Russian Physics Journal, Vol. 44, No. 5, 2001

PLASMA PHYSICS

ESTIMATION OF THE FULFILLMENT OF THE LOCAL THERMODYNAMIC EQUILIBRIUM CRITERION FOR THE PLASMA GENERATED BY LASER PULSES OF VARIOUS SHAPES AT THE SURFACE OF A SOLID TARGET

O. A. Bukin, I. V. Bazarov, A. Yu. Maior, N. S. Bodin, A. A. Il'in, V. I. Tsarev, and V. D. Kiselev

UDC 533.91

The results of experimental estimation of the fulfillment of the local thermodynamic equilibrium (LTE) criterion for the plasma generated by laser pulses of various duration at the surface of a solid target placed in a gaseous atmosphere at standard pressure are given in the present paper. The fulfillment of all the LTE criteria is demonstrated for an ensemble of neutral atoms contained in the plasma generated by a giant laser pulse or by a laser pulse whose complex shape represents several giant pulses against the background of free-running laser oscillations. The plasma excited by the radiation of a Nd : YAG *laser with energy ≤ 0.4 J per pulse is examined. We have recorded a resonance broadening of atomic* Al *and* Mg *lines. This has allowed us to estimate the density of neutral atoms contained in a plasma plume.*

The correct choice of models describing the examined plasma is very important for the correct estimation of the plasma parameters. The adequacy of the model of local thermodynamic equilibrium (LTE) allows the spectroscopic methods for measuring the laser-induced plasma parameters to be used. In particular, the measurements of the emission line intensities for the elements contained in a plasma plume can be used to estimate the plasma temperature [1, 2]. However, for atoms other than hydrogen atoms, simultaneous recording of the Stark broadenings and shifts of the emission line centers for the laser-induced plasma allows the main plasma parameters to be estimated obviating the necessity for the attainment of LTE in the examined volume of the laser plume [3]. Broadenings and shifts of the plasma emission lines caused by the quadratic Stark effect allow the electron concentration and temperature in the emitting plume region to be determined. The sole assumption used in the theory of line broadening due to electron collisions is the Maxwell distribution of electron velocities [4].

The main laser-induced plasma parameters that determine the fulfillment of LTE criteria depend strongly on the character of the laser pulse acting on the target. Thus, the fulfillment of LTE criteria was discussed in [5–7] for the plasma excited by laser pulses of various duration. In that case, the electron temperatures estimated from the spectral line intensities for the Boltzmann distribution of atoms over the energy levels were used to check the fulfillment of the main LTE criterion. In the present paper, we examine plasma plumes excited by a single giant laser pulse or by a complex pulse representing several Q-switched pulses against the background of free-running laser oscillations (up to four 20-ns pulses with a pulse repetition period of 30 μs against the background of a 200-μs pulse of free-running laser oscillations). The main plasma parameters are determined by methods that obviate the necessity for the *a priori* Boltzmann distribution.

We observed abnormal self-inversion and a considerable increase in half-widths of resonance emission transitions in the plasma excited by the complex laser pulse at an aluminum target [8]. The observed increase of the resonance transition half-width and the self-inversion of emission lines are due to the increased optical thickness and the enhanced concentration of neutral aluminum atoms. When the concentration of neutral atoms in the plasma increases significantly, the contribution

---

Institute of Physics and Information Technologies at Far-Eastern State University. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 5, pp. 24–28, May, 2001. Original article submitted January 18, 2000.

of the resonance mechanism to the resonance line half-width broadening may be of the order of or even greater than the corresponding Stark line broadening. The concentration of atoms contained in the plasma plume can be estimated from the resonant broadening of spectral emission lines [9]. An increase in the plasma density and a change in the degree of ionization due to an increased number of neutral atoms in the plasma plume that are carried away from the target surface by the portion of the laser pulse representing free-running laser oscillations lead to the change of the plasma parameters that influence the LTE existence.

In this paper, we present experimental half-widths and shifts of emission lines of the plasma generated by a complex laser pulse and a Q-switched laser pulse of 20-ns duration at half maximum at the surface of an aluminum (AMG-type alloy) target placed in the standard atmosphere. We used the experimental setup described in [3]. The only difference was that the laser pulse energy was ~0.2 J for the giant pulse and ~0.4 J for the complex pulse. The resonance Al I $3s^23p^2\ P^0_{3/2,1/2}$ – $3s^24s^2\ S_{1/2}$ doublet (3961.5 and 3944 Å) and the Mg I $3s3p\ ^3P^0_{0,1,2}$–$3s4s\ ^3S_1$ (5167.3, 5172.7, and 5183.6 Å) triplet were studied. The magnesium concentration in the target material was ~5%. A photodiode line was used as a photodetector, which allowed us to record the emission spectrum in the range of ~200 Å for a single laser pulse. The integral line intensity was measured for the period of plasma plume glowing [3].

Figure 1 shows the emission spectra of the resonance Al I doublet of the plasma generated by a single Q-switched 20-ns laser pulse (*a*) and by pulses with different relative contributions of free-running laser oscillations (*b* and *c*). Crosses in Fig. 1*a* indicate positions of nonshifted spectral line centers. The dashed curve in Fig. 1*c* is the approximation of the instrumental spectrum by the Lorentz profile.

Table 1 gives line broadenings $\Delta\lambda_{1/2}$ with allowance for the instrumental function and shifts $\Delta\lambda_S$ of emission line centers for the corresponding aluminum doublet and magnesium triplet recorded for the plasma generated by the giant pulse. Table 2 gives line broadenings and shifts for the laser pulse with a high portion of free-running laser oscillations. These data were averaged over five laser pulses. In this case, the resonance aluminum line half-width was estimated for the reconstructed Lorentz line profile. The measurement of resonance Al lines shifts (Table 2) was seriously impeded by the self-inversion and large widths of these lines.

According to the theory of line collisional broadening, the corresponding components of the aluminum doublet and magnesium triplet should have the same Stark shifts and line widths for each component (oscillator forces for both components of the resonance aluminum doublet are $f = 0.12$, whereas for the components of the magnesium triplet they are $f = 0.14$ [10]). In this case, the Stark shifts and widths of the examined Mg I triplet must be approximately 1.6–2.1 times greater than those for the resonance Al I transition [4, 11]. Indeed, this dependence was obeyed within the limits of errors in measuring the shift values in our experiments with plasma excitation by the giant laser pulse. The difference between the half-widths of the resonance aluminum doublet components and the values predicted by the Stark broadening theory indicated the contribution of the non-Stark mechanisms to the resonance line broadening (Table 1).

Second in importance mechanism of line broadening for a dense plasma that leads to the Lorentz line profile is the pressure or resonance broadening, which is not accompanied by line shifts. In the collisional approximation, the line half-width $\Delta\lambda'_{1/2}$ caused by the resonance broadening is determined by the expression [9]

$$\Delta\lambda'_{1/2} \approx \sqrt{\frac{g_1}{g_2}} \cdot \frac{e^2 f}{m_e c} \lambda^2 N\,, \tag{1}$$

where e and m_e are the electron charge and mass, g_1 and g_2 are statistical weights of the lower and upper energy levels, f is the transition oscillator force, λ is the transition wavelength, and N is the concentration of atoms of the given species. According to Eq. (1), the half-widths of resonantly broadened components of the examined Al I doublet must be in a $\sqrt{g'_1} : \sqrt{g_1} \approx 1.41 : 1$ ratio, where g'_1 and g_1 are statistical weights of $3s^23p\ ^2P^0_{3/2}$ and $3s^23p\ ^2P^0_{1/2}$ energy levels, respectively. Exactly this ratio of half-widths is tabulated in Table 2 for Al, that is, in this case the pressure broadening dominates for the resonance transition. From the known resonance broadening, the concentration of neutral atoms contained in the plasma can be estimated (Table 3). Resonantly broadened components of the magnesium triplet should be in the $\sqrt{5} : \sqrt{3} : 1 \approx 2.24 : 1.73 : 1$ ratios. The contribution of resonance broadening $\Delta\lambda'_{1/2}(\mathrm{Mg})$ to the Mg I $^3P_0$–$^3S_1$ line half-width, according to Eq. (1), is $\Delta\lambda'_{1/2}(\mathrm{Mg}) \approx 1.51 \cdot \Delta\lambda'_{1/2}(\mathrm{Al}) \cdot \alpha$, where $\Delta\lambda'_{1/2}(\mathrm{Al})$ is the resonantly broadened Al I $^2P_{1/2}$–$^2S_{1/2}$ line half-width and

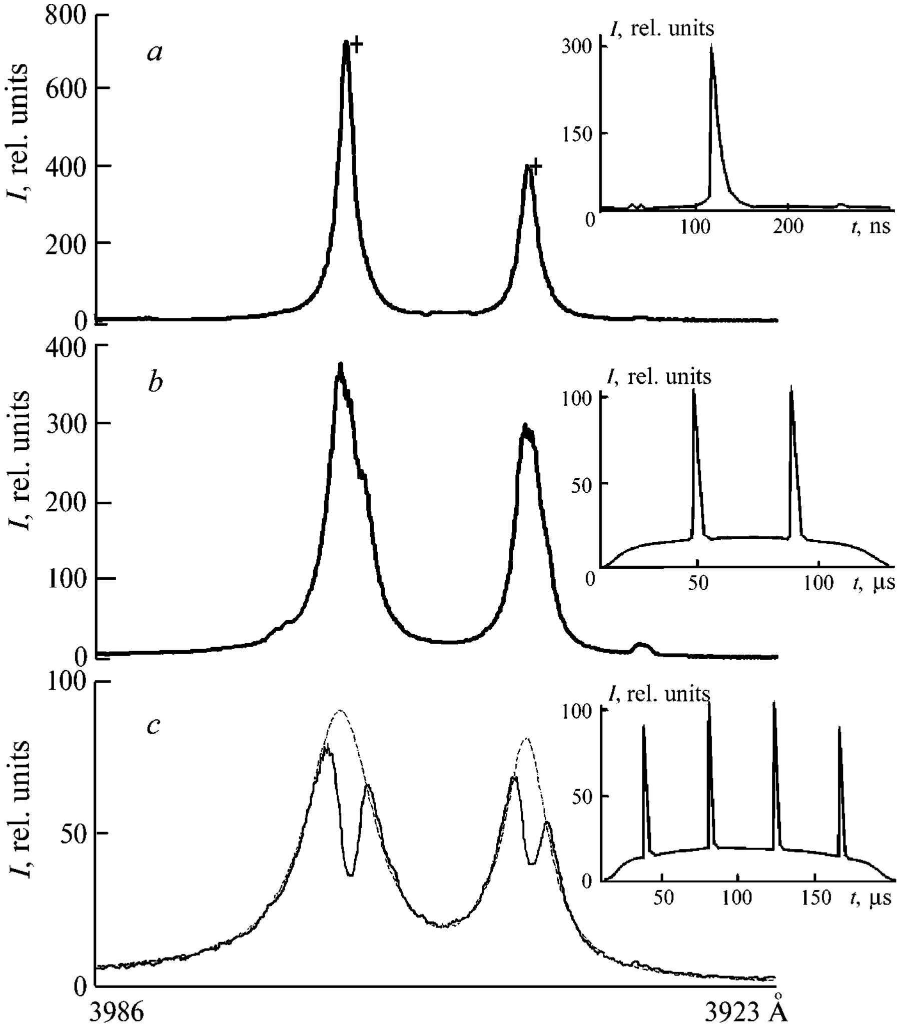

Fig. 1. Emission spectra of the Al I plasma generated by laser pulses of various shapes.

α is the ratio of concentrations of Al and Mg atoms. Taking $\alpha = 0.05$, we obtain that the contributions of the pressure broadening to the triplet magnesium components are 0.4, 0.6, and 0.8 Å, respectively. In addition to the resonance broadening, magnesium lines may be broadened by van der Waals forces when the number density of aluminum atoms is high. The estimated van der Waals contribution (Table 2) to magnesium lines at a density of aluminum atoms of $5 \cdot 10^{19}$ cm^{-3} (calculated by Eq. (1) for the resonance broadening of the Al I $^2P_{1/2}$–$^2S_{1/2}$ line equal to 5 Å) yields 0.2 Å for the half-width and less than 0.1 Å for the shift toward red wavelengths. Considering successively the resonance and van der Waals components of the Mg I line broadening, we obtain that the Stark component of the Mg I triplet half-width is equal to 0.6 Å.

In the case where the plasma is generated by the Q-switched laser pulse (Table 1), the non-Stark mechanisms of line broadening can be neglected. Different magnesium triplet components are broadened and shifted identically, as predicted by the theory of the Stark effect. The ratio of the half-widths of resonance aluminum transition components is about 1.1. Since magnesium triplet lines are broadened by the Stark effect and their Doppler broadening can be neglected (with an error <5%), the contribution of the pressure broadening to the $^2P_{1/2}$–$^2S_{1/2}$ aluminum line half-width is $\Delta\lambda_{1/2}(\mathrm{Al}) - k^{-1}\Delta\lambda_{1/2}(\mathrm{Mg}) \approx 0.4$, where k is the ratio of the Stark half-widths of magnesium triplet and aluminum doublet, $k \approx \left(C_4(\mathrm{Mg})/C_4(\mathrm{Al})\right)^{2/3}$, and C_4 is the parameter of the quadratic Stark effect [4]. For the examined transitions, k lies in the

TABLE 1

Transition, Å	Al I		Mg I		
	$^2P_{3/2}-{}^2S_{1/2}$	$^2P_{1/2}-{}^2S_{1/2}$	$^3P_2-{}^3S_1$	$^3P_1-{}^3S_1$	$^3P_0-{}^3S_1$
$\Delta\lambda_{1/2}$	1.3	1.2	1.4	1.4	1.4
$\Delta\lambda_S$	0.4	0.4	0.7	0.7	0.7

TABLE 2

Transition, Å	Al I		Mg I		
	$^2P_{3/2}-{}^2S_{1/2}$	$^2P_{1/2}-{}^2S_{1/2}$	$^3P_2-{}^3S_1$	$^3P_1-{}^3S_1$	$^3P_0-{}^3S_1$
$\Delta\lambda_{1/2}$	7.2	5.0	1.6	1.4	1.2
$\Delta\lambda_S$	–	–	0.5	0.5	0.5

range 1.6–2.1. Thus, the pressure broadening in the plasma generated by the Q-switched pulse (Table 1) is less than the resonance broadening in the case of the pulse of free-running oscillations (Table 2).

From the known Stark shift and width for the Mg I line, the electron temperature and the laser-induced plasma density can be determined. According to Grim's calculations [11], the width and shift are given by the following approximate formulas:

$$\Delta\lambda_{1/2} = 2[1+1.75\cdot 10^{-4} N_e^{1/4}\alpha(1-0.068 N_e^{1/6} T_e^{-1/2})]10^{-16} w N_e \ \text{Å}, \tag{2}$$

$$\Delta\lambda_S = \left[\left(\frac{d}{w}\right) + 2.0\cdot 10^{-4} N_e^{1/4}\alpha(1-0.068 N_e^{1/6} T_e^{-1/2})\right]10^{-16} w N_e \ \text{Å}, \tag{3}$$

where $2w$ and d are the line half-width and shift (in Å) caused by electron collisions at the given electron temperature T_e for an electron density of 10^{16} cm^{-3} reported in [11], T_e is in K, and α is the ion broadening parameter [11]. As a rule, the second terms in Eqs. (2) and (3) that describe the contributions of ion broadening are very small; therefore, $\Delta\lambda_{1/2}$ and $\Delta\lambda_S$ are caused by electron collisions. The parameter d/w is very sensitive to the electron temperature. Neglecting the contribution of ion broadening, which introduces additional errors in the determination of d/w less than 1% when we calculate the Mg I triplet spectra, we can write

$$\left(\frac{d}{w}\right) \approx 2\frac{\Delta\lambda_S}{\Delta\lambda_{1/2}}. \tag{4}$$

Knowing the parameter d/w, we can find T_e. For the Mg I $3s3p\ ^3P^0_{0,1,2}$–$3s4s\ ^3S_1$ triplet, the parameter d/w depends on $\log T_e$ practically linearly in the temperature range $T_e = 0.5$–7 eV [11]. Consideration of the Doppler broadening for the examined plasma decreases the electron temperature by 4%. The line half-width can be used to find N_e. The plasma parameters tabulated in Table 3 were estimated from the line broadenings and shifts presented in Tables 1 and 2.

We now consider the LTE criteria for the plasma. The first criterion requires that the collision processes of energy level excitation dominate over the spontaneous transitions in the plasma and imposes the following restriction on the electron density [12]:

$$N_e \geq 1.1\cdot 10^{14}(z+1)^6\sqrt{T_e}\,E^3(p,q), \tag{5}$$

where z is the ion charge, T_e [eV] is the temperature, and $E(p, q)$ [eV] is the difference between the energies of excitation into levels p and q. According to Eq. (5), the population density of the Al I resonance level differs by 10% from that

TABLE 3

Tabulated data	N_{Al}, cm^{-3}	N_e, cm^{-3}	T_e, eV
Table 1	$4\cdot10^{18}$	$1.4\cdot10^{17}$	1.9–4.3
Table 2	$5\cdot10^{19}$	$0.7\cdot10^{17}$	0.6–2.7

specified by the Boltzmann distribution for the plasma generated by the giant pulse at $N_e = (4.7\text{–}7.1)\cdot10^{15}$ cm^{-3}, whereas for the plasma generated by the complex pulse this 10% difference is attained at $N_e = (2.6\text{–}5.6)\cdot10^{15}$ cm^{-3}. The same difference is obtained for the resonance Al II level of singly ionized aluminum for the plasma excited by the giant pulse when $N_e = (1.0\text{–}1.5)\cdot10^{18}$ cm^{-3}, and for the plasma excited by the complex pulse it is obtained at $N_e = (0.5\text{–}1.2)\cdot10^{18}$ cm^{-3}. From Eq. (5) it follows that, in both cases, the population of the aluminum atom energy levels corresponds to the LTE plasma model. However, the energy levels of singly ionized aluminum ions do not obey the equilibrium distribution. This is confirmed by the fact that the degree of ionization estimated from the experimental data is much less than that calculated for the LTE model using the Saha formula for the obtained electron temperatures.

In addition, the main plasma parameters must not change significantly during the period of LTE establishing. The time of LTE establishing can be estimated from the formula $\tau = C^{-1}\chi$, where C is the rate of collisional transition from the ground into the resonance level per atom, and the factor χ considers the relative fraction of atoms to be excited or ionized. The characteristic times were estimated using the expression for *C* derived in [11]. For the laser-induced plasma they were of the order of several fractions of a second for the giant pulse and several nanoseconds for the complex pulse. According to Ng *et al*. [7], who investigated the laser-induced plasma with close values of N_e and T_e, the laser plasma parameters change significantly (by ~10%) during the period from several tens to several hundreds of nanoseconds. This means that the steady-state plasma criterion is fulfilled.

The spatially homogeneous plasma criterion should also be analyzed. The average distance *d* [cm] traveled by an atom before excitation or ionization upon electron collisions is determined by the formula [11]

$$d \approx 6\cdot10^{14}\,A^{-1/4}\left(\frac{T_e}{\text{Ry}}\right)^{1/2}\left(\frac{E(p,q)}{f\cdot\text{Ry}}\right)^{1/2}\exp\left(\frac{E(p,q)}{2T_e}\right)\left[\left(N_{\text{Al I}}+N_{\text{Al II}}\right)\left(N_{\text{Al I}}+10N_{\text{Al II}}\right)\right]^{-1/2}, \tag{6}$$

where *A* is the atomic weight, Ry is the Rydberg constant, and $N_{\text{Al I}}$ and $N_{\text{Al II}}$ are concentrations of atoms and ions, respectively. The necessary LTE condition is that the spatial variations of the main plasma parameters at distances of the order of *d* are small. Considering that $N_{\text{Al II}} \approx N_e$, we obtain $d \sim 0.6$ μm for the giant pulse and ~0.1 μm for the complex pulse. The spatial variations of the electron temperature in plasma become significant only at distances equal to several tens of microns [7].

Thus, our analysis demonstrates the fulfillment of the LTE criterion for the atomic system of the laser-induced plasma excited by the giant pulse or by the complex pulse with energy of the order of several tenths of joule per pulse. Already for singly ionized ions, the fulfillment of LTE criteria requires a special consideration for each ion energy level with allowance for the energy of the exciting laser pulse.

The fulfillment of LTE criteria has been estimated for the values of T_e, N_e, and N_{Al} averaged over the period of plasma plume glowing. It should be noted that these criteria may be violated at some moments of plasma existence. Thus, Ng *et al*. [7] observed the deviation from the LTE in the late stages of plasma plume dispersion.

REFERENCES

1. Zh. V. Vasil'chenko, V. V. Azharonok, and I. I. Filatova, Kvant. Elektron., **23**, 831 (1996).
2. M. Sabsabi and P. Cielo, Appl. Spectrosc., **49**, 499 (1995).
3. O. A. Bukin, I. V. Bazarov, and N. S. Bodin, Kvant. Elektron., **25**, 705 (1998).
4. L. A. Vainshtein, I. I. Sobel'man, and E. A. Yukov, Excitation of Atoms and Spectral Line Broadening [in Russian], Nauka, Moscow (1979).

5. M. Ignatavichyus, E. Kazakavichyus, and G. Orshevski, Kvant. Elektron., **18**, 1325 (1991).
6. Yu. M. Vasil'kovskii, I. A. Gordeeva, and R. E. Rovinskii, *ibid.*,1085.
7. C. W. Ng, W. F. Ho, and N. H. Cheung, Appl. Spectrosc., **51**, 976 (1997).
8. O. A. Bukin, E. A. Sviridenkov, and N. V. Sudhilov, Kvant. Elektron., **24**, 725 (1997).
9. N. G. Preobrazhenskii, Spectroscopy of an Optically Dense Plasma [in Russian], Nauka, Moscow (1971).
10. G. A. Kasabov and V. V. Eliseev, Spectroscopic Tables for a Low-Temperature Plasma [in Russian], Atomizdat, Moscow (1973).
11. G. Grim, Plasma Spectroscopy [in Russian], Atomizdat, Moscow (1973).
12. L. S. Polak, Low-Temperature Plasma Physics and Chemistry [Russian translation], Nauka, Moscow (1971).