Asymmetry of spectral line profile of an atom in an external electric field

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The influence of collisional excitation mechanisms on the spectral line shape of an atom in an external electric field is investigated theoretically. The formation of line profiles is studied in the density matrix representation for $4\,^1S_0 - 2\,^1P_1$, $4\,^1P_1 - 2\,^1S_0$, $4\,^1D_2 - 2\,^1P_1$, $4\,^3S_1 - 2\,^3P_{0,1,2}$, $4\,^3P_{0,1,2} - 2\,^3S_1$ transitions of the He atom excited by the electron impact in an external electric field.

The spectral line shape is a sensitive instrument for diagnostics of plasma. The knowledge of line profiles allows us to study the role of various processes in plasma and to determine the distribution functions of the disturbing particles, especially, of those that have pronounced anisotropic properties. The diagnostics based on the spectral line shape is indispensable when studying overlapping spectra.

Collisional processes are among the main mechanisms of the formation of line contour. Besides the collisional mechanisms, the characteristics of plasma emissions are strongly affected by the external electric field, which leads to the change of polarization and angular characteristics of radiation and whose contribution is comparable with those from the effects of anisotropic collisions.

In this paper, we study theoretically the joint effect of the collisional excitation mechanisms on the spectral line shape in the external electric field using, as an example, radiation of an atom excited by the electron impact.

1. Spectral line shape of an atom in an external electric field

The spectral line shape can be described as a Fourier transform of the correlation function $F(t)$ describing the time dependence of the energy state of an atom

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty F(t)\,\mathrm{e}^{-i\omega t}\mathrm{d}t\,. \qquad (1)$$

In the density matrix representation, the correlation function is described by the elements of the density matrix $\rho_{M_0M_0}$ of the state $|M_0\rangle$ of an atom after photon emission. This matrix is connected with the density matrix $\rho_{MM'}$ of the states $|M\rangle$ of the atom before the emission through the operator of radiative transition $\boldsymbol{D}$.

In the presence of an external electric field, the state of the atom should be described by the Stark wave functions $|M\rangle$ and $|M_0\rangle$, which have the following form once resolved over the wave functions $|J'M\rangle$ of an isolated atom:

$$|M\rangle = \sum_{J'} C_{J'}(M)\,|J'M\rangle\,. \qquad (2)$$

Let the atom after emitting a photon be in the state $|M_0\rangle$, which is not disturbed by the field: $|M_0\rangle = |J_0\,M_0\rangle$.

Introduce the tensor of radiation polarization $\Phi_q^{(k)}$ through the series expansion over the spherical components of the polarization vector $\mathbf{e}_\lambda$:

$$\Phi_q^{(k)} = \sum_{q_1 q_2}(-1)^q\sqrt{2k+1}\begin{pmatrix}1 & 1 & k\\ q_1 & -q_2 & -q\end{pmatrix} e_{q_1}^{(1)}\, e_{q_2}^{(1)}. \qquad (3)$$

Then for the transition $J \to J_0$ the spectral line profile in the dipole approximation can be written as a superposition of the Fourier transforms of the density matrix components $\rho_{MM'}$:

$$I(\omega) = \frac{a_0^2 e^2}{2c^3}\sum_M\sum_{M_0}\sum_{J'J''}\sum_{\substack{k\,q\\ q_1 q_2}}(-1)^{q_1}\sqrt{2k+1}\begin{pmatrix}1 & 1 & k\\ q_1 & -q_2 & -q\end{pmatrix}\times$$

$$\times\,\Phi_q^{(k)}\,\langle J_0M_0|D_{q_1}^{(1)}|J'M\rangle\,\langle J_0M_0|D_{q_2}^{(1)}|J''M\rangle^*\times$$

$$\times\, C_{J'}(M)\,C_{J''}^*(M)\,\omega_{J''M}^{3/2}\,\omega_{J'M}^{3/2}\,\frac{1}{\pi}\mathrm{Re}\int_0^\infty \rho_{MM}(t)\,\mathrm{e}^{-i\omega t}\mathrm{d}t. \qquad (4)$$

The Fourier transform of the Mth component of the density matrix will be called the Mth component of the line contour $I_M(\omega)$.

The time dependence of the density matrix $\rho_{MM}(t)$ is determined by the kinetic processes, in which the atom took part before the emission.

2. Kinetic equations for the elements of the density matrix in an external electric field

The kinetic equation for the elements of the density matrix $\rho_{MM}(t)$ is written with the allowance for the excitation of the atom by electron impact and spontaneous emission:

$$\dot{\rho}_{MM} = -(\Gamma_M - i\omega_M)\rho_{MM} + \sum_{M_0} G_{MM}^{M_0M_0}\, \rho_{M_0M_0}, \quad (5)$$

where Γ_M is the inverse lifetime of the Mth atomic level; $G_{MM}^{M_0M_0}$ is the matrix of excitation of the Mth atomic state by the electron impact.

In the case of the quasi-stationary excitation, the Mth component of the contour can be a combination of the Lorentz and dispersion profiles:

$$I_M(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty \rho_{MM}(t)\,\mathrm{e}^{-i\omega t}\mathrm{d}t =$$

$$= \frac{1}{\pi\Gamma_M}\left(\frac{\mathrm{Re}\sum\limits_{M_0} G_{MM}^{M_0M_0}\, \rho_{M_0M_0}}{\Gamma_M^2 + \omega_M^2}\right)\frac{\Gamma_M^2}{\Gamma_M^2 + (\omega - \omega_M)^2} +$$

$$+ \frac{1}{\pi\Gamma_M}\left(\frac{\mathrm{Im}\sum\limits_{M_0} G_{MM}^{M_0M_0}\rho_{M_0M_0}}{\Gamma_M^2 + \omega_M^2}\right)\frac{\Gamma_M\,(\omega_M - \omega)}{\Gamma_M^2 + (\omega - \omega_M)^2}\,. \quad (6)$$

The presence of the dispersion term in the Mth component of the line contour is determined by the value of the imaginary part of the excitation matrix $G_{MM}^{M_0M_0}$.

By comparing the result obtained with that for the case of spontaneous excitation, we can see that the excitation determines population of the M states of the atom.

3. Matrix of the atom excitation by the electron impact in an external electric field

The excitation matrix $G_{M'M''}^{M_0'M_0''}$ describes the change of the state in the system "atom + colliding electron" after averaging over the function of electron distribution $f_\mathrm{e}(\mathbf{k}_0)$ over the momentum of colliding electrons $\mathbf{k}_0$. In the basis of atomic wave functions, the excitation matrix can be represented as

$$G_{M'M''}^{M_0'M_0''} = N_e\,\frac{\pi a_0^2 e^2}{\hbar}\sum_{J'J''} C_{J'}^*(M')\,C_{J''}(M'') \times$$

$$\times \int f_\mathrm{e}(\mathbf{k}_0)\,\mathrm{d}\mathbf{k}_0\, G_{J'M'\ J''M''}^{J_0'M_0'\ J_0''M_0''}(\mathbf{k}_0). \quad (7)$$

Let us write the distribution function $f_\mathrm{e}(\mathbf{k}_0)$ of colliding electrons over the momentum $\mathbf{k}_0$ as a combination of slow (Maxwell) and fast (beam) electrons:

$$f_\mathrm{e}(\mathbf{k}_0) = W[(1-\gamma)\exp\left(-\frac{(\mathbf{k}_0 - \mathbf{k}_\mathrm{d})^2}{\bar{\mathbf{k}}^2}\right) +$$

$$+ \gamma\delta\,(\mathbf{k}_0 - \mathbf{k}_\mathrm{b})]. \quad (8)$$

Here, the slow electrons are characterized by the velocity of thermal motion $\bar{\mathbf{k}}$ and the drift velocity $\mathbf{k}_\mathrm{d}$, and the beam electrons are characterized by the velocity $\mathbf{k}_\mathrm{b}$ and the relative contribution γ; W is the normalization coefficient.

Let us write a series expansion of the distribution function of slow electrons over the multipole moments $f_0^{(k)}(k_0)$:

$$f_\mathrm{e}(\mathbf{k}_0) = W\,[(1-\gamma)\sum_k f_0^{(k)}(k_0)\,Y_0^{(k)}(\Omega_{k_0}) +$$

$$+ \gamma\delta\,(\mathbf{k}_0 - \mathbf{k}_\mathrm{b})]. \quad (9)$$

The multipole moments $f_0^{(k)}(k_0)$ in the series expansion of the distribution function of slow electrons can be determined from the inverse transformation:

$$f_0^{(k)}(k_0) = \int \exp\left(-\frac{(\mathbf{k}_0 - \mathbf{k}_\mathrm{d})^2}{\bar{\mathbf{k}}^2}\right) Y_0^{(k)*}(\Omega_{k_0})\,\mathrm{d}\Omega_{k_0}. \quad (10)$$

To derive the excitation matrix $G_{M'M''}^{M_0'M_0''}$ for helium atom, we took into account both the direct and exchange interaction of the electron with atom.

For the direct excitation in the Born approximation the excitation matrix $G_{J'M'\ J''M''}^{J_0'M_0'\ J_0''M_0''}(\mathbf{k}_0)$ can be written, in the collisional coordinate system, as

$$G_{J'M'\ J''M''}^{J_0'M_0'\ J_0''M_0''}(\mathbf{k}_0) = \frac{8\pi^2}{k_0^2}\int_{k_0-k}^{k_0+k}\frac{\mathrm{d}q}{q^3}\sum_{xq'}(2x+1)\times$$

$$\times \langle J'M'|\,C_q^{(x)}\, j_x(qr)\,|J_0'\,M_0'\rangle \times$$

$$\times \langle J''M''|\,C_q^{(x)}\, j_x(qr)\,|J_0''\,M_0''\rangle^*. \quad (11)$$

For the exchange interaction in the Ochkur approximation, we obtain

$$G^{J_0'M_0'\,J_0''M_0''}_{J'M'\,J''M''}(\mathbf{k}_0) = \frac{8\pi^2}{k_0^6}\int\limits_{k_0-k}^{k_0+k} q\,\mathrm{d}q \sum_{\kappa q'} (2\kappa+1)\times$$

$$\times \langle J'M' \,|\, C^{(\kappa)}_{q'}\, j_\kappa(qr) \,|\, J_0'\, M_0' \rangle \times$$

$$\times \langle J''M'' \,|\, C^{(\kappa)}_{q'}\, j_\kappa(qr) \,|\, J_0''\, M_0'' \rangle^*. \qquad (12)$$

In such an approach, the angular and radial integrals can be easily separated, thus considerably simplifying further analysis.

It was shown theoretically that in the Born approximation the excitation matrix $G^{M_0'M_0''}_{M'M''}$ has a significantly real form. Consequently, the Mth component of the line contour does not include the dispersion component. Therefore, the asymmetry of the line shape can be explained by the population and frequency ratios between different M components.

The excitation was calculated numerically for both singlet $4\,^1S_0$, $4\,^1P_1$, $4\,^1D_2$, $5\,^1D_2$ and triplet $4\,^3S_1$, $4\,^3P_{1,2}$ states of the helium atom. The calculations have shown that the relative population of magnetic sublevels of the atomic excited state changes with the increase of the external electric field strength. Therefore, as is seen from Eq. (6), the external electric field leads to the change of the amplitudes of the Mth components of the line shape.

4. Calculated results

The line contours of unpolarized radiation were calculated for the following transitions: $4\,^1S_0 - 2\,^1P_1$, $4\,^1P_1 - 2\,^1S_0$, $4\,^1D_2 - 2\,^1P_1$, $4\,^3S_1 - 2\,^3P_{0,1,2}$, and $4\,^3P_{0,1,2} - 2\,^3S_1$ in the helium atom at the external field strength varying from 0 to 100 kV/cm at the gas pressure of 1–10 Torr and the gas temperature of 330 K.

The most characteristic dependences of the effect of atom excitation by electron impact on the shape of a spectral line in the presence of an external electric field are depicted in Figs. 1 and 2. The plots show the relative radiation intensity I as a function of the transition wavelength.

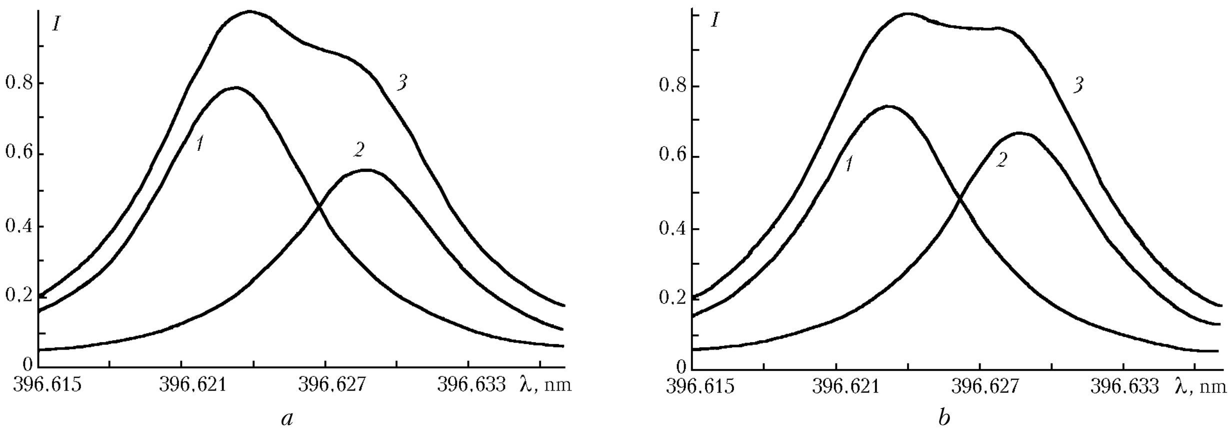

Fig. 1. Line contours of unpolarized radiation of the transitions $4\,^1P_1 - 2\,^1S_0$ (396.64 nm) at isotropic population of magnetic sublevels (*a*) and at population of magnetic sublevels by electron impact (*b*) for the external electric field strength of 15 kV/cm: line shape for $M = 0$ (*1*), $|M| = 1$ (*2*), and the combined contour (*3*).

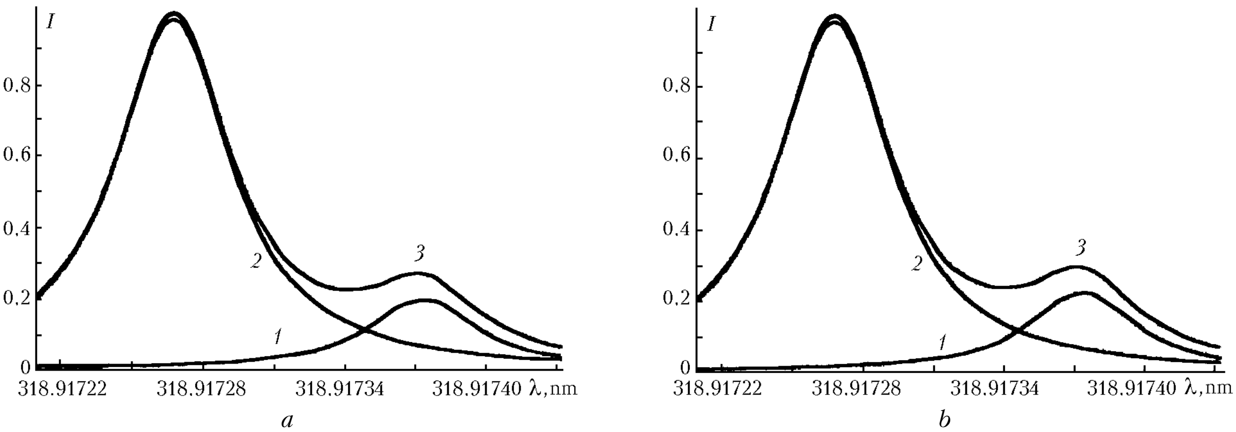

Fig. 2. Line profiles of unpolarized radiation of the transitions $4\,^3P_1 - 2\,^3S_1$ (318.91 nm) at isotropic population of magnetic sublevels (*a*) and at population of magnetic sublevels by electron impact (*b*) for the external electric field strength of 30 kV/cm: line profile for $M = 0$ (*1*), line profile for $|M| = 1$ (*2*), and combined profile (*3*).

The calculations have shown that the external electric field contributes considerably to the formation of the emission line contour of the helium atom excited by the electron impact. The electric field causes splitting of atomic magnetic sublevels and, correspondingly, the shift of the M components of the line shape. For some transitions the separation between the M components can achieve 1 nm.

In the absence of the external electric field, the excitation by slow (Maxwell) electrons leads to isotropic population of the atomic magnetic sublevels. With the increase of the external field, the drift velocity of the slow electrons increases and the population becomes anisotropic. The beam component intensifies anisotropy. Redistribution of populations of magnetic sublevels of the excited state of the atom in the electric field leads to prevalent population of one of the M components, and, according to Eq. (6), this manifests itself in the amplitude of the corresponding M component of the line contour.