

# Simulation of resonance functions in the theory of spectral line collisional broadening

V.I. Starikov<sup>1,2</sup> and N.N. Lavrentieva<sup>2</sup>

<sup>1</sup>Tomsk State University of Control Systems and Radioelectronics

<sup>2</sup>Institute of Atmospheric Optics,  
Siberian Branch of the Russian Academy of Sciences, Tomsk

Received June 13, 2007

Resonance functions for semiclassical molecular line broadening theory are calculated in the exact trajectory model for molecules envired by neutral gas atoms. The calculations are performed for a set of values of the Lennard–Jones potential parameters. Model analytic representations are constructed for resonance functions dependent on these parameters. The model functions are tested in the calculations of the scattering cross section of rotational lines of the HCl molecule in the system HCl–Ar and rotational line half-widths of the radical OH in the system OH–Ar.

## Introduction

The collisional broadening of molecular spectral lines has been studied experimentally and theoretically for tens of years. The theory of spectral line shapes near the line center and at low pressures for nonoverlapping lines is well developed and reduces to computation of the complex scattering matrix  $S$ , from which the broadening coefficients  $\gamma$  and the line center shift coefficients  $\delta$  are determined. At present, several approaches to the computation are used.<sup>1,2</sup> In completely quantum methods, such as  $CC$  method,<sup>3</sup> intramolecular motions (rotation and vibration), and relative translation motion are considered from the quantum positions. This requires a large computer resource, therefore, the method is realized by now for simple systems of interacting molecules.

The relative motion trajectory in semiclassical calculation methods is defined by classical motion equations, including isotropic interaction potential  $U(R)$ , where  $R$  is the distance between centers of mass of interacting molecules. The special case  $U(R) = 0$  results in approximation of linear trajectories. The most complete form of the semiclassical approach is developed in Ref. 4 ( $NG$  approach); where the relative motion trajectory is computed for a series of points, which then are used to compute the matrix elements of the intermolecular potential in the basis of rotational-vibrational wave functions of an absorbing molecule. The  $NG$  formalism is considered as a classical analogue of the quantum  $CC$  method. Similar to the  $CC$  method, this formalism is realized for simple systems of  $XY-A$  type, where  $A$  are atoms of neutral gases.

Certain approximations in classical motion equations and simulation of isotropic intermolecular potential in the form of Lennard–Jones allowed one to introduce the parabolic trajectory ( $PT$ ) model.<sup>5</sup> The method is known as the Robert–Bonamy formalism and is widely used. It significantly simplifies the scheme of  $\gamma$  and  $\delta$  calculation as compared to  $CC$  and

$NG$  methods. Resonance functions, included into the method, were obtained in analytical form with accounting for the dependence on parameters of intermolecular interaction potential, in contrast to the straight-line trajectory approximation.

$S$ -matrix in the second order of perturbation theory is represented as the sum of products of line strengths and resonance functions. The resonance functions enter into the  $S$ -matrix computation scheme as multipliers. They are Fourier transforms of intermolecular interaction potential; their arguments are determined by the balance of the internal energy, released and received in collisions of interacting molecules. A general expression for resonance functions, following from the classical motion equations, is given in Ref. 6 for any form of isotropic intermolecular potential. The expression was used<sup>1,7,8</sup> for computing real and imaginary parts of resonance functions for electrostatic and polarization (induction and dispersion) contributions, where the model potential was used for the latter.

This paper continues our earlier works<sup>7,8</sup> and presents computational results for resonance functions for the intermolecular potential, chosen in the form of sum of pair interaction potentials. Besides, the parameters of model resonance functions, obtained in Refs. 1, 7, and 8, are improved. The improvement relates to the fact that numerical values of the resonance functions have been obtained for a wider set of parameters of the model isotropic potential in the form of Lennard–Jones. Model resonance functions have been tested in calculations of scattering cross section of HCl rotational lines in the system HCl–Ar and of the broadening coefficient  $\gamma$  of rotational lines of radical OH in the system OH–Ar.

## 1. General relations

The relative motion trajectory of interacting particles (i.e., two variables: the distance  $R(t)$  and

polar angle  $\varphi(t)$  is required for the resonance function computation. The trajectory is determined by the isotropic part of the interaction potential with the use of ordinary equations of classical mechanics,<sup>9</sup> which have the form

$$t(y) = \left(\frac{r_c}{v}\right) A_0(y); \quad (1)$$

$$\varphi(y) = \left(\frac{b}{r_c}\right) A_2(y); \quad (2)$$

$$A_n(y) = \frac{1}{2} \int_1^y \frac{dy}{y^{n/2} \{f(y)\}^{1/2}}, \quad n = 0, 2, \quad (3)$$

where  $y = (R/r_c)^2$ ;  $v$  is the relative velocity of colliding particles;  $b$  is the impact parameter;  $r_c$  is the closest approach distance; function  $f(y)$  depends on the isotropic interaction potential, which is defined as the sum

$$V = V^{\text{elec}} + V_{1,2}^{\text{at-at}} = V^{\text{elec}} + \sum_i \sum_j V_{1i,2j} = V^{\text{elec}} + \sum_i \sum_j \left\{ \frac{d_{ij}}{r_{1i,2j}^{12}} - \frac{e_{ij}}{r_{1i,2j}^6} \right\} \quad (4)$$

of electrostatic ( $V^{\text{elec}}$ ) and atom–atom ( $V_{1,2}^{\text{at-at}}$ ) potentials of interaction between molecules 1 and 2, which is determined by the pair Lennard–Jones potentials. The  $V_{1,2}^{\text{at-at}}$  potential simulates the polarization contribution into the intermolecular potential; in which the isotropic part is distinguished

$$V_{\text{isot}} = U(R) = 4\epsilon \left[ -\left(\frac{\sigma}{R}\right)^6 + \left(\frac{\sigma}{R}\right)^{12} \right] = 4\epsilon \left[ -\beta^6 \left(\frac{r_c}{R}\right)^6 + \beta^{12} \left(\frac{r_c}{R}\right)^{12} \right], \quad (5)$$

used for resonance functions computation, and anisotropic one, which is reduced to the same form as  $V^{\text{elec}}$  and then is used to compute the transition functions  $S(b)$  dependent on the parameters  $d_{ij}$  and  $e_{ij}$ , from the matrix  $S$ .

When the potential  $U(R)$  is chosen in form (5),

$$f(y) = (y - 1) + \lambda[\beta^{12}(1 - y^{-5}) - \beta^6(1 - y^{-2})]; \quad (6)$$

$$(b/r_c) = (v_c/v) = \sqrt{1 - \lambda(\beta^{12} - \beta^6)};$$

$$\beta = (\sigma/r_c);$$

$$\lambda = 8\epsilon/(mv^2), \quad (7)$$

where  $m$  is the reduced mass of colliding molecules (particles), the velocity  $v_c$  is defined like in Ref. 5. The real parts  ${}^{(l_1, l_2)}f_p^p(k_c)$  of the resonance functions are defined by the equation<sup>2</sup>

$${}^{(l_1, l_2)}f_p^p(k_c) = N \sum_{m=-l}^l I_{lm}^p(k_c) I_{lm}^{p'}(k_c), \quad (8)$$

where  $N$  is the normalization factor;  $l_1$  and  $l_2$  are the numbers determining the multipolarity of potential (4) expansion;  $l = l_1 + l_2$  and  $k_c = 2\pi cb(\omega_{i'i'} + \omega_{22'})/v$ ;  $\omega$  are the transition frequencies of the main (with indices  $l$  and  $i'$ ) and perturbing (with indices 2 and 2') molecules. In terms of the variables  $u = (y - 1)^{1/2}$ ,

$$I_{lm}^p(k_c) = 2 \sum_s a(l, m, s) \int_0^\infty \frac{e^{ik_c A_0(u)} (\cos \varphi)^m (\sin \varphi)^s u \, du}{(1 + u^2)^{p/2} \{f(u)\}^{1/2}}. \quad (9)$$

The coefficients  $a(l, m, s)$  are obtained from the equations, connecting spherical harmonics with the trigonometric functions  $\cos \varphi$  and  $\sin \varphi$  (see, e.g., Ref. 10). The closest approach distance  $r_c$  is defined as the solution of equation

$$\lambda[\beta^{12} - \beta^6] + (b^*)^2 \beta^2 - 1 = 0, \quad (10)$$

where  $b^* = b/\sigma$ . A general expression for resonance functions, dependent on the integrals in Eq. (9), was obtained in Ref. 6. The Robert–Bonamy computation scheme,<sup>5</sup> where resonance functions, obtained in the model of “exact” trajectories (by equations from Ref. 6), are used instead of the parabolic trajectory model, is called *ET (exact trajectory)* approximation.

## 2. Approximations

The integrals in Eq. (9) in a number of cases can be expressed analytically. In the first approximation (straight-line trajectory approximation)  $U(R) = 0$  ( $\lambda = 0$  or  $\beta = 0$ );  $f(y) = (y - 1)$  from Eq. (6),  $r_c = b$  from Eq. (10), which gives  $A_0(y, \lambda = 0) = u$  and  $R^2 = b^2 + vt^2$ ,  $A_2(y, \lambda = 0) = \arctan(u)$ . Resonance functions for this case were computed in a series of works.<sup>2, 11–13</sup> To obtain the second approximation, let us expand the function  $f(y)$  from Eq. (6) in a Taylor series about  $y_0 = 1$  and limit it to the first terms:

$$f(y) = f(y_0 = 1) + f'(y_0 = 1)(y - 1) + \dots \quad (11)$$

Here  $f(y_0 = 1) = 0$ ,

$$f'(y_0 = 1) = 1 + \lambda[5\beta^{12} - 2\beta^6] = (v'_c/v)^2. \quad (12)$$

The velocity  $v'_c$  was introduced in Ref. 5.

Equation (3) is integrated analytically and results in equations

$$R(t)^2 = r_c^2 + (v'_c t)^2; \quad (13)$$

$$\varphi(y) = (v_c/v'_c) \arctan(R^2/r_c^2 - 1)^{1/2}. \quad (14)$$

What about interactions, for which  $R \cong r_c$  and  $v_c \cong v'_c$ , then the coefficient in Eq. (14) can be inserted into the argument; in this case

$$\sin^2 \varphi = \frac{(v_c t)^2}{r_c^2 + (v_c t)^2}. \quad (15)$$

Equation (15) differs from the corresponding one for  $\sin^2 \varphi$  [Ref. 15] in the denominator, where the velocity  $v_c$  is replaced by  $v'_c$ . Equations for a series of

resonance functions in the Robert–Bonamy formalism (in the parabolic trajectories approximation) are given in Ref. 5.

### 3. Computation scheme

At the first stage, the integrals  $A_n(y, \lambda, \beta)$  from Eq. (3) for different  $y$ ,  $\lambda$ , and  $\beta$  are computed at the step  $\Delta y = 0.2$  for  $1 \leq y \leq 5$  and at the step  $\Delta y = 0.5$  for  $5 < y \leq 9$  at the points  $\lambda = 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5$  at  $\beta = 0.3; 0.5; 0.7; 0.8; 0.85; 0.9; 0.95; 1.0; 1.01; 1.02; 1.04; 1.08$ . At the second stage, the integrals  $A_n(y, \lambda, \beta)$  are approximated by the equations

$$A_0(u, \lambda, \beta) = t(u) \frac{v\beta}{\sigma} = \frac{b_1(\lambda, \beta)u}{1 + b_2(\lambda, \beta)u}, \quad (16)$$

$$A_2(u, \lambda, \beta) = c_1(\lambda, \beta) \arctan(u), \quad (17)$$

where

$$\begin{aligned} b_1(\lambda, \beta) &= \frac{1 + b_{11}\lambda\beta^6(\beta^6 - b_{12})}{1 + b_{13}\lambda\beta^6(\beta^6 - b_{12})}, \\ b_2(\lambda, \beta) &= \frac{b_{21}\lambda\beta^6(\beta^6 - b_{22})}{1 + b_{23}\lambda\beta^6(\beta^6 - b_{22})}, \\ c_1(\lambda, \beta) &= \frac{1 + c_{11}\lambda\beta^6(\beta^6 - c_{12})}{1 + c_{13}\lambda\beta^6(\beta^6 - c_{12})}. \end{aligned} \quad (18)$$

When approximating by Eqs. (17) and (18), the fact that  $A_0(y, \lambda = 0) = u$  and  $A_2(y, \lambda = 0) = \arctan(u)$  in the straight-line trajectory approximation is taken into account. Parameters from Eq. (18) are given in Table 1.

**Table 1. Parameters from Eq. (18) determining the trajectory of interacting particles for the Lennard-Jones potential**

Parameter	Value	Parameter	Value	Parameter	Value
$b_{11}$	0.2867	$b_{21}$	-0.3374	$c_{11}$	0.3513
$b_{12}$	0.5577	$b_{22}$	0.5173	$c_{12}$	0.5441
$b_{13}$	1.7291	$b_{23}$	1.4561	$c_{13}$	1.5409

Using Eqs. (16)–(18) and parameters from Table 1, numerical values of the resonance functions

$$\begin{aligned} &^{(1,0)}f_7^7, \ ^{(1,0)}f_9^9, \ ^{(1,0)}f_{13}^{13}, \ ^{(1,0)}f_{15}^{15} \text{ and } ^{(2,0)}f_8^8, \\ &^{(2,0)}f_{10}^{10}, \ ^{(2,0)}f_{14}^{14} \text{ and } ^{(2,0)}f_{16}^{16} \end{aligned}$$

are obtained from interaction potential (5) for each pair of  $\lambda$  and  $\beta$  and the argument  $k_c$  from 0 to 7.5. These resonance functions appear in the transaction functions  $S(b)$  for the “molecule–neutral gas atom” systems ( $l_2 = 0$ ), when the expansion of atom–atom potential (4) is limited to the terms with  $l_1 = 1, 2$ . Model interaction potentials are often considered in the literature as well. Thus, the system HCl–Ar is considered in Ref. 5 to test the suggested method; the interaction potential was chosen in the form

$$\begin{aligned} V(R, \theta) &= V_0(R) + V_1(R, \theta) + V_2(R, \theta) = \\ &= 4\epsilon\{(\sigma/R)^{12} - (\sigma/R)^6\} + \{R_1(\sigma/R)^{12} - A_1(\sigma/R)^7\} \times \\ &\times P_1(\cos\theta) + \{R_2(\sigma/R)^{12} - A_2(\sigma/R)^6\}P_2(\cos\theta), \end{aligned} \quad (19)$$

where  $P_1(\cos\theta)$  and  $P_2(\cos\theta)$  are the Legendre polynomials ( $\theta = \pi/2 - \varphi$ ). For this potential, the addition resonance functions  $^{(1,0)}f_7^{12}$ ,  $^{(1,0)}f_{12}^{12}$ ,  $^{(2,0)}f_6^6$ ,  $^{(2,0)}f_{12}^{12}$ , and  $^{(2,0)}f_6^{12}$  should be known. The functions  $^{(1,0)}f_{12}^{12}$  and  $^{(2,0)}f_6^6$  were also computed in Ref. 5. Computations show that the functions  $^{(4,l_2)}f_p^p$  with  $p \neq p'$  can be defined by the equation

$$^{(4,l_2)}f_p^p = \left( ^{(4,l_2)}f_p^p \cdot ^{(4,l_2)}f_{p'}^{p'} \right)^{1/2}. \quad (20)$$

### 4. Approximation of the real parts of resonance functions

To use resonance functions in computations of coefficients of line broadening and shift, it is necessary to know their explicit dependence on  $\lambda$  and  $\beta$ , because  $\gamma$  and  $\delta$  computation schemes in general case include integrating over  $b$  (or  $r_c$ ) and the velocity  $v$ , but, according to Eqs. (7) and (10),  $\lambda = \lambda(b, v)$ ,  $\beta = \beta(b, v)$ . In this work (like in Refs. 1, 7, and 8) the resonance functions  $f(x, \lambda, \beta)$  (all indices are omitted,  $x \equiv k_c$ ) are approximated by the functions

$$\begin{aligned} f^{(m)}(x, \lambda, \beta) &= a_1(\lambda, \beta) (\tanh[z(\lambda, \beta)] - 1); \\ z(\lambda, \beta) &= \alpha(\lambda, \beta) [x - x_e(\lambda, \beta)], \end{aligned} \quad (21)$$

where

$$\begin{aligned} a_1(\lambda, \beta) &= a_{10} + a_{11}\{\tanh[a_{1\beta}(\beta - \beta_{1e})] + \\ &+ (\tanh[a_{1\beta}(\beta - \beta_{1e})])^2\}; \\ \alpha(\lambda, \beta) &= \alpha_0 + \alpha_{\lambda\beta\beta} \lambda\beta^2; \\ x_e(\lambda, \beta) &= x_{e0} + x_{e\lambda\beta\beta} \lambda\beta^2. \end{aligned} \quad (22)$$

The parameters  $a_{10}$ ,  $a_{11}$ ,  $a_{1\beta}$ ,  $\alpha_0$ , ...,  $x_{e\lambda\beta\beta}$  in Eq. (22) were determined from fitting of the  $f_{l_1 l_2}^{(m)}(x, \lambda, \beta)$  to the values of exact functions  $^{(4,l_2)}f_p^p(x, \lambda, \beta)$  for different  $x$ ,  $\lambda$ , and  $\beta$ . Functions (21) can be considered as the model representations for resonance functions, obtained in the model of exact trajectories (MET resonance functions). Parameters for these functions are given in Tables 2 and 3.

Figure 1 shows the comparison of the resonance function  $g_1(x) = ^{(2,0)}f_6^6(x)$ , obtained in different approximations.

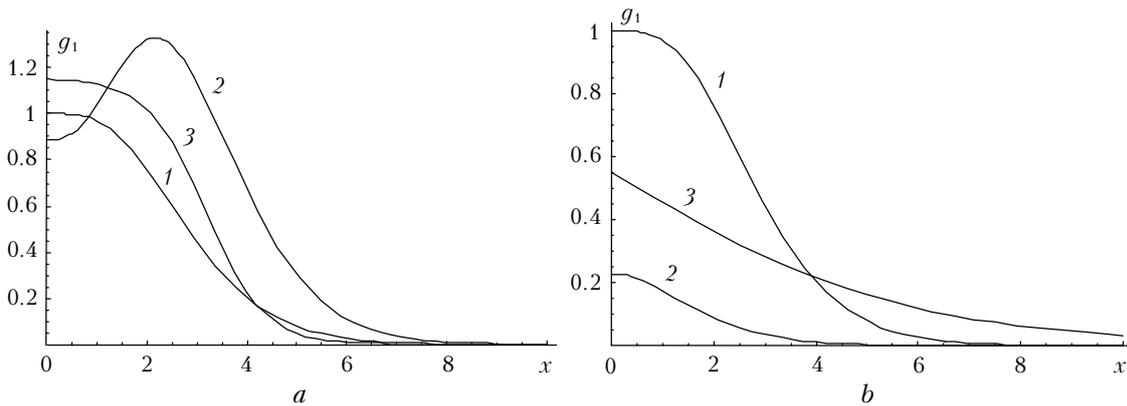
For exact comparison, the expression for  $g_1(x)$  from the PT model<sup>5</sup> is multiplied by  $(v'/v)^2$ , which enters into the transaction functions  $S(b)$  as a multiplier, in contrast to the multiplier  $(1/v)^2$  for the MET function  $S(b)$ . The behavior of  $g_1(x)$  evidently differs in different approximations, especially at  $\beta \geq 1$ . This is true for all functions considered in this work.

**Table 2. Parameters of the model  $^{(1,0)}f_p^p$  functions**

Parameter	$^{(1,0)}f_7^7$	$^{(1,0)}f_9^9$	$^{(1,0)}f_{12}^{12}$	$^{(1,0)}f_{13}^{13}$	$^{(1,0)}f_{15}^{15}$
	$\beta \leq 1.0$				
$a_{10}$	$-0.6593 \pm 0.0072$	$-0.6839 \pm 0.01368$	$-0.775 \pm 0.013$	$-0.7472 \pm 0.0168$	$-0.7714 \pm 0.0187$
$a_{11}$	$0.2965 \pm 0.0060$	$0.3371 \pm 0.01558$	$0.360 \pm 0.005$	$0.3726 \pm 0.0162$	$0.3854 \pm 0.0164$
$a_{1\beta}$	$8.3947 \pm 0.2986$	$6.911 \pm 0.632$	$9.054 \pm 0.250$	$7.178 \pm 0.667$	$7.277 \pm 0.681$
$\beta_{1e}$	$0.8159 \pm 0.1685$	$0.805 \pm 0.003$	$0.810 \pm 0.017$	$0.800 \pm 0.0041$	$0.800 \pm 0.004$
$\alpha_0$	$0.3957 \pm 0.01714$	$0.3263 \pm 0.0218$	$0.274 \pm 0.007$	$0.2392 \pm 0.0171$	$0.2132 \pm 0.0157$
$\alpha_{\lambda,\beta\beta}$	$0.2773 \pm 0.0233$	$0.3099 \pm 0.0369$	$0.131 \pm 0.013$	$0.2642 \pm 0.0308$	$0.2464 \pm 0.0286$
$x_e$	$1.6878 \pm 0.0407$	$1.886 \pm 0.0736$	$1.572 \pm 0.0332$	$1.946 \pm 0.101$	$1.957 \pm 0.112$
$x_{e\lambda,\beta\beta}$	$0.35463 \pm 0.0244$	$0.2469 \pm 0.0364$	$0.720 \pm 0.0353$	$0.3740 \pm 0.0470$	$0.4392 \pm 0.0515$
	$\beta > 1.0$				
$a_{10}$	$-0.5781 \pm 0.0123$	$-0.5166 \pm 0.0133$	$-0.5093 \pm 0.0410$	$-0.4708 \pm 0.0128$	$-0.4550 \pm 0.0125$
$\alpha_0$	$0.2460 \pm 0.0062$	$0.1933 \pm 0.0063$	$0.1647 \pm 0.0069$	$0.15193 \pm 0.00531$	$0.13331 \pm 0.0049$
$\alpha_{\lambda,\beta\beta}$	$-0.03106 \pm 0.0013$	$-0.02680 \pm 0.0013$	$-0.02258 \pm 0.003$	$-0.02149 \pm 0.0010$	$-0.01897 \pm 0.0009$
$x_e$	0.0	0.0	0.0	0.0	0.0
$x_{e\lambda,\beta\beta}$	$-1.8498 \pm 0.140$	$-2.9427 \pm 0.1659$	$-3.3316 \pm 0.93$	$-3.9942 \pm 0.2648$	$-4.6549 \pm 0.3182$

**Table 3. Parameters of the model  $^{(2,0)}f_p^p$  functions**

Parameter	$^{(2,0)}f_6^6$	$^{(2,0)}f_8^8$	$^{(2,0)}f_{10}^{10}$	$^{(2,0)}f_{12}^{12}$	$^{(2,0)}f_{14}^{14}$	$^{(2,0)}f_{16}^{16}$
	$\beta \leq 1.0$					
$a_{10}$	$-0.5539 \pm 0.0032$	$-0.5723 \pm 0.007$	$-0.5986 \pm 0.0083$	$-0.586 \pm 0.002$	$-0.6491 \pm 0.0107$	$-0.6716 \pm 0.0118$
$a_{11}$	$0.2527 \pm 0.0064$	$0.2521 \pm 0.0100$	$0.2724 \pm 0.0102$	$0.292 \pm 0.006$	$0.3053 \pm 0.0103$	$0.3187 \pm 0.0110$
$a_{1\beta}$	$6.9429 \pm 0.2582$	$6.806 \pm 0.515$	$6.942 \pm 0.511$	$6.921 \pm 0.246$	$7.164 \pm 0.511$	$7.256 \pm 0.513$
$\beta_{1e}$	$0.8221 \pm 0.1658$	$0.797 \pm 0.003$	$0.7956 \pm 0.003$	$0.822 \pm 0.001$	$0.794 \pm 0.003$	$0.7930 \pm 0.003$
$\alpha_0$	$0.4023 \pm 0.00853$	$0.3925 \pm 0.025$	$0.3254 \pm 0.0204$	$0.318 \pm 0.006$	$0.2454 \pm 0.0155$	$0.2188 \pm 0.014$
$\alpha_{\lambda,\beta\beta}$	$0.1928 \pm 0.0145$	$0.3016 \pm 0.042$	$0.2625 \pm 0.0353$	$0.170 \pm 0.011$	$0.2207 \pm 0.027$	$0.2082 \pm 0.025$
$x_e$	$2.8459 \pm 0.0275$	$2.9533 \pm 0.0651$	$2.9759 \pm 0.0765$	$2.860 \pm 0.035$	$2.9844 \pm 0.0979$	$2.9825 \pm 0.1081$
$x_{e\lambda,\beta\beta}$	$0.4416 \pm 0.0201$	$0.25456 \pm 0.0368$	$0.30078 \pm 0.0423$	$0.531 \pm 0.023$	$0.3891 \pm 0.051$	$0.4325 \pm 0.0550$
	$\beta > 1.0$					
$a_{10}$	$-0.6797 \pm 0.0151$	$-0.5979 \pm 0.0131$	$-0.5492 \pm 0.0129$	$-0.5248 \pm 0.0109$	$-0.4926 \pm 0.0124$	$-0.47450 \pm 0.0122$
$\alpha_0$	$0.2400 \pm 0.0074$	$0.1938 \pm 0.0054$	$0.1651 \pm 0.0050$	$0.1405 \pm 0.0039$	$0.1321 \pm 0.0045$	$0.1220 \pm 0.0044$
$\alpha_{\lambda,\beta\beta}$	$-0.0293 \pm 0.0032$	$-0.0255 \pm 0.0012$	$-0.02254 \pm 0.0010$	$-0.01999 \pm 0.0008$	$-0.01848 \pm 0.0010$	$-0.01711 \pm 0.0008$
$x_e$						
$x_{e\lambda,\beta\beta}$	$-1.7284 \pm 0.1506$	$-2.5585 \pm 0.1306$	$-3.2862 \pm 0.1797$	$4.2271 \pm 0.2136$	$-4.4295 \pm 0.2851$	$-4.8757 \pm 0.3428$



**Fig. 1.** Resonance function  $g_1(x) = ^{(2,0)}f_6^6(x)$ , obtained for two sets of intermolecular potential parameters ( $\lambda = 2.0$ ;  $\beta = 0.75$ ) (a) and ( $\lambda = 2.0$ ;  $\beta = 1.0$ ) (b) in the straight-line (the function is independent of potential parameters) (1) and parabolic (2) trajectory approximations; 3 corresponds to model function (21) with the parameters from Table 3.

### 5. Imaginary parts of resonance functions

Imaginary parts  $I^{(l_1 l_2)} f_p^p(x, \lambda, \beta)$  of the resonance functions were computed by the equation

$$I^{(l_1 l_2)} f(x, \lambda, \beta) = \frac{1}{\pi} P.P. \int_{-\infty}^{\infty} dx' \frac{{}^{(l_1 l_2)} f^{(m)}(x', \lambda, \beta)}{x - x'}, \quad (23)$$

where *P.P.* means the principal part of the integral

$$If(x) = \frac{1}{\pi} \left\{ \int_{-A}^0 \frac{f(-y)}{x-y} dy + \int_0^{x-\delta} \frac{f(y)}{x-y} dy + \int_{x+\delta}^A \frac{f(y)}{x-y} dy \right\} + \frac{a_2(\lambda, \beta)}{\cosh[\alpha_2(\lambda, \beta)(x - x_e(\lambda, \beta))]} \quad (24)$$

at  $A = 400$  and  $\delta = 10^{-12}$ , while for real parts of resonance functions their model approximations (21) and (22) were used with parameters from Tables 2 and 3.

To approximate the values of functions  $If(x, \lambda, \beta)$  (with an arbitrary set of indices), obtained by Eq. (23), the model

$$If^{(m)}(x, \lambda, \beta) = \sinh[\alpha_0(\lambda, \beta)x] \times \left\{ \frac{a_1(\lambda, \beta)}{\cosh[\alpha_1(\lambda, \beta)(x - x_e(\lambda, \beta))]} + \right.$$

was chosen, where  $a_n(\lambda, \beta)$ ,  $\alpha_n(\lambda, \beta)$ , and  $x_e(\lambda, \beta)$  are defined by Eq. (22), i.e.,

$$\begin{aligned} a_n(\lambda, \beta) &= a_{n0} + a_{n1} \{ \tanh[a_{n\beta}(\beta - \beta_{ne})] + \\ &+ (\tanh[a_{n\beta}(\beta - \beta_{ne})])^2 \}, \quad n = 0, 1, \\ \alpha_n(\lambda, \beta) &= \alpha_{n0} + \alpha_{n\lambda, \beta} \lambda \beta^2, \quad n = 0, 1, 2, \\ x_e(\lambda, \beta) &= x_{e0} + x_{e\lambda\beta} \lambda \beta^2. \end{aligned} \quad (26)$$

The parameters, obtained through the fitting of Eqs. (25) and (26) to the values of resonance functions, computed by Eq. (23) in the model of real trajectories, are given in Tables 4 and 5.

**Table 4. Parameters of the model  $I^{(1,0)}f_p^p$  functions**

Parameter	$I^{(1,0)}f_7^7$	$I^{(1,0)}f_9^9$	$I^{(1,0)}f_{12}^{12}$	$I^{(1,0)}f_{13}^{13}$	$I^{(1,0)}f_{15}^{15}$
	$\beta \leq 1.0$				
$a_{10}$	0.8686 ± 0.0361	0.9589 ± 0.0762	1.4151 ± 0.0819	1.3273 ± 0.0663	1.4305 ± 0.0685
$a_{11}$	3.0165 ± 0.1247	3.2679 ± 0.1605	5.0427 ± 0.287	4.6717 ± 0.2290	5.0632 ± 0.2379
$\beta_{1e}$	1.051 ± 0.002	1.060 ± 0.002	1.069 ± 0.002	1.0633 ± 0.0026	1.064 ± 0.0025
$a_{1\beta}$	8.937 ± 0.178	7.664 ± 0.169	6.952 ± 0.1370	7.257 ± 0.1490	7.208 ± 0.1441
$a_{20}$	0.0219 ± 0.0015	0.01721 ± 0.0020	0.03032 ± 0.0027	0.0177 ± 0.0026	0.01769 ± 0.0027
$\alpha_0$	0.6046 ± 0.0194	0.6261 ± 0.0216	0.3936 ± 0.0163	0.5122 ± 0.0158	0.48417 ± 0.0139
$\alpha_{0\lambda, \beta\beta}$	-0.0509 ± 0.0022	-0.06527 ± 0.0026	-0.04106 ± 0.0021	-0.0723 ± 0.0022	-0.0723 ± 0.0020
$x_e$	0.1392 ± 0.0403	-0.1558 ± 0.0605	-0.8004 ± 0.1009	-0.9093 ± 0.0906	-1.16800 ± 0.0967
$x_{e\lambda, \beta\beta}$	0.5053 ± 0.0775	0.6212 ± 0.0246	0.9696 ± 0.0375	0.9828 ± 0.0330	1.1138 ± 0.0345
$\alpha_{10}$	0.7930 ± 0.0674	0.7615 ± 0.0194	0.5297 ± 0.0129	0.6046 ± 0.0138	0.5640 ± 0.0121
$\alpha_2 = \alpha_0$					
	$\beta > 1$				
$a_{10}$	0.3432 ± 0.0066	0.2975 ± 0.0068	0.2949 ± 0.0065	0.2855 ± 0.0082	0.2622 ± 0.0064
$\alpha_0$	0.6021 ± 0.0162	0.4766 ± 0.0148	0.4007 ± 0.0119	0.3801 ± 0.0146	0.3114 ± 0.010
$\alpha_{0\lambda, \beta\beta}$	0.02428 ± 0.0015	0.02284 ± 0.0017	0.01904 ± 0.0015	0.0229 ± 0.0199	0.01787 ± 0.0016
$x_{e\lambda, \beta\beta}$	-0.6721 ± 0.0212	-1.0418 ± 0.0369	-1.2133 ± 0.0420	-1.5143 ± 0.0645	-1.8000 ± 0.0662
$\alpha_{10}$	0.7241 ± 0.0138	0.5735 ± 0.0125	0.4808 ± 0.0099	0.4601 ± 0.0121	0.3767 ± 0.0083

**Table 5. Parameters of the model  $I^{(2,0)}f_p^p$  functions**

Parameter	$I^{(2,0)}f_6^6$	$I^{(2,0)}f_8^8$	$I^{(2,0)}f_{10}^{10}$	$I^{(2,0)}f_{12}^{12}$	$I^{(2,0)}f_{14}^{14}$	$I^{(2,0)}f_{16}^{16}$
	$\beta \leq 1.0$					
$a_{10}$	0.680 ± 0.031	0.6961 ± 0.0295	0.6835 ± 0.0292	0.720 ± 0.027	0.7227 ± 0.0272	0.7675 ± 0.0295
$a_{11}$	1.9647 ± 0.0186	2.2212 ± 0.0948	0.2251 ± 0.0962	2.4028 ± 0.0206	2.4420 ± 0.0910	2.6497 ± 0.1004
$\beta_{1e}$	1.074 ± 0.001	1.062 ± 0.028	1.063 ± 0.0030	1.078 ± 0.0013	1.061 ± 0.002	1.064 ± 0.0025
$a_{1\beta}$	7.50 ± 0.162	7.353 ± 0.166	7.248 ± 0.171	7.200 ± 0.144	7.185 ± 0.144	7.041 ± 0.139
$a_{20}$	0.0326 ± 0.0011	0.0220 ± 0.0016	0.01788 ± 0.0018	0.02492 ± 0.0017	0.01294 ± 0.0019	0.0115 ± 0.0021
$\alpha_0$	0.4378 ± 0.0022	0.4497 ± 0.0171	0.4776 ± 0.0177	0.4317 ± 0.0032	0.4748 ± 0.0144	0.4624 ± 0.0137
$\alpha_{0\lambda, \beta\beta}$	-0.0216 ± 0.0017	-0.0262 ± 0.0022	-0.0345 ± 0.0022	-0.0314 ± 0.0021	-0.0432 ± 0.0020	-
$x_e$	1.328 ± 0.016	1.1936 ± 0.0261	0.9001 ± 0.0354	0.6680 ± 0.0273	0.4813 ± 0.0478	0.2578 ± 0.0578
$x_{e\lambda, \beta\beta}$	0.4401 ± 0.0146	0.4324 ± 0.0180	0.5512 ± 0.0232	0.7751 ± 0.0235	0.7704 ± 0.0275	0.8752 ± 0.0310
$\alpha_{10}$	0.7016 ± 0.0028	0.6541 ± 0.0132	0.6336 ± 0.0145	0.5721 ± 0.0023	0.5767 ± 0.0125	0.5482 ± 0.0121
$\alpha_2 = \alpha_0$						
	$\beta > 1$					
$a_{10}$	0.3834 ± 0.0068	0.3515 ± 0.0071	0.3212 ± 0.0070	0.2321 ± 0.0029	0.2880 ± 0.0067	0.2759 ± 0.00667
$\alpha_0$	0.5149 ± 0.0123	0.4749 ± 0.1313	0.3998 ± 0.0117	0.3391 ± 0.0068	0.3067 ± 0.0096	0.2771 ± 0.0090
$\alpha_{0\lambda, \beta\beta}$	0.02481 ± 0.0011	0.0207 ± 0.0014	0.0193 ± 0.0015	0.0252 ± 0.0009	0.0176 ± 0.0015	0.01698 ± 0.0015
$x_{e\lambda, \beta\beta}$	-0.5985 ± 0.0184	-0.9191 ± 0.0298	-1.1973 ± 0.0406	-1.50 ± 0.26	-1.7504 ± 0.0623	-2.007 ± 0.0731
$\alpha_{10}$	0.6307 ± 0.0102	0.5707 ± 0.0110	0.4817 ± 0.0097	0.3947 ± 0.0065	0.3714 ± 0.0078	0.3355 ± 0.0073

Note that, if necessary, an asymptotic representation for the resonance functions  $I_f(x)$  should be used for large  $x$ , which can have an analytical form when using Eq. (21) for real parts of these functions. Really, according to Ref. 13,

$$I_f(x) \cong \frac{1}{x} \frac{2}{\pi} \int_0^{\infty} dx' f(x') \quad (27)$$

at large  $x$ . Substituting closed-form Eq. (21), obtain the asymptotic representation

$$I_f^{(m)}(x) \cong \frac{2}{(\pi x)} \left\{ -\frac{a_1}{\alpha} \ln[1 + e^{2\alpha x}] \right\}. \quad (28)$$

For  $x > 9$ , Equation (28) gives almost the same value for  $I_f^{(m)}(x)$  as integral (24). The resonance functions  $I^{(1,0)}f_7^7(x)$  and  $I^{(2,0)}f_6^6(x)$  (2) are shown in Fig. 2.

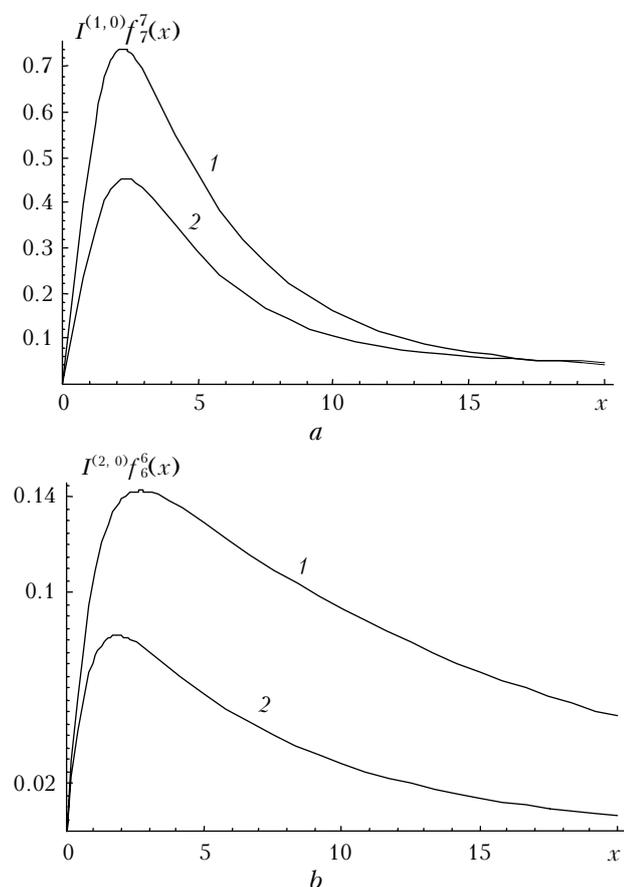


Fig. 2. Resonance functions  $I^{(1,0)}f_7^7(x)$  (1) and  $I^{(2,0)}f_6^6(x)$  (2), obtained in the *ET* approximation for two sets of intermolecular potential parameters ( $\lambda = 2.0$ ;  $\beta = 0.75$ ) (a) and ( $\lambda = 2.0$ ;  $\beta = 1.0$ ) (b).

## 6. Calculation of broadening coefficients

Obtained model representations (21) and (25) for resonance functions were tested in calculations of Ar-pressure broadening coefficients of rotational lines

of HCl and OH molecules. In such calculations, the first-order transaction functions  $S_1(b)$ , determined by the difference between intermolecular potential in different vibrational states, can be neglected. All the calculations were carried following the Robert–Bonamy scheme,<sup>5</sup> with integration over  $r_c$  when determining  $\gamma$  and  $\delta$ . The integration over  $\beta = \sigma/r_c$ ,  $\beta_0 \leq \beta \leq \infty$  ( $\beta_0 = \sigma/r_{c0}$ ,  $r_{c0}$  is given in Ref. 5) is more convenient. In addition, the mean thermal velocity  $v$  is used in calculations.

The system HCl–Ar is thoroughly studied both experimentally and theoretically.<sup>3,5,14</sup> The scattering cross section for the line half-width (differing from the half-width  $\gamma$  in the multiplier<sup>2</sup>) of the rotational molecule spectrum was calculated<sup>5</sup> with the use of the *PT* model and model potential (19) with parameters

$$\varepsilon/k_B = 202 \text{ K}, \quad \sigma = 3.37 \text{ \AA};$$

$$R_1 = 0.37; \quad R_2 = 0.65; \quad A_1 = 0.33; \quad A_2 = 0.14.$$

All functions, required for the transaction function  $S(b)$ , are given in Ref. 5, including the resonance functions  $^{(1,0)}f_7^7$ ,  $^{(1,0)}f_7^{12}$ ,  $^{(1,0)}f_{12}^{12}$  and  $^{(2,0)}f_6^6$ ,  $^{(2,0)}f_6^{12}$  and  $^{(2,0)}f_{12}^{12}$ . We used the same functions for  $S(b)$  except for the above-obtained functions (21) and (25) instead of resonance ones in the *PT* model ( $^{(1,0)}f_7^{12}$  and  $^{(2,0)}f_6^{12}$  were determined from Eq. (20)).

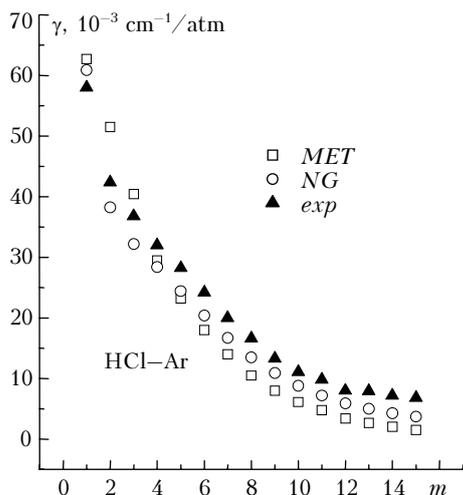
The computational results are given in Table 6 in comparison with the results of similar computations, carried out by other authors.<sup>5</sup> A good agreement of our calculations with those from Refs. 3 and 14 is evident: there is a small undervaluation of the calculated cross sections for the rotational quantum number  $J = 5$  as compared to the *NG* method at an energy of 398 K. In comparison with the parabolic trajectories, our results are regularly lower.

Table 6. Scattering cross section ( $\text{\AA}^2$ ) for the HCl rotational transitions in the system HCl–Ar for different reduced energy  $E^* = mv^2/k_B$

$J$	$E^* = 398 \text{ K}$			$E^* = 808 \text{ K}$		
	<i>MET</i>	<i>NG</i> <sup>3,5</sup>	<i>PT</i> <sup>5</sup>	<i>MET</i>	<i>SGC</i> <sup>3,14</sup>	<i>PT</i> <sup>5</sup>
0	80.0	79.9	80.3	66.1		
1	62.8	57.4	68.2	54.0	57.2	58.7
2	45.4	45.2	55.1	41.7	43.1	47.4
3	34.3	37.4	45.1	35.2	36.5	40.2
4	26.1	30.6	36.6	31.4	31.2	34.8
5	20.1	23.7	29.4	27.7	26.9	30.2

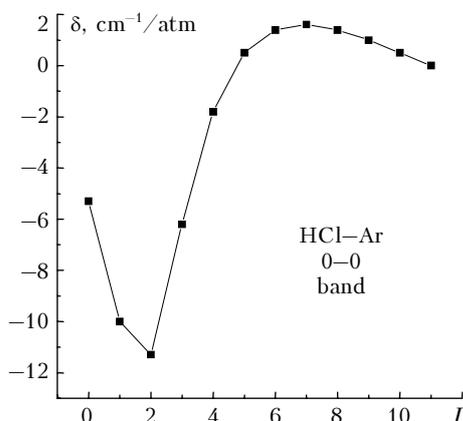
The coefficients  $\gamma$  for the rotational band, computed with model potential (19), are shown in Fig. 3.

The experimental<sup>15</sup>  $\gamma$  for the absorption band  $1 \leftarrow 0$  are shown here for comparison. In Ref. 15,  $\gamma$  and  $\delta$  were computed by the *NG*-method for the bands  $1 \leftarrow 0$  and  $2 \leftarrow 0$  with the use of interaction potential, extended in comparison with Eqs. (4) and (19), being in good agreement with experimental results.



**Fig. 3.** Coefficient  $\gamma$  for the HCl rotational band in the system HCl–Ar computed with model potential (19). Experimental and NG method computed values of  $\gamma$  correspond to the  $1 \leftarrow 0$  band.

The vibrational dependence of the parameters was not taken into account in model potential (19), therefore, line shifts are undetectable. The contribution of the second-order transaction functions was assessed and turned out to be quite significant for small  $J$  (Fig. 4).



**Fig. 4.** Contribution of second-order transaction functions into the shift of HCl molecule rotational lines in the system HCl–Ar (with the use of model potential (19)).

The broadening coefficients  $\gamma$  for the system OH–Ar were theoretically computed earlier by the Robert–Bonamy<sup>14</sup> and  $ET^{17}$  methods. The parameters of atom–atom intermolecular interaction potential from Eq. (4) and other parameters of the molecule are given in Ref. 16 and 17. The OH radical has two branches  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  due to the presence of the unpaired electron.

In this work,  $\gamma$  were computed for the both branches with accounting for virtual intrabranch transitions; interbranch transitions were not taken into account, that, according to Ref. 16, undervalues the computed  $\gamma$  by about 8%. The computational results are given in Table 7.

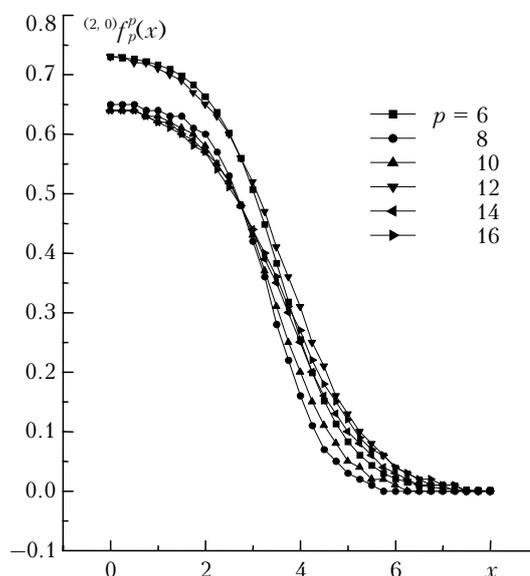
**Table 7.** Experimental and computed OH line half-widths ( $10^{-3} \text{ cm}^{-1}/\text{atm}$ ) for rotational transitions in the OH–Ar system

$J$	${}^2\Pi_{3/2}$			${}^2\Pi_{1/2}$	
	Exp. <sup>18</sup>	MET	ET <sup>17</sup>	MET	ET <sup>17</sup>
1/2	–	–	–	44.6	50.3
3/2	49.9	48.8	46.9	36.4	44.2
5/2	–	40.8	39.8	32.9	37.8
7/2	–	35.4	28.3	29.8	27.2

The obtained  $\gamma$  well correlate with computations in the  $ET$  model, however, our computation results are a little overvalued at  $J = 3.5$  for the branch  ${}^2\Pi_{3/2}$ . At the same time, note a good agreement between the computation for  $J = 1.5$  and the only experimental value.

## 7. Resonance function simulation for large values of index $p$

Expansion of the atom–atom potential is poor convergent for a number of systems of interacting molecules, which results in the necessity to take into account items, including the resonance functions  $f_p^p$  with large  $p$ . The behavior of such resonance functions can be determined from the behavior of already computed ones. The behavior of the model resonance functions  $({}^{2,0})f_p^p(x)$  with  $p = 6, 8, 10, 12, 14,$  and  $16$  is exemplified in Figs. 5 and 6 for  $\lambda = 2.0$  and different  $\beta$ .



**Fig. 5.** Model resonance functions  $({}^{2,0})f_p^p(x)$  for  $\lambda = 2.0$  and  $\beta = 0.9$ .

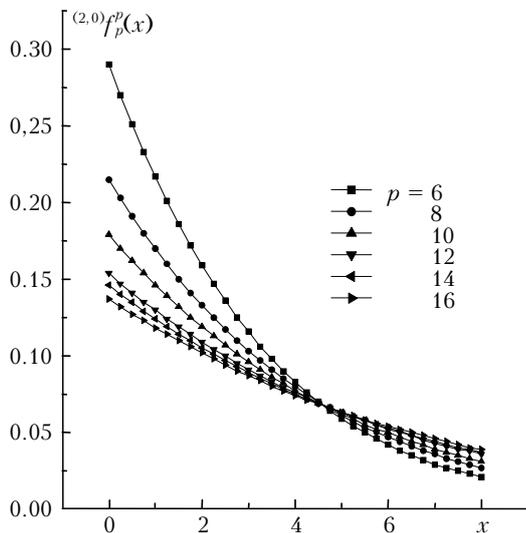
The  $p$ -dependence of the functions

$$f^{(m)}(x, \lambda, \beta; p) = a'_1(\lambda, \beta; p)(\tanh[z'(\lambda, \beta; p)] - 1);$$

$$z'(\lambda, \beta; p) = \alpha'(\lambda, \beta; p)[x - x'_e(\lambda, \beta; p)] \quad (29)$$

**Table 8. Parameters of model resonance functions (29)**

Parameters	$\beta \leq 1$ ( $y_{\alpha x} = 0, 0$ )				
	$a'_{10}$	$a'_{11}$	$a'_{1\beta}$	$\beta'_e$	$y_a$
$^{10}f_p^p$	$-0.2858 \pm 0.0154$	$0.1369 \pm 0.0075$	$7.379 \pm 0.162$	0.8	$0.2927 \pm 0.0206$
$^{20}f_p^p$	$-0.5278 \pm 0.0305$	$0.2440 \pm 0.0144$	$6.845 \pm 0.148$	0.8	$0.7804 \pm 0.0514$
	$\alpha'_0$	$\alpha'_{\lambda, \beta\beta}$	$y_\alpha$	$x'_e$	$x'_{e\lambda, \beta\beta}$
$^{10}f_p^p$	$0.8604 \pm 0.1393$	$0.6811 \pm 0.1159$	$0.1878 \pm 0.04468$	$1.7443 \pm 0.0340$	$0.4634 \pm 0.01787$
$^{20}f_p^p$	$0.4975 \pm 0.0261$	$0.3451 \pm 0.0238$	$0.0566 \pm 0.0078$	$2.8806 \pm 0.0236$	$0.42051 \pm 0.0144$
	$\beta > 1$				
	$a'_{10}$	$y_a$	$\alpha'_0$	$\alpha'_{\lambda, \beta\beta}$	$y_\alpha$
$^{10}f_p^p$	$-0.6482 \pm 0.0093$	$0.0013 \pm 0.0001$	$0.2105 \pm 0.0036$	$-0.0286 \pm 0.0007$	$0.0012 \pm 0.0001$
$^{20}f_p^p$	$-0.7169 \pm 0.0078$	$0.0011 \pm 0.0001$	$0.1928 \pm 0.0026$	$-0.02522 \pm 0.0005$	$0.00075 \pm 0.0001$
	$x'_e$	$x'_{e\lambda, \beta\beta}$	$y_{\alpha x}$		
$^{10}f_p^p$	0.0	$-6.2577 \pm 0.4254$	$1.7512 \pm 0.1162$		
$^{20}f_p^p$	0.0	$-4.2901 \pm 0.2455$	$1.2264 \pm 0.0694$		

**Fig. 6.** Model resonance functions  $^{(2,0)}f_p^p(x)$  for  $\lambda = 2.0$  and  $\beta = 1.03$ .

can be defined by the  $p$ -dependence of parameters of these functions. In this work, this dependence for  $\beta \leq 1$  is chosen in the form

$$\begin{aligned} a'_i(p) &= a'_i p / (1 + y_a p), \\ \alpha'(p) &= \alpha' / (1 + y_\alpha p); \\ x'_e(p) &= x'_e \end{aligned} \quad (30)$$

and for  $\beta > 1$

$$\begin{aligned} a'_i(p) &= a'_i / (1 + y_a p), \\ \alpha'(p) &= \alpha' / (1 + y_\alpha p); \\ x'_e(p) &= x'_e p / (1 + y_x p). \end{aligned} \quad (31)$$

The parameters of model functions (29) were determined from the fitting of Eqs. (29)–(31) to

different  $p$  and the values of functions  $^{(4,2)}f_p^p(x, \lambda, \beta)$  for different  $x$ ,  $\lambda$ , and  $\beta$  simultaneously (see Table 8).

## Conclusion

The principal results of this work are given in Tables 1–5, which, along with Eqs. (21) and (25), allow one to define *MET* resonance functions for the atom–atom potential from Eq. (4) or model potential (19) for the interaction of molecules with neutral gas atoms, i.e., to specify model representation for the resonance functions, numerically obtained in approximation of the exact trajectories (*ET*). This resonance functions are in the closed form, that significantly simplifies computations of spectral line broadening coefficients in the *ET* approximation. The accuracy of these functions depends on the accuracy of approximations (21) and (25). Test computations, carried out in this work and Refs. 1, 7, and 8, show that these functions give the computation results comparable with those obtained in *ET* or *NG* approximations.

## References

1. V.I. Starikov and N.N. Lavrent'eva, *Collisional Broadening of Absorption Spectral Lines of Atmospheric Gases Molecules* (Publishing House of IAO SB RAS, Tomsk, 2006), 307 pp.
2. R.P. Leavitt, *J. Chem. Phys.* **73**, 5432–5450 (1980).
3. S. Green, *J. Chem. Phys.* **92**, 4679–4685 (1990).
4. W.B. Neilsen and R. Gordon, *J. Chem. Phys.* **58**, 4149–4170 (1973).
5. D. Robert and J. Bonamy, *J. de Phys. (Fr.)* **40**, 923–943 (1979).
6. A.D. Bykov, N.N. Lavrent'eva, and L.N. Sinita, *Atmos. Oceanic Opt.* **5**, No. 11, 728–730 (1992).
7. N.N. Lavrentieva and V.I. Starikov, *Mol. Phys.* **104**, 2759–2766 (2006).

8. N.N. Lavrentieva and V.I. Starikov, *Atmos. Oceanic Opt.* **18**, No. 9, 729–734 (2005).
9. L.D. Landau and E.M. Lifshitz, *A Course of Theoretical Physics*. V.1. *Mechanics*, 3rd ed. (Pergamon Press, Oxford, 1976).
10. L. Biedenharn and J. Lauk, *The Angular Momentum in Quantum Physics* [Russian translation] (Mir, Moscow, 1984), 647 pp.
11. C.J. Tsao and B. Curnutte, *J. Quant. Spectrosc. and Radiat. Transfer* **2**, No. 1, 41–91 (1962).
12. A.D. Bykov and N.N. Lavrent'eva, *Atmos. Oceanic Opt.* **4**, No. 7, 518–523 (1991).
13. C. Boulet, D. Robert, and L. Galatry, *J. Chem. Phys.* **65**, 5302–5314 (1976).
14. E.W. Smith, M. Giraud, and J. Cooper, *J. Chem. Phys.* **65**, 1256 (1976).
15. C. Boulet, P.M. Flaud, and J.M. Hartmann, *J. Chem. Phys.* **120**, 11053–11061 (2004).
16. A. Khayar and J. Bonamy, *J. Quant. Spectrosc. and Radiat. Transfer* **28**, 199–212 (1982).
17. S. Benec'h, J. Buldyreva, and M. Chrysos, *J. Mol. Spectrosc.* **210**, 8–17 (2001).
18. J.P. Burrows, D.I. Cliff, P.B. Davies, G.W. Harris, B.A. Thrush, and J.P.T. Wilkinson, *Chem. Phys. Lett.* **65**, 197–200 (1979).