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Features of the formation of the emission spectrum of the decaying plasma of a low-pressure pulsed barrier discharge

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In this paper, the role of the processes of electron-ion recombination of Ne^+, Ne_2^+, and Ne^{++} ions in the formation of the optical properties of decaying neon and helium-neon plasmas is compared by means of kinetic spectroscopy. The plasma source was a low-frequency (80–160 Hz) pulsed dielectric barrier discharge, which creates a sufficient number of doubly charged Ne^{++} ions for spectroscopic observations in the recombination afterglow. Results are presented showing the possibility of solving the problem by analyzing, along with the intensities of individual spectral lines in the afterglow of the discharge, also plasma radiation in „white" light.

Keywords: dielectric barrier discharge, doubly charged ions, collisional–radiative recombination, decaying plasma, elementary processes.

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Introduction

When used as a method for plasma production for the study of elementary processes, a dielectric barrier discharge (DBD) has certain advantages over other discharge types [1]. First, it is important in this regard that a DBD has the capacity to produce doubly charged ions, which manifested themselves in the spectroscopic experiment performed in [1] by enriching the emission spectrum of neon plasma with ion lines at the active DBD stage and in the early afterglow under a gas pressure below several torr. Second, plasma formations produced by a DBD under such conditions are almost uniform in space [2] and extensive (several tens of centimeters) with an easily adjustable electron density. The latter was used in [3,4] to analyze the rate of collisional–radiative recombination (CRR) of Ne^{++} ions with electrons based on the pattern of decay of ion line intensities at the plasma decay stage. One of the conclusions made in this study, which was performed with due account for the data of mass spectroscopy experiments [5,6] on mobility of doubly charged ions and the charge transfer in $Ne^{++}+Ne$ collisions, was that the actual CRR rate of these ions is much higher than the one predicted theoretically [7]. In the present study, the results of a spectroscopic experiment characterizing the contribution of Ne^{++} recombination-related filling of excited levels of a neon ion to the emission of decaying plasma dominated in its ion composition by Ne^+ and Ne_2^+ are reported.

Experimental setup

The design of experiments on low-frequency pulsed barrier discharge was detailed in the papers cited above. For the sake of consistency, we provide here just a brief overview of this technologically simple (Fig. 1) and fairly versatile method for gas ionization within a wide pressure range. The key element of the setup is a flyback transformer operated with a 12 V power supply in the pulsed mode. Its parameters (frequency and duration T_p of a pulse turning transistor Tr on) set the level of energy accumulated in transformer T and, consequently, the DBD electrode voltage upon switching the transistor off. Oscilloscope records of current in the electrode circuit reveal that function $i(t)$ consists of two half-waves of opposite polarities with a base width of approximately 3 μs, which differ slightly in amplitude and duration. In the experiment under consideration (under a gas pressure of 1.7–0.5 Torr), the electrode

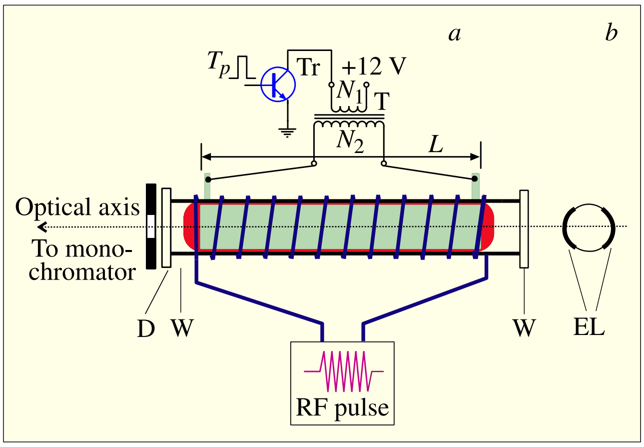

Figure 1. (a) Diagram of superposition of barrier and pulsed radio-frequency discharges (RF Pulse). D — diaphragm 5 mm in diameter; W — are quartz windows. (b) Positioning of DBD electrodes (EL) on the external side surface of a discharge tube $L \sim 20$ cm in length.

voltage could be adjusted within the 1000−6000 V range at turn ratio $N_2/N_1 = 10$, providing an opportunity to produce plasma with electron density $[e] \sim (10^{10}{-}5 \cdot 10^{11})\,cm^{-3}$ at the center of the tube 3.9 cm in diameter. The experimental data presented below were obtained at electron density $[e] \sim 10^{11}\,cm^{-3}$ in the early afterglow.

The added radio-frequency (tens of megahertz) discharge spiral (RF in Fig. 1) has several research applications. In the pulsed mode with a variable radio-frequency voltage amplitude, it makes it easy to induce short-term „heating" of decaying plasma electrons, thus allowing one to examine the mechanisms of filling of excited levels of Ne^* and Ne^{+*} by analyzing the intensity variations of spectral lines. The RF pulse duration in experiments of this kind is normally $\Delta t \le 1\,\mu s$. Longer-term (tens or hundreds of microseconds) heating with monitoring of the population of level $2p^5 3s(^3P_1)$ is used in our research [1] to estimate electron density $[e](t)$ by comparing the $[^3P_1](t)$ variation with the results of calculations based on the known rate constant of process $^3P_2 + e \leftrightarrow {}^3P_1 + e$. In addition, the enrichment of the afterglow spectrum of the used barrier discharge with ion lines (relative to an RF discharge) is indicative of the emergence of Ne^{++} ions in plasma at a reduced gas pressure. The recombination radiation associated with these ions responds to electron „heating" no less vividly than the radiation related to CRR of Ne^+ ions.

Results and discussion

The afterglow spectra of DBD in neon and in a He−Ne mixture under comparable total pressures and the same discharge conditions are shown in Figs. 2, *a, b*. Measurements were performed using the multichannel photon counting technique with a FEU-106 photomultiplier tube and time gating of the FEU-106 signal, which helped exclude the contribution of discharge and early afterglow at a high electron temperature sufficient for direct and stepwise excitation. Thus, the presented spectra characterize the recombination afterglow component; notably, the gating interval included radiation associated with CRR of both singly and doubly charged ions:

$$Ne^+ + e + e \xrightarrow{\alpha_{1cr}} Ne^* + e, \quad (1)$$

$$Ne^{++} + e + e \xrightarrow{\alpha_{2cr}} Ne^{+*} + e, \quad (2)$$

where α_{1cr}, α_{2cr} are the rate constants of processes. Since the data in Fig. 2 correspond to the minimum gas pressure in our experiments, they illustrate most clearly the contribution of process (2) to the afterglow spectrum in the near ultraviolet region. As the neon pressure rises, the kinetics of Ne^{++} ions is influenced more and more by the process of charge transfer:

$$Ne^{++} + Ne \xrightarrow{k_{Ne}} Ne^+ + Ne^+. \quad (3)$$

The data on this process at a particle temperature of $\sim 300\,K$ found in [5,6] contain contradictory

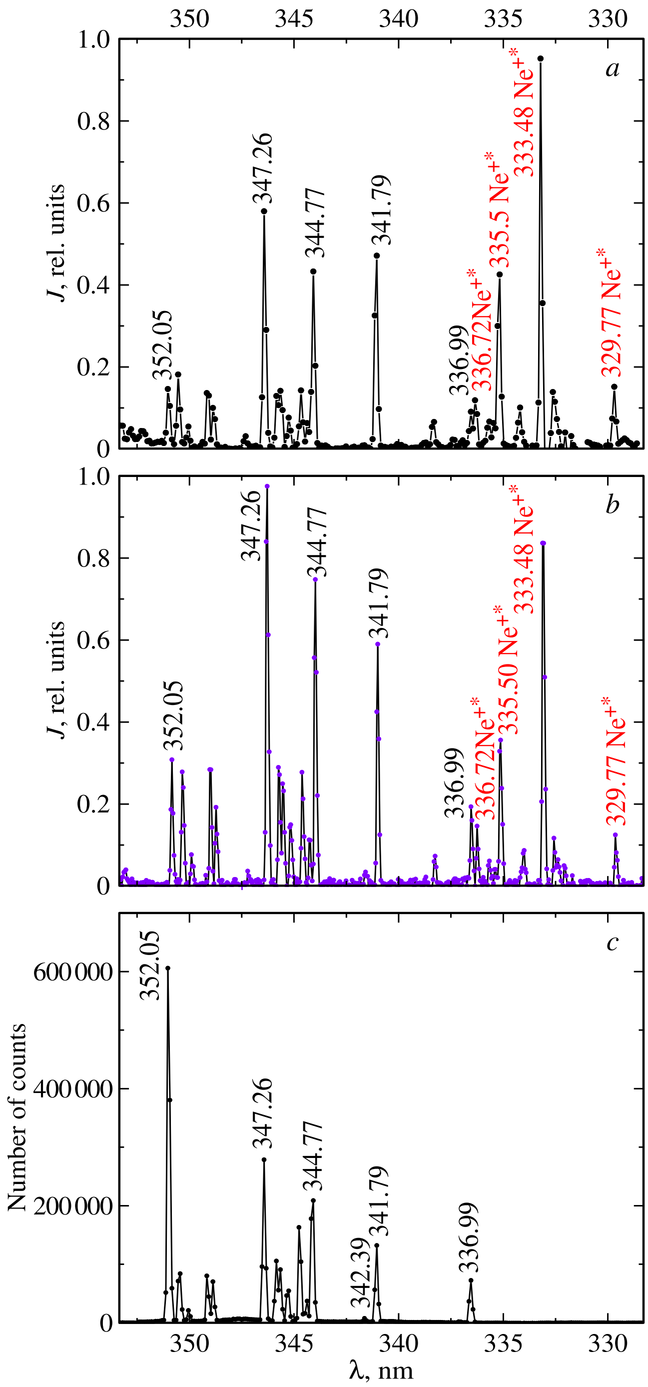

Figure 2. Afterglow spectra: (*a*) He−Ne mixture with component pressures of 0.4 and 0.2 Torr, respectively; (*b*) Ne (0.5 Torr); (*c*) RF discharge in neon (0.5 Torr).

estimates of rate constant k_{Ne}: according to [5], $k_{Ne} = (9 \pm 2) \cdot 10^{-14}\,cm^3 s^{-1}$, while the authors of [6] provide different rate constants for three lower states ^1S, ^1D, and ^3P of a Ne^{++} ion: 2.7 ± 0.3, 1.9 ± 0.2, and 2.1 ± 0.2, respectively (the units of measurement are the same). Using the α_{1cr} rate constant estimate from [7] within the approximation of purely collisional kinetics of an excited electron in (1) (it is worth reminding that the recombination flux is then specified by the rate of diffusion of a highly excited electron, which was produced in a recombination event, toward the ground state of an atom in collisions with plasma electrons; at moderate quantum numbers and electron densities, which are established in the discussed experimental conditions, the recombination flux is carried by radiation) and dependence $\alpha_{Z\mathrm{cr}} \sim Z^3$ of the recombination rate on the ion charge proposed in [7], one determines readily that process (3) is the primary channel of destruction of doubly charge ions under pressures $P_{\mathrm{Ne}} > 1$ Torr, electron density $[\mathrm{e}] \sim 10^{11}\,\mathrm{cm}^{-3}$, and electron temperature $T_e \sim 300$ K. It follows from Fig. 2 that ion lines are the most intense in the examined spectral region when the neon content is at its minimum ($P_{\mathrm{Ne}} = 0.2$ Torr). The wavelengths of certain lines are indicated in the figure. In contrast, the radio-frequency discharge spectrum (Fig. 2, *c*) contains none of these lines, even though all $4p \to 3s$ transition lines down to the weakest ones (e.g., the 342.39 nm line with intensity $J \sim 3000$ counts) with transition probability $A_{ik} \sim 10^5\,\mathrm{s}^{-1}$ are present in it.

As for the entire wavelength range that may be probed in the experiment (300–850 nm), there is little point in comparing the intensities of individual ion and atomic lines directly as it was done in Fig. 2. According to the NIST database [8], the ion spectrum of neon is an order of magnitude denser than the atomic one; therefore, even low-intensity Ne^{+*} emission lines may produce a significant contribution to the total radiation flux of decaying plasma. In the present study, „white-light“ emission (in the zeroth order of the monochromator diffraction grating) was analyzed in order to compare these fluxes. To simplify the task, a discharge in pure neon under a pressure of 1.7 Torr, which is considerably higher than the one corresponding to Fig. 2, was examined experimentally. The results of modeling of processes in decaying barrier discharge plasma [3] suggest that the time dependences of atomic $J_{\mathrm{a}}(t)$ and ion $J_{\mathrm{i}}(t)$ lines are affected, to a certain extent, by the ratio of initial ion densities $[\mathrm{Ne}^{++}]/[\mathrm{Ne}^{+}]$ if their values, which are unknown at the present moment, are comparable; in contrast, at $[\mathrm{Ne}^{++}]/[\mathrm{Ne}^{+}] << 1$, ion conversion $[\mathrm{Ne}^{++}] \to [\mathrm{Ne}^{+}]$ (3) contributes to the fulfillment of the indicated inequality and has no influence on $J_{\mathrm{a}}(t)$ in the afterglow.

Some data on the evolution of afterglow under a neon pressure of 1.7 Torr are presented in Fig. 3. It can be seen that intensities $J(t)$ form three specific groups (this is observed for all atomic and ion spectral lines found within the 300–8500 nm wavelength interval), which represent the contribution of three processes to the production of excited particles. The third process, which is added to (1) and (2), is the dissociation recombination (DR) of a molecular ion:

$$\mathrm{Ne}_2^{+} + \mathrm{e} \overset{\alpha_{\mathrm{DR}}}{\to} \mathrm{Ne}_2^{*} \to \mathrm{Ne}^{*} + \mathrm{Ne}. \quad (4)$$

Intensities *1, 3–5* in Fig. 3 are associated with DR, which is the fastest plasma deionization process with its rate constant α_{DR} exceeding $10^{-6}\,\mathrm{cm}^3/\mathrm{s}$ [9,10] for certain ions. It is characterized by a marked selectivity, since the set of output process channels is limited. This selectivity is especially

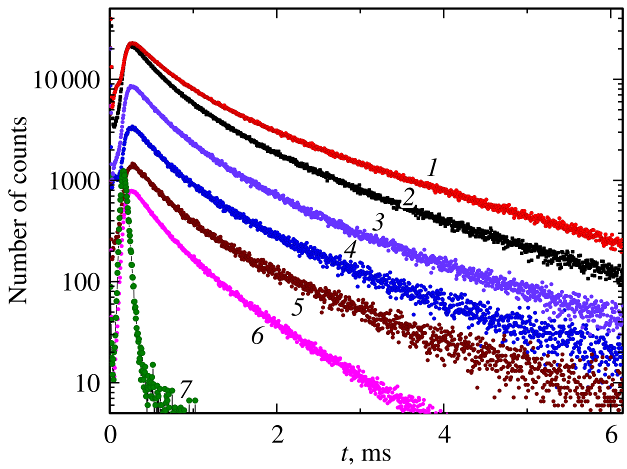

Figure 3. Time $t = 0$ corresponds to the onset of afterglow, the neon pressure is 1.7 Torr, and electron density $[e]$ $(t = 0) \sim 10^{11}\,\mathrm{cm}^{-3}$. *1, 3–6* — intensities J_λ of lines $\lambda = 585.2$ (transition $3p{-}3s$), 344.7 ($4p{-}3s$), 345.4 ($4p{-}3s$), 705.9 ($3d - 3p$), and 576.4 nm ($4d{-}3p$), respectively; *2* — „white“ light; *7* — 333.48 nm ion line.

well-pronounced in neon: level $3p_3$ [11] (in the Paschen notation) of the $2p^5 4p$ configuration with excitation energy $U \sim 20.26$ eV is the threshold one for the process in plasma decaying at electron temperature $T_e \sim 300$ K, while the filling of higher-energy levels is associated with CRR (1), which is represented by the 576.4 nm line in Fig. 3. In view of the above-mentioned specifics of formation of a recombination flux, excited atoms in any state may emerge in plasma with atomic ions.

The $[\mathrm{Ne}^{++}](t)$ density kinetics is represented by the 333.48 nm ion line (curve 7 in Fig. 3). The mechanisms of recombination of Ne^{++} (2) and Ne^{+} (1) ions are identical, and only the rates of processes ($\alpha_{Z_{\mathrm{cr}}} \sim Z^3$) differ. This is illustrated by Fig. 3, which reveals a much faster decay of intensities of ion lines. Since process (2) is the least well-studied in the (1), (2), (4) chain in terms of the influence on optical properties of decaying plasma, it will be discussed in most detail.

It is fairly evident how the data from Fig. 3 should be interpreted in the context of comparison of processes (1) and (3): levels $4d$ are inaccessible to DR, and the photon flux in the 576.4 nm line is

$$J_{576.4}(t) \sim \alpha_{1\mathrm{cr}}[\mathrm{e}]^2[\mathrm{Ne}^{+}]. \quad (5)$$

In addition to a certain fraction of flux (5), the lines from levels $3p$, $4p$, and $3d$ contain contribution (4) of DR of molecular ions, which emerge in the afterglow owing to the well-studied [10] conversion in triple collisions

$$\mathrm{Ne}^{+} + \mathrm{Ne} + \mathrm{Ne} \to \mathrm{Ne}_2^{+} + \mathrm{Ne},$$

and pairwise collisions of excited neon atoms $\mathrm{Ne_M}$ in metastable states

$$\mathrm{Ne_M} + \mathrm{Ne_M} \to \mathrm{Ne}_2^{+} + \mathrm{e}.$$

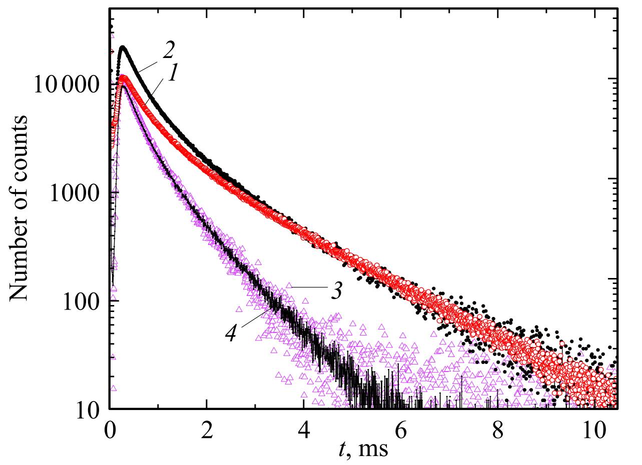

Figure 4. *1* — Intensity $J_{585.2}$ of the 585.2 nm line, *2* — $J_{\mathrm{W}k}$, *3* — difference D_1, and *4* — intensity of the 576.4 nm line superposed with D_1.

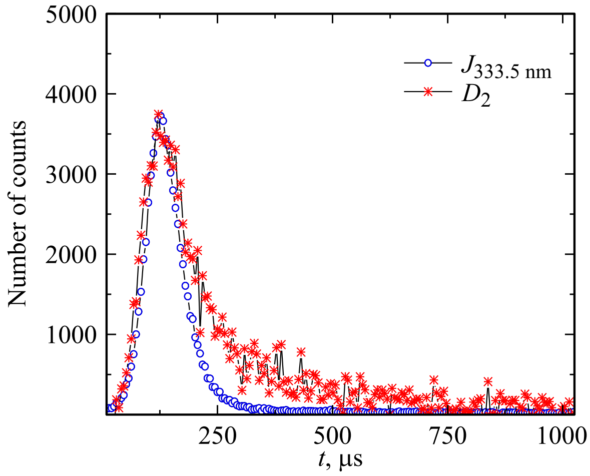

Figure 5. Difference D_2 and intensity of the 333.48 nm line superposed at the maximum.

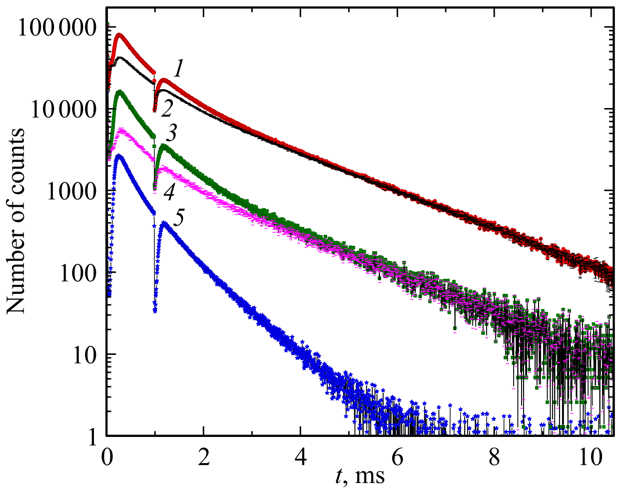

Figure 6. Afterglow with pulsed electron „heating" *1, 3, 5* — intensities of the 585.2, 724.5, and 576.4 nm lines; *2, 4* — intensities of the 585.2 and 724.5 nm lines without the CRR contribution.

Molecular-ion recombination (4) produces a photon flux competing with (1):

$$J_{\mathrm{DR}} \sim \alpha_{\mathrm{DR}}[\mathrm{e}][\mathrm{Ne}_2^+]. \quad (6)$$

It is evident that the problem at hand is solved by excluding recombination fluxes (5) and (6) from „white" light. Let us present the experimentally recorded „white-light" quantum flux as a sum of three components:

$$J_{\mathrm{W}} = a_1 J_{576.4} + a_2 J_{\mathrm{DR}} + a_3 J_{\mathrm{Ne}^{++}}, \quad (7)$$

where

$$J_{\mathrm{Ne}^{++}} \sim \alpha_{2\mathrm{cr}}[\mathrm{e}]^2[\mathrm{Ne}^{++}].$$

As a first step, we substract the intensity of the 585.2 nm line, which is the least affected by CRR (1) (Fig. 3), from the intensity of „white" light. This line was chosen for the following reasons. Since the solution algorithm relies on comparison of time dependences of intensities $J(t)$ of spectral lines, the lines representing the studied processes to the fullest extent and remaining unaffected by concomitant factors, chief among which is the reabsorption of radiation at transitions to the most populated states of a neon atom of the $2p^5 3s$ configuration, should be chosen for analysis. The 585.2 nm line emission is not distorted by reabsorption, since the lower state of the transition is the upper resonance state $^1P_1$, which is much less populated than state $^3P_1$ mentioned above. At the same time, almost the entire radiation flux from level $2p_1$ [8], at which a significant fraction of the DR flux of molecular ions is directed [12], is carried in the 585.2 nm line.

Further development of the algorithm involves finding coefficient k such that the sum of squares of intensity differences $\Sigma_i (J_{585.2} - J_{\mathrm{W}}k)_i^2$ between the 585.2 nm line and „white" light is minimized for points i at times $t > 4.5$ ms in the afterglow when CRR contribution (1) to both of the examined intensities becomes negligible ($J_{576.4}(t)$ in Fig. 3 provides a clear illustration of this). The following difference is then written:

$$D_1(t) = J_{\mathrm{W}}k - J_{585.2}.$$

It is evident that $D_1(t)$ corresponds to the „white-light" flux exclusive of the contribution of DR and, in part, flux (5). Figure 4 presents D_1 together with $J_{585.2}(t)$ and $J_{\mathrm{W}}(t)k$; $J_{576.4}(t)$ superposed with D_1 at $t > 1$ ms, when the afterglow is free from ion lines, in the same way as J_{W} and $J_{585.2}$ is also shown. It can be seen that difference $D_1(t)$ obtained by subtracting the DR contribution from „white" light is almost identical to the CRR flux of Ne^+ ions. It is clear that if the considered model of formation of the radiation flux of decaying plasma is correct (i.e., the flux has only three components), the obtained result implies that the contribution of process (2) to integral plasma radiation is small compared to (1) and (4), although still noticeable (due mostly to short-wavelength emission). Having calculated difference $D_2(t)$ between superposed $D_1(t)$ and $J_{576.4}(t)$ and plotted it in Fig. 5 together with the $J_{333.48}(t)$ ion line (with the intensity of the latter normalized so that it becomes similar to D_2 in the region of the maximum), we find that D_2 is fairly close to $J_{333.5}(t)$.

The presented experimental data are insufficient to tell whether a difference between $D_2(t)$ and $J_{333.5}(t)$ being outside the margin of statistical error is representative of certain real processes in plasma. In any case, the above reasoning demonstrates that a joint spectroscopic analysis of „white" light and line emission of a known origin readily allows one to separate contributions and examine various processes of filling of excited atomic states in plasma of a complex ion composition. We note in conclusion that a similar algorithm for separation of fluxes filling excited levels may be applied to processes (1) and (2). In order to determine the photon fluxes in the 585.2 and 724.5 nm lines free from CRR (1), a more informative experiment with electron „heating" by a weak pulsed (with a duration of 1 μs) radio-frequency field was carried out (see Fig. 6). In concordance with the temperature dependence of rate constant $\alpha_{1cr}(T_e) \sim T_e^{-4.5}$ [7], the 576.4 nm line responds much stronger to T_e variations than the 585.2 and 724.5 nm lines. It is also evident that the response of these lines to electron heating becomes closer to weak dependence $\alpha_{DR}(T_e)$ typical of DR when the CRR contribution to their intensity is „subtracted."

Conclusions

The emission of decaying plasma with a complex ion composition produced by an extended barrier discharge in low-pressure neon was examined by kinetic spectroscopy within the 300−850 nm wavelength range. An algorithm for separating the contributions of processes of recombination of Ne^+, Ne_2^+, and Ne^{++} ions with electrons to the production of excited particles of decaying plasma was developed based on the results of examination of „white-light" plasma emission together with spectral atomic and ion lines. It was demonstrated that CRR of doubly charged neon ions, which enriches the plasma spectrum considerably in the near ultraviolet region, cannot compete with Ne_2^+ and Ne^+ ions when it comes to shaping the overall radiation flux of decaying plasma in the optical range.

Conflict of interest

The authors declare that they have no conflict of interest.

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