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# The response of metal states to interruption of an inductively coupled plasma

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## ABSTRACT

The response to power interruption of excited metal levels has been studied in an argon Inductively Coupled Plasma, experimentally and numerically as well. It appears that the evaporation process of droplets containing the metal is essential and that the evaporation process must be very quick. With this method it is possible to visualize the ionization flow through the atomic system of metals.

## RÉSUMÉ

La réponse à une interruption de puissance des niveaux excités d'un métal a fait l'objet d'une étude expérimentale ainsi que numérique dans un plasma d'Argon couplé par induction. Le processus d'évaporation des gouttelettes contenant le métal s'avère essentiel. Il se trouve que ceci ne peut s'expliquer que si les gouttelettes s'évaporent suffisament rapidement.

Avec cette méthode, il est ainsi possible de visualiser le flux d'ionisation à travers la structure atomique des éléments métalliques.

## 1. INTRODUCTION

In this paper we present the results of an investigation concerning the response of metal states in an atmospheric argon Inductively Coupled Plasma (as shown in fig. 1) during power interruption. This technique is essentially based on the cooling of the electrons from the initial electron temperature $T_e$ to the heavy particle temperature $T_h$. It can be used to obtain information about the population mechanisms of excited states and parameters like the electron temperature $T_e$ and the heavy particle temperature $T_h$ /1,2,3/. The investigation consists of two parts. The first, experimental part, shows the dependency of the response of a simple, but representative metal, Li, as function of the position and the argon flow rates. The second, numerical, part simulates and explains these results by using a time dependent Collisional Radiative Model (CRM).

The background of this research is the fact that excited metal levels react totally different to power interruption than excited Ar levels (see fig. 2). One can explain these differences qualitatively by assuming that excited Ar levels are populated by the Saha balance ($S$) of ionization of and recombination to that level, whereas excited metal levels are completely populated according to the Boltzmann balance ($B$) of excitation of and deexcitation to the ground state. But, one also has to explain why metals are dominated by $B$ and Ar by $S$.

A first attempt for explanation is /3/ that Ar has a large energy gap between the ground state and the first excited level, while met-

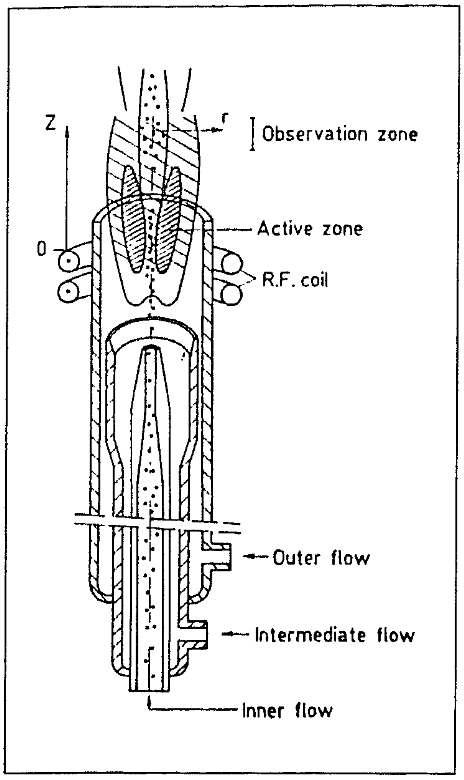

Figure 1. The ICP; note that droplets are injected in the centre of the plasma.

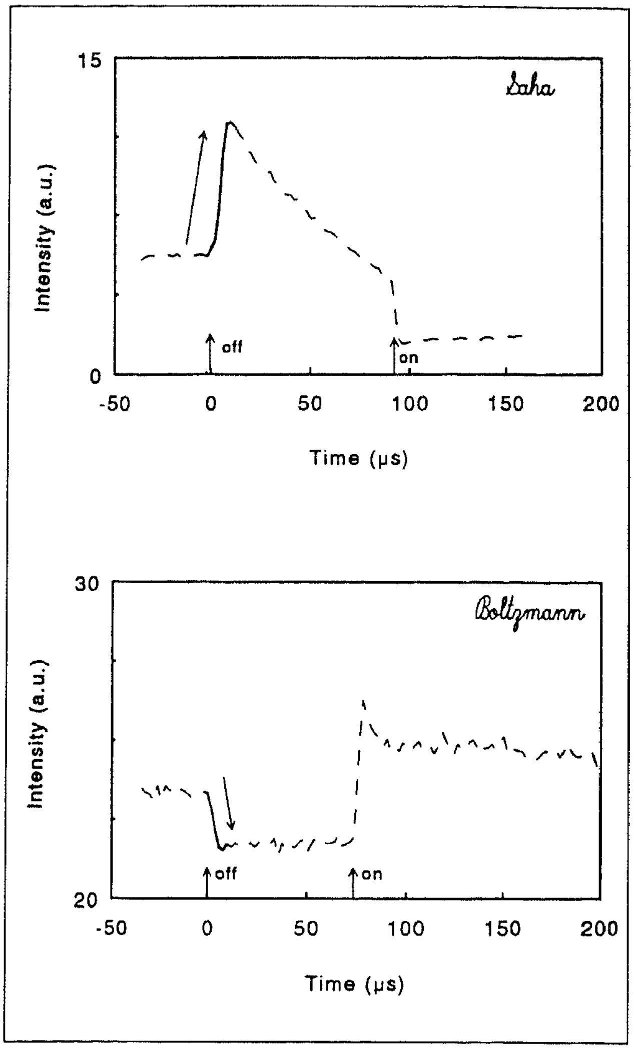

Figure 2. Typical responses for Ar(6d) and Li(2p), which populations are dominated respectively by the Saha and the Boltzmann balance.

als have not. Therefore, the coupling with the ground state is for excited metal levels much better than for Ar. Calculations using a steady state CRM confirm this explanation for Ar: bad coupling to the ground state causes an almost total dominancy of $S$ for the population of excited levels. On the other hand, application of these kinds of models also show that $S$ *and* $B$ are important for metals; the higher the level, the more important $S$ is. This explanation therefore is not satisfactory.

VAN DER MULLEN provides us a second possibility in /4/; due to local production or large gradients of ground state atoms the ground state becomes overpopulated, the whole system ionizing and the influence of $B$ on excited levels larger. This possiblity is realistic, since the metal is introduced in the centre of the plasma by means of very small droplets ($\approx 2\ \mu m$ diameter) of an aqeous solution. The evaporation of the droplets creates local sources of metal ground state atoms, which diffuse to outer parts or ionize. In fact, OLESIK and FISTER recently observed seperate droplets in the centre of the plasma /5/. In order to verify this theory we have to find out whether the evaporation process is fast enough to influence the atomic state distribution function (ASDF) so that $B$ becomes dominant. This can be done by comparing experimental and numerical results of responses of Li levels to power interruption, based on a Collisional Radiative Model.

## 2. THEORY

### 2.1. *Simplified interpretation of responses of balances*

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. The most important are the Boltzmann balances and the Saha balance. In order to obtain a general view we consider the interactions with the most important levels, the ground state level and the ion level. The reaction equations for the governing balances read respectively:

$$Li(p) + e + (I_p) \longleftarrow S \longrightarrow Li_1^+ + e + e,$$

$$Li(p) + e \longleftarrow B \longrightarrow Li(2s) + e + (E_p), \quad (1)$$

where Li(p) and Li(2s) refer to the $p^{th}$ 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 /3/

$$\eta^S(p) = \eta_+(1)\frac{n_e}{2}\frac{h^3}{(2\pi m_e kT_e)^{\frac{3}{2}}} exp\frac{I_p}{kT_e},$$

$$\eta^B(p) = \eta(2s)\exp\frac{-E_p}{kT_e}, \quad (2)$$

where $\eta = n/g$, with $n(p)$ the level density and g(p) the number of states in level p, and $\eta(2s)$ and $\eta_+(1)$ the number density of respectively the atom and the ion ground state. Letting $\gamma = T_e/T_h$, the ratio of the initial to the final electron temperature $T_h$, the responses of states, dominated respectively by the Saha and the Boltzmann balance will be:

$$ln\frac{\eta^S(p)^*}{\eta^S(p)} = \frac{3}{2}ln\gamma + \frac{\gamma-1}{kT_e}I_p + ln\frac{n_e^*}{n_e} + ln\frac{\eta_+(1)^*}{\eta_+(1)},$$

$$ln\frac{\eta^B(p)^*}{\eta^B(p)} = -\frac{\gamma-1}{kT_e}E_p + ln\frac{\eta(2s)^*}{\eta(2s)}, \quad (3)$$

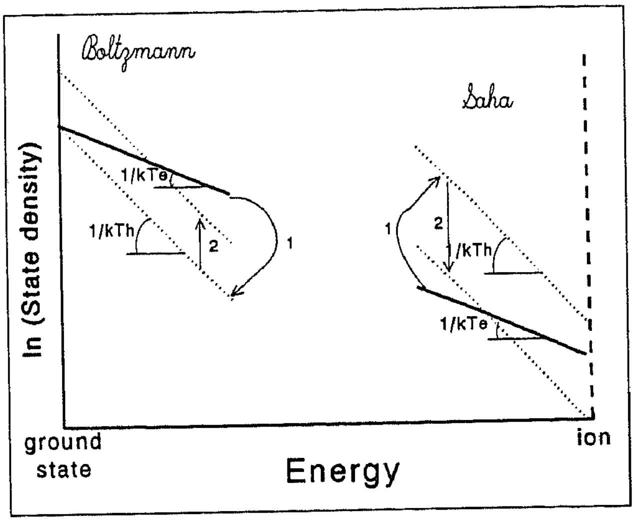

Figure 3. The response to the power interruption for levels which are ruled by the Boltzmann balance or the Saha balance. Two phenomena are visible. First we observe the response to cooling of the electrons from $T_e$ to $T_h$ (indicated by 1 ). Secondly we see the recombination of the ions towards the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

where '*' refers to the off period. When density changes of $n_e$, $\eta(2s)$ and $\eta_+(1)$ are neglected the density of the excited level will increase if 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, due to the fact that recombination to the ground state is much slower /6/. At longer timescales a growth of the ground state density and a decrease of ion density will occur (step 2 in Fig. 3). This can be due to the *recombination to the groundstate* or, in a fast diffusing situation (like around an evaporating droplet), to a *'lack of ionization'* which causes filling up of the ground state and depopulation of the ion state. When during steady state conditions the ion density is larger than the ground state density, then the filling of the ground state will increase substantially and that will be reflected as increase of the density of lower excited states. However, this simplified interpretation does not provide information when and why a flow through the system occurs. For that we need a CRM which can calculate these terms independently (see next subsection).

### 2.2. *A more general view; the Collisional Radiative Model*

A more sophisticated and elaborate way for interpretation is the use of a Collisional Radiative Model (CRM) /7/. It describes the collisional and radiative production and destruction processes of a level p, $S_p^{CR}$, as a source term in the continuity equation

$$\frac{\partial n_p}{\partial t} + \nabla \cdot (n_p \mathbf{w}_p) = S_p^{CR}, \qquad (4)$$

in which $n_p$ represents the number density and $\mathbf{w}_p$ the mean velocity. In this model we will take into account the collisional excitation and deexcitation ($B$), collisional ionization and recombination ($S$), radiative recombination and deexcitation. We assume that radiation escapes. In the model the lower level is the ground state and the upper the ion level. Since $Li^+$ has a He-like configuration we can neglect excitation in the ionic system. Therefore the source terms for atomic levels and the ion read for
atomic levels ($1 \leq p \leq \infty$ ):

$$\begin{aligned} S_p^{CR} &= n_e \sum_{q \neq p} n_q K_{qp} - n_e n_p \sum_{q \neq p} K_{pq} \\ &+ \sum_{q>p} n_q A_{qp} - n_p \sum_{q<p} A_{pq} \\ &+ n_e n_+ (n_e K_{+p} + A_{+p}) - n_e n_p K_{p+}, \end{aligned}$$

ion:

$$\begin{aligned} S^{+CR} &= n_e \sum_q n_q K_{q+} - n_e^2 n_+ \sum_q K_{+q} \\ &- n_e n_+ \sum_q A_{+q}, \end{aligned} \qquad (5)$$

in which $K$ is the $T_e$ dependent rate coefficient for collisional processes and $A$ the transition probability for radiative processes. The subscripts in the coefficients indicate the initial and the final state of the process. Because all transitions occur from one level to another, the sum of all source terms equals zero. Equation 5 shows that all atomic levels contribute to the source term of any other level. Especially important are the adjacent levels since they determine the stepwise ionization and recombination flows through the system. This stepwise flow through the system is treated analytically for highly excited levels which enables us to diminish the number of levels taken into account.

In contrast to the simplified interpretation, given in section 2.1, this method is able to deal with transport and diffusion by introducing $\nabla \cdot (n_p \mathbf{w}_p) \neq 0$. In this model we choose that the *ions are partly removed by diffusion*. This means,

$$\nabla \cdot (n_+ \mathbf{w}_+) \approx \nabla \cdot D_+ \nabla n_+ \approx \frac{D_+ n_+}{L^2} = \gamma_t^+ n_+, \qquad (6)$$

where $D_+$ is diffusion coefficient for ions, L the gradient length and $\gamma_t^+$ a transport frequency. We assume that the *excited levels are not transported*, so in a steady state condition the outflux of ions is equal to the influx of ground state atoms, caused by the evaporation source of analyte ($\nabla \cdot (n_1 \mathbf{w}_1) = -\gamma_t^+ n_+$). For further details of this model we refer to /7/.

## 3. EXPERIMENTAL RESULTS

For the measurement of the response of excited Li levels we use the setup as described in /3,8/. With this setup it is possible to measure the line intensities during interruption; by averaging over a few thousands of repetitions a good signal to noise ratio is obtained. Since the densities of the levels are low we may neglect absorption of radiation.

It appears that the response is very sensitive to changes in plasma parameters and parameters concerning the evaporation. For example, in fig. 4 we show the response of the levels 2p and 4d at various radii at 5 mm above the load coil. During the switching off at $t = 0$ all observed densities jump down, whereby the relative jump depends on the radial position. In this same period the electrons cool down to the heavy particle temperature $T_h$. We can interprete this jump more or less as the direct response of the dominant balance for that level to the cooling of the electrons. Thus, *Li(2p) and Li(4p) are dominated by the Boltzmann balance with the ground state.* Differences occur in the period

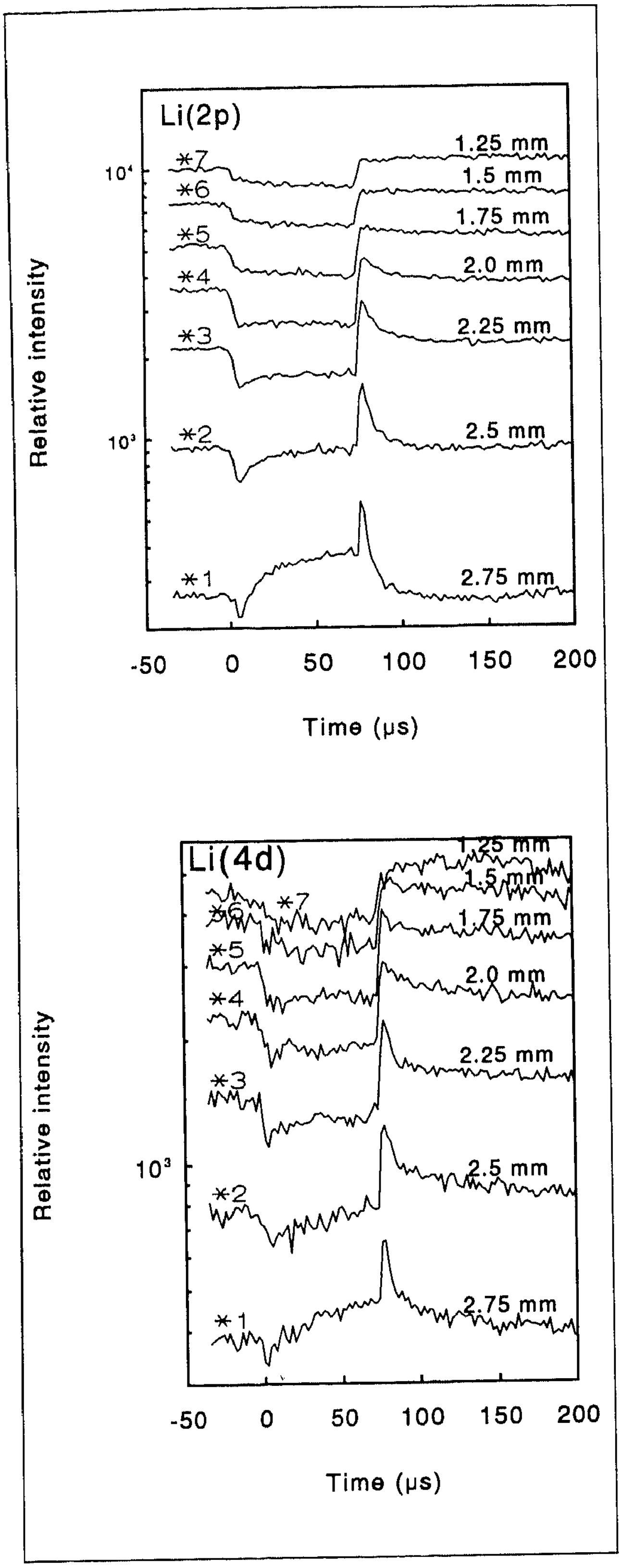

Figure 4. Radially resolved responses of Li(2p) and Li(4d) at 5 mm above the load coil. Plasma power 840 W; outer flow 12 slm, intermediate flow 0.3 slm and central flow 0.7 slm

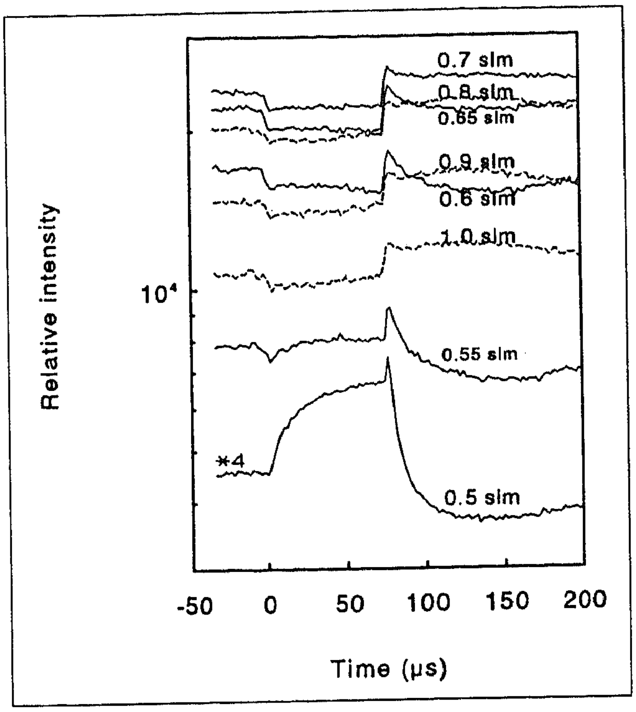

Figure 5. Lateral intensity of Li(2p) in the centre ( r=0, without Abel inversion) as function of central flow. Plasma power 840 W; outer flow 12 slm, intermediate flow 0.3 slm and central flow 0.6 slm

after the cooling; in the centre (at $r$ = 1.25 mm) the density starts to decrease slowly while in the more outer region (at $r$ = 2.75 mm) the density suddenly increases fast. The reaction in the centre can be explained if $T_e$ decreases very slowly due to energy losses of the plasma. In the outer part a density increase of the ground state is very likely. The reason for that can be, as explained in section 2.2, recombination in the system as well as a lack of ionization. One also can explain these results in terms of ionization degree. If the ionization degree is large before switching off, the temperature jump will cause a considerable recombination flow towards the ground state so that the corresponding density will increase quickly.

Another example of the sensitivity for small changes in parameters is given in fig. 5. In this series of experiments the central flow is varied. Increase of flow causes a larger droplet density in the centre and somewhat lower temperatures. At low flow rates the nebulizer which creates the droplets is quite ineffective. According to the response the ionization degree is in this case large. For higher flow rates the ionization degree decreases very quickly.

By also measuring the response as function of height and as function of plasma power (not shown) we get an impression of the central part of the plasma and the evaporation process. We can make the following global model /8/:

1. The droplets are injected in the centre of the plasma and therefore the droplet concentration will be the largest in the centre.
2. Due to the evaporation of the droplets the droplet density or at least the total droplet surface area decreases downstream.
3. Increase of the central flow will (a) increase droplet density, (b) decrease temperatures in the central region (due to smaller residence times), but (c) leaves the droplet size more or less unaltered.
4. The droplet density may become that large that the inter droplet distance becomes smaller than the analyte diffusion lengths around an isolated droplet.
5. Increase of plasma power will change plasma parameters in the skin as well in the centre, especially $n_e$, $T_e$, $T_h$ and skin depth.
6. Heating of the central region is governed by heat conduction from the skin to the centre. Also the EM-field will heat the central region sligthly.

## 4. NUMERICAL RESULTS

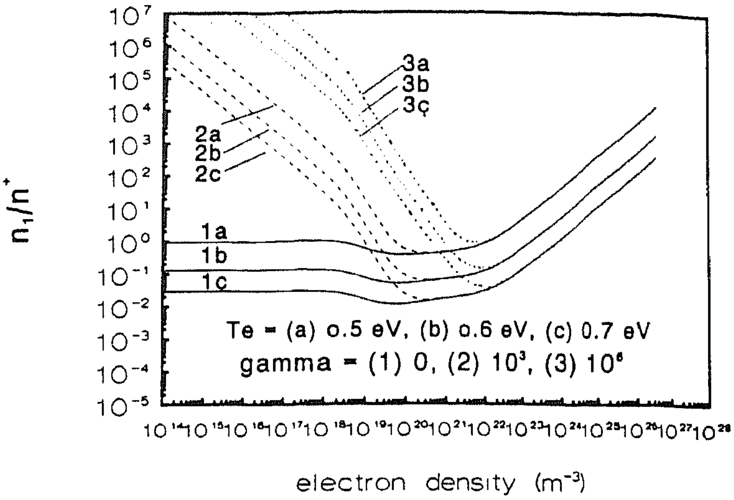

Figure 6. Steady state ratio of $n_1$ and $n_+$ of Li for some transport frquencies and electron temperatures.

A typical result of the CRM, the steady state ratio of $n_+$ and $n_1$, is shown in fig. 6 for some transport frequencies and temperatures as function of $n_e$. We see that the ratio grows with the transport frequency, or in other words; a large flow through the system must be driven by a large overpopulation of the ground state. It appears that for large $n_e$-values the ratio becomes independent of $\gamma_t^+$. The reason for this behaviour is that the influence of transport through the system on the atomic state distribution is limited in case the flow is small compared to the total number of excitations and deexcitations (which grow with $n_e$).

In order to find out whether this whole approximation is able to simulate the power interruption we calculate the time dependent behaviour for some characteristic situations in the centre, given by:

$$\begin{aligned} T_e &= 0.6\ eV,\ T_h = 0.55\ eV, \\ n_e &= 2.5 \cdot 10^{20}\ m^{-3},\ \gamma_t^+ = 1 \cdot 10^4\ s^{-1} \end{aligned}$$

and

$$\begin{aligned} T_e &= 0.5\ eV,\ T_h = 0.45\ eV, \\ n_e &= 2.5 \cdot 10^{20}\ m^{-3},\ \gamma_t^+ = 1.25 \cdot 10^6\ s^{-1}. \end{aligned}$$

It turns out that our expectations are confirmed by the calculations (fig. 7). The density of excited levels jumps downward at switching off and increases later on, when temperature and ionization degree are high during steady state conditions (starting condition $T_e = 0.6$ eV). The increase during the off period is in this case due to a recombination flow to the ground state. In the other case for lower temperature and ionization degree and, partly caused by a large transport frequency, the excited level Li(2p) and the ground state remain more or less constant during the off period. Highly excited states tend to decrease during the off period due to the influence of the Saha balance, since the ion density also decreases. The small increase of the ground state is rather due to lack of ionization than due to a recombination flow. Note that it is possible to approximate the gradient length for ions around the droplets by means of eq. 6. For $\gamma_l^+ = 10^6$ and $D_+ = 10^{-3}$ (an estimation) we find $L \approx 30$ $\mu m$, a value which is approximately a factor 3 smaller than the average distance between the droplets. Therefore this value is quite realistic. On the other hand, one can estimate with simple calculations that in this case an evaporation time of some hundreds of microseconds is necessary, which is also rather realistic. This is however not yet measured.

## 5. CONCLUSIONS

Using an experimental setup designed for fast and continuous photon counting, it is possible to observe locally the response of excited Li levels to power interruption. Their responses are dominated by Boltzmann balances and especially the Boltzmann balance to the ground state.

Plasma parameters like $T_e$, $n_e$, $T_h$ and local density gradients of ions and ground state atoms and evaporation from atoms out of droplets are the most important factors for ionization and recombination flows; it appears that the power interruption experiment provides direct information about the ionization degree. Additional information can be obtained by simulation of the interruption by using a time dependent Collisional Radiative Model. When more or less realistic parameters are introduced in this model the simulations are qualitatively good comparable to the measurements. It can be expected that further analysis with this method will provide quantitative information about the plasma parameters.

From the experiments we can conclude that the response of metals to power interruption is influenced by the evaporation process. This is especially the case in the central flow in the plasma where temperatures are relatively low (compared to the hot skin) and droplets densities large.

Finally we want to state that this method is a powerfull tool for analysis of these kinds of non equilibrium situations.

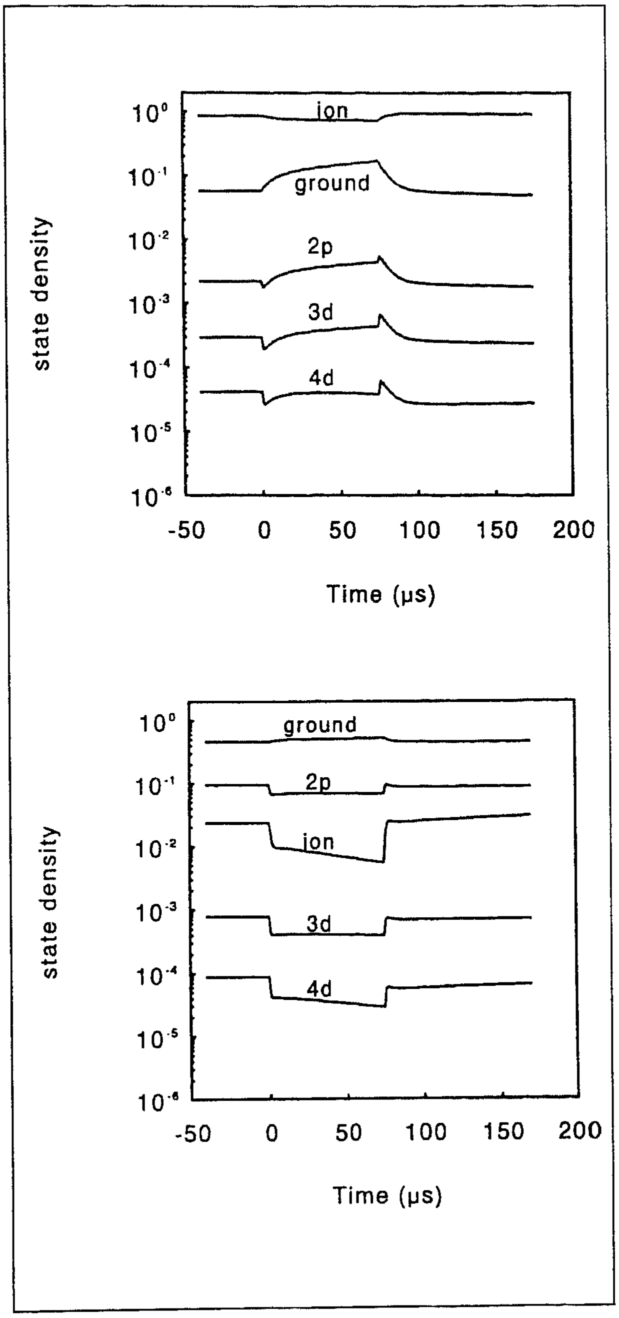

Figure 7. Calculated responses for (a) the conditions $T_e = 0.6$ $eV$, $T_h = 0.55$ $eV$, $n_e = 2.5 \cdot 10^{20}$ $m^{-3}$, $\gamma_l^+ = 1 \cdot 10^4$ $s^{-1}$ and (b) $T_e = 0.5$ $eV$, $T_h = 0.45$ $eV$, $n_e = 2.5 \cdot 10^{20}$ $m^{-3}$, $\gamma_l^+ = 1.25 \cdot 10^6$ $s^{-1}$.

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