Dissociative recombination of heteronuclear molecular ions and electrons in a noble-gas mixture plasma

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(Submitted 22 July 1994)
Zh. Eksp. Teor. Fiz. **106**, 1704–1721 (December 1994)

A method for investigating the dissociative recombination of heteronuclear molecular ions and electrons in a noble-gas mixture plasma is suggested and applied. A helium–neon mixture plasma is used to demonstrate the potentials of the method, which is based on spectroscopic studies of the relaxation processes that develop under pulsed perturbation of the decaying plasma initiated by an electric field. The value and temperature dependence of the rate constant for the recombination of $HeNe^+$ ions are obtained: $\alpha=(1.0\pm0.2)\times10^7\ (T_e/300\ K)^{-1.34\pm0.11}\ cm^3/s$. The conditions are established in which this process plays the dominant role in excited-atom formation in the decaying plasma. Also, some of the outgoing process channels are identified. © *1994 American Institute of Physics.*

1. INTRODUCTION

The dissociative recombination of molecular ions and electrons is the most effective mechanism of volume charge neutralization in weakly ionized plasmas under moderate (tens and hundreds torrs) and high pressures. The cross section of an electron being captured by a molecular ion at thermal energies of the particles reaches a value of approximately 10^{-13} cm^2, with the result that the process plays a key role in the kinetics of the charged plasma particles and the molecular ions. Recent years have seen an upsurge of interest in studies of the recombination of molecular ions of inert gases, whose ionized mixtures B+R have found application as the active media of recombination (plasma) lasers.[1–3] A characteristic feature of these media is the low relative density of the easily ionizable process gas, $[R]/[B]\approx10^{-2}–10^{-3}$, with the pressure of the buffer gas B at one atmosphere or higher. Because of the ion–molecular reactions proceeding in the plasma in these conditions there is intensive production of heteronuclear ions BR, which together with homonuclear molecular ions R_2^+ determine the balance of charged particles and form the recombination flux needed for populating the excited states of atoms. In contrast to dissociative recombination of homogeneous ions,

$$R_2^+ + e \rightarrow R^* + R, \quad (1)$$

which has been extensively studied both experimentally and theoretically (see, e.g. the review articles by Massey,[4] Eletskiĭ and B. M. Smirnov,[5] and Ivanov[6]), the similar process involving heteronuclear ions,

$$BR^+ + e \rightarrow R^* + B, \quad (2)$$

has practically never been studied. The dissociative recombination (1) is considered in kinetic models of active media of noble-gas lasers as a major mechanism by which laser levels are populated.[7] In a number of papers (see, e.g., Ref. 8) the inverted population of the upper laser levels is related to the dissociative recombination of heterogeneous ions. Such models, however, are of a clearly hypothetical nature, since there is no data on the recombination rate of (2) or the process channels. At the same time heterogeneous noble-gas ions are known to have binding energies (0.023 to 0.67 eV) sufficient for forming stable complexes.[9] Such particles have been observed in a number of mass-spectrometer[10–14] and spectroscopic[15–18] experiments.

Heteronuclear ions are also interesting for their direct participation in the formation of the emission spectra of noble-gas mixture plasmas. Under certain conditions the fraction of the energy injected into the plasma and transferred in the molecular bands, which are related to the transitions between different electron–vibrational–rotational states,[19] $B^+R\rightarrow BR^+ + h\nu$, is considerable.[20] This makes it possible to classify these ions as heteronuclear ion molecules, studied in Ref. 21 and promising from the viewpoint of obtaining molecular lasing.

The difficulty in studying the recombination of heteronuclear ions is that the traditional methods based on measuring the rate of decrease in the number density of the charged particles are inapplicable if there are several ion species whose concentrations are comparable. In addition to BR^+ ions, the plasma contains B^+, R^+, B_2^+, and R_2^+ ions, and it is impossible *a priori* to specify the conditions in which processes involving BR^+ ions are predominant in the volume neutralization of charged particles, the more so that there are no reliable data on all the necessary reaction rate constants. This explains the absence of information about the recombination of heteronuclear noble-gas ions.

This paper suggests a method that has been used for the first time to study experimentally the dissociative recombination of heteronuclear ions and electrons. A helium–neon mixture plasma is used to demonstrate the potential of the method, which is based on a spectroscopic analysis of relaxation processes that develop under a pulsed perturbation of the decaying plasma initiated by an electric field. The $HeNe^+$ ions forming in the plasma have the highest binding energy of all heteronuclear ions: $D_e=0.77$ eV (Ref. 22). These ions are stable under thermal dissociation in collisions with thermal atoms and hence, all other things being equal, have the greatest effect, in comparison to other BR^+ ions, on the properties of the plasma.

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We have measured the dissociative-recombination rate constant and found its dependence on the electron temperature T_e in the T_e=300–1000 K range. In this range the rate constant can be represented by the following formula:

$$\alpha(T_e=300\ \mathrm{K})=(1.0\pm0.2)\times10^{-7}\ \mathrm{cm^3/s},$$

$$\alpha(T_e)\propto T_e^{-1.34\pm0.11}.$$

Also, we identify the process channels corresponding to the emergence of excited neon atoms emitting light in the visible and near UV spectral ranges.

2. ION COMPOSITION OF THE PLASMA

In all binary noble-gas mixtures the ion–molecular reactions that lead to formation of heteronuclear ions are similar, with the result that the scheme of the processes in the helium–neon plasma considered below generally reflects the kinetics of ion transformations in other mixtures. The main channel in which BR^+ (below B=He and R=Ne) emerge is conversion in triple collisions:

$$\mathrm{Ne^+ + He + He} \xrightarrow{k_3} \mathrm{HeNe^+ + He}, \tag{3}$$

$$\mathrm{Ne^+ + Ne + He} \xrightarrow{k_3'} \mathrm{HeNe^+ + Ne} \xrightarrow{k_3''} \mathrm{Ne_2^+ + He}, \tag{4}$$

where $k_3=2.1\times10^{-32}$ cm^6/s, and $k_3'+k_3''=3\times10^{-31}$ cm^6/s (Ref. 15). Processes that are the reverse of (3) and (4) can be ignored because the binding energies of $\mathrm{Ne_2^+}$ (1.3 eV) and $\mathrm{HeNe^+}$ (0.77 eV) are much higher than the thermal energies of particles.1) Two processes compete in the decomposition of $\mathrm{HeNe^+}$ ions: an exothermic reaction accompanied by the formation of a homonuclear ion,

$$\mathrm{HeNe^+ + Ne} \xrightarrow{k_4} \mathrm{Ne_2^+ + He}, \tag{5}$$

($k_4=3\times10^{-11}$cm^3/s) (Ref. 15), and dissociative recombination,

$$\mathrm{HeNe^+} + e \xrightarrow{\alpha,\alpha_i} \mathrm{Ne}_i^* + \mathrm{He} \tag{6}$$

(α is the recombination rate constant, and α_i is a partial coefficient characterizing the effectiveness of the reaction in the channel with formation of excited atoms in the state Ne_i^*).

A similar reaction involving a homonuclear ion accompanies (6):

$$\mathrm{Ne_2^+} + e \xrightarrow{\tilde{\alpha},\tilde{\alpha}_i} \mathrm{Ne}_i^* + \mathrm{Ne}, \tag{7}$$

($\tilde{\alpha}=1.7\times10^{-7}$ $(T_e/300\ \mathrm{K})^{-0.5}$ cm^3/s see Ref. 23).

The role played by the various reactions depends on the experimental conditions. However, because of effective decomposition of heteronuclear ions in (5), their observation is possible only when neon content is very low. In such conditions primary ionization is relative, irrespective of the way the plasma was formed, to the emergence of $\mathrm{He^+}$ ions, and all the other ions form in ion–molecular reactions, of which the following, in addition to (3) and (4), play the major role:

$$\mathrm{He^+ + He + He} \xrightarrow{k_1} \mathrm{He_2^+ + He}, \tag{8}$$

$$\mathrm{He_2^+ + Ne} \xrightarrow{k_2} \mathrm{Ne^+ + He + He}, \tag{9}$$

where $k_1=0.65\times10^{-31}$cm^6/s (Ref. 24) and $k_2=1.4\times10^{-10}$cm^3/s (Ref. 25). Thus, the picture of consecutive transformations of ions in a helium–neon plasma consists of the chain $\mathrm{He^+\rightarrow He_2^+\rightarrow Ne^+\rightarrow HeNe^+\rightarrow Ne_2^+}$, concluded by the formation of $\mathrm{Ne_2^+}$ ions.

In modeling the system of processes that form the ion composition of the plasma we allowed for ionization with participation of metastable atoms,

$$\mathrm{He}(2^3S)+\mathrm{He}(2^3S) \xrightarrow{\beta_{11}} \mathrm{He^+ + He} + e \rightarrow \mathrm{He_2^+} + e, \tag{10}$$

and metastable molecules,

$$\begin{aligned} \mathrm{He_2}(2s^3\Sigma_u^+)+\mathrm{He_2}(2s^3\Sigma_u^+) &\xrightarrow{\beta_{22}} \mathrm{He^+ + 3He} + e \\ &\xrightarrow{\beta_{22}} \mathrm{He_2^+ + 2He} + e \\ &\xrightarrow{\beta_{22}} \mathrm{He_3^+ + He} + e \\ &\xrightarrow{\beta_{22}} \mathrm{He_4^+} + e, \end{aligned} \tag{11}$$

$$\begin{aligned} \mathrm{He_2}(2s^3\Sigma_u^+)+\mathrm{He}(2^3S) &\xrightarrow{\beta_{12}} \mathrm{He^+ + 2He} + e \\ &\rightarrow \mathrm{He_2^+ + He} + e \\ &\rightarrow \mathrm{He_3^+} + e, \end{aligned} \tag{12}$$

which noticeably affect the balance of charged particles. The rate constants of the reactions (10)–(12) are known: $\beta_{11}=(1.5\pm0.3)\times10^{-9}$ cm^3/s, $\beta_{22}=(1.5\pm0.5)\times10^{-9}$ cm^3/s, and $\beta_{12}=(2.5\pm1.5)\times10^{-9}$ cm^3/s (Ref. 24).

Thus, as the above reasoning implies, in the system of reactions considered the only unknown quantity is the rate constant of dissociative recombination of heteronuclear ions, which can be found by processing the experimental data. To interpret the experimental results we set up a kinetic model of the processes in the plasma. This model included seven differential equations for the number densities of the $\mathrm{He^+}$, $\mathrm{He_2^+}$, $\mathrm{Ne^+}$, $\mathrm{Ne_2^+}$, and $\mathrm{HeNe^+}$ ions, of the metastable atoms $\mathrm{He}(2^3S)$, and of the $\mathrm{He_2}(2s^3\Sigma_u^+)$ molecules. One of the model parameters was the unknown rate α of dissociative recombination of $\mathrm{HeNe^+}$ ions and electrons. Its value was found by the maximum likelihood method, in which the results of measuring the temporal dependence of the intensities of spectral lines of the neon atom were compared to the results of numerical calculations of the recombination flux on the basis of the constructed model.

3. THE METHOD AND EXPERIMENTAL CONDITIONS

The set of the above ion–molecular reactions suggests the possibility of a number of recombination processes in the helium–neon plasma in which different ions participate. To set up an experiment for studying such a plasma requires resorting to methods that make it possible to separate the

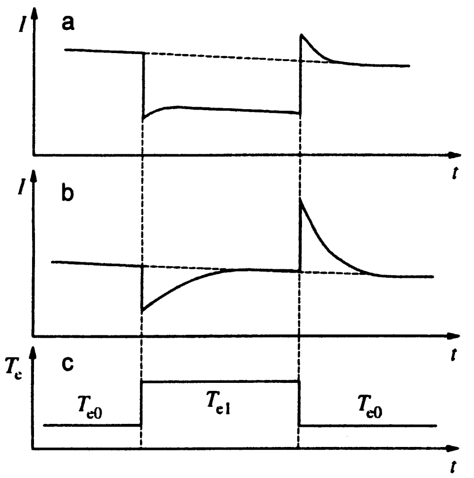

FIG. 1. Response of the intensities of the spectral lines to a perturbation of the electron temperature T_e when a nonrecombination process whose rate does not depend on T_e dominates the ion-concentration balance (a) and when a recombination process dominates the balance (b).

competing processes. The best approach is to use spectroscopic methods, which employ the fact that in each recombination act a neutral particle in an excited state is formed and hence the radiation emitted by the recombining plasma carries information about the effectiveness of the processes (their rate constants) and about the channel along which they proceed. In our research the spectroscopic study was combined with analyzing the relaxation processes that develop under a pulsed perturbation of the decaying plasma initiated by a weak longitudinal electric field.[2)] Our experiment was based on a method, suggested in Ref. 28 and developed in Ref. 29, in which a semi-self-maintained discharge was effected, with the strength and temporal dependence of the external longitudinal electric field $E(t)$ fixed by an external signal. Application of the electric field and the resulting increase in the electron temperature $T_e(E/N)$, where N is the number density of the atoms, lead to disruption of the quasistationary balance of the number of charged particles in the decaying plasma that is determined by the dependence of the rate constants of the recombination processes on the electron temperature $T_e(E/N)$. The variation of the recombination fluxes in turn clearly manifests itself in the intensities of the spectral lines emitted by the decaying plasma.

A characteristic response of the radiation of a decaying helium–neon plasma to pulsed electron heating is depicted in Fig. 1. In our experiment (helium pressure amounted to tens of torrs) the time of electron-energy relaxation caused by elastic collisions with helium atoms proved to be shorter than 10^{-6} s, which is smaller by a factor of ten than the characteristic times of variation of the charged-particle number density, so that on this time scale the variation of $T_e(E(t)/N)$ practically follows that of $E(t)$. In such a situation the drop in intensities of atomic and molecular lines at the fronts of variation of T_e is determined by the temperature dependencies of the respective partial recombination rates, and the relaxation processes caused by disruption of the quasistationary balance become obvious in the intensities of the spectral lines NeI (Fig. 1) and reflect the temporal variation of the number densities of the recombining ions at $T_e(E/N)$ within the electron-heating pulse and at $T_e(E=0)=300$ K after termination of the pulse. This suggests that the experiment conducted at different values of E/N makes it possible to determine both the temperature dependence of the partial recombination rates for the ions participating in the process and the absolute values and temperature dependencies of the total recombination rates of the same ions.

In our experiments the plasma was created by a weak-current ($i<100$ mA) pulsed periodic discharge in a helium–neon mixture that filled a cylindrical glass tube 2.8 mm in diameter. The pressure of the components of the mixture was as follows: $P(\mathrm{He})=40$ torr and $P(\mathrm{Ne})=(10^{-5}-10^{-2})$ $P(\mathrm{He})$. The rate of recombination of HeNe^+ ions and electrons was determined from the results of experiments in which a mixture with extremely low neon content ($[\mathrm{Ne}]\simeq 10^{-5}[\mathrm{He}]$) was used. Such neon content in the mixture is comparable to that in commercially available high-purity helium; consequently, the helium required additional decontamination from impurities. This was done by filtering the gas in an auxiliary discharge cell in which the separation of helium and neon was achieved through cataphoresis. In addition, atmospheric gases and other easily liquefiable components were adsorbed in a trap with activated carbon cooled to 77 K, through which the gas being studied passed. Application of these purifying methods made it possible to lower neon content by at least a factor of 100, so that $[\mathrm{Ne}]/[\mathrm{He}]$ amounted to less than 10^{-7}.

To keep the mixture from separating in the discharge tube because of cataphoresis in a longitudinal field, we uses low pulse repetition frequencies f (tens of hertz) and short (≈ 100 μs) lengths τ_p of the current pulse generating the plasma, with $f\tau_p<10^{-2}$.

The light fluxes emitted by the narrow near-axis region in the plasma were registered in the longitudinal direction (relative to the axis) by the multichannel photon-counting method using a monochromator with a linear dispersion of 20 Å mm and a FÉU-77 photomultiplier. The average electron number density $[e](t)$ was found from the plasma's conductivity by solving the equation for the current through the discharge tube:

$$i(t)=2\pi e b_e T_e(E/N)E\int_0^R [e](r,t)r\,dr, \tag{13}$$

where $b_e(E)$ is the electron mobility in helium.

Specifying the initial conditions for modeling the processes in a decaying plasma requires knowing the distribution of the electron number density along the tube's radius, $[e](r,t)$, in the final stage of the discharge pulse. This quantity was found by measuring the radial intensity profile $I(\lambda,r,t)$ of the bremsspectrum of electrons decelerated by helium atoms at a wavelength of $\lambda=5310$ Å. In a weak-current discharge, $[e](r,t)\propto I(\lambda,r,t)$ in the absence of noticeable temperature inhomogeneities. The radial profiles of the bremsspectrum continuum was registered by the standard procedure of scanning the image of the discharge tube in the plane of the entrance slit of the monochromator.

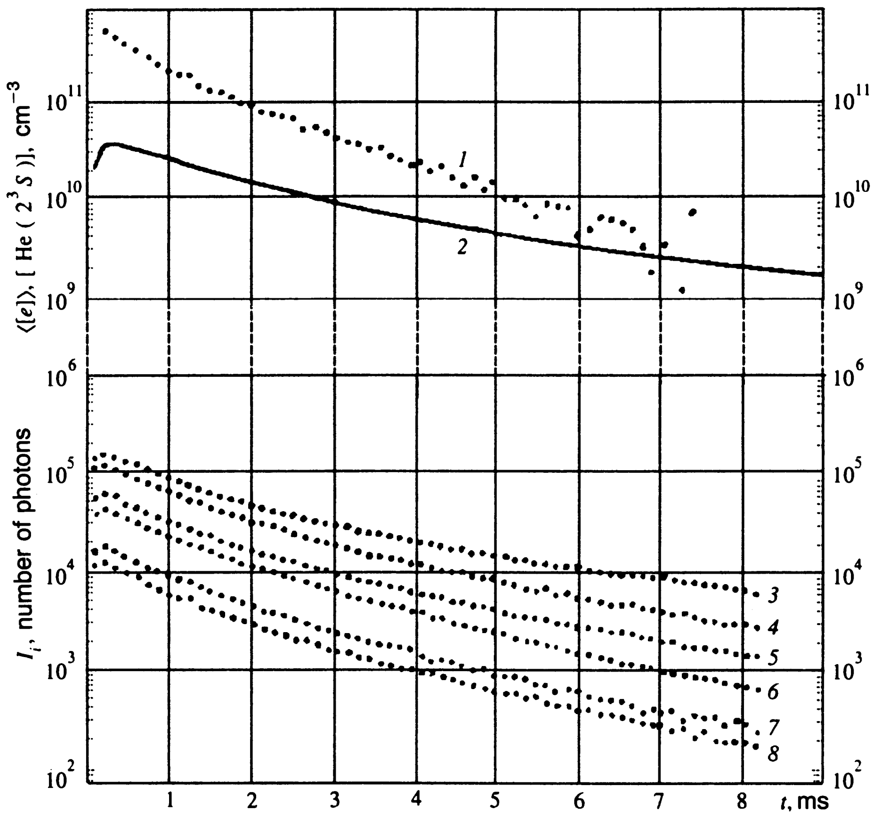

FIG. 2. The dependence on the time in afterglow of the concentration of the metastable atoms $[He(2^3S)]$ on the axis of the discharge tube (points *1*), the electron number density averaged over the cross-sectional area of the discharge tube $\langle[e]\rangle$ (curve *2*), and the intensities of the atomic spectral lines of neon: 5852 Å NeI (points *3*), 7245 Å (points *4*), 6383 Å (points *5*), 3520 Å (points *6*), 5341 Å NeI (points *7*), 5764 Å (points *8*), at $[Ne]/[He]\approx 10^{-5}$ and $P_{He}=40$ torr.

Determining the temporal dependence of the concentration of metastable helium atoms, $[He(2^3S)]$, required measuring the relative absorption on the 3889-Å HeI line. As for the absolute value of $[He(2^3S)]$, analysis of the results of measurements has shown that a more reliable way to find the absolute value of $[He(2^3S)]$ is to use the experimental data on the increase in the electron number density at the initial stage in plasma decay (Figs. 2 and 3), caused primarily by pair collisions of metastable atoms (10)–(12).

The number densities of the metastable molecules, which must be known in order to allow for the ionization processes (11) and (12), was calculated by solving the balance equation and employing the rate constants of the processes of their formation and decomposition.[24,30]

The temperature T_e of electrons3) was found from the energy balance equation with allowance for electron acceleration in the electric field and elastic atomic collisions.

4. THE RESULTS OF EXPERIMENTS

We start with the results of the experiment in studying the helium–neon plasma with low neon content, $[Ne]\approx 10^{-5}[He]$. Variations in the electron number density and the radiation emitted by the plasma in the discharge and afterglow stages are depicted in Figs. 2 and 3.

Analysis of the spectral composition of the emitted radiation revealed an extremely weak glow of NeI lines against the background of bright HeI lines (Fig. 4). This reflects the fact that excitation and hence ionization are due primarily to collisions of electrons and helium atoms.

In our conditions the characteristic time of conversion $He^+\rightarrow He_2^+$ (Eq. (8)) amounted to roughly 10^{-5}s, while the charge exchange between the He_2^+ ions and neon atoms lasts approximately 10^{-3}s, i.e., by the end of the discharge pulse ($\tau_p=100\ \mu s$) the He_2^+ ions dominate in the ion composition. The other ions, i.e., He^+ and ions that have emerged in the afterglow phase preceding the discharge, and the Ne^+, $HeNe^+$, and Ne_2^+ ions constitute only a small fraction in the ion composition of the plasma. The very weak glow initiated by the atomic transitions in neon in the early afterglow stage suggested that the relative concentrations $[Ne^+]/[e]$, $[HeNe^+]/[e]$, and $[Ne_2^+]/[e]$ are low (Fig. 3). Further variation in the spectral composition of the radiation emitted by the decaying plasma reflects the kinetics of the ion-molecular reactions (3), (5), (8), and (9) comprising the chain of transformations $He^+\rightarrow He_2^+\rightarrow Ne^+\rightarrow HeNe^+\rightarrow Ne_2^+$.

In addition to the recombination mechanism, excited neon atoms can appear in a decaying helium–neon plasma as a result of the following well-known excitation-transfer processes:[30–32]

$$He(2^1S)+Ne\xrightarrow{k_6'}Ne^*+He,\quad k_6'=6.46\times 10^{-11}cm^3/s \tag{14}$$

(see Ref. 32),

$$He(2^3S)+Ne\xrightarrow{k_6}Ne^*+He,\quad k_6=3.85\times 10^{-12}\ cm^3/s \tag{15}$$

(see Ref. 32), and

$$He(2s^3\Sigma_u^+)+Ne\xrightarrow{k_7}Ne^*+2He, \tag{16}$$

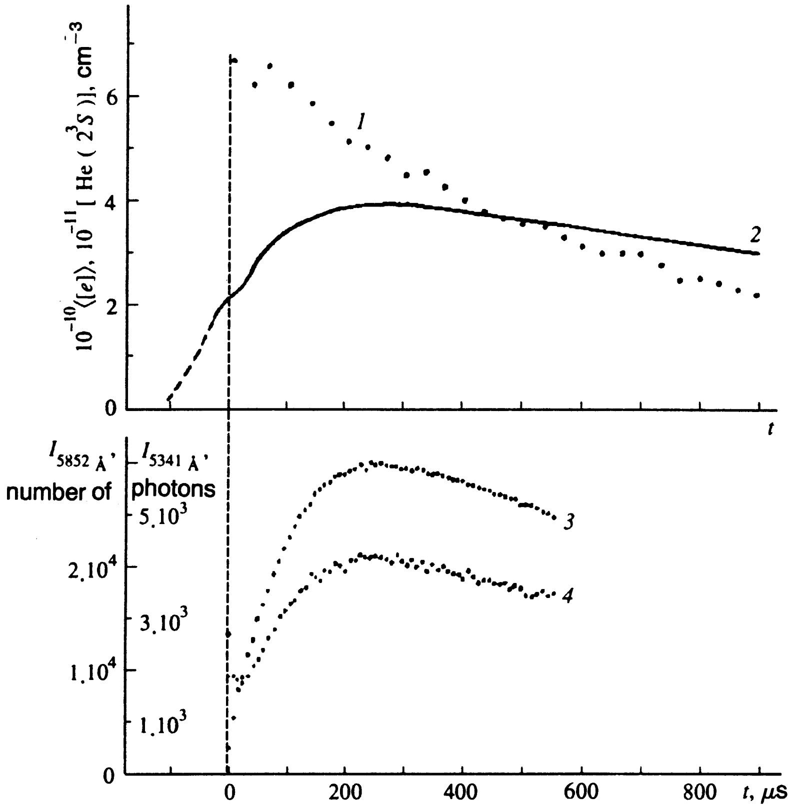

FIG. 3. The temporal dependencies of the concentrations $[\mathrm{He}(2^3S)]$ of the metastable atoms (points *1*), of the electron number density averaged over the cross-sectional area of the discharge tube $\langle[e]\rangle$ (curve *2*), and of the intensities of the 5852-Å NeI line (points *3*) and the 5341-Å NeI line (points *4*) in the initial afterglow phase, at $[\mathrm{Ne}]/[\mathrm{He}] \approx 10^{-5}$ and $P_{\mathrm{He}} = 40$ torr.

$$k_7 = 4.4 \times 10^{-11}\,\mathrm{cm}^3/\mathrm{s}$$

(see Ref. 30).

Hence using the glow of the decaying plasma to study the recombination process (6) requires reliable identification of the excitation source. Let us now discuss the experimental results depicted in Fig. 2 and 3.

The qualitative differences in the temporal dependencies of the intensities of the NeI lines and the relative absorption on the 3889-Å HeI (3^3P–2^3S) line determined by the concentration of the metastable atoms, $[\mathrm{He}(2^3S)]$, suggest that the process (15) cannot contribute considerably to the population of the excited atomic states of neon.

More than that, the results of an experiment that measured the response of line intensities on the pulsed perturbation of the electron temperature by an electric field (Fig. 5) exclude the other excitation-transfer processes, (14) and (16), in addition to excluding (15), from the main channels of population of the states $2p^53p$, $2p^54p$, and $2p^54d$. The truth is that the rate constants of these processes do not depend on the electron temperature, while the experiment clearly reveals a sudden decrease in the intensity of the NeI lines as the electrons are heated. Such behavior of the intensities of the spectral lines indicates recombinational population of the excited states and reflects the dependence of the recombination rate on T_e.

Following the jumps in intensities (Figs. 1 and 5) there is a transient process in which $I(t)$ relaxes to a new quasistationary value at a constant electron temperature $T_e = T_{e1}$ within the heating pulse or at another electron temperature $T_e = T_{e0}$ after termination of the pulse. Such relaxation processes were observed by a number of researchers,[33,34] who studied electron–ion recombination in a noble-gas mixture plasma. They reflect the variation in the ion number density caused by the decrease in the recombination rate constant. This makes it possible to find the values and temperature dependencies of the recombination rate constants by analyzing the relaxation processes.

Notice that the characteristic response of the intensity of the molecular band of He_2^* to electron heating, whose manifestation is related to the recombination of He_2^+ ions and electrons:

$$\mathrm{He}_2^+ + e + e(\mathrm{He}) \rightarrow \mathrm{He}_2^* + e(\mathrm{He}). \tag{17}$$

In the given case the dependence of the intensity on time is close to rectangular. This behavior of the recombination flux occurs if the recombination rate is low compared to the rate of other processes of ion decomposition.

The Ne^+-ion recombination flux must behave in a similar manner:

$$\mathrm{Ne}^+ + e \xrightarrow{\alpha_{\mathrm{Ne}^+}} \mathrm{Ne}^* + e, \tag{18}$$

where α_{Ne^+} is the rate constant for an electron temperature $T_e > 300$ K and an electron number density $[e] < 10^{11}\,\mathrm{cm}^{-3}$ and does not exceed $10^{-9}\,\mathrm{cm}^3/\mathrm{s}$ (Ref. 35).

Hence the process (18) cannot ensure that the response of the intensity to a pulse heating of the electron gas is of the type depicted in Fig. 5, since the ion number density $[\mathrm{Ne}^+]$ is controlled by the conversion reaction (3), with a

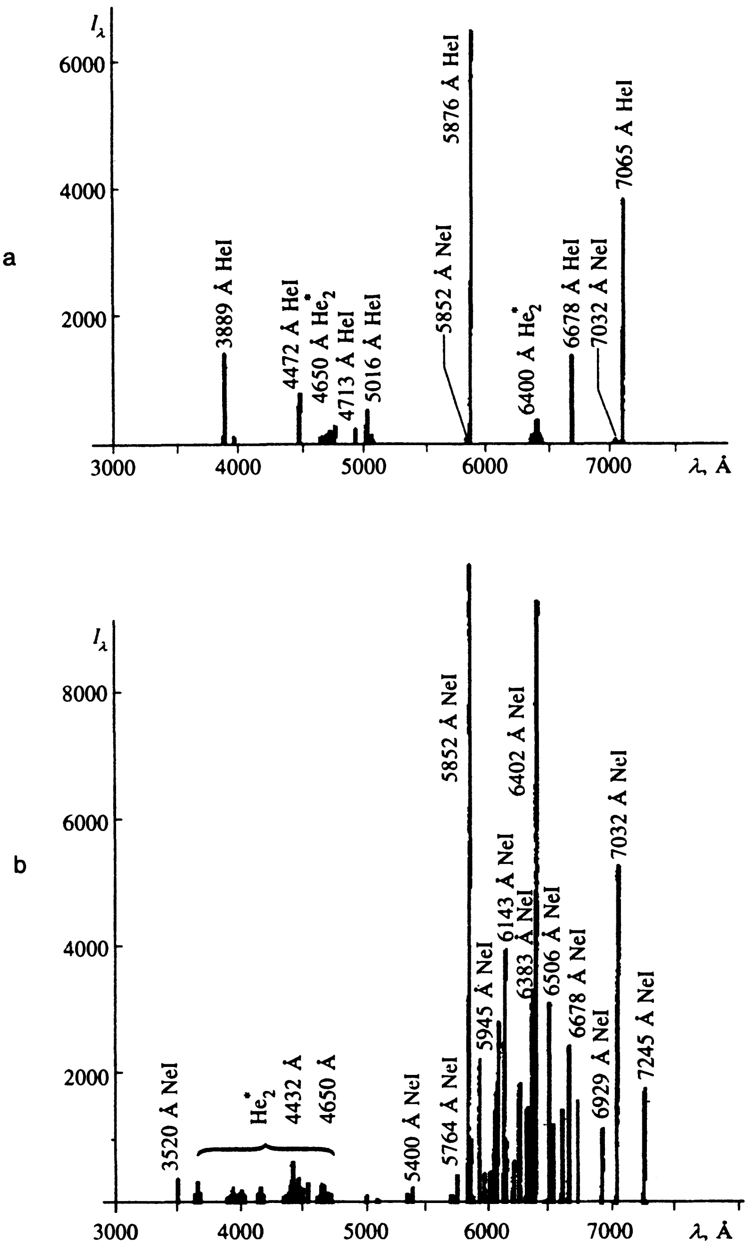

FIG. 4. The emission spectra of the helium–neon plasma: (a) discharge phase, and (b) afterglow phase ($[\mathrm{Ne}]/[\mathrm{He}] \approx 10^{-5}$ and $P_{\mathrm{He}} = 40$ torr).

rate much higher than that of the recombination (18) and, obviously, independent of the electron temperature.

Thus, the appearance of excited neon atoms in the decaying plasma in these conditions can be related only to the mechanism of dissociative recombination (6) and (7). We examine the possible ways of separating these processes. First, because the difference in the binding energies of the Ne_2^+ and $HeNe^+$ ions is so great (Fig. 6), the reactions (6) and (7) can be assumed to have different sets of outgoing channels. As the practice of studying dissociative recombination shows,[6] in a weakly ionized plasma the process leads to the population, with a varying probability, of every energy level of noble-gas atoms that lies below, or is in resonance with, the ground vibrational level of the respective molecular ions.[4)] For instance, in the case of neon, the population of lower levels of the $2p^54p$ configuration and the $2p^53d$ and $2p^53p$ levels is related to the dissociative recombination of Ne_2^+ ions.[6] Hence in the presence of $HeNe^+$ in the plasma, the upper levels of the $2p^54p$ group and the $2p^54d$ levels can be expected to become populated in addition to the levels just mentioned, and the population of these "new" levels correlates with $[HeNe^+]$. (Fig. 6)

Indeed, in the initial afterglow phase, the emission spectrum of the plasma contains transitions from all of the atomic states of neon just mentioned. Here, as Fig. 2 shows, the intensities of the lines emitted in the transitions from all the states behave in a similar manner, and so does the response of the intensities of the $3p$–$3s$, $4p$–$3s$, and $4d$–$3p$ lines to pulsed heating of the electron gas (Fig. 5). Beyond several milliseconds we observed an extremely rapid drop in the intensities of the lines emitted in the transitions from the states $2p^54d$ and $2p^54p$ of neon atoms. Here, as Fig. 5 shows, the temporal dependence of the intensities of these

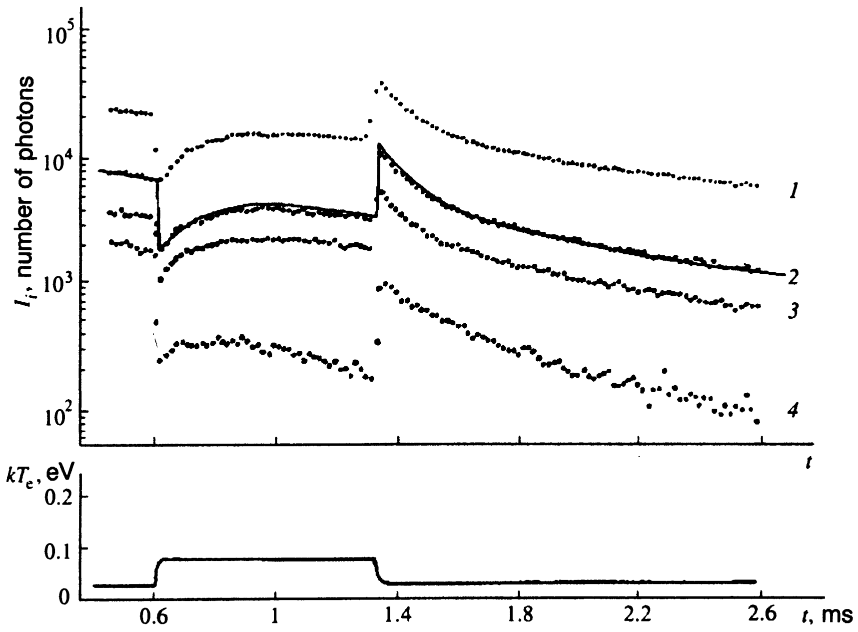

FIG. 5. The response of the intensities of the following spectral lines to an electron-temperature perturbation at $[Ne]/[He] \approx 10^{-5}$ and $P_{He}=40$ torr: (1) 5852 Å NeI, (2) 5764 Å NeI, (3) 3520 Å NeI, and (4) 4432 Å He_2^*.

lines is well-described on the basis of the kinetic model by the recombination flux of $HeNe^+$ ions:

$$\Gamma_{HeNe^+}(t) \propto [e][HeNe^+].$$

Hence one process, the dissociative recombination (6), can be assumed to be the source of population of all the atomic states of neon considered here, ($2p^5 3p$, $2p^5 4p$, and $2p^4 d$), in the initial afterglow phase.

Now let us turn to the results of the analysis of experiments in pulsed heating of electrons. Figure 7 depicts the temperature dependencies of the recombination fluxes to different atomic levels of neon obtained by analyzing the jumps in the intensities of the respective lines and the fronts of the heating pulse in early afterglow. Clearly, these dependencies, differing somewhat for different lines, can be described fairly well by the following function:

$$\alpha_i(T_e = \alpha_{0i} T_e^{-\gamma_i}), \quad \gamma_i = 1.2 \pm 0.1.$$

Note that in view of the multichannel nature of dissociative recombination, the temperature dependencies of the partial rate constants $\alpha_i(T_e)$ may differ considerably both from each other and from the temperature dependence of the rate constant of molecular-ion recombination: $\alpha = \Sigma_i \alpha_i$. The quantities $\alpha_i(T_e)$ are determined by the nature in which the molecular-ion state crosses the states of the atoms interacting in the outgoing channel. In a weakly ionized plasma, where there is no electron "mixing" of excited levels, the functions $\alpha_i(T_e)$ may differ even for the levels of one configuration. For instance, the fluxes of dissociative recombination of Ar_2^+ ions to the $3p^5 4p$ levels of the argon atom follow the temperature dependence $\alpha_i \propto T_e^{-0.5}$ for the main group of levels and $\alpha_i \propto T_e^{-1.5}$ for the lower level of the given configuration.[36] Significant differences in the functions $\alpha_i(T_e)$ were also discovered in xenon-plasma studies.[37,38]

The temperature dependencies of the partial rate constants of the recombination of Ne_2^+ and electrons have been measured by a number of researchers.[39–41] According to their data, $\tilde{\alpha}_{3d} \propto T_e^{-0.3}$ and $\tilde{\alpha}_{3p} \propto T_e^{-0.5}$. For the $2p^5 4d$ levels, which are 0.5-eV above the bottom of the potential well of the Ne_2^+ ion, an increase in $\tilde{\alpha}_{4d}$ with T_e was discovered.[41] Such a dependence reflects the threshold nature of the process, with the participation of ions in the highest populated states of $Ne_2^+(v=0)$, where v is the vibrational quantum number. Thus, the $\alpha_i \propto T_e^{-1.2 \pm 0.1}$ dependence obtained in this paper for the partial rate constants is additional proof that the process (6) is predominant over the process (7) in the formation of the radiation emitted by the decaying plasma.

To measure the recombination rate constant $\alpha(T_e)$ we analyzed relaxation processes of the type depicted in Fig. 5. We used the data on the temporal dependence of the intensities of two ($2p^5 4d \rightarrow 2p^5 3p$) lines: 5764 Å NeI and 5341 Å Ne I. The curves obtained in the experiment were compared with the results of numerical solution of the system of equations describing the balance of the number of particles in the helium–neon plasma (Fig. 8):

1. He^+ ions:

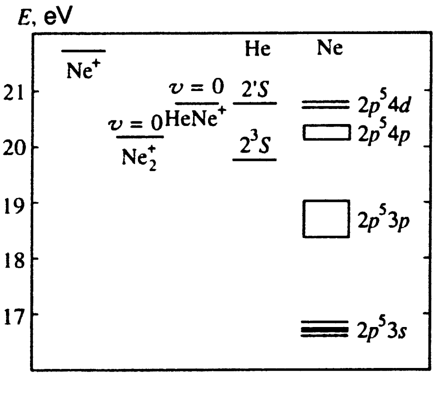

FIG. 6. The energies of the ground states of the Ne^+, Ne_2^+, and $HeNe^+$ ions and the excited states of helium and neon atoms.

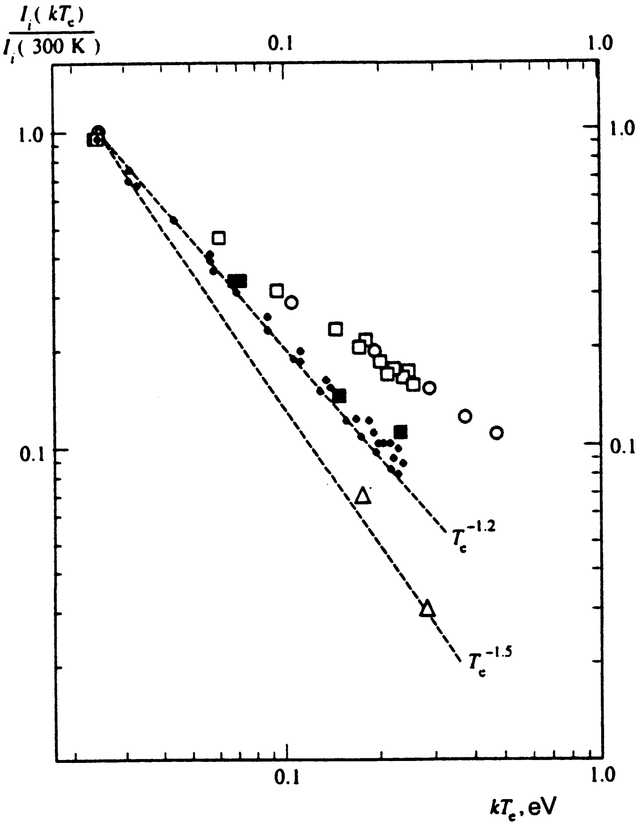

FIG. 7. The intensities of lines in afterglow vs the electron temperature in the recombinational population of excited states. (1) the △ correspond to 4432 Å He_2^*, the ■ to 5764 Å NeI, and the ● to 5852 Å NeI at $[\mathrm{Ne}]/[\mathrm{He}]=10^{-5}$; (2) the ○ correspond to 5852 Å NeI at $\langle[e]\rangle=0.4\times10^{10}\mathrm{cm}^{-3}$ and $[\mathrm{Ne}]/[\mathrm{He}]=10^{-2}$, and the □ correspond to 5852 Å NeI at $\langle[e]\rangle=2.2\times10^{10}\mathrm{cm}^{-3}$ and $[\mathrm{Ne}]/[\mathrm{He}]=10^{-2}$.

$$\frac{d[\mathrm{He}^+]}{dt}=-\eta P^2[\mathrm{He}^+]-\frac{[\mathrm{He}^+]}{\tau_{a1}}+\tfrac{1}{2}(\beta_{11}[\mathrm{He^m}]^2+\beta_{12}[\mathrm{He^m}][\mathrm{He_2^m}]+\beta_{22}[\mathrm{He_2^m}]^2), \qquad (19)$$

where ηP^2 is the rate of the conversion process (8), $\eta=67\mathrm{s}^{-1}\mathrm{torr}^{-2}$ (Ref. 24), τ_{ai} (here and in what follows) is the ambipolar diffusion time, and β_{11}, β_{12}, and β_{22} are the rate constants of the processes (10)–(12). The reciprocal ambipolar-diffusion time is related to the coefficient of ambipolar diffusion of ions by the well-known formula

$$\frac{1}{\tau_{\mathrm{ai}}}=\left(\frac{2.405}{R}\right)^2 D_{\mathrm{ai}},$$

and the ambipolar diffusion coefficient can be calculated if the ion mobility is known:

$$D_{\mathrm{ai}}=\frac{b_i(kT_{\mathrm{e}}+kT_{\mathrm{i}})}{e},$$

with

$$b_i=K_{0i}\frac{760T_{\mathrm{g}}}{273.16P}$$

(Ref. 42), where

$$K_{01}=(10.40\pm0.10)\mathrm{cm}^2/\mathrm{V}^{-1}\cdot\mathrm{s}$$

(here and in what follows) is the reduced ion mobility (in our case in helium).

2. He_2^+ ions:

$$\frac{d[\mathrm{He}_2^+]}{dt}=\eta P^2[\mathrm{He}^+]-\frac{[\mathrm{He}_2^+]}{\tau_{a2}}-k_2[\mathrm{He}_2^+][\mathrm{Ne}]-(\alpha_{\mathrm{e}2}[e]+\alpha_{\mathrm{a}2}[\mathrm{He}])[\mathrm{He}_2^+][e], \qquad (20)$$

with $\alpha_{\mathrm{e}2}[e]+\alpha_{\mathrm{a}2}[\mathrm{He}]$ the rate constant of the recombination process (17),

$$\alpha_{\mathrm{e}2}=(4.0\pm0.5)\cdot10^{-20}(T_{\mathrm{e}}/293\ \mathrm{K})^{-4.0\pm0.5}\ \mathrm{cm}^6/\mathrm{s},$$

$$\alpha_{\mathrm{a}2}=(5\pm1)\cdot10^{-27}(T_{\mathrm{e}}/293\ \mathrm{K})^{-1\pm1}\ \mathrm{cm}^6/\mathrm{s}\ \text{(Ref. 24)},$$

$$K_{02}=(16.70\pm0.17)\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}\ \text{(Ref. 42)}.$$

3. Ne^+ ions:

$$\frac{d[\mathrm{Ne}^+]}{dt}=k_2[\mathrm{He}_2^+][\mathrm{Ne}]-k_3[\mathrm{Ne}^+][\mathrm{He}]-\frac{[\mathrm{Ne}+]}{\tau_{a3}}, \qquad (21)$$

with $K_{03}=(24\pm3)\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ (Ref. 42).

4. HeNe^+ ions:

$$\frac{d[\mathrm{HeNe}^+]}{dt}=k_3[\mathrm{Ne}^+][\mathrm{He}]-\frac{[\mathrm{HeNe}^+]}{\tau_{a4}}-\alpha[\mathrm{HeNe}^+][e]-k_4[\mathrm{HeNe}][\mathrm{Ne}], \qquad (22)$$

with $K_{04}=(20\pm2)\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ (Ref. 42).

5. Ne_2^+ ions:

$$\frac{d[\mathrm{Ne}_2^+]}{dt}=k_5[\mathrm{HeNe}^+][e]-\tilde{\alpha}[\mathrm{Ne}_2^+][e]-\frac{[\mathrm{Ne}_2^+]}{\tau_{a5}}, \qquad (23)$$

with $K_{05}=17.5\ \mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ (Ref. 42).

6. Metastable $\mathrm{He}(2^3S)$ atoms, $[\mathrm{He}(2^3S)]=[\mathrm{He}^m]$:

$$\frac{\partial[\mathrm{He^m}]}{\partial t}=-(\beta_{11}[\mathrm{He^m}]^2-\tfrac{1}{2}\beta_{12}[\mathrm{He^m}][\mathrm{He_2^m}])-\delta P^2[\mathrm{He^m}]-\gamma_1[e][\mathrm{He^m}]+\frac{D_{m1}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial[\mathrm{He}^m]}{\partial r}\right)-k_6[\mathrm{He^m}][\mathrm{Ne}]+\chi_1(\alpha_{\mathrm{e}2}[e]+\alpha_{\mathrm{a}2}[\mathrm{He}])[\mathrm{He}_2^+][e], \qquad (24)$$

with χ_1 the branching factor of the recombination flux, $\chi_1=1$ for $P>40$ torr (Ref. 24), the conversion rate of the metastable atoms in the process

$$\mathrm{He}(2^3S)+\mathrm{He}+\mathrm{He}\rightarrow\mathrm{He}_2(2s^3\Sigma_u^+)+\mathrm{He},$$

$\delta=0.2\mathrm{s}^{-1}\ \mathrm{torr}^{-2}$, $\gamma_1=4.2\times10^{-9}\ \mathrm{cm}^3/\mathrm{s}$ the rate of collisions of the second kind of $\mathrm{He}(2^3S)$ atoms with electrons (Ref. 24), and $D_{m1}P=420\ \mathrm{cm}^2\cdot\mathrm{torr/s}$ the coefficient of diffusion of the metastable atoms.

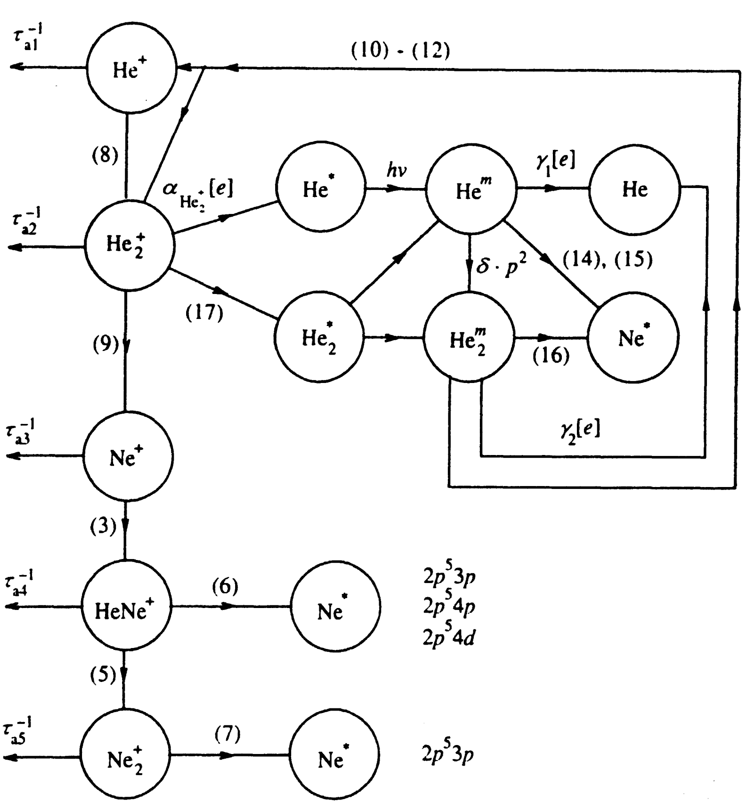

FIG. 8. The diagram of particle transformations in the afterglow plasma produced by a discharge in a helium–neon mixture.

7. Metastable $He_2(2s^3\Sigma_u^+)$ molecules, $[He_2(2s^3\Sigma_u^+)] = [He_2^m]$:

$$\frac{\partial[He_2^m]}{\partial t} = \delta P^2[He^m] + \frac{D_{m2}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial[He_2^m]}{\partial r}\right)$$
$$-[He_2^m](\gamma_2[e]+k_7[Ne])$$
$$-\tfrac{1}{2}\beta_{12}[He^m][He_2^m]-\beta_{22}[He_2^m]^2$$
$$+\chi_2(\alpha_{e2}[e]+\alpha_{a2}[He])[He_2^+][e], \qquad (25)$$

with $D_{m2}P = 380$ cm² torr/s (Ref. 24), $\chi_2 = 0$ for $P \gtrsim 40$ mmHg (Ref. 24), and $k_7 = 4.4 \times 10^{-11} cm^3/s$ the rate of collisions of the second kind of $He_2(2s^3\Sigma_u^+)$ molecules with electrons.

Measurements of the relative absorption A on the 6143 Å NeI $(2p^5 3s[3/2]^0 - 2p^5 3p[3/2]2-2)$ line have shown that in our conditions A does not exceed 0.02, i.e., the concentration of metastable neon atoms, $[Ne^m]$, is lower than $10^9 cm^{-3}$. Because this value is small, we ignored processes with neon metastable atoms in the balance of the number of charged particles.

In Fig. 5 the results of our model calculations are depicted by a solid curve. The maximum likelihood method was used to find the values of the rate constant of the dissociative recombination of $HeNe^+$ ions and electrons, $\alpha(T_e)$. The dependence of α on the electron temperature can be represented by the following formula:

$$\alpha(T_e) = (1.0 \pm 0.2) \cdot 10^{-7}\ (T_e/300\ K)^{-1.34 \pm 0.11}\ cm^3/s.$$

Note the closeness of the values of the partial rate constant α_i $(\gamma_i \approx 1.2)$, and the recombination rate constant $\alpha(T_e)$ $(\gamma = -1.34 \pm 0.11)$ obtained from independent measurements of the temperature dependencies and also their difference from the dependence characteristic of the Ne_2^+ ion: $\tilde{\alpha}_{Ne_2^+} \sim T_e^{-0.5}$.

We did additional verifying experiments with the aim of observing the response of the line intensities to an electron-temperature perturbation at a considerably higher neon content in helium: $[Ne]/[He] \approx 10^{-2}$. The results of measurements with the 5852 Å NeI $(2p^5 3p \rightarrow 2p^5 3s)$ line are shown in Fig. 7. As expected, the temperature dependence of the partial rate constant proved to be weaker than when $[Ne]/[He] = 10^{-5}$, a fact reflected in the variation of the ion content in the direction of a larger fraction of the Ne_2^+ ions due to the reaction (5).

The found value of the rate constant of the dissociative recombination of $HeNe^+$ ions and electrons exceeds severalfold the value $\alpha = 2 \times 10^{-8} cm^3/s$ at $T_e = 300K$ obtained through experiments in measuring the rate of decreases in the charged-particle number density.[43] In this connection we note that in the conditions specified in Ref. 43 $(P_{He} + P_{Ne} = 18$ torr and $[He]/[Ne] = 0.06\%)$ the ion number density $[HeNe^+]$ can be so low owing to the reaction (5) that the ions have hardly any chance of manifesting themselves in the kinetics of the charged and excited particles.

Thus, in this paper we have, for the first time in the practice of studying noble-gas mixture plasmas, discovered the participation of heteronuclear molecular ions in the formation of the recombination flux of the population of excited atomic levels. We have also shown that there are conditions in which this mechanism of excited-atom formation is predominant. Several channels of the dissociative recombination of HeNe$^+$ ions and electrons have been identified, and the value and temperature dependence of the recombination rate constant $\alpha_{\mathrm{HeNe}^+}(T_e)$ have been obtained.

[1] The volume–temperature equilibrium is assumed to set in quickly at least for vibrational states in collisions of molecular ions with atoms whose temperature T_g is 300 K.

[2] The first to perform such an experiment were Goldstein, Anderson, and Clark,[26,27] who used microwave heating of the electrons from the decaying plasma.

[3] By the electron temperature we mean the quantity $2w/3k$, where w is the average electron energy, and k is the Boltzmann constant.

[4] This, for one thing, reflects of the fact that asically several lower vibrational levels of molecular ions are populated in the plasma.

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Translated by Eugene Yankovsky