POSSIBLE USE OF RECOMBINATION FOR SELECTIVE EFFECTS ON THE POPULATIONS OF EXCITED ATOMIC AND IONIC LEVELS. I

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Studies of recombination in a plasma of moderate density are reviewed. Conclusions are drawn regarding the possible use of ternary recombination to produce elevated populations of high-lying excited atomic and ionic levels and regarding the conditions in a gas-discharge plasma which provide the sharpest differences among these populations, with the higher-lying levels populated predominantly. There are additional recombination processes which could produce elevated populations in certain cases in the high-lying excited levels of atoms and ions having displaced levels: radiationless two-particle recombination and ternary recombination of ions formed by the stripping of an electron from an inner shell.

The possible production and use of selective population of excited atomic and ionic levels is of considerable interest in connection with many problems of plasma diagnosis and quantum electronics. Below we analyze the use of recombination processes for this purpose.

At moderate plasma densities ternary recombination must be taken into account. Belyaeva and Budker [1] discussed recombination leading to the formation of an atom in its ground state and in which the third particle is an electron. Such a recombination process, which involves the transfer of much energy (on the order of the ionization energy of the atom) to a third particle does not readily occur. Studies of recombination involving the formation of atoms in high-lying excited states and accompanied by the transfer of a relatively small energy to a third particle have been reported recently. As might be expected, this type of recombination is more efficient. D'Angelo [2] was the first to show that recombination involving the formation of excited atoms in a hydrogen plasma (especially with the main quantum numbers p = 5, 6) occurs much more efficiently than recombination to the ground state. A calculation of pure recombination – recombination involving the formation of an atom in its ground state – taking into account recombination through all possible excited states yields much higher recombination coefficients than those found if these excited states are not taken into account. This result means that recombination directly to the ground state of the atom is essentially negligible. In treating atomic transitions from atomic states to the ground state, D'Angelo took into account spontaneous transitions and ionization of excited atoms due to collisions with electrons. Drawin [3] wrote the coefficient α for pure recombination in a manner consistent with D'Angelo's study:

$$\alpha = \alpha_{\text{rad}} + \left\{ Q_{3,1}(T_e) + \sum_{p=2}^{p^*} \frac{\sum\limits_{q=1}^{p-1} A_{pq} Q_{3,p}(T_e)}{n_e K_{p,c}(T_e) + \sum\limits_{q=1}^{p-1} A_{pq}} \right\}, \tag{1}$$

where α_{rad} is the radiative-recombination coefficient; T_e and n_e are the electron temperature and density; $Q_{3,p}$ is the effective cross section for ternary recombination to state p; A_{pq} is the probability for the spontaneous $p \to q$ transition; $K_{p,c}(T_e)$ is the effective cross section for the ionization of an atom in state p; and p^* is the main quantum number of the highest-lying state which must be taken into account ($E_{p^*} \sim \kappa T$).

In refined calculations [4-6], transitions between excited states due to collisions with electrons were also taken into account. Simultaneous account of transitions between excited states due to collisions with

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electrons and of spontaneous radiation as well as of electron-collision ionization of excited atoms is possible only statistically because of the interrelationships among these processes, which cannot be treated separately. Coefficient α cannot be described in a simple graphic manner. Since the recombination rate is governed by the lifetime of the excited states, α turns out to be a complicated function of the electron density, the particle energy distribution, and the conditions for the emission of radiation. The particle energy distribution for an optically thin layer has been found from the system of equations made up of the balance equation for each of the excited states:

$$\frac{dn_{p}}{dt} = -n_p\{n_e[K_{p,c}+\sum_{q\neq p}K_{p,q}]+\sum_{q<p}A_{p,q}\}+n_e\sum_{q\neq p}n_q K_{q,p}+\sum_{q>p}n_q A_{qp}+n_e n^+(n_e Q_{3,p}+\alpha_{\mathrm{rad}},p).$$

The last term takes into account the appearance of excited states p due to ternary and radiative recombination. A Maxwell velocity distribution was adopted for this calculation. Under the assumption that recombination occurs slowly in comparison with the time between electron conditions, the condition $(dn_p/dt) = 0$ was adopted. In a further simplification adopted for solving the system of equations it was assumed that there was a Boltzmann distribution among the high-lying excited states, since there is little radiation from these states, and account need be taken only of the upper limit on the number of states, p^*. Finally, the assumption $N_0 = 0$ was made, corresponding to the assumption that atoms which have descended to the ground state participate no further in collisions. This system of equations was solved [4-6] for the electron flux (dn_e/dt) descending to the ground state, which governs the pure-recombination coefficient. Here the coefficient α was called the "coefficient for collisional-radiative recombination." The values of α calculated on a computer for a hydrogen plasma are shown in Table 1.

In an effort to determine the effect of the structure of the atomic levels on this coefficient, an analysis was made of the case in which the ground state is treated as the first excited state of the hydrogen atom; this level structure corresponds to an alkali metal atom (the ground and first excited states are close together). It was found that α is relatively insensitive to the structure of singly charged ions.

These calculations were very complicated, requiring knowledge of many atomic constants, not involving an analytic expression for α, and using the classical cross sections found by Grizinsk for transitions between excited states (the Grizinsk cross sections were found under the assumption that the energy transferred in the collision is large in comparison with the electron energy; low-energy transfer is important during recombination). Furthermore, the computer solutions of the system of the equations prevented evaluation of the roles of the individual excited states in the redombination.

In a study of decaying H and He plasmas ($n_e \sim 10^{13}$ cm^{-3}), Hinnov and Hirschberg found experimental data confirming well to the calculations of [4-6]. There have been other experimental verifications. The errors in the cross sections used apparently lie within the experimental error.

A simple and graphic method is the narrow-region method proposed by Byron [8] for evaluating the coefficient for ternary collisional-radiative recombination. Byron assumed that the ternary-recombination coefficient is governed by the rate of passage through the "narrowest" energy gap $p^*\to p^*-1$, which characterizes the minimum deexcitation of level p^* due to collisions and radiation:

$$\alpha_{\mathrm{tr}} = \left[A^{p^*}+n_e K_{p^*,p^*-1}+\sum_{q=p^*+1}^{\infty}\sum_{p=1}^{p^*-1}A_p^q n_q^0\right]\frac{n_{p^*}^0}{n_e^2}.$$

This method is based on the different behavior of the probability for level deexcitation due to collisions and due to radiation involving a change in p (as p increases, the probability for deexcitation through collisions increases, while that for deexcitation through radiation decreases).

The quantity A^{p^*} represents the rate at which the level p^* is deexcited through radiation; for the hydrogen atom, taking into account the averaging over internal quantum numbers l with an account of the associated statistical weights, we find that

$$A^{p^*} = 166\cdot 10^8\frac{1}{p^{4.5}}\,\mathrm{sec}^{-1}.$$

The quantity $n_e K_{p^*,p^*-1}$ represents the rate at which the level is deexcited due to collisions with electrons. The third term gives the contribution of radiative processes from levels $p > p^*$ directly to levels $p < p^*$. As a rule, this term is unimportant. The quantities n_q^0 and $n_{p^*}^0$ are the equilibrium populations of the highly excited states having $q \geq p^*$; these populations obey the Saha equation. For hydrogen atoms, we have $n_q^0 = q^2 n_e^2 (2\pi\hbar^2/m\kappa T_{el})^{3/2}\cdot T^{-3/2}\exp(E_q/\kappa T_{el})$. Evaluation of α_{tr} from this relation yields values of $\alpha = \alpha_{tr} + \alpha_{rad}$

which agree well with the values found in [4]. The transition $p^* \rightarrow p^*-1$ is singled out on the basis of the strong effect of the energy gap on the probability for collisional processes. States having $p > p^*$ make essentially no contribution to recombination because of the high ionization probability. Practical use of the equation proposed for α requires an estimate of p^*, for which the corresponding deexcitation rate is minimal. It was shown that α can be evaluated within a coefficient γ which varies from 1 to 1/4, depending on how clearly the deexcitation minimum is defined. Although a special method was used to evaluate α for a hydrogen plasma, this method was recommended for evaluating α for other atoms. The properties of the particular atom enter through E_{p^*}, the constants, and the effective cross sections.

The narrow-region method for describing recombination was applied in [9] to a low-temperature plasma; Biberman et al. [10] have reported a series of corresponding theoretical studies. Here, as in previous studies, recombination has been treated as a downward diffusion of electrons in energy space. The discrete nature of the levels, the actual conditions on the radiation emission, and possible deviation from the Maxwell distribution (function F_p) were taken into account. In taking into account the opposite flux of electrons, responsible for the ionization ($n_1 n_e \beta$) under the conditions of a steady-state low-temperature plasma, one can speak of a narrow region, taking into account by Byron. Taking into account the electron flux $j = n_1 n_e \beta - n_e n^+ \alpha$ in energy space, introducing the reduce populations $Y_p = (n_0/n_p^0)$ of the excited levels, and introducing the electron densities $Y_e = (n_e/n_e^0)$ (where n_p^0 and n_e^0 are the equilibrium values of n_p and n_e given by the Saha equation), Biberman et al., found

$$Y_1 - Y_e^2 = \sum_{p \geq 1}^{p^*} \frac{j\, n_p^0}{F_p K_{p,\,p+1}(T_e)}.$$

This equation can be used to evaluate the contributions of various levels to the difference between the relative populations of the ground level and the excited level p^* for which we have $Y_{p^*} = Y_e^2$.

The populations of the highly excited levels having $p > p^*$ vary slightly since they are at equilibrium with the continuum. Lower-lying levels, near the ground level, may be at equilibrium with it. Intermediate levels are characterized by a rapid change in population; these levels constitute the narrow region for the recombination process. In contrast with the Byron study, the narrow region here can be thought of as a set of energy levels. The rate at which the narrow region is passed determines α. Evaluation of the position of this narrow region yields $\Delta E = ((3/2)T_e - 7/2T_e)$ (reckoned from the ionization energy). At low temperatures the narrow region moves toward the highly excited states, so the levels can be treated as being hydrogen-like. At high temperatures the region shifts toward lower levels by an amount $E_1 - E_2$.

Biberman et al. [9] found analytic expressions for α both for these limiting cases and for a broad temperature range; for the broad temperature range, α can be written as

$$\alpha = 4.3 \cdot 10^{-32} (R_y/T_e)^{9/2} \left[1 + \frac{\Sigma_i}{g_1} \left(\frac{\Delta E_1}{T_e}\right)^{1+b} (R_y/T_e)^{3/2} \exp(-E_2/T_e) + (13.3a)^{-1}\right]^{-2} \text{cm}^6/\text{sec}$$

for $T_e \leq 0.07 \Delta E_1$ we have $a = 3.2 \cdot 10^{-2}$ and $b = 4/9$, while for $T_e \geq 0.07 \Delta E_1$ we have $a = 0.25$ and $b = 5/6$. Analysis of these expressions for α led to the conclusion that at low T_e ($T_e < 6000$°K) the coefficient α is essentially independent of the nature of the atom. At higher temperatures, the properties of the atom are reflected through the gap $E_1 - E_2$ and through Σ_i/g_1. Calculation of $\alpha = f(T_e)$ for H, He, K, and Cs yields α values agreeing well with the Bates calculations (for H), experimental data (H, He) [7], and data calculated for (Cs) [11] at low temperatures. At these temperatures the nature of the atom is of only minor importance. At higher temperatures there are discrepancies among the α values calculated by different investigators, apparently traceable to the different cross sections used. The more complicated case in which the radiation emission must be taken into account was also analyzed. As was mentioned above, the rate of radiative transitions falls off rapidly with increasing p, while the rate of collisional transitions increases. This circumstance allows the entire energy range to be divided into two regions: $E > E_R$ (corresponding to radiative recombination) and $E < E_R$ (collisional recombination). At low T_e, level E_R lies below the narrow region ($E_R \geq 7/2T_e$), and the radiation is inconsequential, since the recombining electron spends most of its time passing through the highly excited states, and we have $\alpha = f$ (collisional processes): $\alpha = \alpha_{tr} + \alpha_{rad}$. At high temperatures, E_R falls in the narrow region, and radiation strongly affects the value of α. Collisional and radiative processes must both be taken into account. An expression was proposed for α for this case.

TABLE 1

p	E (eV)	10^{12} cm^{-3}		10^{13} cm^{-3}		10^{14} cm^{-3}	
		4000° K	8000° K	4000° K	8000° K	4000° K	8000° K
2	3,40	$4{,}6\cdot10^3$	$1{,}0\cdot10^3$	$2{,}0\cdot10^6$	$2{,}4\cdot10^5$	$1{,}7\cdot10^9$	$1{,}1\cdot10^8$
3	1,51	$1{,}8\cdot10^4$	$3{,}2\cdot10^3$	$1{,}1\cdot10^7$	$1{,}2\cdot10^6$	$3{,}8\cdot10^9$	$2{,}9\cdot10^8$
4	0,85	$6{,}6\cdot10^4$	$1{,}0\cdot10^4$	$1{,}6\cdot10^7$	$2{,}2\cdot10^6$	$2{,}2\cdot10^9$	$2{\cdot}8\cdot10^8$
5	0,54	$1{,}1\cdot10^5$	$2{,}1\cdot10^4$	$1{,}6\cdot10^7$	$2{,}8\cdot10^6$	$1{,}7\cdot10^9$	$3{,}0\cdot10^8$
6	0,38	$1{,}4\cdot10^5$	$3{,}0\cdot10^4$	$1{,}6\cdot10^7$	$3{,}5\cdot10^6$	$1{,}6\cdot10^9$	$3{,}6\cdot10^8$

Biberman et al made an important contribution in deriving expressions for α for the general case, which can be used to trace the effect of T_e, the nature of the atom, the radiation emission, and the deviation of the electron distribution from a Maxwell distribution on the value of α. Significantly, these expressions for α were reduced to a simpler form suitable for numerical calculations for various atoms on the basis of such simple atomic properties as E_1-E_2, E_2, and Σ_i/q_1. Although the calculations were simplified, they give quite reliable results for recombination in a steady-state low-temperature plasma in the ionization regime.

Studies of the atomic distribution with respect to excited states in a nonequilibrium plasma are interesting in connection with the topic of this review. Bates and Kingston [12] and McWhirter and Hearn [13] analyzed the populations of excited states of hydrogen atoms and hydrogen-like ions, respectively, in a nonequilibrium plasma. Taking into account the linear dependence of the excited-state populations on the ground-state population, they wrote reduced populations in the form $Y_p = r_0(p) + r_1(p)Y_1$. Here the coefficients $r_0(p)$ and $r_1(p)$ are complicated functions of T_e and n_e and the structure of the atomic states. The $r_0(p)$ and $r_1(p)$ values which they calculated for hydrogen and hydrogen-like ions in an optically thin plasma for various T_e and n_e, taking into account all collisional and radiative processes, are shown in the accompanying Table 1. Setting $r_1(p) = 0$, i.e., treating recombination alone, we can determine the population distribution among excited states due to recombination.

Table 1 shows n_p values which we calculated from $(n_p/n_p^0) = r_0(p)$ for $p = 1$–6; $n_e = n^+ = 10^{12}$, 10^{13}, and 10^{14} cm^{-3}; and $T_e = 4000°$ and 8000°K. We see that during recombination the most favorable conditions for the production of sharp population differences among the excited states of H atoms, with the higher-lying states populated predominantly, are $T = 4000$°K and $n_e = 10^{13}$ cm^{-3}.

Vorob'ev [14] evaluated the analogous coefficients $r_0'(p)$ and $r_1'(p)$ $[Y_p = n_e^2 r_0'(p) + r_1'(p)]$ for H atoms, taking only collisional processes into account; these results were formulated as $Y_p = f(E)$ dependences for three values of T_e and for $Y_e^2 = 10^2$ and 10^{-2}. It was found that in a hydrogen plasma in the recombination regime sharp population differences can be produced with the higher states populated predominantly. These results can also be used for an optically dense plasma, since in this case radiative transitions will be balanced by radiation absorption.

Drawin [15] analyzed the effect of radiation absorption on the population distribution among various states of H atoms. The population distribution was found by solving the system of equations taking into account, in addition to the processes treated by Bates, Kingston, and McWhirter, processes due to radiation absorption. The following terms were added to the equations for (dn_0/dt):

$$\sum_{q<p} n_p (1-\Lambda_{p,q}) A_{pq} - \sum_{q>p} n_q (1-\Lambda_{q,p}) A_{q,p} - n^+ n^- (1-\Lambda_p) \alpha_{\mathrm{rad}}\, p;$$

where $(1-\Lambda)$ is a factor taking into account the effective absorption in the spectral lines $(\Lambda_{p,q})$ and in the continuum (Λ_p), $(1-\Lambda) = 0$ corresponds to a thin plasma, $(1-\Lambda) = 1$ corresponds to a dense plasma, and $0 < (1-\Lambda) < 1$ corresponds to the intermediate case. The calculated Y_p and Y_p/Y_1 dependences were plotted as Y_p and Y_p/Y_1 vs N_e for two values of T_e and for different absorption intensities in the lines and in the continuum [15]. These graphs also showed the dependences for an optically thin plasma.

It follows from these studies that ternary recombination produces atoms in highly excited states, and there are excited states through which it is difficult for electrons to pass (there is a narrow region). There are sharp changes in the populations of states in this narrow region. These are the most nonequilibrium states and are the most interesting states in this review.

In a nonequilibrium steady-state plasma, with two oppositely directed electron fluxes, due to recombination and ionization ($Y_e < 1$), the $Y_p = f(E)$ distribution usually has the normal form, with the lower-lying states populated predominantly. Even in this case, however, as can be seen from the figure in [15] for an optically thin hydrogen plasma at $T_e = 12{,}000°K$ and with $n_e \sim 10^{12}$-10^{13} cm^{-3}, we have $Y_{10} > Y_4 > Y_3$. Cooling intensifies these inequalities.

In a plasma in the recombination regime ($Y_e > 1$) the population distribution $Y_p = f(E)$ has a negative slope, reflecting the predominant population of the highly excited states due to recombination.

For relatively high populations in the highly excited states, and for sharp population changes due to ternary recombination, the plasma should be in the recombination regime, T_e should be low (or α should be high), and n_e must be such that ternary recombination predominates over radiative recombination, but n_e must not be too high (the plasma conditions must be far from equilibrium). Furthermore, radiative transitions between lower-lying excited states, not offset by absorption, are favorable; these transitions lead to a sharp population change in the narrow region. Radiation absorption causes the population distribution among various states to approach the equilibrium distribution.

Two-particle recombination may occur in the case of certain atoms and ions through free-bound radiationless transitions resulting in the formation of a highly excited atom (or ion) whose excitation energy exceeds the first ionization energy (E_{i1}). During this two-particle recombination an electron is captured into an excited state, and the excess energy is transferred to a different atomic electron. The resulting atom has two excited electrons. This recombination process would be expected in a plasma containing atoms and ions having displaced states, most of which have energies above the first ionization energy. This type of recombination is more efficient than two-particle radiative recombination, whose cross section contains the factor $(e^2/hc = 1/137)^3$. Two-particle radiationless recombination must be taken into account in analyzing recombination in plasmas containing atoms and ions having displaced states.

The density of highly excited atoms ($E_\alpha > E_{i1}$) which are formed is low, because of autoionization, however, this type of recombination may be stabilized, both because of downward radiative transitions (dielectronic recombination) and because of transitions to states which undergo relatively little autoionization in collisions with electrons or atoms (recombination stabilized by collisions). The coefficient for recombination through free-bound radiationless transitions stabilized by some process can be written as [16]

$$\alpha^{\text{stab}} = \frac{A^{\text{stab}} A_a}{A^{\text{stab}} + A_a} T^{-3/2} \frac{w_d}{w_i} \cdot 2.1 \cdot 10^{-16} \exp\left(-\frac{E_{di}}{\kappa T}\right),$$

where A^{stab} and A_a are the stabilization and ionization probabilities; w_d and w_i are the statistical weights of the autoionized state of the atom and the ground state of the ion; and E_{di} is the difference between the energies of these states. Since at moderate densities of a nonequilibrium plasma we usually have $A_a > A^{\text{stab}}$ for the ionization levels, we can write α as

$$\alpha^{\text{stab}} = A^{\text{stab}} \cdot T^{-3/2} \frac{w_d}{w_i} \cdot 2.1 \cdot 10^{-16} \exp\left(-\frac{E_{di}}{\kappa T}\right).$$

In the case of dielectronic recombination, $A^{\text{stab}} = A^r$ are the probabilities for radiative transitions to level κ, and we have $\alpha^{\text{stab}} = \alpha^{\text{diel}}$. We see that α^{diel} depends exponentially on E_{di}, so that only displaced states having E_{di} approximately equal to E_{i1} are important for dielectronic recombination up to $E_{di} \sim \kappa T$. According to the literature, the dielectronic contribution to pure recombination is apparently slight. Under certain conditions in a gas-discharge plasma, stabilization of two-particle radiationless recombination through collisions with electrons and atoms may be efficient ($A^{\text{stab}} = A_{\text{coll}}$). Furthermore, account must be taken of the possible participation in recombination of ions formed by the stripping of inner electrons, rather than valence electrons. Accordingly, other mechanisms involving the formation of highly excited atoms may be operating in the case of atoms having displaced states.

The literature reveals no study simultaneously taking into account ternary recombination and two-particle radiationless recombination. Nor has there been a study of recombination involving ions formed by the stripping of inner electrons.

In a subsequent paper we will analyze the effect of recombination on the level population and on the radiation of atoms having displaced states.

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