Regularities of the Dynamic Stark Effect for Rare Gases in a High-Frequency Discharge[1]

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Abstract – A new theoretical approach was applied to model the Stark effect in the circular polarized electric field for rare gases He, Ne, Ar and Kr. Calculations of the shifts and splitting of the energy levels of rare gases in the electric field were carried out with computer program package STARKD. The regularities of the shifts and splitting of the energy levels in the circular polarized electric field are studied. Dependencies of the dynamic Stark effect on the frequency and strength of the electric field are investigated. The obtained results can be applied to the plasma produced by both a high-frequency discharge and an optical excitation.

1. Introduction

An electric field in a gas discharge is one of the most important discharge parameters. In plasma physics, the Stark effect is widely used for plasma diagnostics, in particular, for the determination of energy distribution functions, density and temperature of electrons, etc. The application of different techniques for measuring electric fields in discharges is based on the Stark effect for the species presented in the discharge or added to the discharge for diagnostics purposes. A number of techniques are based on an analysis of shifts and/or splitting of energy levels due to the Stark effect [1, 2], and other techniques are based on the Stark mixing of energy levels [3, 4].

Of special interest is the Stark effect in rare gases, because they are widely used for plasma processing. It is obvious, that the experimental data must be compared with the theoretical calculations of shifts and splitting of atomic levels in the electric field for reliable interpretation of the experimental results. In a number of cases a comparison of experimental results and theoretical calculation of the Stark effects allows us to considerable increase sensitivity of some experimental methods for measuring an electric field in a discharge [5]. Moreover, theoretical calculations of the Stark effect are needed for modeling excitation sources.

The atomic spectra subjected to an alternating electric field are determined from a non-stationary Shrödinger equation. The methods of a solution of this equation depend on the type of field polarization (linear, circular or elliptic polarization). In the present work, the dynamic Stark effect in a circular polarized field is considered. The electric fields of such polarization may be observed in high-frequency electrodeless lamps and under optical excitation.

In [6], the general formulas were obtained for calculating the Stark effect within the perturbation theory. However, these formulas are suitable only for calculating an isolated atomic level in the absence of resonances with the electric field. Moreover, if the atoms containing equivalent electron in the shells are considered the formulas given in [6] are applicable only for the calculating the Rydberg states of these atoms.

In the present work, a theoretical method of calculation of the dynamic Stark effect in a circular polarized electric field proposed in [7] is used. In the framework of this approach, free from limitations inherent in the perturbation theory, the Stark effect regularities are studied for rare gases He, Ne, Ar and Kr.

2. Theoretical Method

In a circular polarized electric field, a non-stationary Shrödinger equation is written as

$$i\frac{\partial \psi_n(\vec{r},t)}{\partial t} =$$

$$(\hat{H}_0(\vec{r}) - eF(x\cos\omega t \pm y\sin\omega t))\psi_n(\vec{r},t), \quad (1)$$

where ψ_n is the wave function of the n-th state of a system, $\hat{H}_0(\vec{r})$ is the unperturbed Hamiltonian, and the operator $-eF(x\cos\omega t \pm y\sin\omega t)$ describes perturbation induced by the interaction of an atom with a circular polarized field of frequency ω and strength F. The «+» and «–» signs correspond to the right and left polarization of the field, respectively. To go to a stationary Shrödinger equation, let us use the rotating-wave approximation [8].

In order to go to a rotating coordinate system rotating around the Z-axis with the frequency ω, let us introduce a wave function in this coordinate system

$$\varphi(\vec{r},t) = \exp(i\omega t \hat{J}_z)\psi(\vec{r},t), \quad (2)$$

where $\hat{J}_z$ is the z-component of the total angular momentum operator. After substitution of the wave function (2) in Eq. (1), we get

$$i\frac{\partial\varphi(\vec{r},t)}{\partial t} = \hat{Q}\varphi(\vec{r},t), \quad \hat{Q} = (\hat{H}_0 - \omega\hat{J}_z \pm F\hat{D}_x). \quad (3)$$

As is seen from Eq. (3), the operator $\hat{Q}$ is time-independent. Hence, in the rotating-wave approximation, it is possible to go from the non-stationary Shrödinger equation (1) to the stationary one, and we get

$$\hat{Q}\varphi(\vec{r}) = \varepsilon\varphi(\vec{r}), \quad (4)$$

whence

$$\varphi(\vec{r},t) = \exp(-i\varepsilon t)\varphi(\vec{r}). \quad (5)$$

The operator $\hat{Q}$ is the operator of the energy of an atom in an electric field, and ε and $\varphi(\vec{r},t)$ are the energy and wave function of the atom in the electric field in the rotating coordinate system. Obviously, we can find ε and $\varphi(\vec{r},t)$ using a stationary perturbation theory for solution of Eq. (4). Instead of solution of the Shrödinger equation (4) within the perturbation theory, let us use of the approach suggested in [7].

It was shown in [7] that the wave functions and energies of the atom, being the solutions to the Shrödinger equation (4), can be found from the diagonalization of the $\hat{Q}$ matrix. This matrix can be obtained in the representation of the unperturbed wave functions $\varphi_n^{(0)}$ calculated in the absence of an external electric field. In this representation, the matrix elements of the energy operator $\hat{Q}$ are written as

$$Q_{mn} = E_n^{(0)}\delta_{mn} -$$
$$- \omega < \varphi_m^{(0)}(\vec{r})|\hat{J}_z|\varphi_n^{(0)}(\vec{r}) > \pm F < \varphi_m^{(0)}|D_x|\varphi_n^{(0)} >, \quad (6)$$

where $E_n^{(0)}$ is the energy of the n-th state of the atom in the absence of the external electric field, F and ω are the strength and frequency of the external electric field and D_x is the x-component of the dipole transition operator.

The diagonalization of the energy matrix with elements (6) gives a set of wave functions and the energy spectrum for the n-states of the atom in the electric field. Upon diagonalization of the $\hat{Q}$ matrix, we get the energies ε_n and wave functions as

$$\varphi_n(\vec{r},t) = e^{-i\varepsilon_n t}\sum_k C_{nk}\varphi_k^{(0)}(r) \quad (7)$$

for the n states of the atom in the external electric field in the rotating coordinate system. The coefficients C_{nk} in the wave function (7) depend on the frequency and strength of the external electric field. To find the average energies of the atom in the initial coordinate system, it is necessary to perform averaging over the oscillation period. Upon averaging, the average energy

of the system in the electric field in the initial coordinate system is written in the following form:

$$\bar{E}_n = < \psi_n(\vec{r},t)|H(\vec{r},t)|\psi_n(\vec{r},t) >=$$
$$\varepsilon_n + \omega < \varphi_n(\vec{r})|\hat{J}_z|\varphi_n(\vec{r}) >. \quad (8)$$

It follows from Eq. (8) that $\bar{E}_n$ is time-independent.

The matrix elements of the D_x operator are calculated as follows:

$$< \varphi_m^{(0)}|D_x|\varphi_n^{(0)} >=< \gamma JM|D_x|\gamma'J'M' >= \frac{(-1)^{J-M}}{\sqrt{2}}$$
$$\left[\begin{pmatrix} J & 1 & J' \\ -M & -1 & M' \end{pmatrix} - \begin{pmatrix} J & 1 & J' \\ -M & 1 & M' \end{pmatrix}\right] < \gamma J\|D\|\gamma'J' >, \quad (9)$$

the reduced matrix elements $< \gamma J\|D\|\gamma'J' >$ are calculated depending on a coupling scheme. The LS-coupling scheme is realized for He atom, and the rest rare gas atoms are usually calculated using the J_1 – coupling scheme. The reduced matrix elements are calculated with formulas from [9].

The suggested theoretical approach is free from the limitations inherent in the perturbation theory and it may be applied to a calculation of the dynamic Stark effect for any atom or ion in a circular polarized electric field of an arbitrary frequency and strength. Moreover, this method is suitable for calculation both resonance and non-resonance excitations [7].

3. Results and Discussion

In calculations for He, Ne and Ar atoms the energy levels with the principal quantum number n up to 10 were taken into account, and for a Kr atom the energy levels with $n < 13$ were taken into account. An atom He was calculated in the LS-coupling scheme, and the rest rare gas atoms were calculated in the Jl-coupling scheme. Principal attention was given for investigation of the visible region of the emission spectra of rare gases in the electric field of frequency 100 MHz (it is the electric field frequency in a high-frequency electrodeless lamps) and strength up to 10 kV/cm. Calculations of the shifts and splitting of the energy levels of rare gases in the electric field were carried out with computer program package STARKD written in FORTRAN.

On the basis of the calculations of the Stark effect for He, Ne, Ar and Kr atoms the following regularities were discovered. Firstly, for all calculated spectral lines shift of these lines in the circular polarized electric field has quadratic dependence on the electric field strength. Secondly, in the transition from a higher level, a larger shift and higher splitting are observed than in transition from a lower level. Finally, influence of the circular polarized electric field leads to the total release of the degeneracy of energy levels with respect to the magnetic quantum number.

As illustration, Fig. 1 shows the results of calculation of the shifts and splitting of spectral lines for the $6d\,^3D_1$–$2p\,^3P_0$ ($\lambda = 382.084$ nm) and $7d\,^3D_1$–$2p\,^3P_1$ ($\lambda = 370.617$ nm) transitions for a He atom and Fig. 2 shows the results of calculation for the $8d\left[\dfrac{3}{2}\right]_1 - 3p\left[\dfrac{1}{2}\right]_0$ ($\lambda = 469.667$ nm) and $8d'\left[\dfrac{3}{2}\right]_1 - 3p\left[\dfrac{1}{2}\right]_0$ ($\lambda = 453.072$ nm) transitions of a Ne atom.
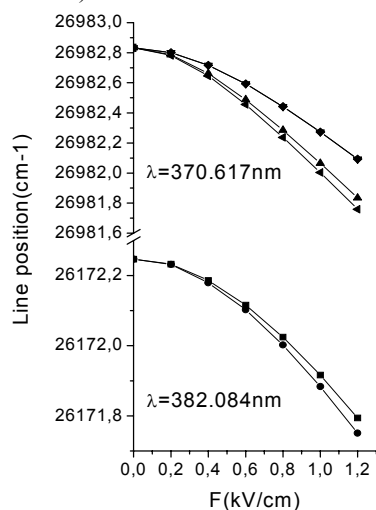

Fig. 1. The shift and splitting of spectral lines for a He atom in the electric field
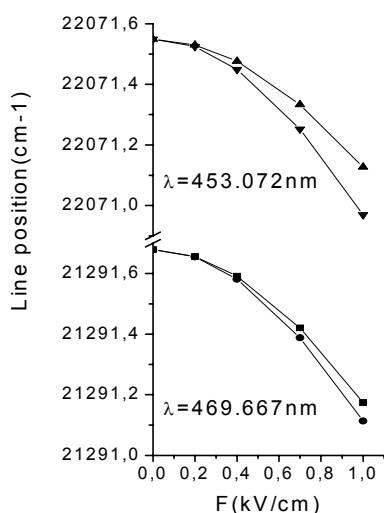

Fig. 2. The shift and splitting of spectral lines for a Ne atom in the electric field

Of interest is to study the general regularities of the Stark effect for rare gases. In order to do it we need to compare the behavior of the same spectral lines for different rare gases. For this purpose, the spectral lines $np\left[\dfrac{1}{2}\right]_0 - n's\left[\dfrac{1}{2}\right]_1$ for Ne, Ar and Kr atoms were calculated. All calculated spectral lines are in the visible spectral region, and transition wavelengths are listed in Table 1.

Table 1. The wavelengths of the transitions for rare gases (nm)

Ne,	$np[1/2]_0$–$3s[1/2]_1$	Ar,	$np[1/2]_0$–$4s[1/2]_1$
n	λ	n	λ
6	281.552	6	360.775
7	272.558	7	337.445
8	267.582	8	325.852
9	264.075	9	318.757

Subsequent analysis of the calculation results of the shifts and splitting of the spectral lines for rare gases in the electric field allows us to do the following conclusions.

Firstly, if the electric field leads to shift of the spectral lines only, then with increase of the nuclear charge for rare gas atom the direction of the shift changes to opposite. For example, for the spectral line $np\left[\dfrac{1}{2}\right]_0 - n's\left[\dfrac{1}{2}\right]_1$ the electric field leads to a shift of spectral lines to the violet spectral region for a Ne atom, whereas for Ar atom the shift of spectral lines occurs to the red spectral region (see Fig. 3). For a Kr atom a further shift of spectral lines to the red spectral region is observed.
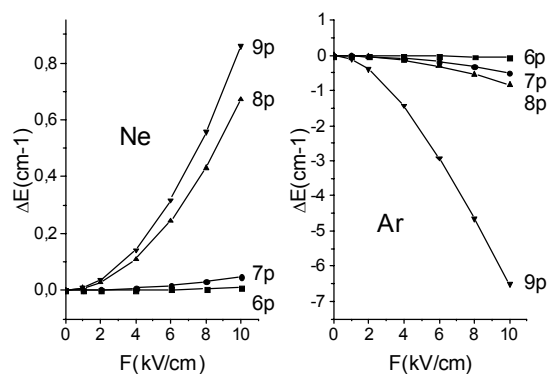

Fig. 3. The behavior of the spectral lines $np\left[\dfrac{1}{2}\right]_0 - n's\left[\dfrac{1}{2}\right]_1$ for rare gases, $n' = 3, 4$ for Ne and Ar atom correspondingly

It should be noted, that these lines are not split in the electric field since the $n's\left[\dfrac{1}{2}\right]_1$ levels are low-lying. For these low-lying levels, the electric field up to 10 kV/cm is weak and it leads only to a small shift of levels, rather than to splitting. It follows from the Fig. 3 that the quadratic dependence of the energy level shifts on the electric field strength is observed, as it was expected. Moreover, the higher energy level from which the transition occurred the more sensitive the corresponding spectral line is to the electric field.

Secondly, as for case where the spectral lines undergo not only shift but also splitting under the influence of the electric field, the careful analysis of the calculation results shows that the behavior of the same spectral lines gets a striking variety for different rare gas atoms. Unfortunately, it is impossible to represent all results in this paper, but the calculation results for

the spectral line $nd\left[\dfrac{3}{2}\right]_1 - n'p\left[\dfrac{1}{2}\right]_0$ for Ne, Ar and Kr atoms are represented as one of the examples in Fig. 4. As is seen from Fig. 4, similar to above considered case, with increase of the nuclear charge for rare gas atom the direction of the shift changes to opposite. In difference from a previous case, for spectral line $nd\left[\dfrac{1}{2}\right]_1 - n'p\left[\dfrac{1}{2}\right]_0$ the electric field leads to a shift of spectral lines to the red spectral region for a Ne atom, whereas for Ar and Kr atoms the shift of spectral lines occurs to the violet spectral region. Hence, knowing a behavior of the spectral lines for someone rare gas atom we can predict a behavior the same spectral lines for other rare gas atoms.
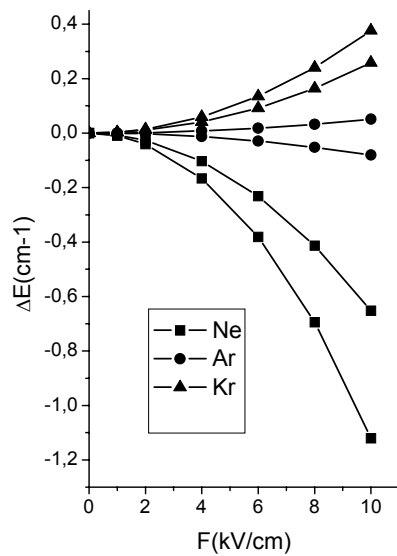

Fig.4. The splitting of spectral lines in the electric field:
Ne atom – $7d[3/2]_1 - 3p[1/2]_0$ line ($\lambda = 481.568$ nm);
Ar atom – $7d[3/2]_1 - 4p[1/2]_0$ line ($\lambda = 563.890$ nm);
Kr atom – $8d[3/2]_1 - 5p[1/2]_0$ line ($\lambda = 608.967$ nm)

Unfortunately, sometimes these regularities are broken and in general case, it is hard to predict the behavior of the each spectral line and we have to calculate the spectral lines for each individual atom.

4. Conclusions

The method suggested in the present work for calculation of the Stark effect for rare gases in a circular polarized field allows us to calculate the shifts and splitting of rare gas spectral lines in the electric field of arbitrary strength and frequency. Such calculations reveal a number of regularities inherent in the behavior of the atoms in the electric field. The obtained results can be used for plasma diagnostics. In particular, a true value of the electric field within a discharge can be found from the comparison of theoretical results with experiment. Finally, these results can be applied to the modeling new excitation sources.

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