ON THE CONTRIBUTION OF THE ORIENTATION AND VELOCITY RELAXATION TO THE ATOMIC LINE SHAPE. II. LOW PRESSURE REGION*

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Formulae describing the intensity distribution in the core of an isolate atomic spectral line in the very low pressure region are given. These formulae can be used for anisotropic interaction potentials too. Test calculations have been carried out for the resonance line of sodium perturbed by argon. The calculated profiles are narrower than the corresponding Voigt profiles and in general asymmetric.

1. *Introduction*

In order to obtain the correct intensity distribution of an atomic line in the low pressure region one has to take into account the combined effect of various phenomena that influence the line profile. Two of them have the fundamental meaning for this problem, namely radiator–perturber collisions and translational radiator motion. Traditionally, it has been assumed that both of these broadening mechanisms are statistically independent so that the line profile can be described by a convolution of an integral of pure Doppler and pure pressure broadening profiles. In most calculations the Doppler effect has been treated in the approximation that collisions do not alter the radiator velocity. In that case the Doppler profile remains Gaussian whereas the pressure broadening theories lead to a Lorentzian profile. Thus straightforward integration of the convolution integral gives a combined profile which is referred to as a Voigt profile. Many authors [1–7] suggest some departure of line profiles from the Voigt profile. Especially Ward et al. [2] showed that all correlation effects are a function of the perturber/radiator mass ratio λ and they can be observed in experimental investigations in systems with $\lambda \geqslant 5$. The present work is the continuation of the previous paper [6], hereafter referred to as I. The formulae for the intensity distribution of atomic lines given in that work have presently been used for numerical calculations. For the sake of further considerations we divide the entire low

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pressure region, where the binary collision approximation holds, into three parts: (*i*) very low pressure region where the Doppler effect dominates correlation effects, (*ii*) intermediate region where neither of our approximations holds and (*iii*) moderate region where the pressure effect dominates the Doppler effect.

In paper I we generalized the formulae derived by Bielicz et al. [3], which describe the intensity distribution of the line in the moderate pressure region, and applied them to the case of anisotropic potentials. Thus reorientation effects have been included in the spectral -line-shape theory. In the present work there are given formulae describing the line profile in the very low pressure region. The derivation of these formulae is based on the previous work of Czuchaj [5], who investigated the influence of radiator motion change due to collisions with perturbers on the line shape in the so-called Doppler limit.

In the next section we will generalize the formula for the line intensity distribution in the Doppler limit for the case of anisotropic potentials.

In Section 3 we will make use of the sudden approximation to express this formula in the form enabling us to use it in numerical calculations. Section 4 is devoted to numerical calculations and the discussion of the obtained results.

2. *Intensity distribution of a spectral line in the Doppler limit*

In paper I we have generalized the spectral line shape theory for the pressure region where the binary collision approximation holds to the case of anisotropic potentials. Particularly, on the basis of the approximation introduced by Bielicz and others [3], we gave formulae describing the line profiles in the moderate pressure region. Now we want to do the same for the very low pressure region.

Let us consider, for example, a transition between two atomic states $\alpha_i j_i$ and $\alpha_f j_f$, where α_a ($a = i$ or f) stands for a principal quantum number and j_a denotes the quantum number of the total angular momentum of the radiator without a nuclear spin. Then the line profile of the transition considered is given by the imaginary part of the statistical average of a resolvent operator as

$$I_{if}^{JM}(x) = -(1/\pi)\,\mathrm{Im}\,\overline{R_{if}^{JM}(x)}, \tag{1}$$

where $x = \omega - \omega_{if}$ and

$$J = |j_i - j_f|, \ldots, |j_i + j_f|, \qquad M = 0, \pm 1, \pm 2, \ldots, \pm J. \tag{2}$$

The explicit form of $\overline{R_{if}^{JM}(x)}$ was given in paper I (cf. Eqs. (6)–(11)). Since the averaged value of the resolvent operator for the isotropic medium does not depend on M, we limit ourselves to the calculation of $\overline{R_{if}^{JM}(x)}$ for $M = 0$ only.

In the papers [4] and [5] one expanded $\overline{R_{if}^{JM}(x)}$ in the power series of the dimensionless quantity $N_0 m_0 \bar{v}/\kappa$, where N_0 is the mean number of atoms in the interacting sphere, m_0 is the mass of the radiator, $\bar{v}$ is the mean velocity of relative motion and κ is the momentum of the photon. Under the condition that

$$N_0 m_0 \bar{v}/\kappa \ll 1, \tag{3}$$

the series can be truncated after the first term. A similar procedure can be performed for the case of the anisotropic potential. Let k_{0z} be the component of the radiator momentum parallel to the direction of the incident photon and $\varrho(k_{0z}^2/2m_0)$ denotes the distribution function of k_{0z}, then $\overline{R_{if}^{J0}(x)}$ is, to the first order of the expansion, given as follows

$$\overline{R_{if}^{J0}(x)} \simeq \int_{-\infty}^{\infty} dk_{0z}\varrho(k_{0z}^2/2m_0)\left[x-\frac{\kappa^2}{2m_0}-\frac{\kappa k_{0z}}{m_0}+\Phi_{if}(k_{0z}, J)\right]^{-1}, \qquad (4)$$

where κ is the propagation vector of the photon, and $\Phi_{if}(k_{0z}, J)$ is the collisional relaxation operator $\hat{v}_{if}(\infty)$ defined as in paper I (cf. Eq. (10)) after averaging over the perpendicular components of the radiator momentum with respect to the direction of the incident photon. According to the paper of Fiutak and Paul [4] the function $\Phi_{if}(k_{0z}, J)$, defined for the $i \to f$ transition, is to be put in the form

$$\Phi_{if}(k_{0z}, J) = \tfrac{1}{2}\,[\Phi(k_{0z}, \alpha_i, j_i)-\Phi^*(k_{0z}, \alpha_f, j_f), \qquad (5)$$

where the function $\Phi(k_{0z}, \alpha_a, j_a)$ is expressed by matrix elements of the transition operator T diagonal in the quantum number m_a and the relative momentum $\boldsymbol{k}$. As was mentioned in paper I, all the elements of the T diagonal in m_a are equal. According to Eq. (10) of paper I we have

$$\Phi(k_{0z}, \alpha_a, j_a) = n(2\pi)^3 \int d\boldsymbol{k}_1\varrho(k_1^2/2m_1) \int d_2k_{0\perp}\varrho(k_{0\perp}^2/2m_0)T_{kk}(\alpha_a, j_a), \quad a = i(f), \qquad (6)$$

where n is the perturber density, $m_1, \boldsymbol{k}_1$ denote respectively the mass and momentum of the perturber and $\varrho(k_1^2/2m_0)$ stands for the distribution function of the perturber momenta. In contradistinction to the analogical expressions derived in [4] and [5] the last formulae cover the reorientation effect of atoms as well.

3. *The reorientation effects*

The aim of our present consideration will be to express the diagonal elements of T in the form that enables us to calculate the considered line profile numerically. Although, the present form of the transition operator T covers the reorientation of atoms, we will use the traditional straight line trajectory approximation in our further consideration. In this approximation any diagonal element of T can be expressed as

$$T_{kk}(\alpha_a, j_a) = -\frac{iv}{(2\pi)^2}\int_0^{\infty} dbb[1-S(\alpha_a, j_a; -\infty, +\infty, v, b)], \qquad (7)$$

where b is the impact parameter. The function $S(\alpha_a, j_a; -\infty, t, v, b)$ satisfies the well-known equation

$$\frac{\partial}{\partial t}S(\alpha_a, j_a; -\infty, t, v, b) = -iV(\alpha_a, j_a)S(\alpha_a, j_a; -\infty, t, v, b) \qquad (8)$$

with the interacting potential $V(\alpha_a, j_a)$ depending on quantum numbers m_a.

In the case of $j_a = 0$ and $j_a = 1/2$ the potential is degenarate with respect to quantum number m_a and the solution to equation (8) is as follows

$$S(\alpha_a, j_a; -\infty, t, v, b) = \exp\left[-i \int_{-\infty}^{t} V(\alpha_a, j_a)dt'\right]. \tag{9}$$

For the case $j_a = 1$ equation (8) means a set of equations analogical to that occurring in paper I (compare Eq. (30)). This would allow us to solve them with the numerical method proposed in the first part of this work. On the other hand, the analysis made by us there showed, that satisfactory results may be obtained in the so-called sudden approximation. In this approximation one gets:

$$S(\alpha_a, j_a; -\infty, +\infty, v, b) = \langle \exp\left[-iP^{(j_a)}\right]\rangle, \tag{10}$$

where $\langle \ldots \rangle$ denotes the average over all possible orientations of atoms, and $P^{(j_a)}$ with $j_a = 1$ and $j_a = 3/2$, according to (8), express the matrix elements of the interaction operator in the following way

$$P^{(1)}_{1,1} = P^{(1)}_{-1,-1} = \int_{-\infty}^{\infty} \{V^1(\alpha_a, 1) + \tfrac{1}{2}[V^0(\alpha_a, 1) - V^1(\alpha_a, 1)] \sin^2 \beta\}dt,$$

$$P^{(1)}_{1,-1} = P^{(1)}_{-1,1} = -\tfrac{1}{2} \int_{-\infty}^{\infty} [V^0(\alpha_a, 1) - V^1(\alpha_a, 1)] \sin^2 \beta dt,$$

$$P^{(1)}_{0,0} = \int_{-\infty}^{\infty} \{V^0(\alpha_a, 1) - [V^0(\alpha_a, 1) - V^1(\alpha_a, 1)] \sin^2 \beta\}dt,$$

$$P^{(3/2)}_{3/2,3/2} = P^{(3/2)}_{-3/2,-3/2} = \int_{-\infty}^{\infty} \{V^{3/2}(\alpha_a, 3/2) + \tfrac{3}{4}[V^{1/2}(\alpha_a, 3/2) - V^{3/2}(\alpha_a, 3/2)] \sin^2 \beta\}dt,$$

$$P^{(3/2)}_{1/2,1/2} = P^{(3/2)}_{-1/2,-1/2} = \int_{-\infty}^{\infty} \{V^{1/2}(\alpha_a, 3/2) - \tfrac{3}{4}[V^{1/2}(\alpha_a, 3/2) - V^{3/2}(\alpha_a, 3/2)] \sin^2 \beta\}dt,$$

$$P^{(3/2)}_{3/2,-1/2} = P^{(3/2)}_{-1/2,3/2} = P^{(3/2)}_{-3/2,1/2} = P^{(3/2)}_{1/2,-3/2}$$

$$= -\frac{\sqrt{3}}{4} \int_{-\infty}^{\infty} [V^{1/2}(\alpha_a, 1/2) - V^{3/2}(\alpha_a, 3/2)]dt, \tag{11}$$

where argument β is exactly defined in paper I (see Fig. 1 and 2). The other elements of $P^{(1)}_{m_a,m'_a}$ and $P^{(3/2)}_{m_a,m'_a}$, are equal to zero.

Now, inserting the last expression into (10) and averaging over all possible orientations of the atoms we get

$$S(\alpha_a, 1; -\infty, +\infty, v, b) = 1 - \tfrac{1}{3}\exp(-iP^{(1)}_{0,0}) - \tfrac{2}{3}\cos(P^{(1)}_{1,-1})\exp(-iP^{(1)}_{11}), \tag{12}$$

$$S(\alpha_a, \tfrac{3}{2}; -\infty, +\infty, v, b) = 1 - \cos(\Gamma)\exp\left[-i(P^{(3/2)}_{3/2,3/2} - P^{(3/2)}_{1/2,1/2})\right], \tag{13}$$

with

$$\Gamma = \left[(P^{(3/2)}_{3/2,3/2} - P^{(3/2)}_{1/2,1/2})^2/4 + (P^{(3/2)}_{3/2,-1/2})^2\right]^{1/2} \tag{14}$$

After inserting the above expressions into (6) we finally get the diagonal elements of the operator T.

In the next section we will evaluate the profile of the resonance line of sodium perturbed by argon for several values of pressure. However, the reorientation effects do not play any role in this case, the analogical calculations may be carried out for other transitions occurring in atomic spectroscopy.

4. *Numerical calculation*

To illustrate our theoretical considerations we have carried out the test calculations for the resonance line of sodium perturbed by argon. For the transition under consideration the interaction potential is isotropic for both states and hence the reorientation effect does not influence the line profile in question. For the numerical calculations we have assumed an interaction potential of the Lennard-Jones type

$$V(\alpha_a, j_a, R) = \varepsilon_m^{(a)}\left[\frac{6}{n-6}\left(\frac{R_m^{(a)}}{R}\right)^n - \frac{n}{n-6}\left(\frac{R_m^{(a)}}{R}\right)^6\right] \tag{15}$$

with $n = 12$ (see Mahan [9]). We have to remember, however, that the Lennard-Jones potential does not describe the interaction between two atoms accurately. Nevertheless, the proceeding seems to be sufficiently justified as our calculations have in general a qualitative character. By taking this potential the calculations become considerably simplified. The corresponding parameters $R_m^{(a)}$ and $\varepsilon_m^{(a)}$ for the $3P_{1/2}$ state are taken from York et al. [10], but the ones for the $3S_{1/2}$ state are taken from Pascale et al. [11]. Thus we put

$$\varepsilon_m^{(i)} = 549.16\ \text{cm}^{-1}, \quad R_m^{(i)} = 3.2\ \text{Å} \quad \varepsilon_m^{(f)} = 43.58\ \text{cm}^{-1}, \quad R_m^{(f)} = 5.0\ \text{Å}. \tag{16}$$

The calculations were carried out separately for the very low pressure region and moderate pressure region, in both cases for the temperature $T = 300°$K.

(*i*) Very low pressure region

Inserting Eq. (9) into (7) and according to (6) we get that

$$\Phi(u, \zeta^{(a)}, \alpha) = \pi n\bar{v}(R_m^{(a)})^2[-\overbrace{d(u, \zeta^{(a)}, \alpha)} - i\overbrace{w(u, \zeta^{(a)}, \alpha)}] \tag{17}$$

and

$$\overbrace{d(u, \zeta^{(a)}, \alpha)} = 2[(\alpha+1)/\pi]^{1/2}\int\limits_0^\infty dye^{-y}\int\limits_{-\infty}^{\infty} dze^{-(\alpha+1)z^2}$$
$$\times[y+(u-z)^2]^{1/2}d\{\zeta^{(a)}/[y+(u-z)^2]^{1/2}\},$$
$$\overbrace{w(u, \zeta^{(a)}, \alpha)} = 2[(\alpha+1)/\pi]^{1/2}\int\limits_0^\infty dye^{-y}\int\limits_{-\infty}^{\infty} dze^{-(\alpha+1)z^2}$$
$$\times[y+(u-z)^2]^{1/2}w\{\zeta^{(a)}/[y+(u-z)^2]^{1/2}\}, \tag{18}$$

where

$$\alpha = m_1/m_0, \quad u = k_{0z}/\bar{v}m_0, \quad \zeta^{(a)} = \varepsilon_m^{(a)}R_m^{(a)}/\bar{v}, \tag{19}$$

but the functions $d\{...\}$ and $w\{...\}$ with the 6–12 Lennard–Jones potential take the form

$$d(x) = 2\int_0^\infty d\varrho\varrho \sin\left[\frac{3\pi x}{4}(\varrho^{-5}-\tfrac{21}{64}\varrho^{-11})\right],$$

$$w(x) = 2\int_0^\infty d\varrho\varrho\left\{1-\cos\left[\frac{3\pi x}{4}(\varrho^{-5}-\tfrac{21}{64}\varrho^{-11})\right]\right\}. \tag{20}$$

In the case under consideration $\alpha = 1.76$, $\zeta^{(i)} = 56.6$ and $\zeta^{(f)} = 7.0$.

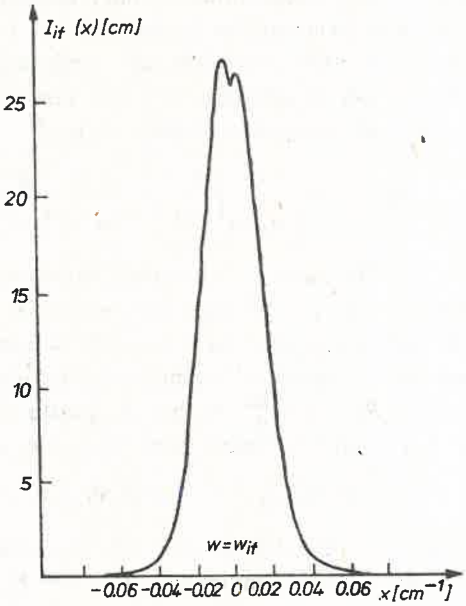

Fig. 1. The line profile obtained according to formula (21) at the pressure 0.154 torr

Inserting now the functions $\Phi(u, \zeta^{(a)}, \alpha)$ for $a = i$ and $a = f$ into Eq. (5) and according to (4) and (1) we obtain the following expression for the line profile in the Doppler limit

$$I_{if}^{JM}(x) \simeq \left[\frac{R_m^{(i)}R_m^{(f)}(\alpha+1)}{2\pi\alpha}\right]^{1/2}\frac{N_0}{\pi\bar{v}}\int_{-\infty}^{\infty} du \exp\left[-(\alpha+1)u^2\right]\left[\overbrace{\gamma w(u, \zeta^{(i)}, \alpha)}\right.$$

$$\left.+\overbrace{\gamma^{-1}w(u, \zeta^{(f)}, \alpha)}\right]\cdot\{[\xi+\eta u+N_0\gamma d(u, \zeta^{(i)}, \alpha)/2-N_0\gamma^{-1}d(u, \zeta^{(f)}, \alpha)/2]^2$$

$$+N_0^2[\gamma w(u, \zeta^{(i)}, \alpha)+\gamma^{-1}w(u, \zeta^{(f)}, \alpha)]^2/4\}^{-1}, \tag{21}$$

where

$$N_0 = \pi n(R_m^{(i)}R_m^{(f)})^{3/2}, \quad \xi = \frac{(x+\kappa^2/2m_0)(R_m^{(i)}R_m^{(f)})^{1/2}}{\bar{v}}$$

$$\gamma = R_m^{(i)}/R_m^{(f)}, \quad \eta = \kappa(R_m^{(i)}R_m^{(f)})^{1/2}. \tag{22}$$

Here $\gamma = 0.64$, $\eta = 4.26\times10^{-3}$ and $\xi = 1.07\times10^{-7}+0.129$ [cm^{-1}]x. We note that condition (3) defining the Doppler limit is satisfied below 6 torr. Fig. 1 presents the line profile for $p = 1.54$ torr. It is shown that the profile is asymmetric and at the resonance frequency ω_{if} one observes a small dip. Similar profiles have been obtained for the pressures 3.105, 1.54, 1.0, 0.5 and 0.154 torr. It is noticed that the observed asymmetry and depth of the dip decreases when the pressure goes down from 3.105 to 0.5 torr and becomes negligible at 0.154 torr (see Table I). All the profiles obtained are narrower from the appropriate Voigt profile.

TABLE I

Asymmetry coefficient defined as a ratio of the red part of the half-width of the line to the violet one for the very low pressure region

p [Torr]	Asymmetry coefficient
3.105	1.8±0.2
1.54	1.5±0.2
1.0	1.3±0.2
0.5	1.1±0.1
0.154	1.0±0.1

(*ii*) Moderate pressure region

At present we want to calculate the line profile of the same transition in the moderate pressure region considered in detail in paper I. As was shown exactly in [3] the intensity distribution of the line in the considered pressure region is given by the general function

$$I_{if}^{JM}(x) = \frac{1}{2\pi}\left\{\frac{\pi n\bar{v}R_m^2\overline{w(\zeta)}+\mathrm{Im}\,(\overline{\hat{Y}_{if}^2})^{1/2}}{[x+\pi\bar{v}R_m^2\overline{d(\zeta)}+\mathrm{Re}\,(\overline{\hat{Y}_{if}^2})^{1/2}]^2+[\pi n\bar{v}R_m^2\overline{w(\zeta)}+\mathrm{Im}\,(\overline{\hat{Y}_{if}^2})^{1/2}]^2}\right.$$
$$\left.+\frac{\pi n\bar{v}R_m^2\overline{w(\zeta)}-\mathrm{Im}\,(\overline{\hat{Y}_{if}^2})^{1/2}}{[x-\pi n\bar{v}R_m^2\overline{d(\zeta)}-\mathrm{Re}\,(\overline{\hat{Y}_{if}^2})^{1/2}]^2+[\pi n\bar{v}R_m^2\overline{w(\zeta)}-\mathrm{Im}\,(\overline{\hat{Y}_{if}^2})^{1/2}]^2}\right\} \tag{23}$$

with

$$\overline{\hat{Y}_{if}^2} = n^2[(\overline{\hat{v}_{if}(\infty)})^2-(\overline{\hat{v}_{if}(\infty)})^2]+\overline{\hat{h}_{0k}^2}+(\overline{\hat{h}_{0k}})^2. \tag{24}$$

The other quantities occurring here are defined in paper I. As was shown there the line profile depends on the two functions $\overline{d(\zeta)}$ and $\overline{w(\zeta)}$ taken at two different values of the parameter ζ. In our case $\zeta = 0.54$ and $\zeta' = 0.255$, and

$$\overline{d(0.54)} = 1.2110,\quad \overline{w(0.54)} = 0.9361,\quad \overline{d(0.255)} = 0.5584,\quad \overline{w(0.255)} = 0.6254 \tag{25}$$

According to the condition

$$(\overline{\hat{Y}_{if}^2})^{1/2} < n\overline{v_{if}(\infty)}, \tag{26}$$

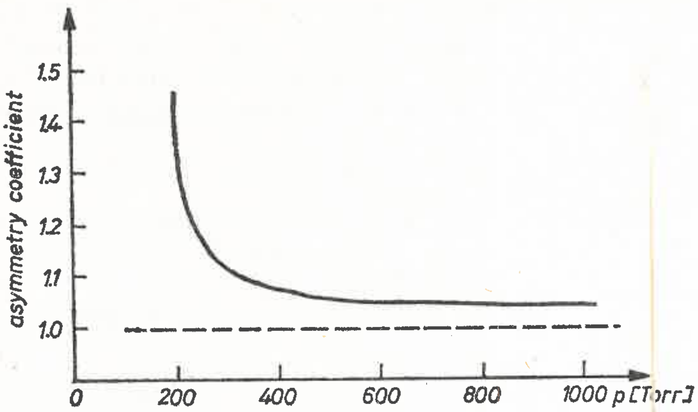

Fig. 2. Asymmetry coefficient defined as a ratio of the violet part of the half-width of the line to the red part for the moderate pressure region

the moderate pressure region in the considered case lies above 150 torr. Our results show that the line profiles in this region are narrower than the appropriate Voigt profiles and display a red asymmetry decreasing gradually with increasing pressure. Fig. 2 shows the asymmetry coefficient of the calculated profiles in the considered pressure region.

5. *Summary and calculations*

A method for calculating line profiles in the very low pressure region, taking into account both radiator velocity change due to collisions with perturbers and reorientation of atoms, has been presented. As was shown, this method allows one to obtain relatively simple expressions for a line profile in the case of anisotropic potentials. Owing to the lack of corresponding potentials our test calculations could not be performed for other transitions and for the system which would allow us to verify both the method presented here and the method described by Ward et al. [2]. Nevertheless the calculated profiles indicate clearly a departure from the appropriate Voigt profiles. They are much narrower than the Voigt profiles and in general asymmetric. A little dip appearing at the resonance frequency of the profiles in the very low pressure region could for example be a result of our approximation. So far the higher terms of the expansion of the resolvent operator were not examined by us. We believe that corresponding experiments able to verify the results of our calculations will be performed in the future. It is also noticeable that we have obtained a departure from the Voigt profile for the system for which the ratio of a perturber mass to a radiator mass lies much below the value at which this effect can be observed at all according to Ward et al. [2].

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