PRAMANA
— journal of
physics

Vol. 65, No. 6
December 2005
pp. 1075–1083

Optical emission from laser-produced chromium and magnesium plasma under the effect of two sequential laser pulses

V N RAI[1], F Y YUEH[2] and J P SINGH[2]
[1]Laser Plasma Division, Centre for Advanced Technology, Indore 452 013, India
[2]Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, 205 Research Boulevard, Starkville, MS 39759, USA
E-mail: vnrai@cat.ernet.in

MS received 4 August 2004; revised 9 June 2005; accepted 2 July 2005

Abstract. Parametric study of optical emission from two successive laser pulses produced chromium and magnesium plasma is presented. The line emission from chromium and magnesium plasma showed an increase by more than six times for double laser pulse excitation than for single-pulse excitation. An optimum increase in emission intensity was noted for inter-pulse delay of ∼2–3 μs for all the elements. The experimental observations were qualitatively explained on the basis of absorption of second laser pulse in the pre-formed (by first laser) coronal plasma by inverse Bremsstrahlung process, which were found responsible for the excitation of more ions and atoms in the plasma. This process starts as the plasma scale length becomes greater than the laser wavelength. This study further indicated the suitability of this technique in the field of elemental analysis.

Keywords. Laser–plasma interaction; laser-induced breakdown spectroscopy; plasma heating; visible emission.

PACS Nos 52.38.-r; 42.62.Fi; 52.50.Jm; 32.30.Jc

1. Introduction

Investigation of high-intensity laser–matter interaction has been an active topic of research not only in plasma physics but also in many fields of research and analysis [1–5]. The capability of lasers to vaporize, dissociate, excite or ionize species from any kind of material (laser-induced ablation) shows its potential of becoming a powerful analytical tool. The hot laser-produced plasma radiates various types of emissions ranging from x-rays to visible wavelength regions. The spectroscopic study of line emission from such microplasma (atomic emission spectroscopy) can provide information about the composition of the target material and is popularly known as laser-induced breakdown spectroscopy (LIBS). Application of this technique is often limited because of insufficient sensitivity of the system (emission characteristics) compared to the other atomic spectrometric methods such as spark

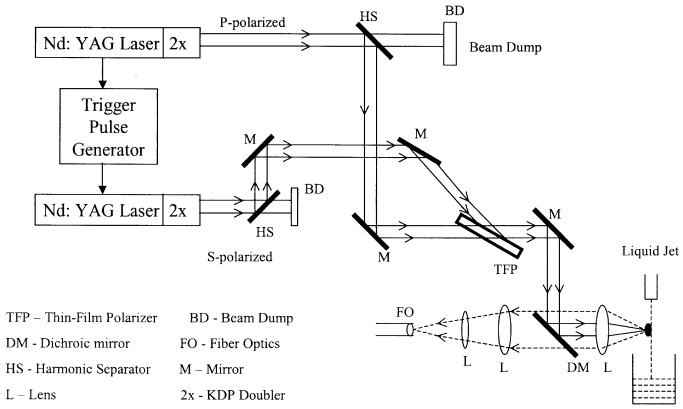

Figure 1. Schematic diagram for recording LIBS under double laser pulse excitation as well as the ray diagram for making two synchronized lasers collinear.

discharge or inductively coupled plasma atomic emission and mass spectrometry (ICP-AES and ICP-MS). Various techniques have been utilized to enhance the sensitivity of LIBS system; that is, to increase the emission intensity from laser-produced plasma. This includes oblique incidence of laser on the sample surface [6], double laser pulse excitation [7,8], introduction of purge gas around the microplasma [9] etc. Earlier, pulsed as well as DC external magnetic field have also been used to enhance the emission from laser-induced plasma in different experimental conditions [10–12]. During double laser pulse experiment, the first laser pulse generated pre-formed plasma, which was further excited by the second laser pulse after few microsecond time duration [7,8]. It is expected that the volume of plasma formed after second laser pulse is more than that formed with a single laser. Along with an increase in the volume of emitting plasma an increase in plasma temperature as well as increased ablation are expected as the reason for enhancement in plasma emission. However, very little information is available about these interaction processes. Considering that most of the earlier experiments were performed on the solid samples, it was found interesting to study the emission as well as the interaction process from liquid samples under the double laser pulse excitation. This study was also considered helpful in evaluating the double pulse LIBS for making a technetium (Tc) monitor, which is a long lifetime radioactive element encountered in the solvent flows during the processing of the nuclear waste.

2. Experimental set-up

The schematic diagram of the experimental set-up for making the two laser beams collinear for recording the laser-induced breakdown emission from the liquid sample under double laser pulse excitation is shown in figure 1. It consisted of two Q-switched, frequency-doubled Nd:YAG laser (Continuum Surelite III and Quanta-Ray DCR-2A-10) that delivers ∼300 mJ energy at 532 nm in 5-ns time duration.

Table 1. Spectroscopic notation of upper and lower states of all the transitions studied from Mg, Cr and Re.

Element	λ (nm)	Upper state	Lower state
Mg	[2.79.55 280.27] –	$2p^6 3p\ ^2P_{1/2}$	$2p^6 3s\ ^2S_{1/2}$
	They are due to Mg^+	$2p^6 3p\ ^2P_{3/2}$	$2p^6 3s\ ^2S_{1/2}$
	285.20 Mg	$2p^6 3s3p\ ^1P_0$	$2p^6 3s^2\ ^1S_0$
Cr	425.44	$3d^5 4p\ ^7P^0_4$	$3d^5 4s\ ^7S_3$
	427.48	$3d^5 4p\ ^7P^0_3$	$3d^5 4s\ ^7S_3$
	428.97	$3d^5 4p\ ^7P^0_2$	$3d^5 4s\ ^7S_3$
		(components of the same $^7P_0$ state)	
Re	346.04	$5d^5 6s6p\ ^6P^0_{7/2}$	$5d^5 6s^2\ ^6S_{5/2}$
	346.47	$5d^5 6s6p\ ^6P^0_{3/2}$	$5d^5 6s^2\ ^6S_{5/2}$

Both the lasers were operated at 10 Hz during this experiment and were focused on the target (in the center of the liquid jet). The detailed description of the experimental set-up has already been reported [7,11]. A teflon nozzle of diameter $\leq$1 mm was used with a peristaltic pump (Cole-Parmer Instrument Co.) to form a laminar liquid jet as a target for this experiment. The aqueous solution of Mg, Cr and Re was used for this experiment. The concentrated solution of Mg, Cr and Re ($\sim$1000 ppm) present in 2% HNO_3 (E M Science, New Jersey) was used to make dilute solutions of various concentrations used in this experiment. Emission spectra were recorded mainly using 2400-l/mm grating for a better spectral resolution. Around 100 pulses were accumulated to obtain one spectrum and 30 such spectra were recorded for each experimental condition in order to increase the sensitivity of the system and reduce the standard deviation.

3. Result and discussion

3.1 *Spectral effect*

Optical emissions from Mg, Cr and Re that are the surrogate elements of technetium (radioactive material) [13] were studied. These elements have very sensitive triplet line emissions in the UV–VIS region of the spectrum because their higher excitation cross-sections are similar to the cross-section of technetium [14]. The Mg emission consists of two lines from Mg ions (279.55 and 280.27 nm) and one (285.2 nm) from neutral magnesium, whereas Cr and Re line emissions are mainly from neutral atoms (table 1).

Figure 2 shows the spectra of Mg recorded in double laser pulse excitation mode, when the inter-pulse delay between both the lasers was zero and 3 μs. A very small increase in the emission intensity was noted for zero delay in comparison to single pulse experiment, mainly due to the addition of intensity from both the lasers.

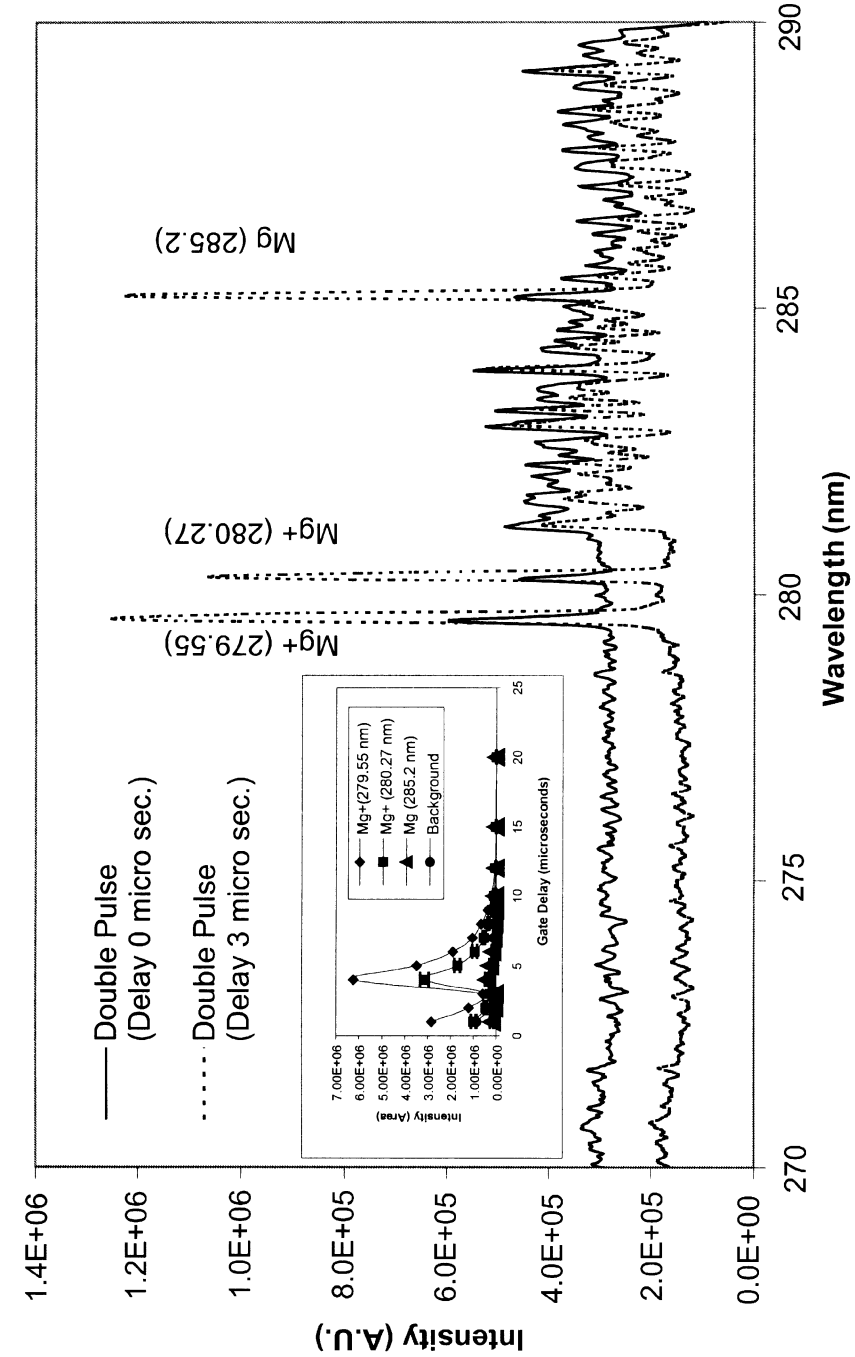

Figure 2. Emission spectra of magnesium (5 ppm) in double laser pulse excitation mode with change in inter-pulse delay (0 and 3 μs) between lasers [laser (1) = 100 mJ, laser (2) = 120 mJ, gate delay/gate width = 10 μs/10 μs]. (In the inset) Variation in the line and background emission from magnesium plasma (5 ppm) with respect to detector gate delay from the first laser [Laser (1) = 130 mJ, laser (2) = 100 mJ and inter-pulse delay between lasers 2 μs, gate width = 0.1 μs].

However, emission intensity was enhanced nearly 4 times (peak to peak), when the delay was increased to 3 μs and the spectra were recorded at 10 μs gate delay. The spectra recorded at 10 μs gate delay made the line emission dominant, whereas at 4 μs emission was dominated by the background emission [8]. At 10 μs gate delay ionic as well as atomic lines from magnesium were found equally strong, because by that time plasma became relatively cool providing large number of neutral atoms as a result of electron–ion recombination [15]. Similar enhancement was noted in neutral line emission also. At the same time, background emission decreased with an increase in inter-pulse separation because the lighter elements of the solution matrix (H, O and OH) contributing mainly to background emission (Bremsstrahlung emission due to frequent electron and light ion collision) expanded and cooled faster in comparison to the heavier element of Mg. Similar enhancement (4–10 times) in emission was reported under double laser pulse excitation for aluminum line emission from a solid target [16]. It was found that emission intensity increases with an increase in intensity of the first or second laser up to a certain level, after which saturation was observed. The occurrence of saturation with an increase in laser intensity is possible either due to self-absorption of emission in the cold high-density plasma (due to more ablation) or due to loss in absorption of laser light as a result of generation of instability in the plasma at higher laser intensity, which is expected [1,11].

From the above experimental observation it seems that the first laser pulse produced the plasma, which expanded normal to the target surface, and the second laser interacted with pre-formed expanding plasma. The interaction of the second laser pulse with expanding plasma may be increasing the probability of its absorption in the plasma plume, which seems to be reheating the plasma and finally exciting more number of plasma particles to its excited state. Even the second laser may contribute in terms of an increase in ablation of more material from the sample target resulting in an increase in the number of emitting species. Similar behavior was noted when Cr and Re solution was used to record the LIBS spectra in double laser pulse excitation.

The time-dependent emission properties of plasma plume were studied in double laser pulse excitation mode by changing the gate delay from the first laser, which enabled us to see the variation in the emission intensity from magnesium after the first as well as the second laser pulse. During this experiment the inter-pulse delay between both the lasers was kept $\sim$2 μs, whereas, gate delay was varied from 1 to 20 μs (gate width $\sim$0.1 μs) with respect to the first laser pulse. Initially, only the first laser was operating at 130 mJ energy (fluence $\sim$1500 W/cm^2) and emission due to this laser was recorded up to 3 μs gate delay. The second laser ($\sim$100 mJ) was started when the gate delay was 4 μs. Figure in the inset of figure 2 shows that up to 3 μs gate delay, emission intensity was small and decreasing in nature because only the first laser-induced plasma was contributing to emission. Line emission intensity increased $\geq$12 times, when second laser started operating than the emission intensity at 3 μs gate delay. The background emission intensity also increased at 4 μs gate delay. The fast decay of background as well as line emissions indicated that the plasma excited by the second laser pulse also started cooling down due to its expansion. In fact the second laser was started when the gate delay was 4 μs, but actually pre-formed plasma interacted with the second laser

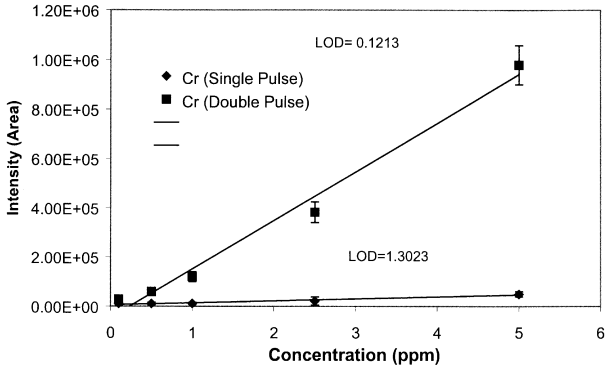

Figure 3. Variation in emission (425.44 nm) from chromium with concentration under single [laser = 140 mJ, gate delay/gate width = 20 μs/10 μs] and double pulse excitation [laser (1) = 140 mJ, laser (2) = 140 mJ, gate delay (from first laser)/gate width = 20 μs /10 μs, delay between lasers = 2.5 μs].

pulse just after 2 μs (inter-pulse delay set for maximum emission) from the first laser for the entire set of experiment. A significant laser absorption and consequent excitation of plasma may take place due to the second laser and pre-formed plasma interaction after 2 μs from the plasma formation by the first laser. Slight increase in the temperature of plasma was indicated by an increase in the background emission just after the interaction, which decayed very fast in comparison to the line emission [8]. This resulted in an enhancement in the line emission from Mg ions and neutrals. However, plasma temperature has been measured earlier in similar experimental condition as $\sim$0.5 eV at 10 μs gate delay [11]. The occurrence of maximum emission was decided mainly by the delay between the two lasers, the plasma temperature and the dynamics of plasma.

It was noted that as the inter-pulse delay between lasers increased, the occurrence of maximum line emission shifted towards higher gate delay. Amplitude of the emission intensity also decreased with an increase in the inter-pulse delay due to fast decay in plasma density (typical density $n_e \sim 5.47 \times 10^{16}$ cm^{-3}) produced by the first laser [11]. This also indicates that enhancement in the emission in this experiment seems to be due to the excitation of more number of ions/atoms as a result of better absorption of second laser in pre-plasma. However, a significant amount of material ablation due to the second laser pulse may also be contributing towards an increase in emission intensity. Similar variation in the LIBS of Cr and Re was also noted, when excited using the dual laser pulses.

3.2 *Absorption of laser light in plasma*

For explaining the above experimental observations, it is better to understand the absorption of laser light in the pre-formed coronal plasma. The possible absorption mechanism in such case is inverse Bremsstrahlung absorption [17], which takes place as a result of electron–ion collision in low-temperature plasma. This is because

when the plasma electrons are subjected to momentum changing collisions as they oscillate back and forth in the laser electric field, the laser light wave feels an effective damping. In this case absorption coefficient (k_{ib}) of plasma can be written as

$$k_{ib} \propto \frac{Zn_e^2}{T_e^{3/2}\left(1-\frac{n_e}{n_c}\right)^{1/2}}. \tag{1}$$

This clearly shows that inverse Bremsstrahlung absorption is strongest for low plasma temperature (T_e), high density (n_e) and high Z plasma. Here n_c is the critical plasma density. This qualitatively explains our observation that when the delay between both the lasers is very less, the temperature of pre-formed plasma remains high giving less probability of absorption of second laser and the corresponding excitation of ions and atoms (less enhancement in emission). Even the high-temperature plasma emits Bremsstrahlung continuum emission, which is observed experimentally in the form of background emission. Plasma temperature goes down as it expands away from the ablation surface resulting is an increase in probability of absorption of the second laser. Nakano *et al* [18] have calculated the absorption of laser light in expanding pre-formed plasma. For this purpose they have solved the Helmholtz wave equation with a density gradient profile $n(x,t)$ [19] (given as the Reimann solution of the hydrodynamic equation [20]) as

$$n(x,t) = n_0\left[\frac{3}{4} - \frac{x}{(4v_{\exp}t)}\right]^3. \tag{2}$$

Here n_0 is the solid or liquid state density and the plasma scale length $L = v_{\exp}t$. This calculation shows that absorption of the second laser started as the plasma scale length $L(v_{\exp}t)$ exceeds the wavelength of laser light λ, that is $L \geq \lambda$. In our experimental condition $T_e \sim 1$ eV corresponds to a plasma expansion velocity $v_{\exp} \sim 5.5\times10^5$ cm/s. The time delay between the two lasers for maximum emission was $\sim$2 μs. The scale length of the plasma was obtained as $L = v_{\exp}t = 1.10$ cm, which is much greater than $\lambda \sim 0.53$ μm. This shows that in this case an efficient absorption of second laser is possible in the pre-formed plasma produced by the first laser. However, any further increase in delay between the lasers will decrease the emission intensity due to drastic decrease in plasma density as a result of the combined effect of electron–ion recombination and plasma diffusion. According to eq. (1) absorption coefficient is directly proportional to n^2, which indicates that any decrease in plasma density will significantly lead to a decrease in the probability of laser absorption in the plasma resulting in less emission even under the double laser pulse excitation. Finally, in the case of quite large delay between lasers, interaction (absorption) of the second laser with pre-formed plasma would be either very less or negligible. In such a case emission will be observed as produced by two separate lasers. The qualitative agreement of this analysis with our observations confirms that the main reason for the enhancement in the emission under double laser pulse excitation is due to better absorption of second laser in the pre-formed plasma produced by the first laser, where optimum absorption (emission) occurs when the plasma scale length $L \sim 1.10$ cm $\gg \lambda \sim 0.53$ μm. Further analysis of the laser–plasma interaction by considering all aspects of plasma formation and its dynamics will provide still better understanding.

3.3 *Application of enhancement in emission*

The variation in the line emission intensity with concentration of Mg, Cr and Re in solution was recorded in the single as well as double laser pulse excitation in order to compare the calibration curve and the limit of detection (LOD) for each element from application point of view. Figure 3 shows the calibration curve for Cr line emission at $\lambda = 425.44$ nm recorded in single and double laser pulse excitation mode. The slope of the linear variation was found more in double laser pulse excitation due to a large enhancement in the emission in the concentration range of 0.1–5 ppm. The limit of detection (LOD) was calculated here as the ratio of three times standard deviation (σ) in the data and the slope of calibration curve (S) as $3\sigma/S$. The limit of detection for Cr was calculated as ∼120 ppb (part per billion) in double laser pulse excitation between 0.1 and 5 ppm concentration range, whereas, it was 1300 ppb in single laser pulse excitation mode, showing an order of magnitude improvement in LOD.

Similar improvement in LOD of Mg and Re were also in double laser pulse excitation for different emission lines. It was noticed that improvement (decrease) in LOD was better for the most sensitive line emission. Maximum improvement in LOD was noted for Cr (425.44 nm), whereas for Mg [8] and Re this was comparatively less, which seems to be due to its lower transition probability in comparison to Cr. Finally double laser pulse excitation was found useful in enhancing the emission from laser-produced plasma, which may be applicable in making the technetium monitor.

4. Conclusion

Optical properties of the emission from laser-produced Mg, Cr and Re plasma under double laser pulse excitation were studied. An increase in line emission intensity by ≥6 times was obtained for the laser inter-pulse separation of 2–3 μs, which was slightly more for neutral atomic emission. Optimum delay of 2–3 μs was found correlated with an optimum expansion of pre-plasma, which is necessary for better absorption of the second laser pulse, which helped in increasing the volume of emitting plasma. The experimental observations were found in good qualitative agreement with the calculation of absorption of laser in the plasma via inverse Bremsstrahlung processes, where the onset of absorption occurs when the plasma scale length $L(v_{\exp}t) > \lambda \sim 0.53$ μm. During the maximum absorption, plasma scale length was calculated as 1.10 cm $\gg \lambda$, which confirms absorption of significant amount of laser energy in the elongated plasma increasing the effective volume of the plasma emitting visible radiation.

Finally an increase in the excitation of ions and atoms, the emitting plasma volume and ablation of the sample material after second laser pulse absorption in pre-plasma contributed towards an increase in the emission intensity. An order of magnitude improvement (decrease) in LOD of Cr under double laser pulse excitation indicated that dual laser pulse LIBS system might be applicable as a technetium monitor. However, further experimental as well as theoretical investigations are

needed to better understand the process of laser–plasma interaction increasing the emission under double laser pulse excitation.

Acknowledgment

This work is supported by U.S. Department of energy cooperative agreement no. DE-FC26-98FT 40395. Authors are grateful to the referee of this paper for his/her constructive comments regarding the improvement of this manuscript.

References

[1] L J Radziemski and D A Cremers, *Laser induced plasma and applications* (Marcel Dekker, New York, 1989)
[2] F Y Yueh, J P Singh and H Zhang, Laser induced breakdown spectroscopy: Elemental analysis, in *Encyclopedia of analytical chemistry* (John Wiley & Sons Ltd, New York, 2000) vol. 3, pp. 2065–2087
[3] O Samek, D C S Beddows, J Kaiser, S V Kukhlevsky, M Liska, H H Telle and J Young, *Opt. Eng.* **38**, 2248 (2000)
[4] D A Rusak, B C Castle, B W Smith and J D Winefordner, *Crit. Rev. Anal. Chem.* **27**, 257 (1997)
[5] I Schechter, *Rev. Anal. Chem.* **16**, 173 (1997)
[6] R A Multari, L E Foster, D A Cremers and M J Ferris, *Appl. Spectrosc.* **12**, 1483 (1996)
[7] J Uebbing, J Brust, W Sdorra, F Leis and K Niemax, *Appl. Spectrosc.* **45**, 1419 (1991)
[8] V N Rai, F Y Yueh and J P Singh, *Appl. Opt.* **42**, 2094 (2003)
[9] S Nakamura, Y Ito, K Sone, H Hiraga and K I Kaneko, *Anal. Chem.* **68**, 2981 (1996)
[10] K J Mason and J M Goldberg, *Appl. Spectrosc.* **45**, 1444 (1991)
[11] V N Rai, A K Rai, F Y Yueh and J P Singh, *Appl. Opt.* **42**, 2085 (2003)
[12] V N Rai, J P Singh, F Y Yueh and R L Cook, *Laser and Particle Beam* **21**, 65 (2003)
[13] W A Spencer, F M Pennebaker, N M Hassan, J E McCarty and C W Jenkins, Rep. No. BNF-003-98-0199 Rev, Feb. 7 (2000) Savannah River Technology Center, Savannah River Site, Aiken, SC
[14] R C Weast (ed.), *CRC handbook of chemistry and physics*, 68 edition (CRC Press Inc., Florida, 1987–88)
[15] J M Dowson, *Phys. Fluids* **7**, 981 (1964)
[16] L St-Onge, M Sabasabi and P Cielo, *Spectrochim. Acta* **B53**, 407 (1998)
[17] C E Max, Physics of the coronal plasma in laser fusion targets, in *Laser plasma interaction* edited by R Balian and J C Adams (North Holland Publishing Co., Amsterdam, 1982)
[18] H Nakano, T Nishikawa, H Ahn and N Uesugi, *Appl. Phys.* **B63**, 107 (1996)
[19] H M Milchberg and R R Freeman, *J. Opt. Soc. Am.* **B6**, 1351 (1996)
[20] R M Moore, K H Warren, D A Young and G B Zimermann, *Phys. Fluids* **31**, 3059 (1988)