MEASUREMENT OF THE COEFFICIENTS OF RESONANCE ELECTRON TRAPPING BY AUTOIONIZATION STATES OF THE CU ATOM

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The coefficients of resonance electron trapping by the autoionization states $5s'^4D_{5/2}$ (7.8 eV) *and* $5s''^2D_{5/2}$ (8.32 eV) *of the* Cu *atom have been measured to be* $4.0\cdot10^{-10}$ *and* $2.5\cdot10^{-10}$ $cm^3\cdot s^{-1}$.

The atom Cu possesses a number of shifted (Beitler) states, most of them (~110, see Ref. 1) lying above the first ionization boundary (Fig. 1). Some energy levels of atom, lying above the first ionization boundary, appear to be unstable. Atoms excited to these levels have a high probability of spontaneous transition to ionized state without change in energy, and this process is referred to as autoionization. For example,

$$\mathrm{Cu}\ (5\,s'^4D_{5/2}) - \mathrm{Cu}\ (^1S_0) + e.$$

The reverse process, resonance recombination (resonance electron trapping)

$$\mathrm{Cu}^+\ (^1S_0) + e - \mathrm{Cu}\ (5\,s'\,^4D_{5/2})$$

is possible too.

Due to autoionization, these states feature rather short lifetime, resulting in smearing (anomalous broadening) of emission lines at transitions from these levels. Shown in Fig. 2 is the spectrum of Cu+Ne laser emission in operating mode, where very strong and wide autoionization lines of Cu from $5s'^4D_{3/2,5/2}$, $5s'^2D_{3/2,5/2}$, and $5s''^2D_{3/2,5/2}$ are clearly seen. The basic parameters of these lines measured by us and by other authors are tabulated in Table I.

The lines corresponding to transitions from the levels $5s'^4D_{5/2}$ with $E_{ex} = 7.80$ eV and $5s'^4D_{3/2}$ with $E_{ex} = 7.88$ eV are strongest.

Autoionization lines of Cu are due to transitions from short-living shifted levels

$$5\,s'\,^4D_{3/2,\,5/2},\ \ 5\,s'\,^2D_{3/2,\,5/2},\ \text{and}\ 5\,s''\,^2D_{3/2,\,5/2}.$$

The probability of autoionization to the level $5s'^4D_{3/2,5/2}$, estimated from the width of corresponding lines, is $W_{ac} \approx 10^{12}$ s^{-1}, which is three-four orders of magnitude greater than the probability of radiative processes. Comparison of the collision and autoionization line widths shows that collision transitions, depleting the levels $5s'^4D_{3/2,\,5/2}$, are also improbable as compared to autoionization. For example, according to Ref. 2, $W_{ao} \approx 10^9$ s^{-1} at $n_e = 10^{16}$ cm^{-3}, where W_{ao} is the frequency corresponding to atomic transition from autoionization to bound state.

Analogous relations for the probability of reverse processes follow from the principle of detailed balance.[5]

Thus, the primary mechanism of the autoionization level population is the resonance trapping of free electron, i.e., the process reverse to autoionization being the first phase of dielectronic recombination.

This is why only autoionization and resonance trapping of free electron[3] should be considered in the balance equation for autoionization level

$$-\,n_a\,W_{ac} + n_e\,n_i\,A = 0, \tag{1}$$

where n_a is the population of autoionization level, n_i is the ion number density, A is the coefficient of resonance electron trapping, related to the coefficient of dielectronic recombination α_d as follows:

$$\alpha_d = AB/(W_{ac} + B), \tag{2}$$

B is the probability of stabilization, and $B \ll W_{ac}$.

The relation between W_{ac} and A follows from the principle of detailed balance

$$n_a^0\,W_{ac} = n_e^0\,n_i\,A, \tag{3}$$

where n^0 are the equilibrium number densities of the ground state of the atom at temperature T.

From Eqs. (1) and (3), using dimensionless parameters $y = n/n^0$, we can obtain $y_a = y_e y_i$, or, if there are ions of only one kind in plasma (under conditions of Cu-vapor laser discharge, one can take into account only ionization of Cu), $y_a = y_e^2$. The last means that the autoionization level is in the relative equilibrium with electron continuum, and its nonequilibrium population $y_a < 1$ can be only due to the ionization nonequilibrium $y_e < 1$. Nonequilibrium due to plasma recombination mode ($y_e > 1$), for example, in collapsing plasma, must result in relative strengthening of autoionization lines, which was observed in our experiment under conditions of copper-vapor laser afterglow (Fig. 2).

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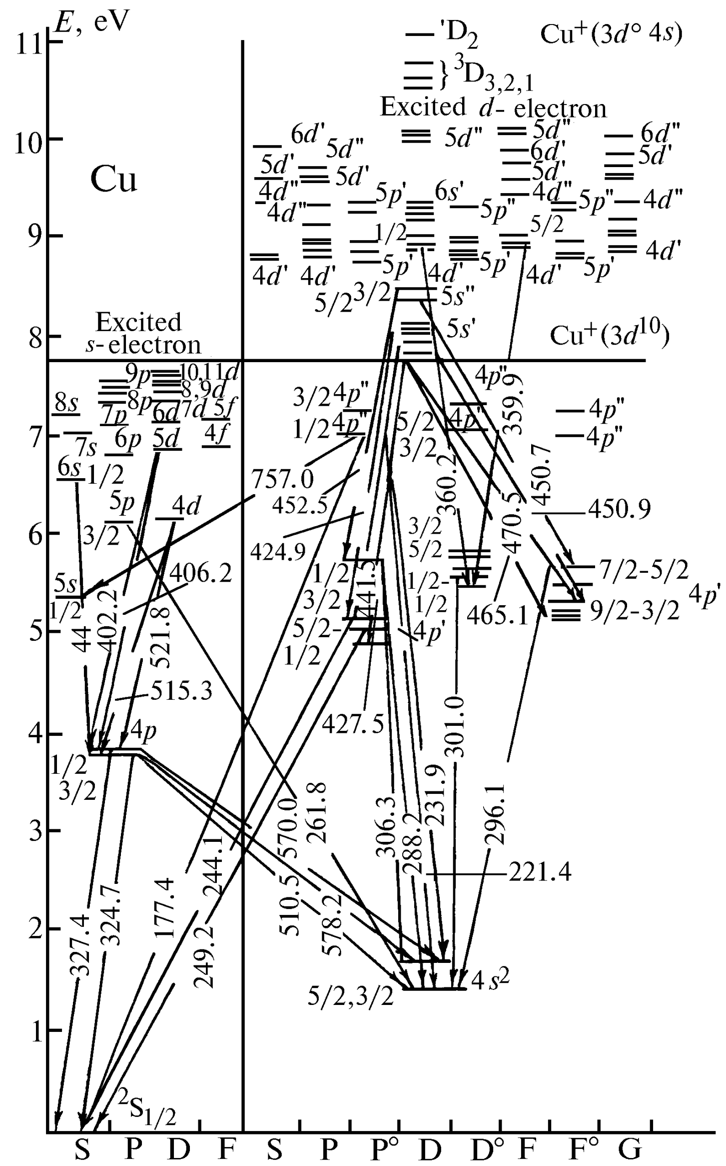

FIG. 1. Scheme of terms of the atom Cu.

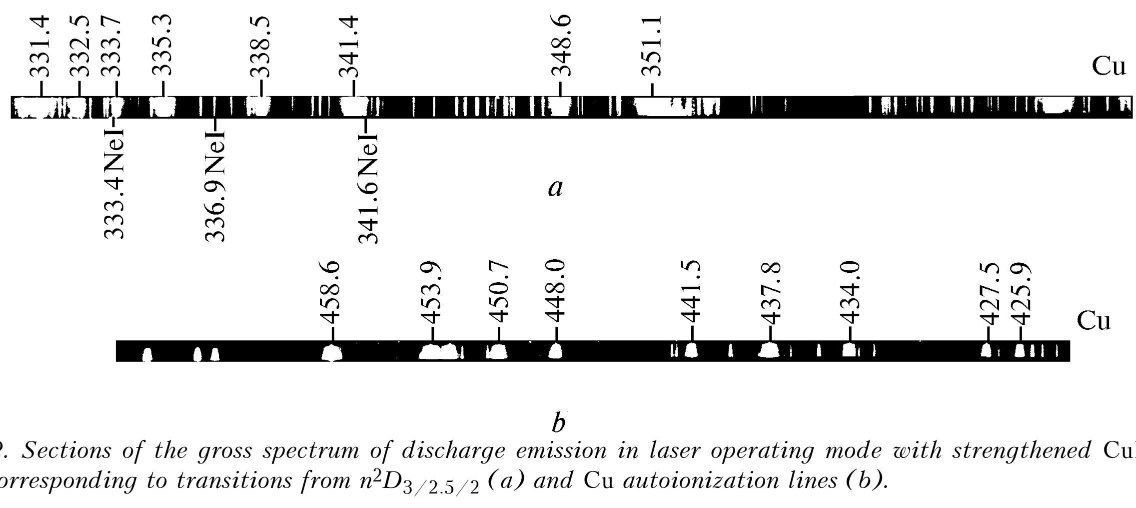

FIG. 2. Sections of the gross spectrum of discharge emission in laser operating mode with strengthened CuI *lines: lines corresponding to transitions from* $n^2D_{3/2,5/2}$ *(a) and* Cu *autoionization lines (b).*

TABLE I.

λ, nm	E_l, eV	E_u, eV	Transition	I	Width, cm^{-1}	
					Our measurements	Refs. 8 and 9
485.6	5.78	8.32	$4\,p'\,^2D^0_{5/2} - 5\,s''\,^2D_{5/2}$	75		3
479.4	5.51	8.09	$4\,p'\,^4D^0_{5/2} - 5\,s'\,^2D_{3/2}$	150	9.2	6.5
476.7	5.72	8.32	$4\,p'\,^2D^0_{3/2} - 5\,s''\,^2D_{5/2}$	75		3
469.7	5.21	7.88	$4\,p'\,^4F^0_{3/2} - 5\,s'\,^4D_{3/2}$	350	4.5	4.5
467.4	5.15	7.80	$4\,p'\,^4F^0_{5/2} - 5\,s'\,^4D_{5/2}$	500	2.8	2.5
464.2	5.42	8.09	$4\,p'\,^2F^0_{5/2} - 5\,s'\,^2D_{3/2}$	150		3
458.6	5.10	7.80	$4\,p'\,^4F^0_{7/2} - 5\,s'\,^4D_{5/2}$	1300		2
453.9	5.15	7.88	$4\,p'\,^4F^0_{5/2} - 5\,s'\,^4D_{3/2}$	800		2
441.5	5.08	7.88	$4\,p'\,^4P^0_{1/2} - 5\,s'\,^4D_{3/2}$	200		2
437.8	4.97	7.80	$4\,p'\,^4P^0_{3/2} - 5\,s'\,^4D_{5/2}$	550		2
425.9	4.97	7.88	$4\,p'\,^4P^0_{3/2} - 5\,s'\,^4D_{3/2}$	150		3
417.6	4.84	7.80	$4\,p'\,^4P^0_{5/2} - 5\,s'\,^4D_{5/2}$	100		2
450.7	5.57	8.32	$4\,p'\,^2F^0_{7/2} - 5\,s''\,^2D_{5/2}$	200	8.5	8.7

Let us calculate the coefficient of resonance electron trapping A for autoionization levels of the Cu atom based on our measurements of populations n_a and plasma parameters n_e and T_e in copper-vapor laser discharge afterglow, which are shown in Figs. 3 and 4 and reported in Ref. 4.

According to the principle of detailed balance, for any autoionization level the condition

$$(W_{ac}/g_c)\,e^{-E_a/T} = W^0_{ca}/g_a, \quad (4)$$

must hold true. In Eq. (4), W_{ca} is the frequency corresponding to the transition from the state of continuous spectrum to autoionization state (or transition probability), $W_{ca} = A n_e$; W_{ac} is the frequency corresponding to reverse transition, i.e., the probability of autoionization; E_a is the energy of autoionization level excitation counted from the boundary energy of continuous spectrum; g_a and g_c are the statistical weights of electron autoionization state and states of continuous spectrum, and due to frequent transitions between these states, they are considered here as one state with the statistical weght[5]

$$g_c = (g_e\,g_i/n_i)\,[m\,T/(2\pi\,h^2)]^{3/2},$$

where g_e and g_i are the statistical weights of electron and ion, respectively; T is electron temperature; and, m is electron mass.

From Eq. (4), having substituted the needed quantities, we obtain

$$A = W_{ac}\,(g_a/2\,g_i)\,[2\pi\,h/(m\,T)]^{3/2}\,e^{-E_a/T}\,. \quad (5)$$

As follows from Eq. (5), to find the value of A, we must know the probability of autoionization W_{ac} and the electron temperature T for the conditions under study.

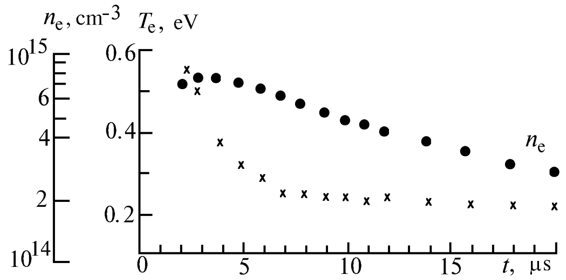

FIG. 3. Temporal behavior of the electron number density and temperature in the period between pulses of Cu*—vapor laser discharge with a pulse repetition rate of 8 kHz.*

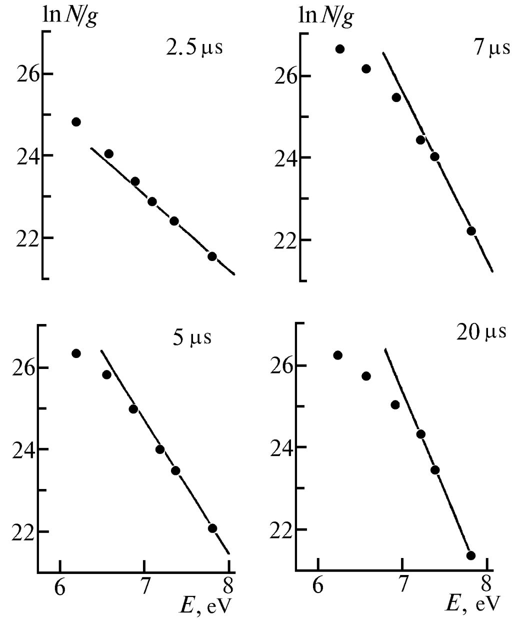

FIG. 4. Distribution of populations over excited states of Cu *atom in the period between pulses of the* Cu*— vapor laser discharge.*

From balance equation (1), the coefficient of electron trapping can be derived as $A = n_a W_{ac}/(n_e\, n_i)$. If only one kind of ions is taken into consideration, which is well satisfied for Cu-vapor laser discharge, then

$$A = n_a\, W_{ac}/n_e^2. \tag{6}$$

To determine A, we must measure the population of the autoionization level n_a and the electron number density n_e.

The calculations were done for the levels: 1) $5s'\,^4D_{5/2}$, E_i=7.80 eV; W_{ac}=0.75·10^{11} s^{-1} (2.5 cm^{-1}), 2) $5s''\,^2D_{5/2}$, E_i=8.32 eV; W_{ac}=2.6·10^{11} s^{-1} (8.7 cm^{-1}) at an instant of maximum afterglow of autoionization line, when T_e dropped down to approximately gas temperature, and n_e was maintained about its maximum value. This instant was within 5 μs after beginning of a current pulse whose duration was 0.3 μs. At this instant, according to our measurements, T_e = 0.3 eV, $n_e = 7{\cdot}10^{14}$ cm^{-3}, $n_a = 3{\cdot}10^9$ cm^{-3} for $5s'^4\mathrm{D}_{5/2}$, and $n_a = 6.5{\cdot}10^8$ cm^{-3} for $5s''^2\mathrm{D}_{5/2}$. The calculated results are presented in Table II.

TABLE II.

Autoionization level of CuI	$A{\cdot}10^{-10}$, cm$^3{\cdot}$s^{-1}	Expression used for calculation
$5\,s'\,^4D_{5/2}$, 7.80 eV $5\,s''\,^2D_{5/2}$; 8.32 eV	4.0 2.4	$A = W_{ac}\dfrac{g_a}{2g_i}\left(\dfrac{2\pi h}{mT}\right)^{3/2} e^{-E_a/T}$
$5\,s'\,^4D_{5/2}$, 7.80 eV $5\,s''\,^2D_{5/2}$, 8.32 eV	4.6 3.4	$A = n_a\, W_{ac}\,/n_e^2$

As shown above, the radiative and collision transitions for autoionization states of copper in collapsing plasma of copper-vapor laser discharge are improbable as compared with autoionization. This means that these states are in thermodynamic equilibrium with electron continuous spectrum under condition that the width of autoionization state Γ_a, corresponding to the decay of this state with emission of a free electron, much greater than its collision width Γ_c, i.e., $\Gamma_a = hW_{ac} \gg \Gamma_c = hW_{ao}$. The width $\Gamma_c < 10^{-18}$ erg, because at $n_e = 10^{16}$ cm^{-3}, according to Ref. 2, $W_{ao} < 10^9$ s^{-1}. For all autoionization levels of the Cu atom, $\Gamma_a \approx 10^{-15}$ erg, i.e., the condition $\Gamma_a \gg \Gamma_c$ holds true.

In this connection, let us consider the explanation for the marked deviation from the Boltzmann law of populations of copper autoionization states and even greater deviation of nearby nonautoionization CuI states, namely, $5s'^4\mathrm{D}_{7/2}$, in a low–pressure arc when n_e is within the range $4{\cdot}10^{15} - 4{\cdot}10^{16}$ cm^{-3} at temperatures of 5000–6000 K (Ref. 2). To explain this effect, in Ref. 2 it was proposed to consider some "new" processes, for example, resonance ion-atom charge exchange, which can proceed "rather efficiently due to low ionization potential."

If we assume that the charge exchange processes of the form

$$\mathrm{CuII}\,(^1S_0)+\mathrm{CuI}(5s'\,^4D_{5/2})=\mathrm{CuI}(5s'\,^4D_{5/2})+\mathrm{CuII}(^1S_0),$$
$$\mathrm{CuII}\,(^1S_0) + \mathrm{CuI}\,(^2S_{1/2})=\mathrm{CuI}\,(5s'\,^4D_{5/2})+\mathrm{CuII}\,(^1S_0)$$

take place, then the rate of the first reaction will be negligibly small for reasonable values of cross sections of charge exchange, $\sigma \approx 10^{-15} - 10^{-14}$ cm^2, under conditions of our experiment in comparison with the reaction of electron trapping, since the population of CuI $5s'^4\mathrm{D}_{5/2}$ is equal to ~10^9 cm^{-3}, and the electron number density is n_e ~ 10^{15} cm^{-3}.

The second reaction is unlikely to proceed, since the cross section of endothermic charge exchange for adiabatic regime of interaction tends to zero.[6]

In Ref. 7, possible violation of Maxwellian distribution of electrons over their energies in the range of excitation of autoionization levels due to the process of resonance electron trapping was proved. However, comparison of characteristic times of resonance electron trapping $\tau_e = 1/An_e \approx 10^{-5}$ s and time of electron maxwellization $\tau_m \approx 10^{-9}$ s (Ref. 5) indicates that under conditions of our experiment the Maxwellian distribution of electrons over their energies cannot violate.

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