Modelling of Atomic Spectra Emitted by Light Sources Based on an Inductive Discharge

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ABSTRACT

In this work, modelling of emission spectra of neon and argon atoms in an inductive discharge is performed. The influence of generated into this discharge alternating electric field on spectral characteristics of light sources is studied. Based on the calculation results, the regularities in the behaviour of spectroscopic properties of Ne and Ar atoms in an alternating circularly polarized electric field have been revealed. Practical applications of the simulation results are considered.

KEYWORDS: simulation of light sources, regularities in the behaviour of atomic emission spectra

1. Introduction

In recent years, light sources based on the principle of electromagnetic induction have received a rapid development. Such light sources are widely used in medicine, biology and ecological monitoring. In particular, high-frequency electrodeless discharge lamps are very suitable for use in atomic spectroscopy. For optimization of light sources and understanding processes taking place in plasma generated in an inductive discharge one needs correct and efficient calculation methods. Different numerical methods were suggested for plasma-parameter calculations in high-frequency electrodeless discharge lamps (see works and references therein). The method of self-consistent solution for the plasma-field system in a high-frequency electrodeless discharge was proposed in works for helium plasma and in work for argon plasma. In works, a 1D self-consistent model with the assumption of the Maxwellian electron energy distribution function was used for argon-mercury lamps. A number of papers were dedicated to the study of the influence of the electric field frequency and strength on spectral line intensities and the emission colour of lamps (see, for example, work and references therein). But a systematic study of dependences of atomic emission spectra on the electric field strength and frequency has never been reported.

The purpose of this paper is the study of characteristic features inherent in the behaviour of atomic emission spectra under changing the strength and frequency of an alternating circularly polarized electric field. Electric fields of such polarization are generated in electrodeless high-frequency discharge lamps, light-emitting diodes, theta discharges and other light sources. It is obvious, switching on the electric field leads to an appearance of the AC Stark effect, and this field influences all spectroscopic properties of atoms, namely: transition probabilities, energy level lifetimes and spectral line intensities. Since transition probabilities are included in the population density balance equations, the population densities of atomic states in the electric field also depend on the electric field strength and frequency. The simulation of atomic emission spectra requires reliable calculation methods. Perturbation theory, by virtue of its limitations, is not suitable to calculate emission spectra excited by electric fields generated by the above mentioned light sources.

In this work, all calculations are performed by the method of the energy matrix diagonalization of an atom in the electric field developed by us in work. This method is free from limitations of perturbation theory and valid for calculating atomic emission spectra in a circularly polarized electric field with the strength and frequency changing in wide ranges. Rare gas atoms are chosen as the subject for study because these gases are widely used in different light sources either as main gases or as buffer gases.

2. Calculation method

In the framework of our method, the energies and wave functions of an atom in a circularly polarized electric field being solutions of the non-stationary Schrödinger equation

\[
\frac{i\hbar}{\partial t} \psi_n(x,t) = (H_0(x) - F(x \cos \omega t \pm y \sin \omega t)) \psi_n(x,t), \quad (1)
\]

are determined by the two-step procedure. In the first step, in the rotating-wave approximation, atomic energies \(E_n\) and wave functions \(\psi_n(x)\) are determined by diagonalization of the energy matrix of an atom in the
electric field. The energy matrix has elements

\[ Q_{mn} = E_n^{(0)} \delta_{mn} - \omega \langle \phi_m^{(0)}(r) | J_z | \phi_n^{(0)}(r) \rangle + F \langle \phi_m^{(0)}(r) | D_z | \phi_n^{(0)}(r) \rangle, \]

(2)

This matrix is obtained in the coordinate system rotating about the Z-axis with frequency \( \omega \). In Eqs. (1, 2), \( F \) and \( \omega \) are the strength and frequency of the electric field; \( \phi_n^{(0)} \) and \( E_n^{(0)} \) are the wave function and energy of the \( n \)-th state of an atom in the absence of the electric field; \( J_z \) is the z-component of the total angular momentum operator; and \( D_z \) is the x-component of the dipole moment operator.

In the second step, after averaging over the oscillation period, the wave functions and average energies of an atom in the electric field in the initial coordinate system are written as

\[ \psi_n(r,t) = \exp(-i(\omega J_z + \epsilon_n)t) \sum_k C_{nk} \phi_k^{(0)}(r), \]

(3)

\[ \overline{E}_n = \langle \psi_n(r,t) | H(r,t) | \psi_n(r,t) \rangle - \epsilon_n + \omega \langle \phi_n(r) | J_z | \phi_n(r) \rangle \]

(4)

where \( C_{nk} \) are the expansion coefficients of the wave functions of the examined atom under the action of the electric field in terms of unperturbed wave functions.

The wave functions and energies of an atom in the electric field specified by equations (3) and (4) are further used for calculating spontaneous transition probabilities between the Stark states \( JM \) and \( J'M' \). These transition probabilities are computed as

\[ A(JM \rightarrow J'M') = 4\alpha_{JM,J'M'}^3 \, 3e^3 |D_{JM,J'M'}|^2, \]

(5)

\[ |D_{JM,J'M'}|^2 = \sum_q \sum_j C_{qj}^{JM} C_{jM'}^{JM'} (-1)^{j-j'} \frac{1}{q - M_i} \left\langle \gamma, J_i | D \right| \gamma', J_j \right\rangle^2, \]

(6)

where \( C_{qj}^{JM} \) and \( C_{jM'}^{JM'} \) are the expansion coefficients from Eq. (3), and \( \alpha_{JM,J'M'} \) is the frequency of the \( JM \rightarrow J'M' \) transition. The matrix elements of the \( D_z \) operator in equations (2) and (6) are determined as

\[ \langle \phi_m^{(0)} | D_z | \phi_n^{(0)} \rangle = \delta_{MN} \langle yJM | D_z | y'J'M' \rangle = (-1)^{j'-j} \left[ \frac{1}{M - M'} \right] \right\langle \gamma, J_i | D \right| \gamma', J_j \right\rangle, \]

(7)

where the reduced matrix elements \( \langle yJM | D_z | y'J'M' \rangle \) are calculated depending on a coupling scheme. The details of calculating the reduced matrix elements were reported in works\(^{3, 11}\).

It follows from the above reasoning that the proposed theoretical approach is free from limitations of perturbation theory and can be used for calculating the dynamic Stark effect in a circularly polarized electric field with the strength and frequency changing in wide ranges. The energies and wave functions in the electric field are determined by the diagonalization procedure, therefore, it allows us to take into account the interaction of all Stark states involved in the energy matrix of an atom in the electric field.

3. Results and discussion

Modelling of atomic emission spectra in the electric field has shown that the behaviour of spectroscopic properties of neon and argon atoms obeys certain regularities under changing the electric field strength and frequency. In this work, the parameters of the circularly polarized electric field were chosen in the range \( \omega = 1-10^6 \) MHz and \( F = 0-10 \) kV/cm.

Let us consider the found regularities.

3.1 The dependence of shifts and splitting of atomic energy levels on the electric field parameters

In our previous works, it was shown that under weak interaction of the Stark states, the dependence of the Stark state shifts on the electric field strength is quadratic, that is, \( \Delta E = F^2 \), where \( \Delta E \) is the shift of atomic energy state with respect to its position in the absence of the electric field. The quadratic dependence is known from perturbation theory, and this fact confirms the validity of our theoretical approach. Then, we have found that the Stark state shifts and splitting in the field increase monotonically with the principal quantum number \( n \) of the outer-shell electron\(^{3, 12}\). Under strong interaction of the Stark states, these regularities are broken.

The dependence of the AC Stark effect on the electric field frequency is much more complicated. To analyze the behaviour of atomic energy levels under changing the electric field frequency, it is convenient to make use of formulas specifying the maximal shifts and splitting of the energy levels in electric fields. The maximal shift of the energy level \( J \) in the electric field is computed as

\[ \Delta E_{\text{shift}} = E_{\text{max}}(JM) - E^{(0)}(J), \]

(8)

where \( E_{\text{max}}(JM) \) is the relative shift of the \( JM \) state, maximally deviating from the given level position in the absence of the electric field. The maximal splitting of the \( J \) level in the electric field is computed as the difference between the Stark states \( JM \) with the maximal and minimal deviations from unperturbed position of this level, that is,

\[ \Delta E_{\text{split}} = E_{\text{max}}(JM) - E_{\text{min}}(JM'). \]

(9)

The analysis of the energy-level maximal shifts and splitting has allowed us to reveal the following regulari-
ties in the behaviour of the Stark states of Ne and Ar atoms in the circularly polarized electric field.

1) For the energy levels, non-splitting in the electric field, an increase in the electric field frequency \( \omega \) leads to a slow decrease in shifts of these levels in the range \( \omega = 1 \times 10^5 \text{MHz} \) (see Table 1). It follows from this table that atomic states from the \( ns \) configuration have the same shift directions for all examined \( \omega \) from the range \( 1 \times 10^5 \text{MHz} \), whereas the energy states from the \( np \) and \( nd \) configurations change not only values but also the state-shift directions with increasing \( \omega \) (see Table 1). In this table, the sign “−” corresponds to the Stark state shift toward the red region, and the sign “+” corresponds to the Stark state shift toward the violet region. As a rule, this change in the sign is accompanied by a sharp increase in the Stark state shifts in the electric field.

2) The energy levels of neon and argon atoms, splitting in the electric field, demonstrate a similar behaviour. It follows from Table 2, in the range \( \omega = 1 \times 10^5 \text{MHz} \), all states of these atoms have invariable state-shift directions, and shifts and splitting of the energy levels slowly decrease with an increase in the electric field frequency. At \( \omega = 10^7 \text{MHz} \), the state-shift directions remain the same for energy states from the \( ns \) configuration, whereas atomic states from the \( np \) and \( nd \) configurations reverse their directions. In most cases, changing the state-shift directions leads not only to a sharp increase in the shift values, but to a drastic increase in splitting of the energy levels under consideration.

It should be noted that changing the state-shift directions at increasing the electric field frequency leads to the change in the emission colour of light sources. As an illustration of this effect, the dependence of the \( 8\delta[1/2]_b \) state (the Ne atom) and the \( 8\delta[1/2]_b \) state (the Ar atom) on the electric field frequency are plotted in Figure 1.

As seen from this figure, an increase in the electric field frequency leads to the change in the emission colour from the blue colour to the red one for spectral lines corresponding to the transitions from these excited states. These results agree with experimental observations of work.8

The found regularities in the behaviour of the shift directions of the Stark states allows us to estimate the influence of changing the electric field parameters on colour characteristics of light sources and broadening of spectral lines observed in experiments.8,13

Let us to compare our theoretical results with experimental data.8,13 First of all, it should be noted that Tables 1 and 2 contain the maximal shifts and splitting
for rather high energy states $nl \, \{J,K\}$, with $n=5-9$. These results are chosen to illustrate the revealed regularities in the best way. All of the rest examined energy states of Ne and Ar atoms demonstrate a similar behaviour in the electric field. In doing so, the higher upper state, which the transition occurs from, the more sensitive spectral characteristics of atomic lines are to changes in the electric field strength and frequency. Moreover, it is known from experiments that spectral lines corresponding to the transitions from the $nl \, \{J,K\}$ states with the minimal values of the principal quantum number $n$ have the maximal intensities, and the intensities decrease with the growth of $n$ (see, for example, work\textsuperscript{15} and the references there). In particular, for the Ne atom, in the absence of the electric field, the relative intensities of the $3s[1/2]_0\rightarrow 3p[1/2]_0$, $3p[3/2]_0\rightarrow 6d[5/2]_0$, $3s[3/2]_0\rightarrow 7p[3/2]_0$ spectral lines are 20000, 3000 and 2000 rel. un., correspondingly\textsuperscript{10}. However, switching on the electric field can lead to an increase in the intensity of spectral lines by an order of magnitude. For example, such increase was obtained for the Stark component $M=\rightarrow -2 \rightarrow M=-1$ of the $2P_{1\rightarrow 3D}_2$ spectral line for the He atom in the electric field with the parameters $\omega=100$ MHz and $F=1$kV/cm. More details about changes in spectral line intensities of rare gas atoms in the electric field are reported in works\textsuperscript{15, 16}.

Further, we would like to add that the knowledge of the positions and transition probabilities of spectral lines corresponding to the transitions from high energy states is necessary for spectroscopic diagnostics in solving many problems of atomic spectroscopy, plasma spectroscopy, and also for constructing new light sources with desirable properties or searching optimal operation modes of existing light sources.

Our calculations have shown that the influence of the electric field on the behaviour of the $3s[1/2]_0\rightarrow 3p[1/2]_0$ (the Ne atom) and $4s[1/2]_0\rightarrow 5p[1/2]_0$ (the Ar atom) spectral lines is rather weak. But, nevertheless, in work\textsuperscript{8} and the references there, the influence of the change in the electric field frequency on the intensity and colour of the radiation of lamps was discussed very actively, and these papers stimulated us to perform a theoretical investigation of this problem.

Now let us to discuss the shift of the $2P_{1\rightarrow 3D}_2$ spectral line of the He atom toward the red region. Detailed comparison of our theoretical results with experimental data\textsuperscript{13} was published earlier\textsuperscript{10}. It was shown\textsuperscript{10} that the values and shift directions of the Stark components, and also the intensity and profile of this line in the alternating circularly polarized electric field obtained in the framework of our theoretical approach practically coincide with those observed in experiments\textsuperscript{13}. In particular, the shift of the Stark component $M=1\rightarrow M'=2$ of the $2P_{1\rightarrow 3D}_2$ spectral line in the electric field is 4.5302 cm$^{-1}$ (our calculation) and 4.5 cm$^{-1}$ (experiment [13]). Such good agreement of our results with experimental data confirms the validity and efficiency of the suggested theoretical approach.

3.2 The dependence of transition probabilities on the electric field parameters

Now let us consider the influence of changing the electric field strength and frequency on transition probabilities in atomic emission spectra. Based on our calculation results, we have found some interesting regularities in the behaviour of transition probabilities in emission spectra of Ne and Ar atoms in the circularly polarized electric field. Let us consider these regularities.

1) Under weak interaction of the Stark states, all $M\rightarrow M'$ transitions are pairwise equiprobable, that is, $A_{M\rightarrow M'}(+M\rightarrow +M')=A_{M\rightarrow M'}(-M\rightarrow -M')$. Transition probabilities do not depend on the electric field frequency. As an illustration, probabilities of different transitions are represented in Table 3.

Analogous results are obtained for probabilities of other transitions in spectra of atoms under consideration.

2) Under strong state interactions, it is significant that we have a great difference between probabilities of all $M\rightarrow M'$ transitions between the Stark components.
Table 3  Dependence of probabilities of the $J^M \rightarrow J'^{M'}$ transitions (in $10^6$ s$^{-1}$) on the electric field strength under weak interaction of the Stark states ($\omega = 1$–$10^6$ MHz).

| Atom | Transition | $A_{\Omega}$ (at $P'=0$) | $M \rightarrow M'$ | $A_{\Omega}(M \rightarrow M')$ |
|------|------------|--------------------------|-------------------|-----------------------------|
| Ne   | 9$p[1/2]_J$–3$p[1/2]_J$ | 0.113 | 0→±1 | 0.038 | 0.036 |
| Ne   | 9$p[3/2]_J$–3$p[1/2]_J$ | 0.078 | ±1→0 | 0.078 | 0.077 |
| Ar   | 7$p[1/2]_J$–4$p[3/2]_J$ | 2.314 | 0→±1 | 0.780 | 0.780 |
| Ar   | 7$p[1/2]_J$–4$p[1/2]_J$ | 0.042 | ±1→0 | 0.042 | 0.042 |
| Ar   | 4$p[3/2]_J$–4$p[3/2]_J$ | 5.960 | ±1→±2 | 3.580 | 3.580 |
| Ar   | 4$p[5/2]_J$–4$p[3/2]_J$ | 22.459 | ±2→±1 | 22.459 | 22.459 |
|      |             |                  | ±1→0 | 11.229 | 11.229 |
|      |             |                  | 0→±1 | 3.745  | 3.745  |

Analogous results are obtained for probabilities of other transitions in emission spectra of neon and argon atoms.

As seen from Figure 2, at $J, J' \leq 1$, probabilities of the $M \rightarrow M'$ transitions between the Stark components of the same spectral line have the same values in the range of $\omega = 1$–$10^6$ MHz, but a further increase in the electric field frequency leads to changes in probability values. At $J=J'$, the difference between probabilities of the $0 \rightarrow 1$

![Figure 2](image1.png)

![Figure 3](image2.png)

![Figure 4](image3.png)
and 0→−1 transitions increases with the electric field frequency. On the contrary, at J< J', the difference between probabilities of the +1→0 and −1→0 transitions decreases with increasing ω.

Now, let us consider the behaviour of transition probabilities under changing the electric field parameters at J, J'≤2. As seen from Figure 3, in case of J, J'≤2 as well as at J, J'≤1, switching on the electric field leads to an immediate drop of all transition probabilities at J< J'. On the contrary, at J> J', at least one of the pair of probabilities A_{jM}(−M→M) and A_{jM}(+M→−M) with the maximal value of M or M' is practically indifferent to changes in the electric field strength, whereas the rest probabilities demonstrate the same behaviour as in the case of J< J'.

Additionally, Figure 4 shows the dependence of transition probabilities A_{jM}(M→M') between the Stark components of the 4d5/2 3p3/2 spectral line on the electric field frequency. As seen from these figures, the transition probabilities A_{jM}(M→M') with the maximal value of M increase with the electric field frequency, and transition probabilities therewith tend to be pairwise equiprobable under an increase in ω.

3) The above-mentioned difference in the behaviour of transition probabilities A_{jM}(M→M') at J< J' and J> J' is valid both for strong and weak mixing of the Stark states (see Table 3 and Figures 2–4). The fundamental reason for this difference is the addition theorem for mutually exclusive events, because the number of allowed M→M' transitions at J< J' is greater than their number at J> J'. By virtue of the theorem, the revealed effect must be observed for probabilities of all transitions in atomic emission spectra, as was obtained in the calculations. By the present time, there are no experimental data for comparison the results of our calculations with experimental data, because these experiments are very complicated. We and Prokhorov General Physics Institute (Russia, Moscow) only begin this work.

4) The calculation results have shown that switching on the electric field leads to ordering of transition probabilities with respect to the magnetic quantum number M. As seen from Table 3 and Figures 2–4, for the J=1→J'=2 transitions, probabilities of the M→max[M'] transitions have maximal values, and these probabilities diminish with M'. The same regularity is observed for the J=2→J'=1 transitions, namely: probabilities of the max[M]→±M transitions are maximal, and these probabilities diminish with M. The found regularity is valid at both weak and strong interactions of the Stark states with the only one distinction, namely: under strong interaction of the Stark states all M→M' transitions are equiprobable, whereas under weak interactions pairwise equiprobability of transitions is observed. Analogous results are obtained for probabilities of other transitions in emission spectra of neon and argon atoms.

The regularities established in the behaviour of transition probabilities allow us to conclude that for all transitions under weak interaction of the Stark states, as well as under strong one, switching on the electric field immediately leads to quenching of spectral lines for J< J' transitions and ordering of transition probabilities with respect to the magnetic quantum number M. These regularities are valid for all transition probabilities and examined values of the electric field strength and frequency. In addition, based on our calculation results, we have found that in case of weak Stark state interactions, the transitions always are pairwise equiprobable and practically insensitive to increasing the electric field frequency, whereas in case of strong Stark state interactions, all transitions are unequivalent at small ω and they have a tendency to be pairwise equiprobable under increasing ω.

4. Conclusions

Regularities in the behaviour of the AC Stark effect and transition probabilities in atomic emission spectra in an alternating circularly polarized electric field, found in this work, are of interest from the theoretical viewpoint. In addition, the established regularities are very useful in practical applications. For example, they allow us to explain processes taking place in plasma, clarify mechanisms of formation of atomic emission spectra in the electric field and understand the reasons for changes in colour characteristics of light sources induced by the electric field. Finally, the results obtained are useful for searching optimal operation modes of existing light sources and for constructing new light sources.

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