Dissociative recombination of molecular ions in noble-gas plasmas

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This review treats the process of dissociative recombination of molecular ions with electrons and its role in shaping the properties of a weakly-ionized plasma of the inert gases and mixtures of them. Data are presented on the rate constants of the process and the efficiency of recombination with formation of excited atoms in various states. We discuss experimental methods that enable study of recombination processes over a wide range of variation of the electron temperature. We analyze the competition of dissociative recombination with alternative mechanisms of formation of excited atoms in recombinatively nonequilibrium plasmas, the manifestation of heteronuclear ions in the kinetics of excited and charged particles, and the mechanisms of relaxation of the energy of vibrational motion in collisions of molecular ions with atoms and dissociation in collisions with electrons. The results are discussed of experiments to study the role of inelastic atom-atom collisions in the formation of the emission spectrum of the plasma with molecular ions.

1. INTRODUCTION

Recent years have marked a considerable growth in the number of publications on the study of processes in noble-gas plasmas at moderate and high pressures (hundreds and thousands of Torr). This involves the successful application of such a plasma in such fields as the conversion of electric and nuclear energy into light energy, the search for new active media, and the invention of new, promising recombinative-type lasers based on transitions in noble-gas atoms. The properties of such a plasma arise to a considerable extent from processes involving molecular ions. The capture cross section of an electron by a molecular ion at thermal particle energies can exceed 10^{-13} cm^2. Therefore their appearance in a plasma, even in a relatively small amount, sharply increases the rate of bulk neutralization of charged particles, is the reason for the nonthermal contraction (pinch) of discharges, and leads to sharply marked selective population of excited atoms in the decaying plasma.

The extensive experimental material accumulated over a more than thirty-year history of study of molecular ions is reflected in rather full volume in a number of reviews and monographs.[1–4] However, the development of new fields, and primarily, the invention of promising lasers based on noble-gas mixtures, has brought to light new problems and advanced to front rank such problems as the study of the efficiency of recombination of molecular ions with electrons to yield specific excited states, the analysis of the competition of various mechanisms of recombination in creating the optical properties of the plasma, the study of processes involving heteronuclear molecular ions, and the development of experimental methods of studying a multicomponent recombinatively nonequilibrium plasma.

The processes that occur in a noble-gas plasma take a special place in the study of the phenomena under discussion. Owing to the accessibility of these gases, experimental studies of relaxation of noble-gas plasmas have been conducted for several decades. Much experience has been accumulated in this field, in particular, indicating that the relaxation processes in a noble-gas plasma prove to be no less complex than in a plasma of molecular gases. This arises from the existence in a noble-gas plasma of molecular ions having a high excitation energy of the noble-gas atoms, comparable with their ionization potentials, and the closeness of the excitation energy of the different states of the atoms. This review is devoted to studying these processes.

2. RATE CONSTANTS OF DISSOCIATIVE RECOMBINATION AND METHODS OF STUDYING THE PROCESS

Dissociative recombination of a molecular ion and an electron occurs by capture of the electron by a repulsive term of the quasimolecule, and separation of the nuclei, which leads to appearance of excited atoms in various states:

$$R_2^+(v) + e \underset{\alpha_\Sigma}{\overset{\alpha_{vi}}{\rightarrow}} (R_2^*) \rightarrow R_i^* + R. \tag{1}$$

This is a multichannel process. Therefore we shall describe it with the set of constants α_{vi} corresponding to formation of atoms in the state i upon recombination of ions existing in the vibrational state v. The relationship of the coefficient α_{vi} with the coefficient of dissociative recombination α_Σ usually measured in experiments to study the rate of decline of the density of molecular ions is rather obvious:

$$\alpha_\Sigma = \sum_v \sum_i g_v \alpha_{vi} = \sum_v g_v \alpha_v = \sum_i \alpha_i; \tag{2}$$

Here $g_v = [R_2^+(v)]/\Sigma_v [R_2^+(v)]$ are the relative populations of the vibrational levels of the molecular ion, $\alpha_v = \Sigma_i \alpha_{vi}$ is the recombination coefficient of an ion in the state v with allowance for all possible exit channels, and $\alpha_i = \Sigma_v g_v \alpha_{vi}$ are the so-called partial recombination coefficients, which indicate the fraction of the recombination flux through the ith channel.

Among the set of quantities α_Σ, α_i, α_v, and α_{vi}, only the last two amount to rate constants of an elementary process, whereas the coefficients α_Σ and α_i usually measured experimentally depend on the character of the population distribution over the vibrational levels of the molecular ion, and thus, depend to some degree on the particular experimental conditions.

The theoretical description of dissociative recombination includes approaches of varying degrees of complexity:

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from the model of a single autoionization state R_2^* in which electron capture is possible,[2] to the multichannel quantum-defect approximation,[5,6] and *ab initio* calculations. The latter have been performed as yet only for a limited set of very simple ions of the type of H_2^+, H_3^+, and He_2^+.[7-9] Therefore, despite a certain success in the development of numerical methods, the gaining of new information on the mechanism of recombination of molecular ions has mainly involved experimental studies. At the same time, to analyze the results of these studies, in a number of cases one can use the simple approximation of a single autoionization states;[2] within this framework the capture cross section for the electron is described by the Breit–Wigner formula

$$\sigma_{vi}(\varepsilon, r) = \frac{\pi\hbar^2}{2m\varepsilon}\frac{\Gamma_i^2}{(\varepsilon - \varepsilon_{vi}(r))^2 + (\Gamma_i^2/4)}; \quad (3)$$

Here ε is the energy of the electron, r is the distance between the nuclei of the molecular ion, $\varepsilon_{vi}(r)$ is the energy difference between the autoionization state $R_2^*(R_i^* + R)$ and the molecular ion R_2^* in the vibrational state v (Fig. 1), and $\Gamma_i(r)$ is the width of the autoionization level.

Taking into account the distribution of the molecular ions over the internuclear distance, we find the following expression for the cross section of dissociative recombination:

$$\sigma_{vi}^{d} = \int \sigma_{vi}(\varepsilon, r)|\psi_v|^2 - \exp(-S_i)dr; \quad (4)$$

Here e^{-S_i} is the so-called "survival factor," which takes account of the probability of autoionization in the motion of the nuclei from the capture point r_c to the crossing with the boundary of the continuous spectrum r_a; $\psi_v(r)$ is the nuclear wave function.

For a Maxwellian energy distribution function of the electrons and in the case $\varepsilon_{vi} \gg \Gamma_i$, the equation (4) for the recombination coefficient α_{vi} implies that[2]

$$\alpha_{vi} = 4\pi\int f(v)v^3\sigma_{vi}^{d}dv = \frac{2\sqrt{2\pi}\hbar^2}{(mkT_e)^{3/2}}\left\langle\Gamma_i\exp\left(-\frac{\varepsilon_{vi}}{kT_e} - S_i\right)\right\rangle. \quad (5)$$

The angle brackets denote averaging over the internuclear distance distribution in the molecular ion.

By summation of (5) over the vibrational states of the molecular ion we find the partial recombination coefficient

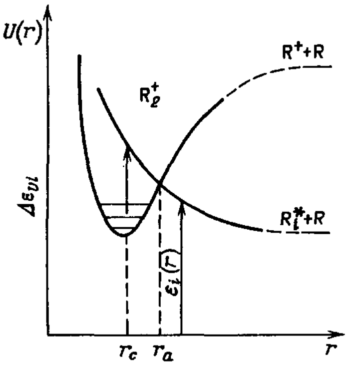

FIG. 1. Illustration of the mechanism of dissociative recombination of molecular ions and electrons.

TABLE I. Dissociative-recombination coefficients of the molecular ions of the noble gases (in units of 10^{-7} cm^3/s at $T_e = 300$ K. k is the approximation parameter of $\alpha_\Sigma(T_e) = \alpha_\Sigma(300\ \mathrm{K})(T_e/300)^{-k}$.

Ion	α_Σ	k	References
He	5.10^{-3}	1 ± 1	[10]
Ne	1,7	0,43	[11]
Ar	8,5	0,67	[12]
Kr	16	0,55	[13]
Xe	23	0,3 — 0,71	[14]

$\alpha_i = \Sigma_v g_v \alpha_{vi}$ and the corresponding recombination flux via the ith exit channel

$$F_i = \alpha_i n_e[R_2^+] = n_e[R_2^+]\sum_v g_v \frac{2\sqrt{2\pi}\hbar^2}{(mkT_e)^{3/2}}\left\langle\Gamma_i\exp\left(-\frac{\varepsilon_{vi}}{kT_e} - S_i\right)\right\rangle. \quad (6)$$

We shall use Eq. (6) below for interpreting the results of spectroscopic experiments to study the temperature dependences of the recombination fluxes into the various excited levels of the noble-gas atoms.

As Eqs. (2) and (5) imply, the function $\alpha_\Sigma(T_e)$ can differ, depending on the conditions under which the process occurs. Experimental practice shows that the lower vibrational levels of the molecular ions are the most populated in situations of practical interest. In this case the channels of the process are optimal that correspond to the terms $\varepsilon_i(r)$ that cross the ground electronic term of the molecular ion near the bottom of its potential well. For them the quantities ε_{vi} are small, and therefore slow electrons can be captured, while the latter mainly determine the efficiency of the process. This happens if the system $R^* + R$ has a high density of terms near the bottom of the potential well of R_2^+. The results of experimental studies show that here one realizes on $\alpha_\Sigma(T_e)$ relationship close to the law $\alpha_\Sigma \sim T_e^{-1/2}$. The values and temperature dependences of the dissociative-recombination coefficients of the molecular ions of the noble gases taken from the most often cited works[10-14] are given in Table I. We see that, except for He_2^+, the coefficients α_Σ exceed 10^{-7} cm^3/s. The peculiarity of the recombination of He_2^+ ions involves the fact that the repulsive terms of $He^* + He$ intersect the potential curve of He_2^+ in the region of vibrational levels $v > 3$. The recombination of He_2^+ ions has been studied in detail theoretically in Refs. 15–17, while Ref. 18 contains an analysis of the experimental studies. Hence we shall not touch on these problems in this review.

We can classify the experimental methods of studying the recombination of molecular ions into several groups, depending on which of the quantities in (2) that one is measuring. Effective methods have been developed in recent decades, including direct measurement of the cross sections of dissociative recombination using ions traps[19] and aligned and crossed beams.[20-24] Extensive experimental material has been obtained by using them, including a large set of ions of molecular gases. However, the difficulties of creating sufficiently intense beams of the molecular ions of the noble gases have not yet been overcome, while the fundamental source of information on them, as before, remains plasma experimentation.

The first study of recombination of molecular ions was undertaken in Ref. 25 by using UHF technique for probing decaying plasmas. In subsequent years these methods have become widespread, both in plasma diagnostics and for microwave "heating" of the electrons of a decaying plasma with a weak high-frequency field[26,27] to measure the recombination coefficients $\alpha_\Sigma(T_e)$. In these experiments the quantities α_Σ are found by analyzing the rate of decay of the electron density

$$\frac{dn_e}{dt} = -\alpha_\Sigma n_e [R_2^+] \tag{7}$$

taking account of the diffusion corrections. Under the very simple conditions commonly used, the densities $[R_2^+]$ and n_e are similar. Hence we have

$$n_e(t) = n_e(0)/(1 + \alpha_\Sigma n_e(0)t). \tag{8}$$

By using different variants of this method, a very large amount of data has been obtained on the recombination coefficients $\alpha_\Sigma(T_e)$ of the ions of atomic and molecular gases. Detailed information on them is found in Ref. 2.

One of the main questions of the kinetics of excited particles of a plasma containing molecular ions is that of the channels of recombination and the distribution of the flux of dissociative recombination among these channels. The only methods of study in this case are the spectroscopic methods. It was found even in the first experiments that dissociative recombination, in contrast to the other mechanisms of electron-ion recombination, has a sharply marked selective character[28] and leads to population of a restricted set of excited states of the noble-gas atoms. This property of the process has stimulated studies designed to seek possibilities of creating an inverted population in the decaying plasma,[29] which successfully completed the development of recombination lasers based on transitions in atoms of the noble gases.[30–32]

The problem of studying the exit channels of recombination can be considered in two aspects. The first involves revealing the group of states of the atoms that can be populated by the dissociative mechanism, while the second involves analysis of the efficiency of the given mechanism as compared with the other processes of formation of excited atoms in the plasma. A substantial contribution toward solving the first problem was introduced by a series of studies on joint mass spectrometric-spectroscopic anlysis of the decaying noble-gas plasma.[33–38] The basis of these studies is observations of correlations of intensities of spectral ines $J_i(t)$ and ion densities $[R_2^+](t)$ in the afterglow plasma. In agreement with Eq. (6), in the dissociative population of excited levels we have $J_i \sim n_e[R_2^+]$. Under the conditions commonly used for this purpose (pressure of the gas or gas mixture of several Torr, density of electrons $n_e < 10^{12}$ cm^{-3}), the only mechanism of recombinative population that competes with (1) is the process of impact-radiation recombination of the atomic ions R^+ with electrons

$$R^+ + e + e \rightarrow R_i^* + e. \tag{9}$$

As is known, in the ternary process of (9), state R_i^* are formed with a binding energy of the order of the thermal energy kT_e. Further, owing to a complex of collisional and radiative processes, an excited electron diffuses into the region of negative energies, and thus atoms in any of the excited states can arise. A number of mass-spectrometric and spectroscopic experiments[33–36,59] have observed a distinct separation of the mechanisms of (1) and (9) according to their contribution to the population of different levels of the noble-gas atoms. It was found that the dissociative-recombination flux in a plasma containing thermal electrons is transported mainly in transitions from $np^5\,(n+1)$p levels (n is the principal quantum number of an unexcited electron), and to a considerably lesser degree, from levels $np^5(n+2)$p.

However, for all their information content, the spectroscopic methods possess a substantial defect involving the restricted region of sensitivity $\delta\lambda \approx 3000$–$8000$ Å of the contemporary receivers (photomultipliers) used in such "standard" experiments for measuring relatively weak light fluxes. Therefore information is practically lacking on the recombination fluxes onto np^5nd levels of atoms of the heavy noble gases (Ar, Kr, Xe), i.e., precisely those fluxes that are of greatest interest for analyzing the kinetics of the populations in the plasma of active media of lasers based on infrared d–p transitions of the stated atoms.

The spectroscopic methods of studying dissociative recombination are applied usually under conditions such that the positively charged particles are represented mainly by molecular ions, i.e., $[R_2^+] \approx n_e$. Then the time course of the intensities of the spectral lines in the decaying plasma is directly determined by the magnitude of the dissociative-recombination coefficient:

$$J_i(t) \sim n_e^2(t), \quad (J_i(t))^{-1/2} \sim 1 + \alpha_\Sigma n_e(0)t.$$

In real plasma systems that are of interest from the standpoint of certain applications, such a situation is not realized in practice. In them dissociative recombination appears as one of a large number of mechanisms of deionization and formation of excited atoms. Therefore, in analyzing such systems, the problem of revealing the role of a certain process in the kinetics of the excited and ionized particles of the plasma arises in the front rank. Let us examine one of the variants of the spectroscopic methods that has proved highly effective in analyzing complex systems. The method consists in spectroscopic analysis of the relaxation processes that develop upon pulsed perturbation of a recombinatively nonequilibrium plasma by a weak electric field. The first experiments were conducted in Refs. 26 and 27 by applying the technique of pulsed UHF heating of the electrons. For a number of reasons, the method of pulsed microwave heating has not been widely applied in studying elementary processes. An alternative approach to solving this problem has been formulated.[39,40] The heating of the electron gas is performed with the longitudinal electric field of a non-self-sustaining discharge in the stage of plasma decay. The rate constants of the processes of formation of excited atoms in the plasma depend on the temperature of the electrons. Therefore the fundamental difficulty of applying the methods being discussed (both microwave heating and the one that uses a longitudinal electric field) consists in the need of maintaining the temperature of the electrons strictly constant within the time interval being analyzed. In Refs. 39 and 40 this problem was solved by using a feedback system that automatically fixed the required value and the time course of the intensity of the longitudinal electric field $E(t)$ of the non-self-sustaining discharge. As is shown by the practice of ap-

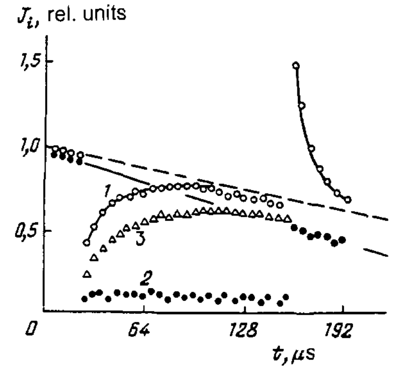

FIG. 2. Response of the intensities of spectral lines of the Xe atom emitted by a decaying He–Xe plasma to pulsed electron heating. Helium pressure is 60 Torr, xenon 1 Torr, electron density $n_e \approx 5\times 10^{10}$ cm^{-3}. *1*–λ = 8280 Å (6p–6s), *2, 3*–λ = 5934 Å (9d–6p). Electron temperature during the pulse: *1, 2*–1000 K, *3*–3000 K. Outside the pulse T_e = 300 K.

plying this method,[41,42] one can carry out the pulsed heating of electrons from a temperature of the order of room temperature $T_e\,(E=0) \approx 300$ K to value of $T_e\,(E)$ that reach 1–2 eV with times of the growth and decay fronts of $E(t)$ on the scale of a few microseconds.

Figures 2 and 3 demonstrate the possibilities of the method in studying the processes in a recombinatively nonequilibrium plasma. The first diagram shows the reaction of the radiation of an He–Xe plasma to pulsed heating of the electrons. The experiment distinctly shows a difference in the mechanisms of poulation of excited levels having different excitation potentials. The characteristic time dependences of relaxation type track the variation in density of molecular ions Xe_2^+ whose recombination with electrons leads to formation of 6p, 6p′, and 7p Xe atoms, whereas the population of all the more highly excited levels of the Xe atom at low electron temperatures arises from the impact-radiative recombination of Xe^+ ions. The specifics of this experiment consists in the fact that $[Xe_2^+] \ll [Xe^+] \approx n_e$ under the stated conditions. Therefore, in line with the

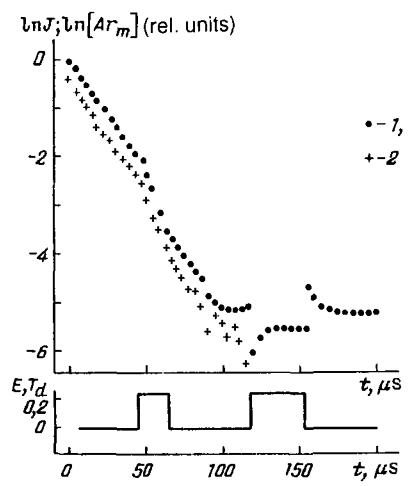

FIG. 3. Intensity trend of the line XeI λ = 4671 Å (7p–6s) (*1*) and the density of metastable argon atoms Ar[$4s^3P_2$] (*2*) in the decaying plasma of an He–Ar–Xe mixture with pulsed heating of the electrons. Argon pressure 1 Torr, helium 3 Torr, xenon 0.006 Torr. Electron density $n_e = 5\times 10^{10}$ cm^{-3}.

$\alpha_\Sigma\,(T_e)$ relationship, the variation in the temperature of the electrons gives rise to a variation in the density of molecular ions in the decaying plasma having the characteristic times $\tau = 1/n_e\alpha_\Sigma\,(T_e\,(E))$ during the pulse, and $\tau = 1/n_e\alpha_\Sigma\,(300\text{ K})$ after it has finished. Hence clearly one can easily find by processing the results of such an experiment the magnitudes and temperature dependences of the coefficients $\alpha_i\,(T_e)$ and $\alpha_\Sigma\,(T_e)$.

The data of Fig. 2 demonstrate another important property of dissociative recombination: the intensities of all the transitions accessible to observation from highly excited states begin with increasing temperature to depend on the time within the limits of the heating pulse in the same way as the intensities of the 6p–6s, 6p′–6s, and 7p–7s transitions. This indicates the dominant role of the process of dissociative recombination in the formation of highly excited atoms in a plasma with elevated T_e. This phenomenon will be discussed in detail in Sec. 4.

In mixtures of noble gases having close-lying ionization potentials, processes of excitation transfer can participate in excitation of atoms, as well as the recombinative processes. The experiment illustrated in Fig. 3 was performed under conditions of competition of the process of excitation transfer

$$Ar(4s^3P_2) + Xe \to Xe_i^* + Ar(^1S_0) \qquad (10)$$

with the dissociative formation of Xe* atoms in a decaying plasma of an He–Ar–Xe mixture. In the early stage of the afterglow the process (10) dominates, and, as we see from the diagram, the heating of the electrons causes only a change in the rate of decay of the intensity $J_i\,(t)$, whereas the dissociative mechanism proves to be the only source for the appearance of excited atoms in the later stage of plasma decay.

Analogously, by using the method being discussed, one can easily identify the process of excitation by electron impact, and also the dissociative population with participation of heteronuclear molecular ions of the noble gases.[43] We note that the processes being discussed are cited (with varying stress, depending on the viewpoint of the authors) to explain the population inversion in active media based on noble-gas mixtures.[44–47]

We note another merit of the method of electron heating with a longitudinal electric field. In a plasma containing a field, the electric current $i(t) = eb_eE\bar{n}_e\,(t)$ flows (b_e is the mobility of the electrons, and $\bar{n}_e$ is the electron density averaged over the cross section of the discharge interval), which is proportional to the electron density $n_e\,(t)$. Since current measurement presents no difficulties, one can easily find the value of $n_e\,(t)$ in experiments of this type.

3. RESULTS OF STUDYING THE TEMPERATURE DEPENDENCES OF THE PARTIAL DISSOCIATIVE-RECOMBINATION COEFFICIENTS

The dissociative recombination of a molecular ion and an electron is a multichannel process. Therefore one of the problems of study involves obtaining data on the probability of occurrence of the process via a given channel. Here one must bear in mind the fact that both the quantities α_i and α_Σ and the rate constants α_{vi}, which do not depend on the character of the vibrational distribution of the molecular ions in the plasma, can have different dependences on the temperature of the electron gas. This follows directly from Eqs. (3) and (4), which show that the character of the $\alpha_{vi}(T_e)$ relationships is determined to a substantial degree by the parameters of the terms ε_{vi} and Γ_i. In agreement with the calculations[60] of the recombination coefficients using various model interaction potentials, the values of α_Σ and α_i can strongly depend in certain cases on the vibrational temperature T_v. Thus the problem of the temperature dependences of the recombination coefficients proves to involve a large number of problems. This implies, in particular, that the experimental solution of the problem must be based on measurements performed over a maximally broad range of variation of the parameters of the plasma. On the other hand, the results of such measurements contain information on the degree of vibration excitation of the molecular ions and the parameters of the terms $\varepsilon_i(r)$ and Γ_i.

Measurements of the temperature dependences of the *partial recombination coefficients are performed in experiments* with pulsed heating of the electrons and are based on comparing the intensities of the spectral lines emitted by the plasma before and immediately after the front of the pulse of the field that heats the electrons. Here the time segment Δt between two successive measurements must appreciably exceed the characteristic relaxation time τ_T of the electron temperature but be smaller than the characteristic time of variation of the density of charged particles $\tau_n : \tau_T < \Delta t < \tau_n$. This condition narrows the applicability of the method by imposing a limit on the degree of ionization of the plasma. If the fundamental exit mechanism of the charged particles is dissociative recombination ($\tau_n = 1/\alpha_\Sigma n_e$), while the relaxation of the energy of the electrons is due to elastic collisions with atoms (as is usually the case), then we have

$$\frac{1}{\tau_T} \approx \frac{2m}{M}\bar{v}_{ea} > \alpha_\Sigma n_e, \quad \frac{n_e}{[\mathrm{R}]} < \frac{2m}{M}\frac{\langle\sigma_{ea}v_e\rangle}{\alpha_\Sigma} \tag{11}$$

($\bar{v}_{ea} = [\mathrm{R}]\langle\sigma_{ea}v_e\rangle$ is the rate of collisions of electrons with atoms). The electrons undergo maximal energy losses in collisions with He atoms. Therefore the condition (11) proves least strict if the experiment is performed in an He–R mixture, in which helium plays the role of a buffer gas. Then, for ions having a recombination coefficient of $\alpha_\Sigma \approx 10^6(T_e/300)^{-1/2}$ cm^3/s, Eq. (11) acquires the form: $n_e/[\mathrm{He}] < 10^{-6}\,T_e/300$. The addition of helium in experiments on electron heating by a longitudinal electric field also enables one to eliminate the effect of the hysteresis character of the dependence of the mean energy on the parameter E/N that is manifested in a plasma of the heavy noble gases.[49,50]

Below we briefy examine the results of measurements of the variations of the recombination coefficients $\alpha_i(T_e)$.

3.1. Ne_2^+ ions

Figure 4(a) shows the temperature dependences of the partial recombination coefficients for certain levels of the neon atom obtained in the experiments of Refs. 50–52 involving electron heating with a longitudinal electric field in a non-self-sustaining discharge. As we see from these data, the temperature dependences $\alpha_i(T_e)$ for the 3p and 3d levels are decreasing functions of the temperature T_e of the type E_e^{-k}, yet with differing exponents: $k_{3d} \approx 0.35$ and $k_{3p} \approx 0.5$, which do not coincide with the approximation constant $k_\Sigma = 0.43$ of the coefficient $\alpha_\Sigma(T_e) \sim T_e^{-k_\Sigma}$. Transition to the 4p levels, which have a larger excitation energy close to the energy of the ground vibrational level of the Ne_2^+ ion ($v = 0$) (Fig. 4b) is accompanied by a qualitative change in the $\alpha_i(T_e)$ relationship, which proves to increase in the region $T_e \approx 300$–800 K. On the qualitative level, all these $\alpha_i(T_e)$ relationships can be interpreted in the approximation of a single (for each of the studied levels) autoionization state of Ne_2^*. Equation (4) implies that, for different parameters of the problem, the dissociative-recombination cross section can have a different dependence on the electron energy:[2] $\sigma^d \sim 1/\varepsilon$, $\sigma^d \sim 1/\varepsilon^3$, $\sigma_d \sim 1/[\varepsilon(\varepsilon - \varepsilon_{vi})^2 + (\Gamma/4)^2]$. The first two cases correspond to temperature dependences of the coefficients $\alpha_i \sim T_e^{-1/2}$, $\alpha_i \sim T_e^{-2.5}$. In the third case, if $\varepsilon_{vi} \gg \Gamma_i$, one can observe an upward trend of the corresponding coefficient $\alpha_i(T_e)$, as occurs for the upper 4p levels of the neon atom. Apparently, in the case of the 3d levels, an intermediate case is realized. Thus, the experiment indicates the possibility of a substantial difference in the temperature dependences of the partial coefficients and the dissociative-recombination coefficient $\alpha_\Sigma(T_e)$. Since $\alpha_\Sigma = \Sigma\alpha_i$, it is of interest to reconstruct the $\alpha_\Sigma(T_e)$ relationsip on the basis of experimental data on the coefficients $\alpha_i(T_e)$. The dissociative-recombination flux of Ne_2^+ ions is transported mainly to the 3d–3p and 3p–3s transitions, while we have $\alpha_{3d}(300\ \mathrm{K}) \approx 0.2\alpha_{3p}$.[53,54,75] Then we

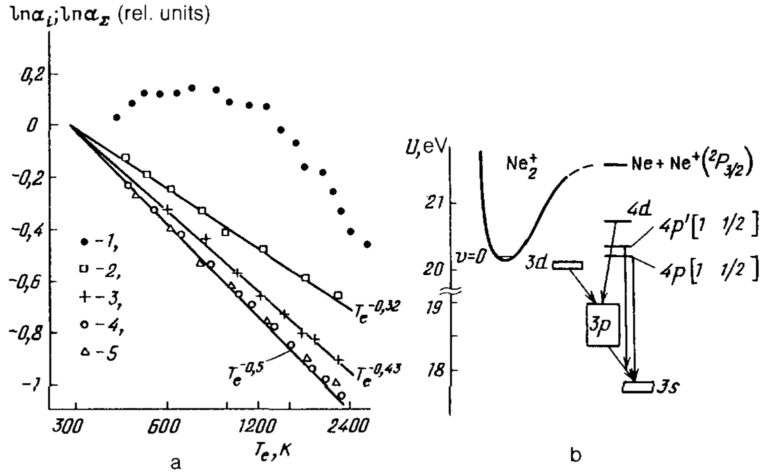

FIG. 4. a–Temperature dependences of the recombination coefficients of the Ne_2^+ ion. *1*–for the upper of the 4p levels 4p'[3/2], *2*–for the 3d levels, *3*–$\alpha_\Sigma(T_e)$, *4*–4p[3/2], *5*–a typical variation of the partial recombination coefficients $\alpha_i(T_e)$ onto the 3p levels of the neon atom. b–Diagram of levels of the neon atom.

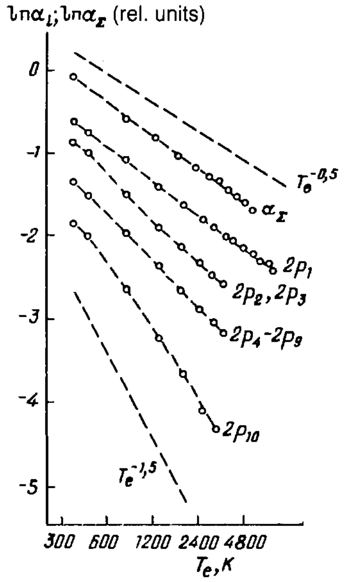

FIG. 5. Temperature dependences of the coefficients $\alpha_i(T_e)$ and $\alpha_\Sigma(T_e)$ of dissociative recombination of the Ar_2^+ ions.[55]

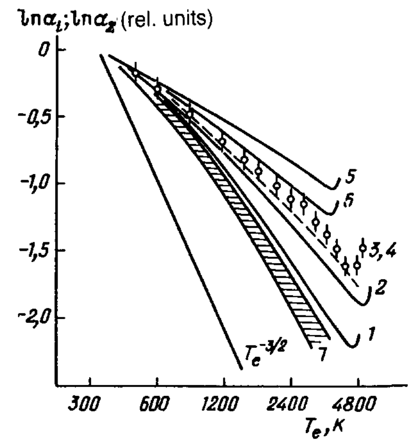

FIG. 6. Temperature dependences of the dissociative-recombination coefficients of the Xe_2^+ ion.[56,57] Dashed line–$\alpha_\Sigma(T_e)$, *1*–for the $2p_5$ level (notation of Paschen), *2*–$2p_6$, *3*, *4*–$2p_7$, $2p_8$, *5*–$2p_9$, *6*–$2p_{10}$, *7*–zone of variation of the coefficients $\alpha_i(T_e)$ for the 6p′ and 7p levels. The accuracy and discreteness of the data are demonstrated by curves *3* and *4*. The sharp increase in the curves at high electron temperatures involves the "turning on" of the process of stepwise excitation of the stated levels by electron impact.

find for α_Σ, in the region of T_e indicated in Fig. 4a, that $\alpha_\Sigma(T_e) \sim T_e^{-0.45}$. This practically coincides with the results of measuring $\alpha_\Sigma(T_e)$ shown in Fig. 4a.

3.2. Ar_2^+ ions

Figure 5 shows the temperature dependences of the coefficients $\alpha_{2p_i}(T_e)$ (Paschen notation). We see there that the $\alpha_{2p_i}(T_e)$ relationships are close to $\alpha_\Sigma(T_e)$ except for $2p_{10}$. This gives grounds for assuming that the predominant part of the recombination flux of Ar_2^+ ions is transported via the levels $2p_1,\ldots,2p_9$. Actually (see Sec. 5) the fraction of this flux amounts to $\approx 80\%$. At the same time, the appreciable difference between the relationsips $\alpha_{2p_{10}}(T_e)$ and $\alpha_\Sigma(T_e)$ indicates a specific character of the intersection of the terms $Ar^*(2p_{10}) + Ar$ and Ar_2^+.

3.3. Xe_2^+ ions

Figure 6 presents the complete set of data on the variations of the coefficients $\alpha_i(T_e)$ for the 7p, 6p′, and 6p levels of the Xe atom. We see from the results of the measurements that the individual features of the terms $Xe_i^* + Xe$ and Xe_2^+ are manifested most sharply in the case of Xe. Thus, even for a group of close-lying 6p levels, the functions $\alpha_i(T_e)$ differ appreciably.

The observed steepening of the $\alpha_i(T_e)$ relationships with increasing T_e can be easily explained by turning to Eq. (4). In a certain region of variation of the mean electron energy, a transition can occur from the relation $\sigma^d \sim 1/\varepsilon$ to the stronger dependence of the recombination cross section on the energy $\sigma^d \sim 1/\varepsilon^3$. Such a transition has been observed, for example, in studying the dissociative recombination of NH_4^+ ions.[58,61] Another mechanism of strengthening the $\alpha_i(T_e)$ relationship can occur: with increasing energy of the electron captured by the ion, the time necessary for separation of the nuclei beyond the region of crossing of the terms of R_2^* and R_2^+ increases. Therefore the probability increases of autoionization of R_2^*, and consequently the recombination cross section becomes smaller than the cross section of the initial capture.[14]

4. FORMATION OF HIGHLY EXCITED ATOMS IN DISSOCIATIVE RECOMBINATION

The $\alpha_i(T_e)$ dependences of the partial coefficients discussed in the previous section for the levels of the atoms that transport the main flux of recombinations had a declining course typical of this process. At the same time, the general formula (4) for the dissociative-recombination cross section predicts the possibility of observing sharply increasing variations $\alpha_i(T_e)$ of the partial coefficients in the case $\varepsilon_{vi} \gg \Gamma_i$. In this situation the process occurs by capture of the electron by the terms $\varepsilon_i(r)$ lying considerably higher than the most populated lower vibrational levels of the molecular ion. Hence it has a threshold character. Evidently the effect of flare-up of the recombination radiation upon heating the electrons of the plasma can be manifested in lines emitted in transitions from the highly excited states of the atoms.[1)]

For a long time the question of the kinetics of highly excited atoms in a plasma containing molecular ions lay outside the attention of investigators. The first experiments that indicated the possibility of observing a threshold process of dissociative recombination in a plasma were performed in the studies of Biondi *et al.*[12–14] They found an enrichment of the emission spectrum of a decaying plasma upon microwave heating of the electrons to value $T_e \approx 6000$–8000 K owing to transitions from highly excited states of Ar, Kr, and Xe atoms. The study of this phenomenon in Refs. 62–65 showed that the threshold mechanism of dissociative recombination is manifested in all the noble gases. A graphic view of the process is given by the results of a study[65] of the temperature dependences of the intensities of spectral lines of highly excited Xe atoms in a decaying plasma (Fig. 7). We see that the $J_i(T_e)$ relationship consists of three characteristic branches that arise from different processes. The sharp decline in the region $T_e < 0.1$ eV is due to the predominant population of the levels by impact–radiative recombination

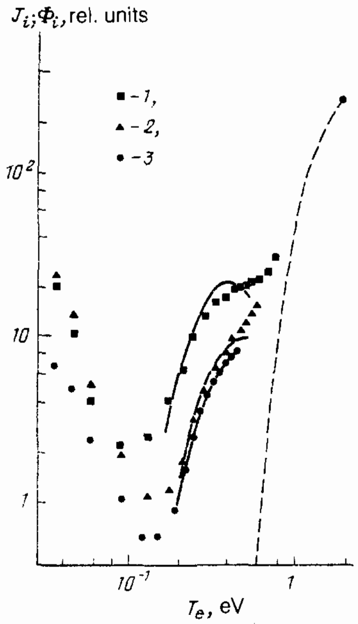

FIG. 7. Temperature dependences of the intensities of spectral lines of the Xe atom $J_i(T_e)$, of the calculated fluxes $\Phi_i(T_e)$ of dissociative recombination of Xe_2^+ ions (solid lines), and of the stepwise-excitation flux (dashed line). 1-λ = 6872 Å (level 6f[9/2], 2-λ = 5488 Å (level 11d[7/2], 3-λ = 5934 Å (level 9d[7/2]).

of Xe^+ ions:

$$Xe^+ + e + e(He) \rightarrow Xe_i^* + e(He),$$

This reflects the strong dependence of the rate of the process on T_e. The sharp increase in the line intensities with heating of the electrons at temperatures $T_e > 0.5$ eV is due to the "turning on" of the stepwise population of the levels being discussed by electron impact. In the intermediate temperature region the mechanism of threshold dissociative recombination dominates.

For a quantitative description of the process one can use Eq. (6), which gives an algorithm for calculating the fluxes $F_i(T_e)$. Equation (6) implies that the recombination fluxes to highly excited levels are sensitive to the location of the term $\varepsilon_i(r)$ with respect to the most populated lower levels of the molecular ion. The parameters of the terms are unknown, and hence the problem of calculating the fluxes $F_i(t_e)$ must be solved jointly with finding the terms $\varepsilon_i(r)$ from the experimental data on the temperature dependences of the line intensities $J_i(T_e)$. This problem was solved[62,65] by a selection by least squares of the parameters of the terms $\varepsilon_i(r)$ under the condition of best agreement of the measured $J_i(T_e)$ relationships with the fluxes $F_i(T_e)$ calculated by (6). The degree of agreement of the $J_i(T_e)$ and $F_i(T_e)$ relationships is demonstrated in Fig. 7, which shows that the threshold mechanism of dissociation recombination is well described in the approximation of a single autoionization level based on the Breit–Wigner formula for the cross section of the process. Figure 8 shows the region of location of one of the found terms, which corresponds to formation of Xe9d atoms and some of the studied levels of the Xe atom.

As we have already mentioned, the manifestation of the character of the dependences of the coefficients $\alpha_i(T_e)$ directly involves the problems of the kinetics of the populations of the vibrational levels of the molecular ions. The fol-

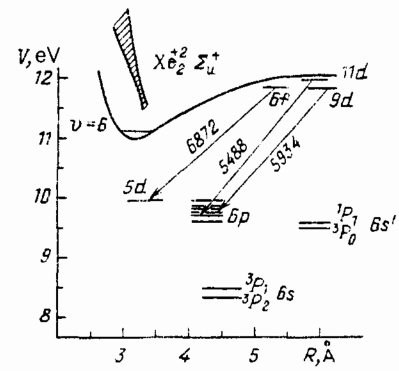

FIG. 8. Location of some of the levels of the xenon atom studied in Ref. 65. The cross-hatched region shows the location of the term Xe*(9d[7/2]) + Xe.

lowing facts were established[62,65] with respect to the distribution $[R_2^+(v)]$ with respect to v. In the case of Xe_2^+ ions the best agreement of the measured and calculated fluxes of population of the highly excited levels was attained upon using in the calculations the equilibrium distribution of $[Xe_2^+(v)]$ with the temperature $T_v = 300$ K. We note that the possible realization in a weakly ionized low-pressure plasma of an equilibrium distribution does not contradict the existing views of the rates of V–T exchange of molecular ions of heavy noble gases with their own atoms,[66,67] according to which the rate constants of V–T exchange are of the order of magnitude of 10^{-11} cm^3/s.

A different situation was observed in studying a neon plasma.[62] In this case the attainment of an equilibrium distribution $[Ne_2^+(v)]$ of ions occurred at neon pressures of tens of Torr. This gives grounds for assuming that V–T exchange in $Ne_2^+ + Ne$ collisions is considerably less effective than for Xe_2^+ ions and Xe. However, here we must mention the alternative viewpoint,[67,68] according to which the rate constants of $v = 1 \rightarrow v = 0$ transitions for all molecular ions in their own gas are of the order of 10^{-11} cm^3/s.

In summarizing the results of the studies on the threshold mechanism of dissociative recombination, we point out the following. In a plasma containing molecular ions, over a broad range of variation of the electron temperature (several

TABLE II. Magnitudes of the partial recombination coefficients of the Ar_2^+ ion estimated from measurements of the absolute intensities of spectral lines of the argon atom. Value of $T_m \approx (3-8) \times 10^3$ K.

Level	α_i, 10^{-11} cm^3/s
6s[3/2]	2,6
4d[1/2]	2,4
5d[7/2]	5
4d'[3/2]	0,7
7s[3/2]	0,6
5p[1/2]	0,8
5d'[5/2]	0,6
5d[3/2]	1
6d[7/2]	1,7
7d[7/2]	0,9
6d[1/2]	1,5
5d'[3/2]	1,3

TABLE III. Distribution of the dissociative-recombination flux of the Ne_2^+ ion over the excited levels of the neon atom in percentages of the total flux. For the 3d and 4p levels a summation was performed over all the levels of $2p^53d$ and $2p^54p$ configurations. The fluxes to the $2p_i$ levels include both direct population and cascades from the 3d levels.

Levels	3d	4p	$2p_1$	$2p_2$	$2p_3$	$2p_4$	$2p_5$	$2p_6$	$2p_7$	$2p_8$	$2p_9$	$2p_{10}$
Flux	11	5,4	6,8	6,9	2,9	11,3	6,9	10,4	5,4	9	13	22

thousand degrees), this process can be the dominant source of formation of highly excited atoms. The data of Table II characterizes its efficiency; here the results are presented of the estimates[69,70] of the absolute magnitudes of the partial coefficients $\alpha_i(T_m)$ at temperatures T_m corresponding to reaching the maxima of the $\alpha_i(T_e)$ relationships. In closing we note that the coefficients of Table II, while small in comparison with the quantities α_Σ, substantially exceed the constants of the process of dielectron recombination of atomic ions.[71] The latter resembles dissociative recombination in that the primary event of electron capture also results in formation of an autoionization (doubly excited) state. The efficiency of the stabilization of the process of dielectron recombination is determined by the relationship of the probabilities of radiative transition A_{rad} to the lower electronic state and that for autoioinization A_a, where we have $A_a \gg A_{rad}$. At the same time, in dissociative recombination the probability of autoionization A_a of the molecule R_2^*, as a rule, is of the order of or smaller than the reciprocal time for separation of the nuclei as they move along a repulsive term.

The discussed mechanism of formation of highly excited atoms finds an explanation based on the general views on dissociative recombination. Therefore we can expect that it will be found also in plasmas of other media containing molecular ions.

5. DISTRIBUTION OF THE RECOMBINATION FLUX OVER THE EXIT CHANNELS OF THE PROCESS

Full information on dissociative recombination as a source for formation of excited atoms is contained in the temperature dependences of the partial coefficients $\alpha_i(T_e)$ and in their absolute magnitudes. The determination of the constants α_i is based on comparing the intensities of a large number of spectral lines emitted by the decaying plasma. Such observations have been performed in a number of studies analyzing neon,[53,72–76] argon,[12,36,77–79] krypton,[13,28,80] and xenon[14,57,81,82] afterglows. The following conditions must be satisfied in these experiments. First, the process studied must be the only source of population of the excited levels of the atoms. Second, the electron density and the gas pressure must be small enough to avoid collisional "mixing" of the excited levels by these particles. Third, the measurements of the line intensities must not be distorted by reabsorption of radiation. And finally, the entire dissociative-recombination flux must be transported in the transitions being studied. These conditions are satisfied in the experiments of Refs. 53, 57, and 79, whose results are given in Tables III–VI. The data on krypton are taken from Ref. 13. The tables lack information on the recombination fluxes onto the levels Ne 4s; Kr 3d; Ar 5s, 4d, 6s, Xe 5d, 7s. However, the stated levels are depleted owing to radiative transitions to the $(n+1)$p levels of the atoms, the radiation from which, together with $(n+2)\text{p} \to (n+1)\text{s}$ transitions, transports the entire dissociative-recombination flux. We note some important consequences of the data presented in Tables III–VI, and above all, the fact that the overwhelming fraction of the recombination flux is transported in the lines of $(n+1)\text{p} - (n+1)\text{s}$ transitions. Here a high selectivity exists in the population of individual $(n+1)$p levels. Thus, about 20% of the total recombination flux goes to the $2p_{10}$ and $2p_9$ levels of Ne and Ar atoms, respectively. The most marked effect is observed in a decaying xenon plasma: almost 40% of the flux goes to the level $2p_6$, i.e., the 8232-Å line ($2p_6 - 1s_5$) transports almost a third of the entire dissociative-recombination flux of the Xe_2^+ ions.

On the level of laser applications, of greatest interest are the data on the fluxes to the *n*d levels of Ar, Kr, and Xe atoms. Such information is lacking at present, although it is known that the *n*d levels are also populated in dissociative recombination.[83] However, from the data of Tables III–VI one can draw quite definite conclusions on the fluxes F_{nd}. Thus, one can point out the following with regard to the upper level $5d[3/2]_1^0$ in the system of 5d levels of the Xe atom, the transitions from which at the wavelength 1730 Å have yielded the most powerful generation in lasers based on Ar–Xe mixtures. In agreement with the probabilities of 6p–5d transitions,[84] about half (0.434) of the radiation flux of the $5d[3/2]_1^0$ Xe atoms goes to the level $2p_7$. At the same time, the flux of quanta in transitions from this level amounts (see Table VI) to $\approx 6\%$ of the total flux of dissociative recombination. Therefore it is clear that no more than 15% of the dissociative-recombination flux of the Xe_2^+ ions goes to the $5d[3/2]_1^0$ level.

The data presented in Tables III–VI correspond to a distribution close to equilibrium of the populations $[R_2^+(v)]$ over the levels v. For Ar_2^+, Kr_2^+, and Xe_2^+, the basis for this is the high velocities of V–T exchange. As regards Ne_2^+ ions, the situation is not so clear. However, one can cite as an argument here the results of studying the contours of spectral lines in the afterglow of a discharge in neon, according to which the fundamental recombination flux to the 3p level at a neon pressure ≈ 1 Torr is formed by the ions

TABLE IV. Distribution of the recombination flux of the Ar_2^+ molecular ion over the excited levels of the argon atom in percentages of the total flux. For the 5p levels an estimate is given of the flux going to levels of configuration $3p^55p$.

Levels	5p	$2p_1$	$2p_2$	$2p_3$	$2p_4$	$2p_5$	$2p_6$	$2p_7$	$2p_8$	$2p_9$	$2p_{10}$
Flux	< 1	3,8	11,6	10,5	6,7	3	13	8,5	9,7	20	14

TABLE V. Distribution of the recombination flux of Kr_2^+ ions over the excited levels of the Kr atom in percentages of the total flux. A summation of the fluxes is performed for the 6p levels.

Levels	6p	$2p_1$	$2p_2$	$2p_3$	$2p_4$	$2p_5$	$2p_6$	$2p_7$	$2p_8$	$2p_9$	$2p_{10}$
Flux	7	3	19	4,6	3,7	3,7	9,2	10	17,5	14	18

Ne_2^+ ($v=0$).[85] The data presented in Table III were obtained under similar conditions.

6. HETERONUCLEAR MOLECULAR IONS IN NOBLE-GAS PLASMAS

The problem of the role of heteronuclear ions in the deionization of a plasma and formation of excited atoms is one of the most important in the kinetics of excited and charged particles of plasmas of noble-gas mixtures. These particles are often cited to explain a population inversion in a recombinatively nonequilibrium plasma of a noble-gas mixture.[44] A number of studies (e.g., Refs. 86 and 87) have treated the possibility of obtaining laser action based on transitions between electronic terms of heteronuclear ions.

The formation of heteronuclear ions occurs in triple collisions of the type

$$R^+ + R + B \xrightarrow{\beta_R} R_2^+ + B, \qquad (12)$$

$$R^+ + R + B \xrightarrow{\beta_{RB}} R^+B + R, \qquad (13)$$

$$R^+ + B + B \overset{\beta_{BB}}{\rightleftarrows} R^+B + B. \qquad (14)$$

Depending on the collision partners, the rate constants β_{RB} of the processes have magnitudes from $\approx 10^{-31}$ for He–Xe^{+}[88] to $\approx 5\times10^{-31}$ cm^6/s for Ar–Xe^+. The experimental methods of studying heteronuclear ions are limited as yet to mass-spectrometric measurements[35,36,89–93,97–99] and spectroscopic analysis of a recombinatively nonequilibrium plasma.[87,94,95,100] Some information on the binding energies of heteronuclear ions has been obtained in experiments[101] to study scattering of ioins by atoms. Figure 9 shows a typical structure of the electronic terms of heteronuclear ions. Table VII shows the results of calculations[102] of the parameters of their ground states $X^2\Sigma_{1/2}$. We see from these data that all the ions, except for $HeNe^+$, $ArKr^+$, and $KrXe^+$, have binding energies $D_0<0.15$ eV. Therefore their concentration in the plasma is determined mainly by the relationship between the rates of the forward and backward reactions,[13,14] i.e., the equilibrium constants of the stated processes. For $ArXe^+$ ions in argon the equilibrium constant at room temperature is $\approx 10^{-20}$ cm^3.[98] That is, the process of dissociation of these ions in collisions with Ar atoms is described by the rate constant $\tilde{\beta}_{BB}\approx 5\times10^{-11}$ cm^3/s. If we allow for the fact that ions of the type of $HeAr^+$, $HeKr^+$, and $HeXe^+$ have even smaller binding energies, we can assume that the corresponding dissociation constants will exceed 10^{-10} cm^3/s. This constitutes the principal difference in the kinetics of hetero- and homonuclear molecular ions. The latter have binding energies $D_0>1$ eV, and hence the reverse reactions play no substantial role, at least until the gas temperature exceeds $T_g\approx 800$–1000 K.[103]

The information and estimates that we have indicated essentially constitute the entire bulk of the current information on heteronuclear ions. Therefore, an analysis of their role in the kinetics of the particles of plasmas clearly can be only an estimate in nature owing to the lack of data on the efficiencies and recombination channels.

The sole exception are the $HeNe^+$ ions. Owing to their large binding energy, these ions are stable with respect to thermal dissociation, which makes possible the study of their recombination with electrons. In Ref. 104 the recombination channels of $HeNe^+$ were identified by spectroscopic analysis of the relaxation response of the emission of a decaying He–Ne plasma to pulsed heating of the electrons. It was shown that, just as in the case of Ne_2^+, the main recombination flux is transported in the 3p–3s transitions of the Ne atom. However, there is a substantial difference between the recombination channels of $HeNe^+$ and Ne_2^+ ions. First, the emission spectrum of a He–Ne plasma contains transitions from levels of configuration $2p^54d$. Second, the partial coefficients $\alpha_i(T_e)$ have a stronger dependence on the electron temperature, close to $\alpha_i\sim T_e^{-1}$. This observation confirms the empirically established rule, according to which dissociative recombination in a decaying noble-gas plasma populates all the excited levels of the atoms lying in resonance with or below the ground vibrational state of the molecular ion.

Let us turn to the heteronuclear ions in plasmas of the heavy noble gases. We shall estimate the degree of ionization at which the destruction of the heteronuclear ions is caused by their thermal dissociation. Let us allow for the fact that the collisions of the ions with electrons at energies of the latter exceeding the binding energy D_0 lead with greatest probability to dissociation of the BR^+ ions, rather than to dissociative capture of an electron. The corresponding rate constants k_d for ions with binding energies of a fraction of an eV can attain values of 10^{-7}–10^{-6} cm^3/s.[105] Then the condition $\tilde{\beta}_{BB}[B]>k_d n_e$ leads to the inequality:

$$\frac{n_e}{[B]}<10^{-3}-10^{-4}.$$

TABLE VI. Distribution of the dissociative-recombination flux of Xe_2^+ ions over the excited levels of the Xe atom in percentages of the total flux according to the data of Ref. 57. A summation of the fluxes is performed for the 7p and 6p′ levels.

Levels	7p	6p′	$2p_5$	$2p_6$	$2p_7$	$2p_8$	$2p_9$	$2p_{10}$
Flux	6	2,6	4,2	36	5,4	39	8,3	< 20

The measurements for the $2p_{10}$ level are least accurate; therefore the table gives an estimate of the recombination flux going to it.

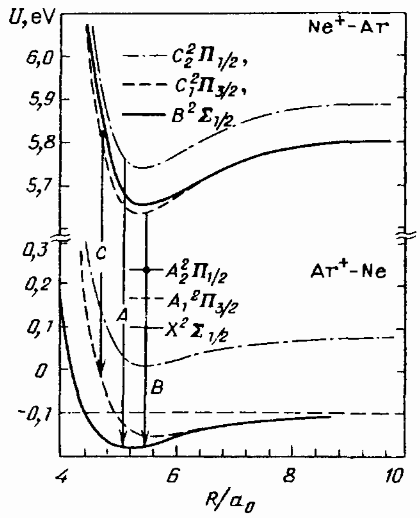

FIG. 9. Terms of heteronuclear ions of the noble gases based on the example of $(NeAr)^+$.

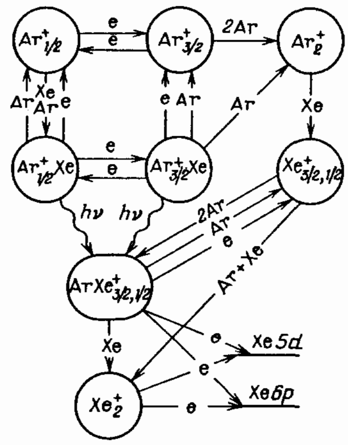

FIG. 10. Diagram of the processes of formation and breakdown of $ArXe^+$ ions in an Ar–Xe mixture.

Noting that this inequality is usually satisfied in media of interest for laser applications, let us find for them the order of magnitude of the ratio of densities of homo- and heteronuclear ions under conditions typical of active media $[B] = \gamma[R]$, $\gamma \approx 10^{+2}$. In estimates of the density $[R_2^+]$ it suffices to take account of the formation of ions in the process (13) and exit by the dissociative-recombination channel. Then we have

$$[R_2^+] = \beta_R [R^+][R][B]/\alpha_\Sigma n_e, \quad [R^+B] = \frac{\beta_{BB}}{\tilde{\beta}_{BB}}[B][R^+], \quad (15)$$

$$\frac{[R^+B]}{[R_2^+]} = \frac{\alpha_\Sigma n_e \beta_{BB}}{\beta_R \tilde{\beta}_{BB}[R]} \approx \frac{10^4 \gamma n_e}{[B]} \approx 10^6 \frac{n_e}{[B]}. \quad (16)$$

The numerical quantity on the right-hand side of Eq. (16) pertains to a plasma in an Ar-Xe mixture (B = Ar, R = Xe). Already this simple estimate (somewhat too high owing to use of a simplified model) shows that the problem of heteronuclear ions is of some current interest. However, despite the large number of studies on these particles, it has not yet been possible to detect the formation of excited atoms involving their recombination. Nevertheless, we can point out the degree of ionization $n_e/[B]$ at which it is expedient to conduct a search for heteronuclear ions from their influence on the populations of excited levels of the noble-gas atoms. According to the spectroscopic study of decaying plasmas of He–Ar, He–Xe, and He–Ar–Xe plasmas,[43,106] the ions $HeAr^+$ and $HeXe^+$, if they can compete with Ar_2^+ and Xe_2^+ in giving shape to the recombination flux, can do so only at high enough degrees of ionization $n_e/[He] > 10^5$. However, even in this case they do not influence the rate of deionization of the plasma.

TABLE VII. Binding energy D_0 and equilibrium internuclear distances r_0 of the lowest electronic states $X^2\Sigma_{1/2}$ of the heteronuclear molecular ions of the noble gases according to the data of Ref. 102.

Ion	D_0, meV	r_0/a_0
$HeNe^+$	699	2,6
$HeAr^+$	26,7	5,0
$HeKr^+$	22,7	5,5
$HeXe^+$	40,6	5,0
$NeAr^+$	77,3	5,2
$NeKr^+$	53,7	5,7
$NeXe^+$	38,6	6,5
$ArKr^+$	607	5
$ArXe^+$	138	7,2
$KrXe^+$	361	6,2

A different situation occurs in an Ar–Xe plasma. In practically all studies on the kinetics of a laser Ar–Xe plasma,[44–47,107] the $ArXe^+$ ions are treated as one of the main sources of the inverted population of the 5d levels of the Xe atom. These ions are distinctly detected, both in plasmas at high[86,87,95] and relatively low (a few Torr)[100,108] pressures. The diagram of the reactions of formation and breakdown of $ArXe^+$ ions shown in Fig. 10, which is constructed from the mass-spectrometric and spectroscopic studies cited above, makes it possible to trace the evolution of the density of these ions in an Ar–Xe plasma formed by different ionization sources. According to the calculations of Refs. 45 and 46, in a beam plasma the contribution of $ArXe^+$ ions to the pumping of the upper laser levels of the Xe atom can reach tens of percent. In a weakly ionized gas-discharge plasma the processes involving $ArXe^+$ ions can fully determine the rate of deionization.[106]

Another interesting property of plasmas of noble-gas mixtures merits attention. The formation of heteronuclear ions is manifested primarily in the appearance of molecular radiation that arises from transitions between the different electronic states $B^+R \rightarrow BR^+$. The most intense emission bands of an Ar–Xe mixture are shown in Fig. 11. Under certain conditions, an appreciable fraction of the energy introduced into the plasma can be transported in these bands. Thus, in an Ar–Xe mixture ionized with α-particles,[86] the radiation power in the 3290-Å band (Fig. 11) reaches 5% of the power introduced into the gas mixture. This points out another promising line of study of heteronuclear ionic molecules[109] as a working material for quantum generators.

Let us study the mechanism of formation of the radiative states of the ion Ar^+Xe. The fundamental contribution to the formation of the spectrum comes from the transitions $Ar^+(^2P_{1/2})Xe - ArXe^+(^2P_{3/2})$ (band A) and $Ar^+(^2P_{3/2})Xe - ArXe^+(^2P_{3/2})$ (bands B and C). As implied by the schema of the processes shown in Fig. 10, the

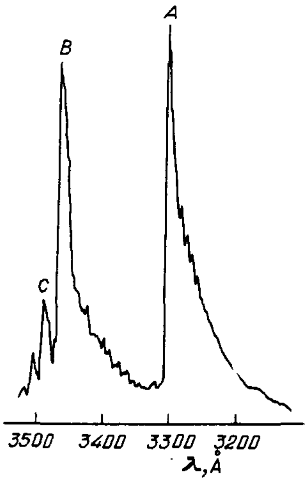

FIG. 11. Emission spectrum of the $(ArXe)^+$ ion in the short-wavelength region. The transitions are indicated in Fig. 9. The classification of the bands is given in Ref. 108.

ions $Ar^+(^2P_{1/2})Xe$ are formed in triple collisions of $Ar^+(^2P_{1/2})$ argon ions with Ar and Xe atoms:

$$Ar^+(^2P_{1/2}) + Ar + Xe \rightarrow Ar^+(^2P_{1/2})Xe + Ar. \qquad (17)$$

As regards the $Ar^+(^2P_{3/2})Xe$ ions, as is shown by the studies of Refs. 87, 95, and 100, the channel analogous to (17) is not dominant, and their appearance is mainly due to the interaction of $Ar^+(^2P_{1/2})Xe$ with the electrons of the plasma:

$$Ar^+(^2P_{1/2})Xe + e \rightleftarrows Ar^+(^2P_{3/2})Xe + e. \qquad (18)$$

This difference in the mechanisms of formation of the indicated states of Ar^+Xe ions is well manifested experimentally. Thus, in a plasma having a low degree of ionization, emission of bands B and C involving $Ar^+(^2P_{3/2})Xe$ ions is lacking.[87,95] Figure 12 shows the dependence measured in Ref. 100 of the intensities of bands A and B on the electron density. We see from these data that the electronic "mixing" of the ions in the states $Ar^+(^2P_{1/2})Xe$ and $Ar^+(^2P_{3/2})Xe$ leads to establishment of an equilibrium ratio of their densities at a degree of ionization $n_e/[Ar] \gtrsim 10^{-5}$. In such a plasma the intensities of bands A and B are determined by two factors: the evolution of the source of formation of heteronuclear ions, i.e., the density of $Ar^+(^2P_{1/2})$ argon ions, and the ratio of the rate constants of the forward and backward processes of (18), i.e., the temperature of the electron gas. The latter situation makes it possible to affect efficiently the ratio of intensities of bands A and B by electron heating. This is demonstrated by the results presented in Fig. 13 of the experiment[100] to study the emission from the heteronuclear Ar^+Xe ions in the decaying plasma of an He–Ar–Xe mixture with pulsed heating of the electrons with a longitudinal electric field.

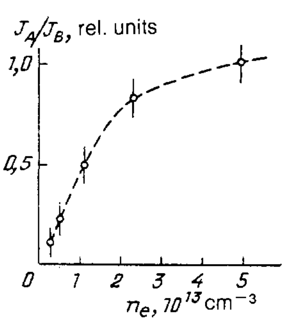

FIG. 12. Dependence of the ratio of intensities of the molecular bands A and B on the concentration of electrons in a decaying Ar–Xe plasma. $p_{Ar} = 37$ Torr, $p_{Xe} = 0.3$ Torr.

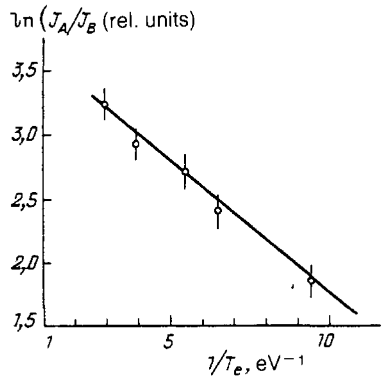

FIG. 13. Dependence of the ratio of intensities of the molecular bands A and B on the temperature of the electrons of the plasma of an He–Ar–Xe mixture. $p_{He} = 30$, $p_{Ar} = 8.2$, $p_{Xe} = 0.3$ Torr. $n_e \approx 10^{13}$ cm^{-3}.

We note that in an Ar–Xe plasma the Ar^+Xe–$ArXe^+$ radiative transitions can make a substantial contribution to the formation of $ArXe^+$ ions in the lower states $X\,^2\Sigma_{1/2}$ and $A\,^2\Pi_{3/2}$, which are the object of analysis when one studies the plasmas of active media based on Ar–Xe mixtures.

7. COMPETITION OF DISSOCIATIVE RECOMBINATION WITH OTHER MECHANISMS OF FORMATION OF EXCITED ATOMS IN A RECOMBINATIVELY NONEQUILIBRIUM PLASMA

The information discussed in the previous sections on molecular ions was obtained mainly in specially designed "standard" experiments, in which the conditions most favorable for study were deliberately selected. In real objects such a situation is not realized. Most often in such objects the only process competing with dissociative recombination proves to be impact-radiative recombination of atomic ions.[9] On the qualitative level the problem of recombination in such a plasma can be treated on the basis of the known modified diffusion approximation.[110,111] However, in a number of cases it has a simple experimental solution. This is demonstrated by Fig. 14, which shows the results of measurements[57] of the temperature dependences of the intensities of spectral lines of the Xe atom performed in experiments with pulsed heating of the electrons of a decaying He–Xe plasma. We see from the presented data that, when $T_e > 500$ K, one observes a change in the mechanism of population of the 7p, 6p′, and 6p levels: from impact-radiative recombination of Xe^+ ions, which has the sharp deline in flux $F \sim T_e^{-9/2}$ typical of this process, to dissociative recombination, which has a considerably weaker dependence of the rate constant of the process on the electron temperature. The formation of ever more highly excited atoms corresponded to the J_{9d} (T_e relationship shown in Fig. 14. Since the relative density of Xe_2^+ ions can be easily estimated (under the conditions of the experiment $[Xe_2^+]/[Xe_e^+] \approx 10^{-4}$, $n_e \approx 3 \times 10^{11}$ cm^{-3}), the data of Fig. 14 can be used as reference data for analyzing

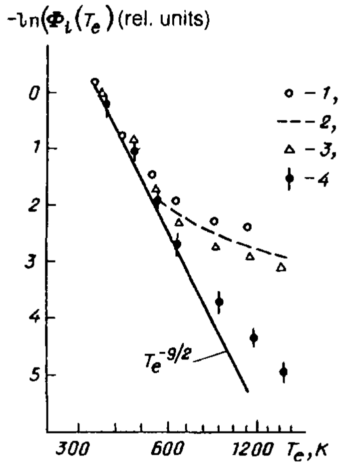

FIG. 14. Dependence of the intensities of spectral lines of the Xe atom on the electron temperature of a decaying He–Xe plasma at $p_{He} = 50$, $p_{Xe} = 0.01$ Torr, $n_e \approx 3\times 10^{11}$ cm^{-3}. 1–for the 7p level, 2–6p′, 3–6p, 4–9d.

the competition of the processes being discussed within the framework of certain models in the formation of the recombination flux of population of levels of the Xe atom. The setup of such experiments under conditions of the plasmas of active media might elucidate the mechanism of formation of the inversion.

In ionized mixtures of gases having close-lying excitation potentials, the reaction of excitation transfer occurs intensively with participation as donor of atoms B_m of the buffer gas in metastable states. In a decaying Ar–Xe plasma one can bring about conditions under which practically all the radiation flux of the plasma arises from this process.[112] Collisions Ar4s($^3P_2$) + Xe can play a substantial role in populating the laser 5d levels of the Xe atom in an Ar–Xe mixture.[46] Figure 3 illustrates the possibility of studying the competition of recombinative population and excitation transfer. Processing of the results of this experiment led to a conclusion important in understanding the kinetics of active media based on Ar–Xe mixtures: no more than 1/3 of the excitation-transfer flux goes into the laser $5d[3/2]_1^0$ level.

8. VIBRATIONALLY EXCITED IONS IN NOBLE-GAS PLASMAS

The problems of the kinetics of the populations of the vibrational levels of molecular ions, which were first touched upon in Refs. 15, 16, 113, and 114 in connection with analyzing the recombination mechanism of He_2^+ ions, do not lose their sharpness even today. They arise unavoidably in studying a plasma containing molecular ions. The latter are produced mainly in highly excited vibrational states in three-particle processes of conversion of atomic ions. Therefore the populations $[R_2^+(v)]$ take shape in the competition of processes of vibrational relaxation in collisions with particles of the plasma and dissociative recombination of $R_2^+(v)$. This implies that the analysis of the kinetics of molecular ions must be constructed on the basis of solving two independent problems: vibrational relaxation proper and elucidation of the dependence of the probability of recombination on the vibrational state of the ion. Allowing for the fact that the problem being discussed is general in character and is not restricted to the molecular ions of the noble gases, for which there are practically no reliable data, let us examine briefly the methods and theoretical models used for studying and describing the vibrational relaxation of small charged molecules.

8.1. Vibrational relaxation of molecular ions

V–T exchange of molecular ions with atoms substantially differs from the vibrational relaxation of neutral molecules. The slow relaxation intrisic to many neutral molecules is caused by the short-range repulsive potential and obeys the Landau–Teller model. The interaction of a molecular ion R_2^+ with an atom B has a different character, which involves the electrostatic interaction $V(r)\sim 1/r^4$ of the ion and the polarized atom. This interaction can lead, owing to the capture of the atom by the ion as the particles move in the polarization potential, to formation of a short-lived intermediate complex

$$R_2^+(v) + B \underset{\tilde{k}_c}{\overset{k_c}{\rightleftarrows}} (R_2^+B)^* \xrightarrow{k_r} R_2^+(v' < v) + B. \tag{19}$$

The decay of this complex is effected with a certain probability by relaxation of the energy of vibrational motion. In this model the rate constant of vibrational relaxation $k_{v,v}$, is determined by the capture constant $k_c = 2\pi e(\alpha/\mu)^{1/2}$ (μ is the reduced mass, and α is the polarizability of the atom), by the ratio of the probabilities of decay by the reverse channel, and by a process analogous to the predissociation of neutral molecules:

$$k_{v,v'} = \frac{k_c k_r}{\tilde{k}_c + k_r}. \tag{20}$$

The quantities $\tilde{k}_c$ and k_r are not known *a priori*. Therefore the vibrational relaxation via an intermediate complex can be analyzed only on the qualitative level. In a number of studies, e.g., Refs. 115–177, the authors resort to the statistical theory of decay,[118–123] within whose framework one can calculate the probability of the distribution of dissociation products with respect to the energy of vibrational, rotational, and translational motion. Thus, numerical calculations[115] of the reaction $NO^+(v=4) + Xe \rightarrow NO^+(v'\leqslant 4) + Xe$ yield the following distribution of probabilities over the numbers v': $P_0 = 0.46$, $P_1 = 0.3$, $P_2 = 0.17$, $P_3 = 0.007$, $P_4 = 0.004$. This example shows that the statistical theory predicts values of $k_{v,0}$ that do not differ strongly from the capture constant $k_c \approx 10^{-9}$ cm^3/s. However, this rule is not general. Actually the greatest difficulties arise in substantiating the statistical theory, rather than in applying it for calculating concrete systems. The theory assumes that during the lifetime of the complex a statistical redistribution of energy can occur over all the degrees of freedom. That is, this time in any case must exceed the vibration and rotation periods. The description of the dynamics of formation of the complex requires information on the interaction potentials of the colliding particles, which are generally lacking. Therefore it is expedient to draw conclusions on the mechanism of vibrational relaxation of concrete molecular ions on the basis of analyzing the experimental material.

In recent years a number of subtle experiments have been performed, which measured the rate constants of vibrational relaxation of the ions O_2^+,[117] N_2^+,[124] NO^+,[125] and CO^+ [116] in different atomic and molecular gasses. Molecular ions with a known distribution over v were created by using selective ion-molecule reactions or, as in the case of

TABLE VIII. Rate constants k_v of vibrational relaxation of O_2^+ ions ($v = 1$) in collisions with various partners. α is the polarizability of the atom or molecule, D is the binding energy of the intermediate complex, k_c is the polarization capture constant, and Z is the probability of loss of vibrational excitation upon collision (decimal exponent indicated in parentheses).

Atom or molecule	k_v, cm³/s	α, Å³	D, eV	k_c	Z
He	< 2(−15)	0,205	0,026	5,6(−10)	< 3,6(−6)
Ne	< 1,3(−14)	0,395	0,1	4,2(−10)	< 3,1(−5)
Ar	1(−12)	1,64	0,3	7,1(−10)	1,4(−3)
Kr	1,1(−11)	2,48	—	7,6(−10)	1,4(−2)
H_2	2,5(−12)	0,808	< 0,2	1,5(−9)	1,6(−3)
CO_2	1(−10)	2,59	0,42	8,7(−10)	0,11
SF_6	1,1(−10)	4,48	—	9,7(−10)	0,11

CO^+, by populating the required states of CO^+ with radiation of a frequency-tunable laser. Some results taken from Ref. 117 are shown in Table VIII. These data, as well as the analysis of a wider set of experimental material,[117] indicate a correlation of the rate constants k_v and the quantities α and D, and lead to the conclusion that V-T exchange in ion-atom and ion-molecule collisions occurs via formation of an intermediate complex if the polarizability of the atom or molecule exceeds the value $\alpha \approx 1$ Å³. Here the binding energy of the complex D proves to be greater than ≈ 0.1 eV. This conclusion enables one to use the information existing in the literature on the binding energies of complex ions (e.g., Ref. 126) for prediction of the efficiency of V–T exchange. Besides this, one can decide on the rates of vibrational relaxation on the basis of data on the rate constants of ion-molecule reactions.[68,127–129] Thus, correlation must exist between the efficiency of vibrational relaxation in the process (19) and the rate of the ternary process $R_2^+ + B + M \to R_2^+B + M$.[129]

As regards molecular ions in a noble-gas plasma, we should expect high rates of vibrational relaxation on the basis of the discussed material. For the Ar_2^+, Kr_2^+, and Xe_2^+ ions in their own gas, the atoms of which have high polarizability, this is evident even from the data of Table VIII. An experiment[66] to observe the photodissociation spectrum of Ar_2^+ ions at various argon pressures yields an estimate of the rate constant $k_v \gtrsim 10^{-11}$ cm³/s.

As regards He_2^+ ions in helium and Ne_2^+ in neon, the situation proves to be not so clear. On the one hand, there are no fundamental differences between He_2^+ and Ne_2^+ ions and the ions of the heavy noble gases, since in all cases an exchange reaction is possible, $R_2^+(v) + R \to R + R_2^+(v')$, which in all probability is accompanied by the removal of vibrational excitation.[68] On the other hand, experimental studies[62,130,131] have revealed considerable populations of vibrationally excited He_2^+ and Ne_2^+ ions that greatly exceed the equilibrium values (for He_2^+ by several orders of magnitude), even at gas pressures of tens of Torr. We note that precisely this circumstance makes it possible to observe the dissociative recombination of He_2^+ ions in a helium plasma.[131]

The discussed model representations, together with experimental data of the type of Table VIII, enable one to analyze the physical pattern of vibrational relaxation of molecular ions R_2^+ in R-B noble-gas mixtures. Here we can study the following situations:

1. The B atoms have a high polarizability (e.g., Xe_2^+ in argon or krypton). In this case V–T exchange can occur via the formation of an intermediate complex. That is, the rate constants can be of the order of $k_v \approx 10^{-11}$ cm³/s.

2. B = Ne or He. These atoms have a low polarizability. Therefore the collisions $R_2^+(v) + \mathrm{Ne}$ or $R_2^+(v) + \mathrm{He}$ correspond to the Landau–Teller model, rather than to formation of an intermediate complex. The rate constants of vibrational relaxation of Ne_2^+ ions in neon and He_2^+ in helium calculated by this model with account taken of the polarization attraction are of the order of magnitude of 10^{-15} cm³/s,[145] which coincides with the value of k_v for O_2^+ ions in He (see Table VIII).

In a plasma with a high degree of ionization, besides the discussed processes, a certain role can be played by inelastic collisions of vibrationally excited molecular ions with electrons:

$$R_2^+(v) + e \xrightarrow{k_e} R_2^+(v-1) + e. \tag{21}$$

The results of calculations[114,132] and experiment[52] show that, for transitions $v = 1 \to v = 0$ caused by the interaction of ions with thermal electrons, in order of magnitude we have $k_e \approx 10^{-7}$–10^{-8} cm³/s. If we take account of the fact that the probability of relaxation increases with increasing v, while the dissociative recombination of the molecular ions of the noble gases declines (see below), the important role becomes evident of collisions (21) in the kinetics of vibrationally excited ions. In plasmas of the heavy noble gases the process (21) can compete with relaxation in collisions with atoms when the degree of ionization is $n_e/[R] \gtrsim 10^{-5}$.

8.2. Recombination of vibrationally excited ions

Allowing for the physical nature of the mechanism of dissociative recombination, we can expect the manifestation of various dependences of the recombination probability on the vibrational state of the ion. Let us examine the different possible situations. The problem is solved relatively simply for recombination via any single channel with formation of excited atoms in concrete states R_i^* if we are dealing with a threshold mechanism. We shall assume that the distribution of populations $[R_2^+(v)]$ is described by the temperature T_v: $[R_2^+(v)] = [R_2^+(0)]\cdot\exp(-\hbar\omega/kT_v)$. Then by using Eq. (6) for the partial recombination coefficients we have:

$$\alpha_i(T_v, T_e) \sim \sum_v \exp\left(-\frac{\hbar\omega v}{kT_v} + \frac{\hbar\omega v}{kT_e}\right)\left\langle \Gamma_i \exp\left(-\frac{\varepsilon_{0i}}{kT_e} - S_i\right)\right\rangle. \tag{22}$$

In the case $T_v \ll T_e$ typical of a weakly ionized plasma Eq. (22) implies that the $\alpha_i(T_v)$ relationships are determined mainly by the Boltzmann factors $\exp(-\hbar\omega v/kT_v)$. If $kT_v \ll \hbar\omega$, the main contribution to the process comes from several deep vibrational levels of the ion. Conversely, in an equilibrium plasma ($T_v = T_e$), the decline in populations $[R_2^+(v)]$ is compensated by the decrease in the energy gap between the terms $\varepsilon_i(r)$ ($R_i^* + R$) and the levels v. Therefore a variation in temperature of the particles of the plasma does not alter the relative contribution of the different vibrational states of the molecular ion to the recombination flux via the ith channel.

In the case $\varepsilon_{vi} \approx \Gamma_i \approx kT_e$ or of crossing of the vibrational levels by the term $\varepsilon_i(r)$, the Breit–Wigner formula is inapplicable. Here model calculations furnish some information. Let us study the three types of crossings of the terms R_2^+ and $R_i^* + R$ shown in Fig. 15. Numerical solution of the problem[60] on the basis of the multichannel approximation of the quantum defect developed in Ref. 6 yields the following results. The increase in the temperature of the distribution T_v in the case of Fig. 15a leads, independently of the electron temperature, to a decrease in the rate of recombination, whereas for the curves of Fig. 15b and c it leads to a growth in the rate. We shall use this conclusion for analyzing the observations of the dependences $\alpha_\Sigma(T_v)$ of the recombination coefficients of the molecular ions of the noble gases. In the experiments of Refs. 133–136 to study dissociative recombination over a broad range of variation of the gas temperature (by the shock-wave method), a strong dependence was found of the quantity α_Σ on the gas temperature T_g: $\alpha_\Sigma \sim T_g^{-1.5}$ (here $T_e = T_g$). The only reason for this is the increase in the degree of vibrational excitation of the molecular ions with increasing T_g. Therefore the results of these experiments unequivocally show that the recombination coefficients α_Σ of the noble-gas ions have $\alpha_\Sigma(T_v)$ relationships of declining type. The analysis of the experiments of Refs. 137–139 performed under the assumption of V–T equilibrium leads to the conclusion of a sharp decline in the coefficients α_v with increasing v: $\alpha_1 \approx 0.3\alpha_0$. Spectroscopic experiment yields a similar result.[52] On this basis we can assume that the terms $\varepsilon_i(r)$ ($R_i^* + R$) that correspond to the most intense recombination channels are grouped near the bottom of the potential well of the R_2^+ molecular ions, and that in type of crossing they belong to the case of Fig. 15a.

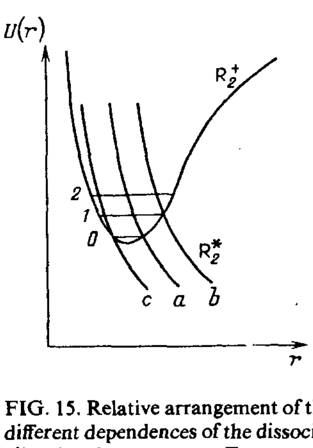

FIG. 15. Relative arrangement of the R_2^+ and R_2^* terms corresponding to different dependences of the dissociative-recombination coefficient on the vibrational temperature T_v.

In closing this section we should stress that the established dependence of the recombination coefficients α_Σ on the degree of vibrational excitation of the molecular ions is not general in character. Naturally, for systems having a high density of autoionization states, the coefficients α_Σ need not show a strong dependence on the vibrational state of the ions. This fact has been established by studying the dissociative recombination of a number of polyatomic ions,[140] and also N_2^+.[141] On the other hand, very simple molecular ions of the type of H_2^+,[7,23,142] He_2^+,[15,16] and H_3^+[143,144] can recombine efficiently only from vibrationally excited states.

9. DISSOCIATION OF MOLECULAR IONS

To analyze the role of molecular ions in the kinetics of charged and excited particles of a plasma, we need information on the ionic composition. Besides the mechanism that we have discussed of breakdown of molecular ions via the channel of dissociative recombination, under certain conditions in a plasma, also other processes occur that lead to a decrease in the density of molecular ions. These processes include the processes of dissociation in collisions of molecular ions with atoms

$$R_2^+ + R(B) \rightarrow R^+ + R + R(B), \tag{23}$$

with electrons

$$R_2^+ + e \rightarrow R^+ + R + e \tag{24}$$

and photons

$$R_2^+ + h\nu \rightarrow R^+ + R. \tag{25}$$

9.1. Dissociation in collisions with atoms

The thermal dissociation of homonuclear molecular ions (23) plays an appreciable role in shaping the properties of constricted discharges,[103] and determines the ionic composition of plasmas under shock-wave conditions, i.e., is manifested in objects having an elevated gas temperature.

The process of thermal dissociation is the reverse of the conversion of atomic ions in triple collisions. Therefore, by using the Saha relationship we can calculate the equilibrium densities of atomic and molecular ions as functions of the gas temperature. Such calculations were performed in Ref. 103, and their results are shown in Table IX. These data indicate the temperatures T_g above which thermal dissociation can be the main mechanism of breakdown of molecular ions. At $T_g \approx 5000$ K the rate constant of dissociation of ions, e.g., Ne_2^+, is of the order of 10^{-12} cm^3/s.[146] In such a plasma dissociative recombination proves to be a less efficient exit channel of molecular ions at degrees of ionization $n_e/[Ne] < 2\times10^{-5}$.

TABLE IX. Values of the temperature at which the densities of molecular and atomic ions of the different gases are equal.

log[R]	He	Ne	Ar	Kr	Xe
16	1530	910	740	780	650
17	1740	1060	870	900	740
18	2100	1250	1010	1050	860
19	2630	1500	1230	1250	1010

9.2. Dissociation of molecular ions by electrons in a plasma

Dissociative recombination is one of the two possible mechanisms of breakdown of molecular ions by electrons. The result of collision with an electron of high enough energy can be the dissociation of the molecular ion in (24). This process should be taken into account at energies of electrons exceeding the binding energy of the molecular ion $D \approx 1$ eV. Therefore the question of the competition of processes of dissociation and dissociative recombination is important for such objects as a gas-discharge plasma, the active media of excimer lasers, and electroionization lasers based on noble-gas mixtures.

Charge neutralization does not occur in the reaction (24). However, in a number of cases the dissociation of molecular ions by electrons can lead to a substantial change in the ionic composition and to retardation of the rate of bulk losses involving the recombination of molecular ions.

In contrast to dissociative recombination, which has been widely studied, both experimentally and theoretically, considerably less attention has been paid to the process (24). For H_2^+ ions, Refs. 147 and 148 have calculated the dissociation cross sections, which proved to agree well with the measurements in beam experiments.[149,150] In Ref. 105 formulas were derived for the dissociation cross sections of the high vibrational states of BR^+ ions owing to direct exchange of the energy of the incident electron with the energy of relative motion of the nuclei. The problem of the dissociation of homonuclear molecular ions of the noble gases was studied in Ref. 151. According to these calculations under equilibrium conditions and at $T_v \approx 300$ K, the process (24) is more probable than dissociative electron capture at energies $\varepsilon \approx 4$–5 eV for Ne_2^+ ions, 3–4 eV for Ar_2^+, 2–3 eV for Kr_2^+, and ≈ 1.5 eV for Xe_2^+.

The only experimental study as yet of the dissociation of molecular ions by the electrons of a plasma was performed in Ref. 152. An uncomplicated experiment was set up in this study in which the method discussed above of the relaxational response of the emission of the decaying plasma to pulsed heating of the electron gas was used to measure the dependence of the total rate $n_e(\alpha_\Sigma(T_e) + k_d(T_e))$ (k_d is the rate constant of dissociation) of breakdown of Xe_2^+ molecular ions due to both dissociative recombination and dissociation in collisions of Xe_2^+ with electrons. The results of the experiment[152] are shown in Fig. 16 together with the data on the value of $\alpha_\Sigma(T_e)$ obtained by the method of microwave heating of the electrons.[14] We see that the constant $k_\Sigma = \alpha_\Sigma + k_d$ undergoes a sharp increase at $T_e \gtrsim 1$ eV owing to "turning on" of the dissociation mechanism at high electron temperatures. The dashed curves in Fig. 16 show the approximation of the experimental data of Ref. 152 by the sum $k_\Sigma = \alpha_\Sigma(T_e) + k_d(T_e)$ as constructed by using the least squares method. Here the Breit–Wigner formula (3) in the approximation of a single autoionization state was used to find the analytic $\alpha_\Sigma(T_e)$ relationship, while the dissociation constant was calculated from the data of Ref. 151 on the energy dependence of the cross section of the process. The data shown in Fig. 16 imply that the results of measurements in the region $T_e \gtrsim 1$ eV are described well by the calculations of Ref. 151. Here the main contribution to the dissociation process comes from transitions between terms of the molecular ion $\mathrm{I}(1/2)_u \to \mathrm{I}(1/2)_g$ and $\mathrm{I}(1/2)_u \to \mathrm{II}(1/2)_g$ (Fig. 17).

We note that, in the theoretical sense, the calculation of the dissociation cross section of Xe_2^+ ions is very difficult owing to the need to take account of the strong spin-orbital interaction. Therefore the agreement of the experimental and calculated values using the cross sections from Ref. 151 of $k_d(T_e)$ thus give grounds for hoping that, even in the case of the lighter noble gases, the calculations of Ref. 151 can be used for estimating the rates of dissociation of molecular ions by electrons.

Let us estimate the influence of dissociation on the ionic composition of a plasma of a noble-gas mixture. Here we shall consider the case $[R] \approx 10^{-2}$ $[B]$, $[B] = 10^{20}$ cm^{-3}, which is of interest on the level of analyzing the recombination population of the excited levels of atoms in active media. According to (15) and taking account of the dissociation process, we have the following expression for the density of molecular ions:

$$[R_2^+]/[R^+] = \beta_R[R][B]/(\alpha_\Sigma + k_d)n_e.$$

The best generation parameters are attained using combination (electroionization) pumping of an Ar–Xe mixture.[44]

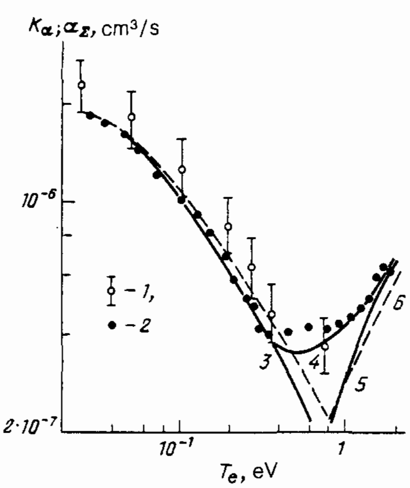

FIG. 16. Rate constants of breakdown of Xe_2^+ molecular ions by electrons. *1*–$\alpha_\Sigma(T_e)$ by the data of Ref. 14, *2*–$k_\Sigma(T_e)$ by the measurements of Ref. 152, *3*, *4* and *5*, *6*–recombination coefficient $\alpha_\Sigma(T_e)$ and rate constant of dissociation for calculated (*3*, *5*) and Maxwellian (*4*, *6*) energy distribution functions of the electrons.

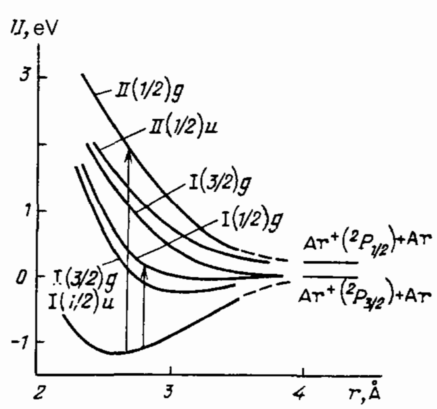

FIG. 17. Terms of the molecular ions of the noble gases based on the example of Ar_2^+.

The electric field intensities of a non-self-sustaining discharge typical of this system amount to 1–3 Td (which correspond to mean electron energies of several eV[153]), while the degree of ionization is $n_e/[\mathrm{Ar}] \approx 10^{-5}$. In such a plasma, as is implied by the data shown in Fig. 16, the breakdown of Xe_2^+ ions is due to their dissociation (the constant k_d exceeds α_Σ by an order of magnitude), while here $[Xe_2^+]/[Xe^+] \ll 1$. At the same time, in the kinetic schemes of active media, even in the most detailed of them,[45–47,107] one considers a single channel of exit of molecular ions–dissociative recombination. This estimate shows that the dissociation of molecular ions by electrons plays a substantial role in shaping the ionic composition of the plasma of active media based on noble-gas mixtures, and hence, in shaping the recombination flux of population of the excited levels of atoms.

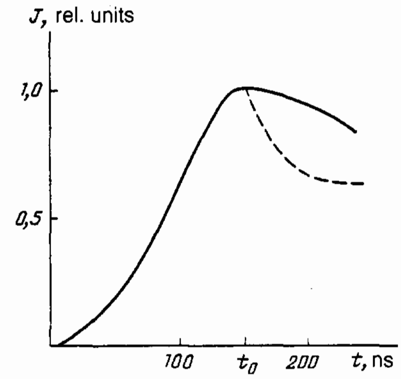

FIG. 19. Trend of variation of the intensity of the 8280-Å line of the Xe atom (6p–6s transition) upon irradiation of a cuvette for $t > t_0$ with a N_2 laser pulse (dashed line) in the experiment of Refs. 158 and 159.

9.3. Photodissociation of molecular ions

The interest in the process of photodissociation (25) of molecular ions arose in connection with analyzing the losses of working radiation in the active media of excimer lasers.[154–157] Just as in the case of dissociation in collisions with electrons, the efficiency of the process is determined by the probabilities of the transitions $\mathrm{I}(1/2)_u \to \mathrm{I}(1/2)_g$, $\mathrm{II}(1/2)_g$. Figure 18 shows a typical form of the dependence of the cross section $\sigma(\lambda)$ of photodissociation on the wavelength of the radiation. We see that for the $\mathrm{I}(1/2)_u \to \mathrm{II}(1/2)_g$ transition the cross section can reach values $\sigma \approx 5 \times 10^{-17}$ cm^2. Such high probabilities of photoionization have the result that, even at relatively low powers of laser radiation, an appreciable fraction of the molecular ions contained in the active medium is broken down. Figure 19 demonstrates the effect of photodissociation upon illuminating a cuvette containing ionized xenon with the radiation of an XeF or N_2 laser ($\lambda \approx 3500$ Å, power ≈ 10 MW/cm^2).[158,159]

The photodissociation spectrum is determined both by the arrangement of the terms of the molecular ion and by the population distribution over the vibrational levels. In a number of studies, e. g., Refs. 66 and 157, this has been used to analyze the character of the vibrational distribution of molecular ions. Thus, the use of the phenomenon of photodissociation for diagnostic purposes substantially expands the potentialities of spectroscopic study of plasmas containing molecular ions.

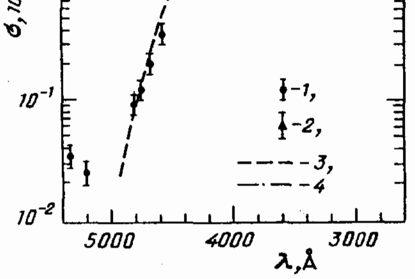

FIG. 18. Photodissociation cross section of Kr_2^+ molecular ions. 1–data of Ref. 157, 2–Ref. 156, 3–Ref. 163, 4–Ref. 155.

The set that we have discussed of alternative reactions to dissociative recombination, together with their quantitative characteristics, offers a rather complete view of the mechanisms of breakdown of molecular ions, and enables one to point out the fundamental processes that determine their kinetics under certain concrete conditions.

10. USE OF THE DISSOCIATIVE MECHANISM OF POPULATING EXCITED LEVELS OF ATOMS TO STUDY COLLISIONAL PROCESSES IN A WEAKLY IONIZED PLASMA

As the material of the preceding sections implies, the distribution of the dissociative-recombination flux $F_i/F_\Sigma = \Sigma_v \alpha_{vi} g_v/\alpha_\Sigma$ over the excited levels of the atoms depends only on the degree of vibrational excitation of the molecular ions. In a weakly ionized gas this distribution is stabilized in the formation of a distribution close to equilibrium of the populations $[R_2^+(v)]$ over the levels v owing to V–T exchange in the collisions of the molecular ions with atoms. In the noble gases with a high rate of vibrational relaxation (constant k_v of the order of 10^{-11} cm^3/s), V–T equilibrium is reached at pressures of fractions to units of Torr.[66] Elevation of the pressure of the gas (or gas mixture) beyond the stated value leads to predominance of molecular ions in the ionic composition of the plasma and to increase in the absolute value of the recombination flux associated with them, which wins over all other processes of formation of excited atoms. Thus molecular ions give rise to an intense recombination flux independent of the density of neutral particles, with a fixed distribution of it over the excited levels of the atoms. This unique property of the dissociative mechanism can be used to investigate the little-studied processes of "mixing" of excited levels in atom-atom collisions:

$$R_i^* + R(B) \to R_k^* + R(B),$$

since the variation of the relative populations of the atoms $[R_i^*]/[R_k^*]$ upon increasing the densities of neutral particles is due only to these processes. The design of the experiments[53,57,79] to observe the deformation of the population distribution over the excited levels of the atoms in He-Ne, He-Ar, and He–Xe mixtures in the controllable dissociative recombination of afterglows enabled discovery of interesting effects arising from collisional processes and playing an important role in the kinetics of excited atoms in plasmas containing molecular ions. Some results of the experiments are demonstrated in Figs. 20 and 21. It is convenient to present the experimental data in the form of ratios of the total quantum fluxes $\Phi_\Sigma^{nl}/\Phi_\Sigma^{n'l'}$ in transitions from levels of different configurations nl. This approach enables one to analyze the role of intermultiplet transitions, since intramultiplet "mixing" has no effect on the ratios of total fluxes of quanta. Let us study first of all the influence of the density [Xe] on the population $[Xe_i^*]$. The rate constants of $[Xe_i^*] \to [Xe_k^*]$ transitions are known.[160–162] Therefore the results of such an experiment can be used to test the feasibility of the approach being discussed. We see from the data presented in Fig. 20 that, when $P_{Xe} > 1$ Torr, one observes a sharp decline (almost an order of magnitude) in the ratio $\Phi_\Sigma^{7p}/\Phi_\Sigma^{6p}$. This character of the dependence of the ratio $\Phi_\Sigma^{7p}/\Phi_\Sigma^{6p}([Xe])$ on the density [Xe] is also implied by a comparison of the data of Refs. 160–162 on the rate constants of collisional quenching of the levels of the 7p and 6p configurations.

When $p_{Xe} < 1$ Torr the collisional processes in the system of 7p and 6p levels are not noticeable against the background of radiative transitions. Under conditions of dissociative population, the increase in the ratio $\Phi_\Sigma^{7p}/\ \Phi_\Sigma^{6p}$ observed in the experiment of Fig. 20 can be associated only with a decline in the degree of vibrational excitation of the Xe_2^+ ions and a concomitant change in the relative recombination fluxes $F_\Sigma^{7p}/F_\Sigma^{6p}$. Starting with this hypothesis and using the data of Fig. 20 in the pressure region $p_{Xe} < 1$ Torr, we can obtain the following estimate of the rate constant of vibrational relaxation of Xe_2^+ ions in xenon:[57] $k_v \approx 3\times 10^{-11}$ cm^3/s, which agrees with the views on the rates of V–T exchange of heavy molecular ions in their own gas. Of special interest are the data of Fig. 20 on the dependence of the ratio $\Phi_\Sigma^{7p}/\Phi_\Sigma^{6p}$ on the density of helium atoms, since information on inelastic collisions of Xe^+ and He is lacking. The analysis[57] of the data shown in Fig. 20 yields the following estimate of the rate constants of collisional quenching of blocks of 7p and 6p levels of the xenon atom by helium owing to intermultiplet transitions (for the 6p levels, 6p–6s): $k_{7p} \approx 5\times 10^{-12}$, $k_{6p} \approx 2\times 10^{-10}$ cm^3/s. This indicates a

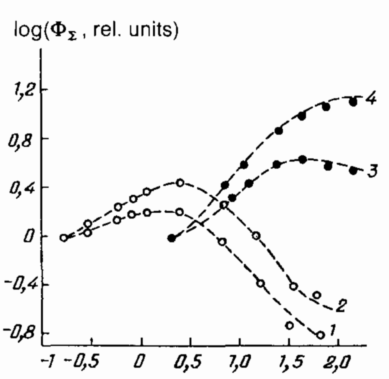

FIG. 20. Dependence of the ratio of fluxes of quanta emitted by the 6p′ (*1*, *3*) and 7p (*2*, *4*) levels to the flux of quanta in the 6p-6s transitions of the xenon atom on the pressure of helium and xenon.

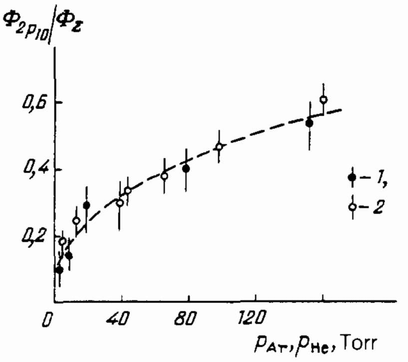

FIG. 21. Dependence of the ratio of fluxes of quanta emitted from the $2p_{10}$ levels of Xe (*1*) and Ar (*2*) atoms to the flux of quanta in the $(n+1)$p–$(n+1)$s transitions of the stated atoms on the pressure of buffer gas in decaying plasmas of He–Ar and Ar–Xe mixtures.

large role of inelastic collisions in shaping the populations of Xe(6p) in plasmas of He–Xe mixtures having a high density of helium. Since a He–Xe mixture is used as the active medium of recombination lasers, we can conclude that, under the conditions typical of these media (atmospheric and higher presure of helium), the lifetimes of the 6p levels of the xenon atom, which are the lower laser levels for 5d–6p transitions, prove to be of the order of 10^{-10} s, and their depletion is caused exclusively by collisional quenching.

Figure 21 demonstrates the curious result of a similar study in He–Ar and Ar–Xe mixtures, which shows that, at a pressure of buffer gas $p_B \gtrsim 200$ Torr, more than 60% of the entire flux of quanta emitted by the decaying plasma comes from transitions from the $2p_{10}$ levels of argon and xenon atoms. Here half of this flux is transported in the 9123-Å line of Ar and 9800 Å of Xe ($2p_{10} \to 1s_5$ transitions). These observations show the possibility of using the selective character of the dissociative mechanism of recombination of molecular ions in combination with intramultiplet collisional "mixing" of excited levels to create media having an extremely high concentration of radiation in one spectral transition.

Let us briefly examine the situation in a He–Ne plasma. This mixture, with admixtures of an easily ionized gas, is used as the active medium of recombination Penning lasers based on the 3p–3s transitions of the neon atom. The best generation parameters are obtained in the $2p_1$–$1s_2$ transition, $\lambda = 5852$ Å. Study of the kinetics of the excited neon atoms in the recombinatively nonequilibrium He–Ne plasma reveals an increase in the relative intensity of the 5852-Å line with increasing helium pressure.[164,165] The authors explain this increase by selecive population of the $2p_1$ level upon dissociative recombination in the He–Ne plasma. As the material being discussed implies, this requires either resorting to the kinetics of the populations of the vibrational levels of the Ne_2^+ ion or adducing a process of dissociative recombination of the heteronuclear ion $HeNe^+$ and an associated population of the $2p_1$ level. However, an explanation of the effect can be found in another context, namely, in a comparative analysis of the probabilities of collisional quenching of the $2p^53p$ levels of the neon atom by neon and helium. There are no literature data on the quenching of the $Ne(2p_1)$ level of the neon atom by helium, while the results of study of the kinetics of $Ne(2p_1)$ atoms in neon plasmas diverge by more than an order of magntiude. Thus, Refs.

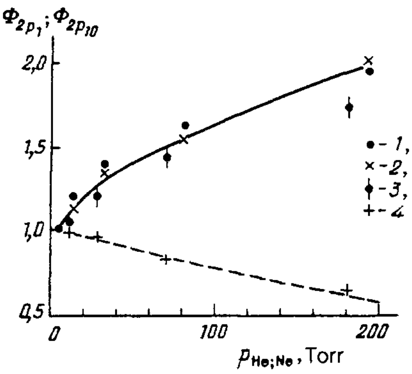

FIG. 22. Dependences of the fluxes of quanta from the $2p_1$ (*2, 4*) and $2p_{10}$ (*1, 3*) levels of the neon atom, referred to the total flux in 1s–2p transitions, to the pressure of helium and neon. $p_{Ne} = 2$ (*1, 2*), $p_{He} = 2$ (*3, 4*) Torr.

166–169 give the following rate constants: $(0.71 \pm 0.13)\cdot 10^{-11}$, $(1.6 \pm 2)\cdot 10^{-11}$, $(2 \pm 3)\cdot 10^{-10}$ and less than 1.5×10^{-12} cm^3/s. Therefore let us turn to the results of an experiment[53] to study the distribution of populations of excited neon atoms in a decaying He–Ne plasma under conditions of dominant dissociative recombination of Ne_2^+ ions. Figure 22 shows the data on the dependences of the relative fluxes of quanta emitted by the $2p_1$ and $2p_{10}$ levels of the neon atom on the pressures of helium and neon. These data imply that quenching of the $2p_1$ level by helium is considerably less efficient than that of the group of other levels of configuration $2p^53p$. This conclusion agrees with the calculations[170] of the interaction potentials of Ne*(3p) + He. According to the data of Fig. 22, we can estimate the effective quenching constant of the block of $2p_2$-$2p_9$ levels by helium owing to intermultiplet transitions: $k \simeq 10^{-11}$ cm^3/s. We should emphasize that the change shown in Fig. 22 in the relative populations of the levels being discussed is caused only by processes of collisional "mixing" of the excited levels, since these changes take place at gas pressures considerably exceeding those necessary for establishment of V-T equilibrium.

We note that in an He–Ne plasma, just as in He–Ar and Ar–Xe mixtures, the effect is manifested of collisional "population" of the lower level $2p_{10}$ in the $2p^53p$ system owing to intramultiplet "mixing" by the buffer gas. Here, under conditions of high enough helium pressure $p_{He} \gtrsim 200$ Torr, more than 30% of the flux of quanta emitted by the decaying plasma is concentrated in the 7032-Å line ($2p_{10}$-$1s_5$).

11. CONCLUSION

The studies of recent years have substantially expanded the views of the dissociative recombination of molecular ions with electrons as a multichannel process. The data on the distribution of the recombination flux over the exit channels of the process obtained over a broad range of variation of the temperature of the electron gas enable us to solve the problem, important in practice, of constructing the level-by-level kinetics of the excited atoms in plasmas containing molecular ions. These data, together with the results of study of the competition of dissociative recombination with alternative mechanisms of neutralization of charged particles and formation of excited atoms make it possible to take the following fundamental step: to proceed from studying dissociative recombination as an elementary process in a plasma to analyzing rather complex plasma systems. Appreciable advances have been noted also in understanding the mechanisms of realization of the populations of vibrational levels of molecular ions, which are a connecting link in the chain of processes of formation and breakdown of molecular ions in plasmas; the role is clarified of heteronuclear molecular ions of the noble gases in shaping the optical properties of a recombinatively nonequilibrium plasma. On the whole, all this allows us to expect progress in creating adequate kinetic models of plasmas of the noble gases and their mixtures.

[1)] Here we understand highly excited levels to be the levels i of atoms R_i^* lying above the ground vibrational level of the corresponding molecular ion R_2^+.

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