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The effect of evaporation on the analyte emission intensities during power interruption in an inductively coupled plasma

F. H. A. G. Fey, J. M. de Regt, J. A. M. van der Mullen* and D. C. Schram
Physics Department, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract—A power interruption technique is used to study the population balances of excited states of analytes in an inductively coupled plasma (ICP). Measurements on Li analyte emission show that the Boltzmann balance of excitation of and de-excitation to the ground state is the dominant population process for the lower excited levels. During the power interruption, changes in the excitation and de-excitation flows are visible and it turns out that the ionization degree of Li depends strongly on position, central flow and plasma power. The results cannot be explained unless evaporation of analyte is assumed to have an important impact on the excitation flow in the Li system.

1. Introduction

The density of excited states of elements in an inductively coupled plasma (ICP) can be interpreted as a result of balances that govern the population and depopulation of the levels [1–4]. Important balances are the Saha balance of ionization of and recombination to an excited state p and the Boltzmann balance of excitation from and de-excitation to the ground state. In these balances, electrons play an important role since they deliver or absorb the process energy. Therefore it is clear that they depend on electron temperature and density, T_e and n_e. Much less known, or at least realized, is the fact that the transport associated with the phenomena of analyte evaporation can strongly affect the balances [3] as well.

In this study we will investigate the population balances of analytes by removing the (energy) source of the temperature inequality of electrons and heavy particles: $T_e > T_h$. This is done by interrupting the electromagnetic (EM) field, based on the technique of Gurevich and Podmoshenskii [5]. At switching off the generator, the electrons cool down to the heavy particle temperature, and consequently during the off-period the plasma will be recombining. When the generator is switched on again, electrons are heated and the plasma returns to its original situation. The line intensities of excited levels reflect the changes in the balances that govern the population and depopulation of these levels. Therefore we are able to investigate the important properties of the plasma during the interruption if we understand the population balances.

For example, a level populated by the Saha balance will jump upward at switching off as a result of the shift of the ionization balance to the lower energy level (the excited state) (Fig. 1(a)). Since the relative jump is a function of T_e, T_h and the ionization energy of the excited level, I_p, it is possible to calculate T_e and T_h when the relative jump is measured as a function of I_p (cf. Section 2) [6, 7]. A demand is that the levels in question should be sufficiently close to local Saha equilibrium. This is valid for the highly excited levels of argon, the main gas of the plasma.

Recently we showed [1] that line intensities of analyte levels have a totally different response (Fig. 1(b)). This can be interpreted as a response of the Boltzmann balance of excitation from and de-excitation to the ground state of that atom. We argued that the difference between the behaviour of an analyte line and an argon line is a consequence of "the relatively small excitation energy of the excited analyte" compared to that of argon (11 eV). However, it is just part of the story. The method of

* Author to whom correspondence should be addressed.

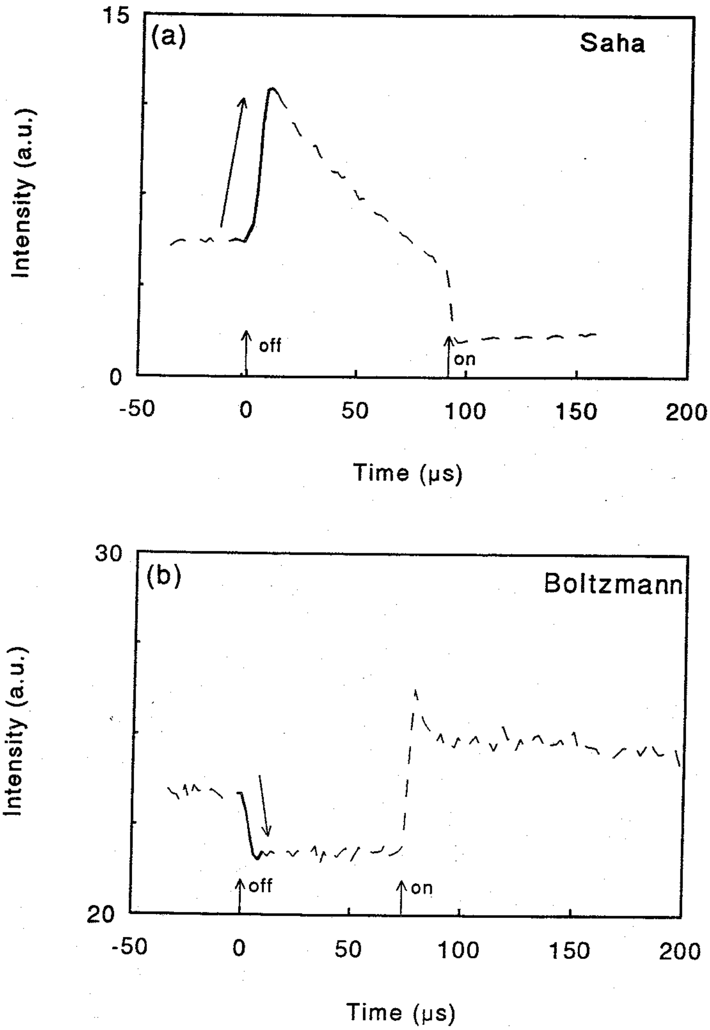

Fig. 1. Typical responses of levels which are populated respectively by (a) the Saha balance of ionization and recombination, and (b) the Boltzmann balance of excitation from and de-excitation to the ground state atom. Note that the Saha dominated level is going upward, whereas the response to cooling (at $t = 0$) for the Boltzmann dominated level is going downward.

introducing elements into the plasma is important as well: argon is introduced as a gas while metals are introduced by means of nebulized solutions. In fact, it will be shown in this and the next paper that the analyte evaporation process is such a large source of ground state atoms that it causes a large overpopulation of the analyte ground state in the environment of the former analyte particle. OLESIK and FISTER [8, 9] recently observed this effect for large vaporizing, desolvated particles. They observed, in time, separated small peaks of Ca I intensity, followed by an increase of Ca II intensity. The peak in the Ca I intensity reflects two processes: first, population of the upper level from the ground state (Boltzmann balance) as the analyte evaporates; second, depopulation of the level by excitation to the ion level. Essentially, the Ca I peak thus reflects the stepwise ionization flow from the ground state to the ion level. This flow is caused by the temporal overpopulation of the ground state. Actually, the initial overpopulation of the ground level is so large that there is hardly a Boltzmann *balance*, i.e. excitation balanced by de-excitation. Instead, it is a one-directional flow.

However, most of the analyte that evaporates is carried by small droplets, which will not show such clear peaks. The reason is that the number density of droplets that

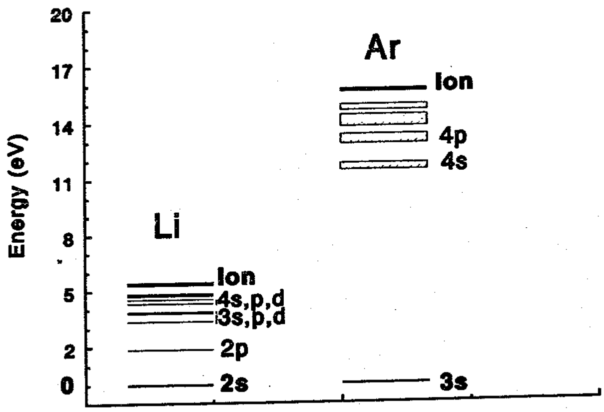

Fig. 2. The systems of Li and Ar. Excitation or charge exchange between these two systems is impossible since the systems do not have (quasi) overlap of energy levels.

enter the plasma is very large, i.e. the order of 10^{10} to 10^{11} m^{-3} (for a cross-flow nebulizer). Therefore, we may expect to observe (measuring with a monochromator) more than one evaporating periphery of a former particle at the same time. In fact, due to overlap in time and space, we will observe a more or less steady state behaviour of ensembles of vaporizing particles which are transported into and out of the observation volume. So, in contrast with Refs [8, 9] where the desolvation and evaporation of individual large droplets were observed, our study is focused on the averaged effect of an ensemble of evaporation processes.

To study the influence of the plasma parameters on the atomic state distribution function theoretically, one can use a collisional radiative model (CRM) [10–12]. Benoy *et al.* [10] already showed that for the argon system such a model can be used to calculate the contributions of the Saha and the Boltzmann balances to the state density separately. These calculations confirm the assumption in our former paper that the highly excited argon levels are very close to Saha equilibrium. Boltzmann processes are, especially due to the large excitation energy, almost negligible. The CR models treating analyte systems [11, 12] show that analyte levels are also mainly ruled by the Saha balance, predicting that the response to power interruption should be in accordance with Fig. 1(a) instead of Fig. 1(b). This conflict with the experimental fact that highly excited metal states behave differently from those of Ar can be traced back to the fact that the CR models use the same gradient lengths to describe the transport phenomena of argon and analytes, i.e. the size of the plasma, typically 1 cm. However, for analytes introduced into the plasma via evaporating droplets, the gradient lengths are much smaller, typically several times the droplet diameter, so that the transport fluxes are consequently much larger than for argon. A future article will be dedicated to a CR model for the Li system. This simple system is chosen since Li^+ has a noble gas structure. Therefore we can neglect excitation effects in the Li^+ system. Also, it is not possible for Li to exchange charge or excitation with Ar, because the atomic levels do not fit each other (Fig. 2). Therefore we are able to apply a simple scheme like the one Benoy *et al.* [10] used for argon.

In the present study, we will confine ourselves to the experimental results which, for the time being, can be interpreted globally by a simple model.

2. Theory: Responses of Balances to Interruption

The response of a level to power interruption is the result of the changes in all balances that govern the population and depopulation of that level. Since we confine ourselves in this paper to a very simple element, Li, we only have to consider the Saha (S) and the Boltzmann (B) balances. In order to obtain a general view, we

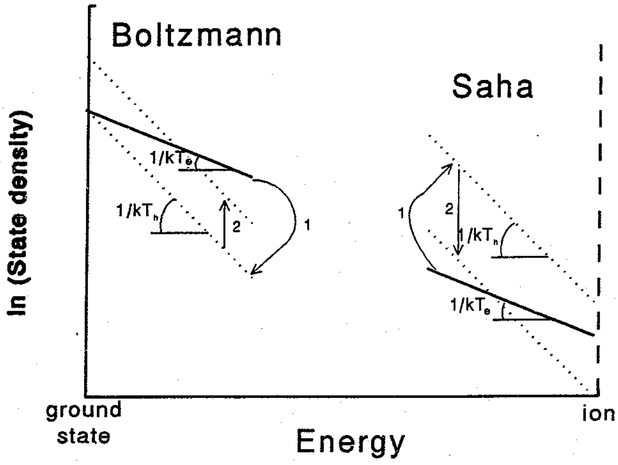

Fig. 3. The response to the power interruption for levels that are ruled by the Boltzmann balance or the Saha balance. Two phenomena are visible. First, we observe the response to cooling of the electrons from T_e to T_h (indicated by 1). Second, we see the recombination of the ions towards the ground state (indicated by 2).

consider the interactions with the most important levels: the ground state and the ion level. The reaction equations for these balances read respectively:

$$\mathrm{Li}(p) + \mathrm{e} + (I_p) \leftarrow \mathrm{S} \rightarrow \mathrm{Li}_1^+ + \mathrm{e} + \mathrm{e} \tag{1a}$$

$$\mathrm{Li}(p) + \mathrm{e} \leftarrow \mathrm{B} \rightarrow \mathrm{Li}(2s) + \mathrm{e} + (E_p) \tag{1b}$$

where Li(p) and Li($2s$) refer to the pth excited state and the ground state, Li_1^+ to the ion ground state, I_p to the ionization energy and E_p to the excitation energy of state p. Clearly, these balances are controlled by electrons and are therefore T_e dependent. The corresponding equilibrium densities are given by [1]:

$$\eta^{\mathrm{S}}(p) = \eta^+(1)\,\frac{n_e}{2}\,\frac{\mathrm{h}^3}{(2\pi m_e \mathrm{k} T_e)^{3/2}}\exp\frac{I_p}{\mathrm{k}T_e} \tag{2a}$$

$$\eta^{\mathrm{B}}(p) = \eta(2s)\exp\frac{-E_p}{\mathrm{k}T_e} \tag{2b}$$

where $\eta = n/g$, where $n(p)$ is the level density and $g(p)$ the number of states of level p, and $\eta(2s)$ and $\eta^+(1)$ are the number densities of the atom and the ion ground state, respectively. If $\gamma = T_e/T_h$, i.e. the ratio of the initial to the final electron temperature T_h, then the responses of a Saha state and a Boltzmann dominated state will be:

$$\ln\frac{\eta^{\mathrm{S}}(p)^*}{\eta^{\mathrm{S}}(p)} = \frac{3}{2}\ln\gamma + \frac{\gamma-1}{\mathrm{k}T_e}I_p + \ln\frac{n_e^*}{n_e} + \ln\frac{\eta^+(1)^*}{\eta^+(1)} \tag{3a}$$

$$\ln\frac{\eta^{\mathrm{B}}(p)^*}{\eta^{\mathrm{B}}(p)} = -\frac{\gamma-1}{\mathrm{k}T_e}E_p + \ln\frac{\eta(2s)^*}{\eta(2s)} \tag{3b}$$

where the superscript * refers to the off-period. If changes of n_e, $\eta(2s)$ and $\eta^+(1)$ are neglected, the density of the excited level will increase when it is Saha dominated and decrease when it is Boltzmann dominated (step 1 in Fig. 3). This assumption is valid during cooling of the electrons, owing to the fact that recombination to the ground state is much slower [13]. However, at longer time scales a growth of the ground state density and a decrease of the ion density will occur (step 2 in Fig. 3). This can be due to recombination to the ground state or, in a situation where inward transport (e.g.

Table 1. Instrumentation

RF-generator	100 MHz generator developed by Philips
RF-coil	coil consisting of two windings with diameter of 35 mm and a height of 15 mm
RF pulse circuit	custom designed by Himmel
HV power supply	Himmel, type NE-002, 0–5.5 kVA
Flow controllers	Brooks flow controller, type 5851, range 0–30 l min^{-1} argon Brooks flow controller, type 5850TR, range 0–6 l min^{-1} argon Brooks flow controller, type 5850TR, range 0–2 l min^{-1} argon
Plasma torch	three concentric quartz tubes, developed by BOUMANS and LUX-STEINER [14]
Nebulizer	cross-flow nebulizer, designed by Philips
TTL pulse generator	homemade generator, based on computer controlled counter time cartridge, Metrabyte type CTM05
Monochromator	1-m monochromator with a 1200 grooves mm^{-1} grating, blazed at 500 nm and variable slits, B&M Spektronik, type BM100
PM tube	EMI 9698QB
Amplifier	variable gain amplifier with 2 ns rise time, Philips, model 777
Discriminator	timing discriminator, Philips, model 715
Multi-channel scaler	computer controlled, multi-channel scaler cartridge, EG&G Ortec, type ACE-MCS

due to the vaporization process) is fast, to a "lack of ionization flow" which causes filling up of the ground state and depopulation of the ion level. If during steady state conditions the ion density is larger than the ground state density, then the filling of the ground state will increase the ground state density substantially and that will be reflected in an increase of the density of lower excited states during the recombination period.

3. EXPERIMENTAL

The experimental set-up used for the measurements is essentially the same as described in Ref. [1]. The instrumentation is listed in Table 1.

Computer controlled triggering starts the interruption of the rf plasma generator and (at the same moment) the time dependent continuous photon counting set-up (Fig. 4). In this way a

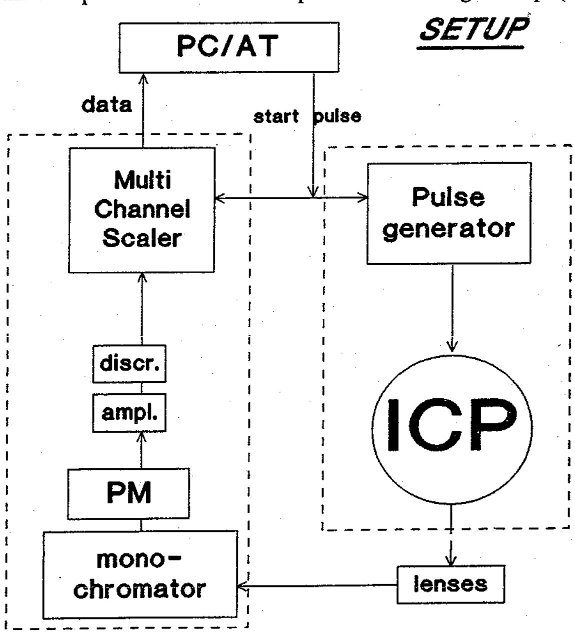

Fig. 4. Schematic view of the set-up. The starting trigger pulse of the power interruption and the multi-channel scaler is created by a counter/timer computer cartridge. During the interruption the multi-channel scalar counts the discriminated photon pulses of the amplified photomultiplier signal. In this way, the time dependent intensity is measured as a function of time, averaged over a programmed number of repetitions.

kind of digital integrating oscilloscope with a total resolution of 2 μs is created to measure a repeating signal of a line intensity. This resolution is sufficient to observe the different steps in Fig. 3. However, we are restricted to those levels that have a substantial density and radiative transition probability in the wavelength interval from 180 to approximately 800 nm.

4. Results

4.1. *Outline*

In order to test and clarify the ideas about the influence of evaporation on analyte emission we should realize experimental conditions in which relevant parameters can be changed more or less independently. The experimental approach will be guided by the following global model:

1. the droplets are injected at the centre of the plasma and therefore the droplet concentration will be the largest at the centre;
2. owing to the evaporation of the droplets, the droplet density or at least the total droplet surface area decreases downstream;
3. an increase of the central flow, ϕ_c, will (a) increase the droplet density for moderate ϕ_c values [15], and (b) decrease the temperatures in the central region (due to smaller residence times). Changes in droplet size will be neglected;
4. an increase of plasma power will change plasma parameters in the skin as well as in the centre, especially n_e, T_e, T_h and the skin depth; and
5. heating of the central region is mainly governed by heat conduction from the skin to the centre, driven by the temperature gradients of T_e and T_h. In the central region from $z = 0$ mm above the load coil (ALC) to at least 10 mm ALC we can expect that T_e and T_h increase downstream since the energy input exceeds the losses.

The global model reveals that the response should be studied spatially resolved, both axially and radially and that the central flow rate and the plasma power P are important parameters. Therefore, lateral scans have been made for three Li levels ($2p$, $3s$ and $4d$). After Abel inversion we obtained the radially resolved information of the relaxation experiments. Afterwards we also varied the observation height, the central flow rate and the plasma power.

4.2. *Dependence on radial position*

As pointed out above, we may expect large radial gradients of analyte concentration due to the fact that the droplets are only present in the centre of the plasma. This is easily observed in the steady-state intensities of the Li levels $2p$, $3d$ and $4d$ (Fig. 5(a)) at a height of 5 mm ALC. In Fig. 5(b)–(d) the corresponding radially resolved responses of the Li levels are shown. First, we take a general view. For each level we observe at $t = 0$ at every position a downward jump directly after switch off. This is the effect of the cooling of the electrons on the Boltzmann balance of the observed level to the ground state. Because the jumps of Li($4d$) are smaller than those of Li($3d$) we have to conclude that, according to Eqns (3a) and (3b), the Saha balance also has some influence on the occupation of Li($4d$). The relative jump is dependent on the radial position and tends to be largest at approximately $r = 2.25$ mm. If we apply Eqn (3b) without taking into account the changes in the ground state density, we find that the value of γ ($= T_e/T_h$) should be a maximum at that position. This is not very likely. In fact, a secondary and mostly much slower effect than the cooling, namely the recombination, also starting at $t = 0$, is important at radial positions larger than $r = 2.25$ mm. In this case, the recombination seems to be as fast as the cooling. This contrasts with the results of Miller's analysis of the argon jumps [13] (Saha dominated), from which he concluded that for argon the relative jump of argon levels at cooling is virtually unaffected by the recombination of Ar^+.

The reason why recombination is important for Li levels at 5 mm ALC and $r \geqslant 2.25$ mm is a consequence of the large ionization degree ($n_+ >> n_1$) at those radii before the switch off of the generator. However, at small radii ($r < 2.25$ mm) the

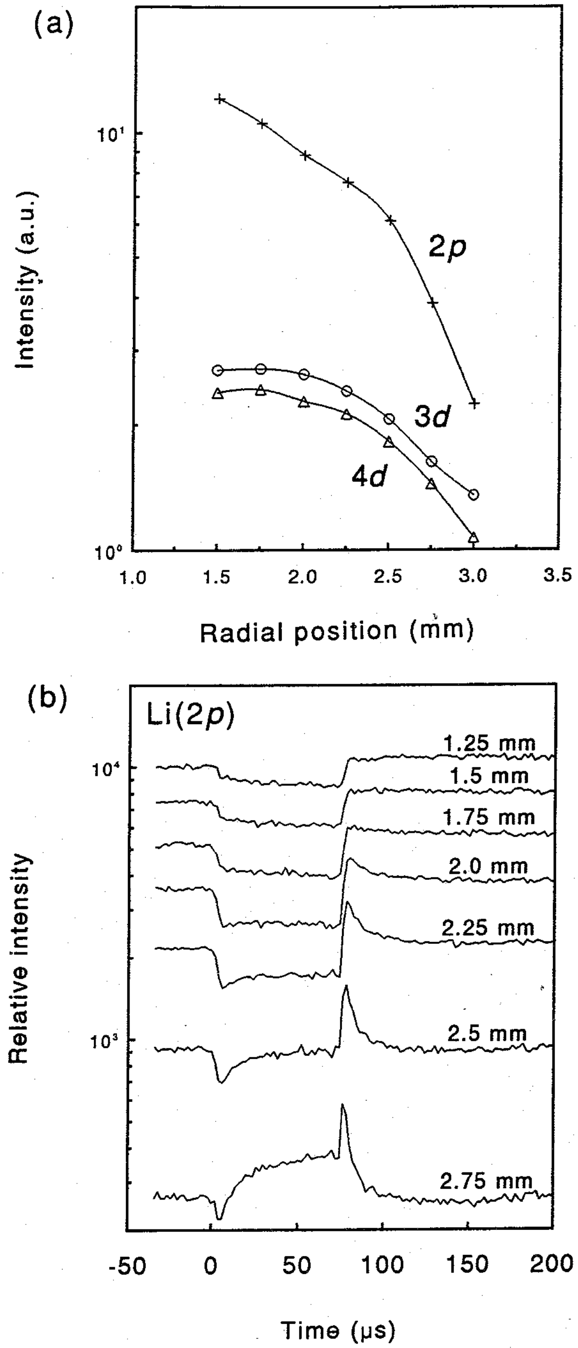

Fig. 5. Continued

ionization degree is apparently much smaller since we observe a further decrease of density after the cooling of the electrons, owing to recombination of Ar ions (time constant of this process is approximately 200 μs [1, 16]). At this height and plasma conditions, T_e is above 0.5 eV in the centre of the plasma according to the measurements of NOWAK *et al.* [17], and, according to the results of Refs [11, 12] it is expected that $n(p) \approx n^S(p)$ so that $n_+ >> n_1$ for Li. However, our measurements show (at least) that $n_+ \lesssim n_1$. Therefore, the latter effect can only be caused by large overpopulation of the ground state; *the rate of vaporization of analyte must be large with respect to the rate of ionization.*

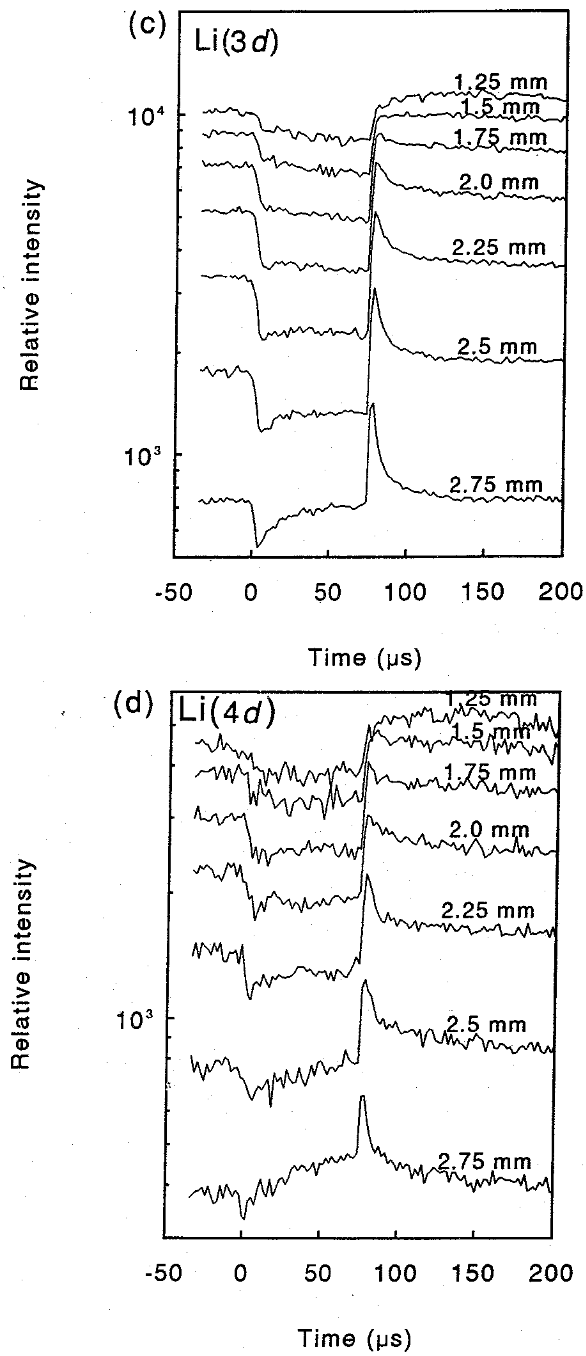

Fig. 5. Radially resolved intensities of the Li levels $2p$, $3d$ and $4d$. In (a) the scaled steady-state intensities of the levels are shown as a function of the radial position. Especially, the Li($2p$) density decreases rapidly with radius. In (b)–(d), the responses are shown of $2p$, $3d$ and $4d$, respectively, to the power interruption for several radial positions, from $r = 1.25$ mm to $r = 2.75$ mm. The relative intensities are shown on a logarithmic scale. The plots have been mutually shifted in the y direction to facilitate the visualization. Note that, at all levels, the jump is downward at switching off, regardless of the radial position. Plasma power 840 W; outer flow 12.0 l min^{-1}; intermediate flow 0.3 l min^{-1}; central flow 0.7 l min^{-1}; number of repetitions is 4000; time per channel 2 μs; and repetition frequency 39.7 Hz.

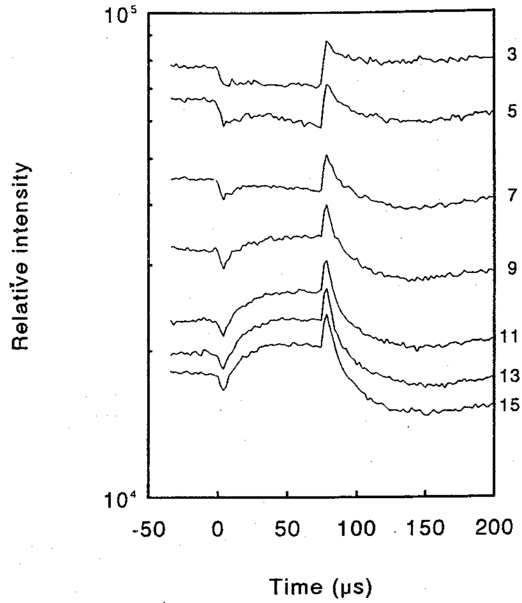

Fig. 6. Response of Li(2*p*) (scaled logarithmically) to interruption in the centre ($r = 0$, without Abel inversion) as a function of the height in the plasma. The plots, shown on a logarithmic scale, were obtained at positions ranging from 3 mm ALC (top) to 15 mm ALC (bottom) as indicated at the right of the diagram. Note that the magnitude of the downward jump at switching off is almost independent of height and that the relative growth of the ground state in the off-period increases with height. This indicates that in the top of the plasma the ionization degree is larger. Plasma power 840 W; outer flow 12.0 l min^{-1}; intermediate flow 0.3 l min^{-1}; central flow 0.6 l min^{-1}; number of repetitions is 4000; time per channel 2 μs; and repetition frequency 39.7 Hz.

4.3. *Dependence on height*

Although the response of the various levels is not exactly the same, we have seen in Section 4.2 that their responses are similar in the centre of the plasma. Also the major amount of radiation is coming from that region. Therefore, we will assume from now on the lateral response of Li(*p*) as indicator for the central region. In Fig. 6 the responses of Li(2*p*) to interruption are shown as a function of height. It shows that the Li(2*p*) steady-state density (and therefore also the ground state density) decreases with height while the increase during recombination after cooling of the electrons is more pronounced in the high than in the lower regions of the plasma. This height dependence of the response to power interruption can be explained by the fact that the ionization degree increases with height. This explanation is confirmed by the decrease of the Li(2*p*) intensity (and therefore also the ground state density).

4.4. *Dependence on central gas flow rate*

In Fig. 7(a) the steady-state intensity of Li(2*p*) at 5 mm ALC is shown as a function of the central flow rate. Note that below approximately 0.55 l min^{-1}, the intensity drops very quickly and that at 0.7 l min^{-1} a maximum is observed. The behaviour depicted in Fig. 7(a) is comparable with the results given in Ref. [15] which show that the efficiency of a cross-flow nebulizer increases with ϕ_c for intermediate ϕ_c-values. Below 0.5 l min^{-1} the nebulizer does not work. Therefore, above 0.5 l min^{-1} the number of droplets reaching the plasma increases rapidly. The difference (above 0.7 l min^{-1}) between the shape of Fig. 7(a) and that of the efficiency of the nebulizer is caused by the fact that the temperature in the centre decreases with central flow due to smaller residence times. This explanation is confirmed by statements 3 and 5 of the global model in Section 4.1.

Under the same conditions, we measured the response of Li(2*p*) to interruption. The results are shown in Fig. 7(b). Below 0.55 l min^{-1}, the intensity increases rapidly

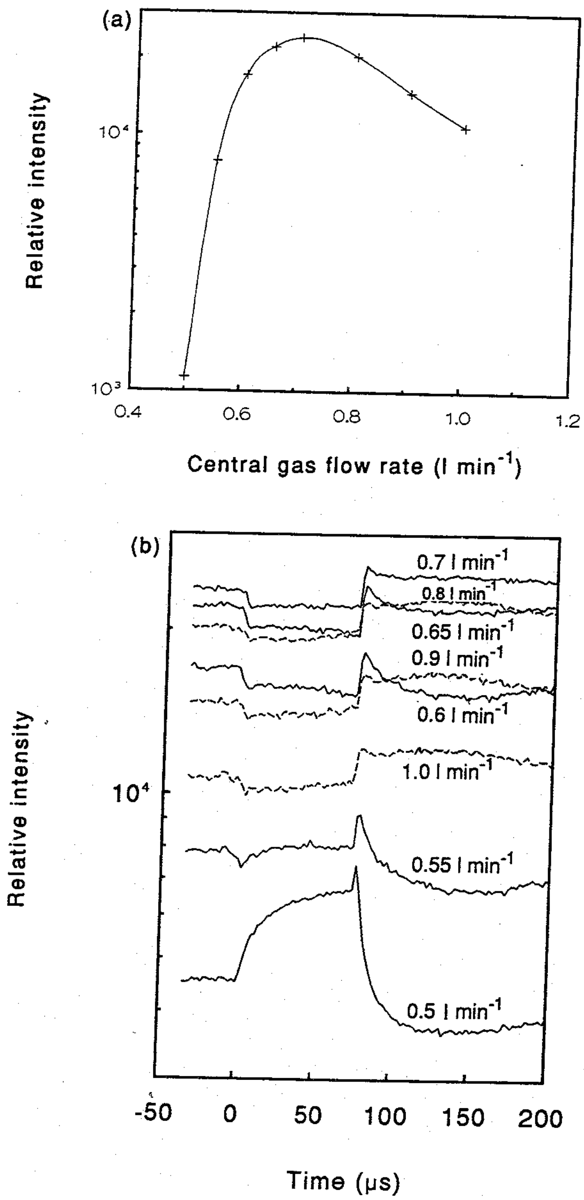

Fig. 7. Lateral intensity of Li(2*p*) (scaled logarithmically) in the centre ($r = 0$, without Abel inversion) as a function of central flow. In (a), the steady-state is shown. The steep cut-off below a central flow of 0.55 l min^{-1} is due to the characteristics of the cross-flow nebulizer, while the decrease of intensity above 0.7 l min^{-1} is due to ineffective heating of the centre at high central flow rates. In (b), the response to power interruption is shown for several central flow rates: 0.5, 0.55, 0.6, 0.65 and 0.7 l min^{-1} (continuous curves) and 0.8, 0.9 and 1.0 l min^{-1} (broken curves). Plasma power 840 W; outer flow 12.0 l min^{-1}; intermediate flow 0.3 l min^{-1}; central flow variable; number of repetitions is 4000; time per channel 2 μs; and repetition frequency 39.7 Hz.

during the off-period, indicating that the ion density is substantially larger than the ground state density. Above 0.55 l min^{-1} we see a fast decrease to a new steady-state indicating the opposite: the neutral density is larger than the ion density.

4.5. *Dependence on plasma power*

The response to interruption is dependent on the plasma power. This is shown in Fig. 8 at 5 mm ALC for two central flows, 0.55 and 0.6 l min^{-1}. These two values are chosen because the responses at these flow rates are critical to variation of parameters

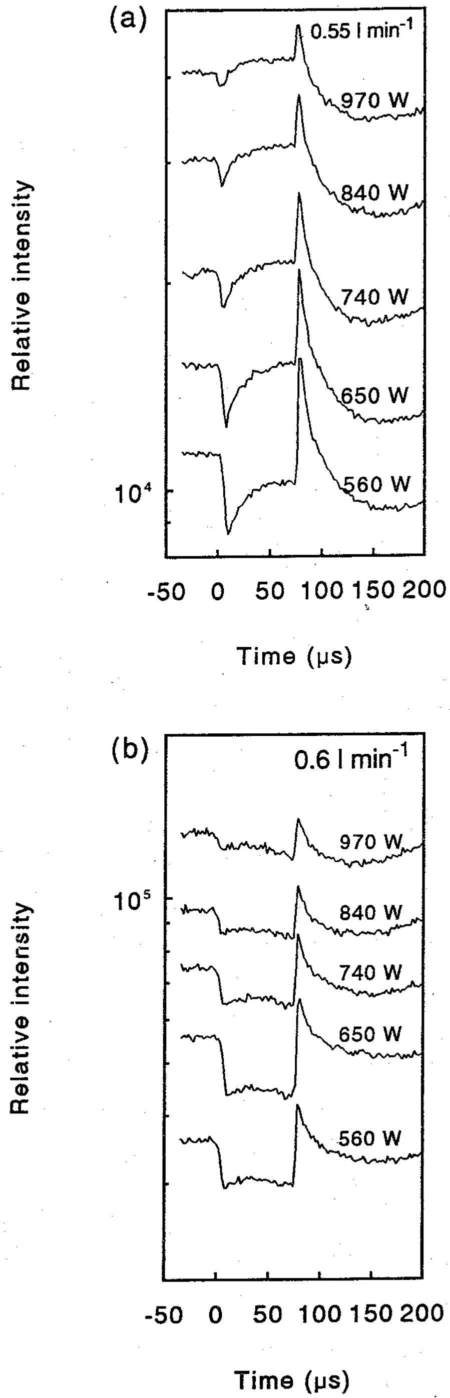

Fig. 8. Lateral intensity of Li(p) (scaled logarithmically) in the centre at 5 mm ALC as a function of power at two central flows. The operated powers are (from bottom to top) 560, 650, 740, 840 and 970 W, respectively. Outer flow 12.0 l min^{-1}; intermediate flow 0.3 l min^{-1}; central flow (a) 0.55 l min^{-1}, (b) 0.6 l min^{-1}. Number of repetitions is 4000; time per channel 2 μs; and repetition frequency 39.7 Hz.

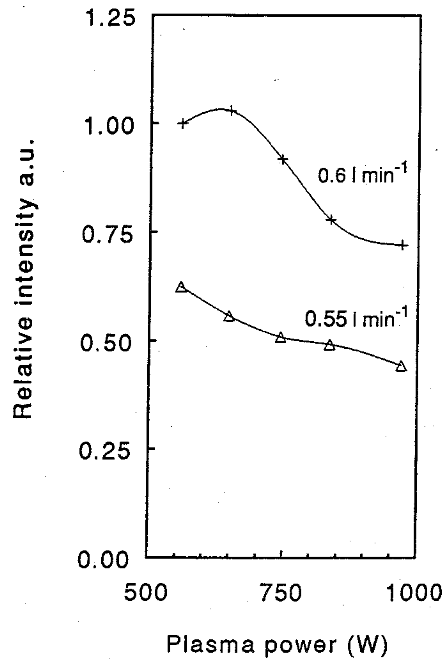

Fig. 9. Steady-state intensity of Li(2*p*) in the centre at 5 mm ALC as a function of power at two central flows. Outer flow 12.0 l min^{-1} min; intermediate flow 0.3 l min^{-1}; central flow (a) 0.55 l min^{-1}, (b) 0.6 l min^{-1}. Number of repetitions is 4000; time per channel 2 μs; and repetition frequency 39.7 Hz.

(see, for example, the former Section). In Fig. 8(a) and (b) we observe that the relative jumps to cooling and heating decrease with power. This means, according to Eqn (3b), that in both cases γ decreases with power. This is strange since one might expect that the temperature difference should increase when more energy is transferred from electrons to heavy particles. However, owing to the higher temperatures (T_e and T_h) in the skin, the electron density increases faster than the power. Moreover, since the electron density and temperature in the skin increases with power, the skin depth of the EM field will decrease; the EM field will be absorbed before it reaches the centre of the plasma. In that case γ will decrease as well.

From Fig. 9, it follows that in both cases considered in Fig. 8, the steady-state ground state density decreases (and ionization increases) with power. This confirms the assumptions used above that electron density and T_e increase with power.

5. Conclusions

From the measurements it follows that the response to power interruption of Li levels largely depends on the plasma parameters. However, in all cases we observe that the most important population mechanism for the Li levels is the Boltzmann balance. This can be concluded from the downward jump of line intensities at switching off. During the off-period we can distinguish two categories. In one category, associated with low ionization degree, line intensities remain unaltered or decrease slowly during the off-period. In the other category, associated with high ionization degrees, line intensities increase fast (with a time constant between 20 and 30 μs) to another steady state. The increase is due to filling of the ground state and is caused by recombination of Li^+ or by a lack of excitation flow from the ground state to the higher levels. The method can be used to classify the analyte regions of the plasma. In the centre, the central channel is clearly visible as a region with low ionization degree. The surrounding region is much more ionized. When the total evaporation of droplets is completed higher in the plasma the slightly ionized central channel disappears. The height at which it has disappeared totally, depends strongly on the energy balance in the centre, which, in turn, is strongly related to the central flow rate and the plasma power.

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