,<sup>3</sup> but with small differences connected because of the fact that the real part of the cross-relaxation parameters in this case is also nonzero.

## Conclusion

So, the spectral exchange of vibrational bands is caused by the isotropic part of the interaction potential, which contributes already in the first order of the perturbation theory. Only the bands having, as a common, either the initial or the final level can interfere. For efficient interference, the bands should be close enough ( $\Delta\omega \leq \sim 30 \text{ cm}^{-1}$ ). Interference of vibrational bands is not reduced to the interference of identical rotational-vibrational lines in the bands, since the relaxation parameters of individual lines depend on both the isotropic and anisotropic parts of the interaction potential, and the isotropic part of the cross-relaxation parameters depends, though weakly, on the rotational quantum numbers.

Interference of vibrational bands (at  $\Delta\omega \sim 30 \text{ cm}^{-1}$ ) manifests itself in the spectrum at rather high buffer gas pressure, at which the cross-relaxation parameters become comparable with the separation between the bands. In this case, the following pattern of the pressure transformation of the spectral shape can be expected: first, some rise of the inner line wings and drop of the

outer wings will be observed ( $p \sim 5 - 20$  atm); then the line shift toward the spectrum centroid will start to manifest itself and, possibly, some transfer of intensity from one band to another will take place ( $p \sim 10 - 50$  atm); at the further pressure increase the bands will become to merge into a single broadened band.

Certainly, this pattern is quite an approximate one being only qualitative. Actually, it will be affected by numerous factors connected both with the ignored effects (such as, for example, line interference within a band, violation of the impact approximation, etc.) and with the actual values of parameters, in particular, line positions in the bands. Particular emphasis should be placed on the characteristic distinctions of the interference of vibrational bands from the interference of lines within a band. At the interference of lines in a band, the pressure increase shifts the lines toward the band centroid and the intensity is transferred from the periphery parts of the band to the central part. If the vibrational bands interfere, then the pressure increase induces the band shift toward their common centroid. As a result, the gap between the bands vanishes and their outer wings drop down.

### Appendix on derivation of Eq. (34)

In Ref. 6 the vectors of the line space and the dipole moment are defined by the following equations (in our designations):

$$|\hat{m}\rangle = \rho_i^{-1/2} |if^+\rangle = \rho^{-1/2} |f\rangle \langle i|; \quad (\text{I})$$

$$|M\rangle = \sum_{\hat{m}} M_{\hat{m}} |\hat{m}\rangle, \quad (\text{II})$$

where

$$M_{\hat{m}} = \rho^{-1/2} P_{fi} \quad (\text{III})$$

and, consequently, the vector  $|M\rangle$  is independent of  $\rho$ . Therefore, the equality  $\hat{\Gamma}|M\rangle = 0$  is valid. This directly results in the expression

$$\begin{aligned} \hat{\Gamma}|M\rangle &= \sum_{\hat{m}} \hat{\Gamma}|\hat{m}\rangle M_{\hat{m}} = \sum_{\hat{m}, \hat{n}, \hat{k}} |\hat{n}\rangle \langle \hat{n} | \hat{\Gamma} | \hat{k} \rangle \langle \hat{k} | \hat{m} \rangle M_{\hat{m}} = \\ &= \sum_{\hat{m}, \hat{n}} |\hat{n}\rangle \langle \hat{n} | \hat{\Gamma} | \hat{m} \rangle M_{\hat{m}} = 0, \end{aligned} \quad (\text{IV})$$

as a consequence, because of the linear independence of the vectors  $|\hat{n}\rangle$ , we have

$$\sum_{\hat{m}} \langle \hat{n} | \hat{\Gamma} | \hat{m} \rangle M_{\hat{m}} = 0. \quad (\text{V})$$

With the help of Eq. (III) this can be written in the form

$$\sum_{\hat{m}} \langle \hat{n} | \hat{\Gamma} | \hat{m} \rangle \rho_i^{-1/2} P_{fi} = 0. \quad (\text{VI})$$

If the scalar product is defined as  $(A, B) = \text{Tr}\{\rho A^+ B\}$ , an arbitrary matrix element of the relaxation superoperator is

$$\langle \hat{n} | \hat{\Gamma} | \hat{m} \rangle = \rho_i^{-1/2} \rho_i^{-1/2} \text{Tr}\{\rho |i'\rangle \langle f'| (\hat{\Gamma} |f\rangle \langle i|)\}. \quad (\text{VII})$$

Using it in the previous equation, we can easily see that its dependence on  $\rho_i^{-1/2}$  is fictitious:

$$\sum_{\hat{m}} \rho_i^{-1/2} \text{Tr}\{\rho |i'\rangle \langle f'| (\hat{\Gamma} |f\rangle \langle i|)\} P_{fi} = 0. \quad (\text{VIII})$$

Reducing it by the factor  $\rho_i^{-1/2}$ , we have

$$\sum_{\hat{m}} \text{Tr}\{\rho |i'\rangle \langle f'| (\hat{\Gamma} |f\rangle \langle i|)\} P_{fi} = 0, \quad (\text{IX})$$

what is equivalent to the standard equation

$$\sum_{\hat{m}} \langle \hat{i}' f'^+ | \hat{\Gamma} | \hat{i} f^+ \rangle P_{fi} = 0, \quad (\text{X})$$

which is the consequence of commutativity of the intermolecular interaction potential with any function of coordinates and, in particular, with the operator of dipole moment.

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### References

1. M. Baranger, Phys. Rev. **112**, No. 2, 494-504 (1958).
2. J. Fiutak, Acta Phys. Polon. **27**, 753-761 (1965).
3. A. Ben-Reuven, Phys. Rev. Lett. **14**, No. 10, 349-353 (1965).
4. A. Ben-Reuven, Phys. Rev. **141**, No. 1, 34-40 (1966).
5. A. Ben-Reuven, Phys. Rev. **145**, No. 1, 7-22 (1966).
6. M.V. Tonkov and N.N. Filippov, Opt. Spektrosk. **54**, No. 6, 999-1004 (1983).
7. J.L. Gersten and H.M. Foley, Phys. Rev. **188**, No. 1, 24-28 (1969).
8. K.S. Lam, J. Quant. Spectrosc. Radiat. Transfer **17**, No. 2, 351-358 (1977).
9. M.R. Cherkasov, Opt. Spektrosk. **40**, No. 1, 7-13 (1976).
10. M.R. Cherkasov, Opt. Spektrosk. **7**, No. 7, 894-902 (1994).
11. R.J. Gordon and R.P. McGinnes, J. Chem. Phys. **49**, No. 5, 2455-2456 (1968).
12. P.W. Rozenkranz, IEEE Trans. Ant. Propag. **23**, 489 (1975).
13. E.W. Smith, J. Chem. Phys. **74**, No. 12, 6658-6673 (1981).
14. A.I. Burshtein, M.L. Strekalov, and S.I. Temkin, Zh. Eksp. Teor. Fiz. **66**, No. 3, 894-906 (1974).
15. V.A. Alekseev and I.I. Sobel'man, Zh. Fiz. Khimii **34**, No. 4, 579-583 (1968).
16. A.I. Petrova and M.R. Cherkasov, Opt. Spektrosk. **48**, No. 1, 43-48 (1980); **48**, No. 2, 256-261 (1980); **48**, No. 5, 870-877 (1980); **53**, No. 3, 429-434 (1982).



17. S. Green, J. Boissoles, and C. Boulet, *J. Quant. Spectrosc. Radiat. Transfer* **39**, No. 1, 33–42 (1988).
18. J. Boissoles, D. Robert, C. Boulet, and S. Green, *J. Chem. Phys.* **89**, No. 2, 625–635 (1989).
19. R. Chen and S. Takeo, *Usp. Fiz. Nauk* **66**, 391–474 (1958).
20. B. Bleaney and J.H.N. Loubser, *Proc. Phys. Soc.* **63A**, No. 2, 483–489 (1950).
21. A.H. Nethercot, J.A. Klein, J.H.N. Loubser, and C.H. Townes, *Nuovo Cimento* **9**, No. 2, 358–363 (1952).
22. R. Abraham, *Nuclear Magnetism* [Russian translation] (Izd. Inostr. Lit., Moscow, 1963), 564 pp.
23. A. Ben-Reuven and A. Lightman, *J. Chem. Phys.* **46**, 2489 (1967).
24. A. Lightman and A. Ben-Reuven, *J. Chem. Phys.* **50**, No. 1, 351 (1969).
25. A.B. Dokuchaev and M.V. Tonkov, *Opt. Spektrosk.* **50**, No. 3, 738–743 (1980).
26. M.R. Cherkasov, *Dep. VINITI*, No. 4281–77 (1977), 21 pp.
27. U. Fano, *Phys. Rev.* **131**, No. 1, 259–268 (1963).
28. N.N. Kuznetsov and A.P. Galtsev, *Preprint No. 9*, (IFA AN SSSR (1990), 40 pp.
29. P.W. Anderson, *Phys. Rev.* **76**, 647–661 (1949).
30. C.J. Tsao and D. Curnutte, *J. Quant. Spectrosc. Radiat. Transfer* **2**, 41–91 (1962).
31. J.S. Murphy and J.E. Boggs, *J. Chem. Phys.* **47**, 691–699 (1967).
32. B.S. Frost, *J. Phys. B: Atom. Molec. Phys.* **9**, 1001–1024 (1967).
33. U. Luk, *Special Mathematical Functions and Their Approximations* [Russian translation] (Mir, Moscow, 1980), 608 pp.