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An approach to the ejection mechanisms of Li atoms from pulsed excimer laser ablation of a $LiNbO_3$ target

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Abstract

A nonequilibrium kinetic model is used for predicting the time evolution of the Li atom concentrations (ground and excited states) in the plasma produced by excimer laser ablation of a $LiNbO_3$ target. The model predicts a very high ionization degree (~0.97) that agrees well with the one obtained experimentally (~1). These results together with the prediction of high (and close to local thermodynamic equilibrium) population densities of the electronically excited Li upper energy levels provide an indirect support for an electronic rather than thermal ablation mechanism of Li atoms.

Keywords: Ejection; Laser ablation; Plasma; PLD

1. INTRODUCTION

Lithium niobate ($LiNbO_3$) is a well known material with excellent nonlinear properties of interest for integrated optical devices and for piezo-electric and electrooptic applications (Voger, 1987). When attempting to produce $LiNbO_3$ films, their low Li content has been the problem more often addressed. When using pulsed laser deposition (PLD), which is one of the most successful techniques for producing complex oxide thin films, the Li deficiency has been overcome by using Li-enriched targets (Shibata *et al*., 1995), O_2 and Ar gas mixtures as ambients (Ogale *et al*., 1992), or more recently, high oxygen pressures (Chaos *et al*., 2001). The latter work has provided a preliminary explanation on the Li transport mechanisms from the target to the growing film during the plasma expansion into a gas environment. However, the ejection mechanism of Li, which appears to have an impact on this loss, is not yet clear. Recent experimental results by Chaos *et al*. (2000) reported a delayed release of Li atoms 2–20 μs after the laser pulse, with Li atoms ejecting from the target at very high velocities that are consistent with an electronic ejection mechanism.

The aim of this work is to provide indirect support for the existence of an electronic rather than thermal mechanism underlying the ablation of a $LiNbO_3$ target with a pulsed ArF laser. Our approach in the present work is based on the use of a collisional-radiative kinetic model (Gordillo-Vázquez, 2001) of the nonequilibrium lithium-like plasmas generated by laser ablation of $LiNbO_3$ targets to theoretically determine the concentration of Li atoms (ground and excited) from measurements of the electron density (N_e) and electron temperature (T_e), both used as input parameters of the model. We have also obtained the time evolution of the ground state population density of Li atoms from available measurements of the optical density (Chaos *et al*., 2000). The above results will allow us to estimate and compare the theoretical and experimental ionization degrees in the plasma.

2. APPROACH

In a plasma, where atom–atom inelastic collisions and particle diffusion are neglected, the net production of excited atoms can be determined by balancing all collisional and radiative processes populating and depopulating each atomic level. Thus, the net production rates of Li atoms excited to the ith level and of electrons in the plasma can be calculated, respectively, by (Kunc, 1988)

$$\frac{\partial N_i}{\partial t} = \sum_{j<i} N_e N_j C_{ji} + \sum_{j>i} N_e N_j R_{ji} + \sum_{j>i} N_j A_{ji} \kappa_{ji} + N_e^2 N^+ \beta_{ci} - N_i \left(\sum_{j>i} N_e C_{ij} + \sum_{j<i} N_e R_{ij} + \sum_{j<i} A_{ij} \kappa_{ij} + N_e S_{ic} \right), \quad (1)$$

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and

$$\frac{\partial N_e}{\partial t} = N_e N_1 S_{1c} - N_e^3 \beta_{c1}, \tag{2}$$

where N_i ($i \neq 1$) and N_1 are, respectively, the population densities of the excited and ground Li atoms, and N_e and $N^+ \approx N_e$ are, respectively, the concentrations of electrons and of all the possible positive ions present in the plasma (not only those of Li) in their ground energy level (for the sake of simplicity, we have only considered ground-state ions); C_{ij} is the rate coefficient for electron-impact excitation of the jth atomic level from the lower level i; R_{ji} is the rate coefficient for electron-impact deexcitation of level j into a lower level i; S_{ic} is the rate coefficient for ionizing collisions of an electron with an atom in its ground or excited level i; β_{ci} is the rate coefficient for three-body recombination producing an atom excited to the ith level; A_{ji} is the transition probability for $j \rightarrow i$ spontaneous emission; and k_{ji} is a radiation escape factor for the radiation emitted in bound–bound transitions in the plasma. We have assumed an optically thin plasma for all the dipole-allowed radiative transitions considered. The rate coefficients in Eqs. (1) and (2) are calculated following Gordillo-Vázquez (2001).

In order to study the kinetics of Li atoms and ions, we need to consider their basic energy level structure. We have considered the five lower energy levels (up to the 3^2D level corresponding to ~4 eV) of the Li atom including the continuum of energy (from 5.4 eV) and ground-state Li ions. The electric dipole-allowed transition probabilities and the statistical weights of the energy levels considered are the same as in Gordillo-Vázquez (2001). If we rewrite Eq. (1) for the case of steady-state plasmas, we find (Kunc, 1988)

$$N_i \left(\sum_{j<i} A_{ij} \kappa_{ij} + N_e \sum_{j<i} R_{ij} \right) = \sum_{j<i} N_e N_j C_{ji} + \delta, \tag{3}$$

where

$$\delta = \sum_{j>i} N_j A_{ji} \kappa_{ji} + N_e \left(\sum_{j>i} N_j R_{ji} + N^+ N_e \beta_{ci} \right) - N_e N_i \left(\sum_{j>i} C_{ij} + S_{ic} \right). \tag{4}$$

The magnitude δ can be neglected in Eq. (3) in many plasmas with medium and high electron density ($>10^{12}$ cm^{-3}) because in such case we have that

$$N_e \sum_{j<i} N_j C_{ji} \gg \delta. \tag{5}$$

If we neglect the quantity δ, the concentrations of the Li atoms excited to the ith energy level (with $i = 2, 3, 4, 5$) can be obtained from the analytic expression

$$N_i = \frac{N_e \sum_{j<i} N_j C_{ji}}{\sum_{j<i} A_{ij} \kappa_{ij} + N_e \sum_{j<i} R_{ij}}, \tag{6}$$

where only rate coefficients for collisional electronic excitations and deexcitations and spontaneous emission are required. Taking into account the above considerations, the population densities of the excited Li atomic levels can be given in Boltzmann-like form

$$\left(\frac{N_j}{N_i} \right)_{neq} = \frac{B_j}{B_i} \left(\frac{N_j}{N_i} \right)_{eq}, \tag{7}$$

with

$$\left(\frac{N_j}{N_i} \right)_{eq} = f_{ji} = \frac{\omega_j}{\omega_i} \exp\left(- \frac{E_j - E_i}{kT_e} \right),$$

where E_i and E_j are the energies of the levels (relative to the ground state), and ω_j and ω_i are statistical weights of the levels. The coefficients B_i measure the deviation of each of the ith excited state of Li atoms present in the plasma from their corresponding thermodynamic equilibrium concentration, and are given by

$$B_i = \frac{\sum_{j<i} B_j \tau_{ij}}{1 + \sum_{j<i} \tau_{ij}}, \tag{8}$$

with

$$\tau_{ij} = \frac{N_e R_{ij}}{\sum_{j<i} A_{ij} \kappa_{ij}},$$

with $B_1 = 1$.

Therefore, according to the above, Eqs. (7) and (8) are enough to calculate the concentration of the excited Li atomic levels $i = 2$, 3, 4 and 5. To derive the concentration of Li atoms in their ground level ($i = 1$), one just needs to solve Eq. (2) for steady-state plasmas. After some calculations we reach

$$N_1^{Theo} = \frac{N_e^2 \beta_{c1}}{S_{1c}} \text{ cm}^{-3}. \tag{9}$$

When the population of an atomic Li level departs (as a result of a small change of plasma parameters) from its steady-state value, then some time (called the relaxation time) is needed to reestablish the steady-state population of the level. The relaxation times for each atomic level (including the ground) of Li can be calculated as (Kunc & Soon, 1989)

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$$\tau_i = \left[\sum_{k<i} (N_e R_{ik} + A_{ik}) + \sum_{j>i} \left(N_E C_{ij} + \frac{N_j}{N_i} (1 - \kappa_{ji}) A_{ji} \right) + N_e S_{ic} \right]^{-1} \text{s}, \quad (10)$$

where ionizing collisions are only taken into account from the ground atomic level, that is, we assume that $S_{ic} = 0$ (for $i = 2$, 3, 4 and 5).

The laser-produced plasmas that concern us in this work are not stationary but time dependent. Therefore, to study such a transient plasma with a stationary kinetic model, we first need to evaluate the time scales of the different processes involved. These processes ($\sim 10^{-8}$ s) are, in general, much longer than the relaxation times ($\sim 10^{-10}$ s–10^{-11} s for our N_e and T_e (Gordillo-Vázquez, 2001)) of the different excited levels of Li atoms but, often, they are shorter than the relaxation time of ground-state Li. However, for plasmas produced by lasers with a pulse duration of several nanoseconds, it happens to be that the relaxation (or thermalization) times of electrons (Kunc, 1989) is much shorter ($\sim 10^{-14}$ s) than any characteristic time scale of the laser-produced plasma. Consequently, the time-dependent rate equations for calculating the concentration of the electrons in the transient plasmas of interest here can be solved by assuming that electrons are in steady state.

The ionization degree (ρ) of Li in our plasma, considered as a cloud of Li atoms and other species such as Nb, O, or O_2 from the ablated target, is calculated by

$$\rho = \frac{N_e}{N_1 + N^+}, \quad (11)$$

where N_1 is taken as the concentration of ground Li atoms and it is assumed that $N^+ \cong N_e$. Most of the electrons in the plasma come from the target and from ionizing collisions of electrons with Li atoms since Li has the lowest ionization threshold (5.4 eV) when compared to those of Nb (6.88 eV), O (13.6 eV), or O_2 (12.07 eV). The value of ρ is likely close to the total ionization degree of the plasma since, according to the stoichiometry of the target, the concentrations of Nb and O in the plasma might be similar to that of Li.

3. EXPERIMENT

To develop a kinetic model that can predict the Li atom concentrations present in the plasma formed by ablation of a $LiNbO_3$ target by means of an ArF laser (193 nm and 20 ns of pulse width) with a fluence of 1.2 J cm^{-2} (typical of PLD experiments), we need to have T_e and N_e as input parameters. The former is derived from the ratio of emission line intensities of successive ionization stages of Nb atoms (NbII 478.9 nm and NbI 407.97 nm) measured by optical emission spectroscopy. The Stark-broadened profiles of the 610.3 nm line of Li I are used for quantifying N_e. Further details can be found elsewhere (Gordillo-Vázquez *et al.*, 2001) and the resulting N_e and T_e are shown in Figure 1. In addition, we have followed the results of Gordillo-Vázquez, (2001) to determine the experimental concentration of ground Li atoms from available measurements (Chaos *et al.*, 2000) of the temporal evolution of the optical density (O.D.), associated to the Li I 670.8 nm transition, performed at $L =$ 11 mm from the target. Whereas the ablation experiments to determine N_e and T_e were performed at a fluence of 1.2 J cm^{-2}, that is, the one typically used to produce stoichiometric films (Chaos *et al.*, 2001), the ones to measure the optical density were carried out at a much lower fluence (0.06 J cm^{-2}). This was necessary to minimize the light emitted by the plasma that overlaps the absorption signal.

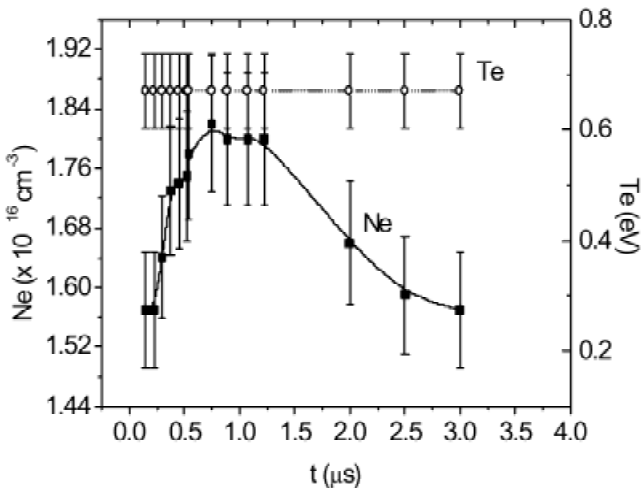

Fig. 1. Experimental values of Ne (■) and Te (○) at 11 mm from the target as a function of the time after the laser pulse is off. The laser fluence used for ablation of the $LiNbO_3$ target was 1.2 J cm^{-2}. The lines are the best fits.

The approximate expression for the temporal evolution of the experimental concentration of ground Li atoms is taken from Gordillo-Vázquez (2001) as

$$N_{\text{Li}(i=1)}^{Exp}(t) \cong \frac{2.3026 \times \Delta\lambda_{1/2}^{1\to 2}(t)}{L \times 1.52 \times 10^{-14}} \log\left(\frac{I_0^{\lambda_{12}}}{I_L^{\lambda_{12}}(t)} \right), \quad (12)$$

where the O.D. corresponds to the logarithmic term and where the full width at half maximum (FWHM), $\Delta\lambda_{1/2}^{2\to 1}$, of the emission line 670.8 nm of Li I was obtained as in Gordillo-Vázquez (2001).

4. RESULTS AND DISCUSSION

In this section, we will describe and discuss two issues: (1) the main predictions from the kinetic model as well as their comparison with the experimental results available from studies of the plasma produced by laser ablation of $LiNbO_3$ targets in vacuum, and (2) their implications in connection with the possible ejection mechanisms of Li atoms from $LiNbO_3$ targets.

Figure 2a and 2b show, respectively, the predicted temporal evolution of the concentrations of ground and excited

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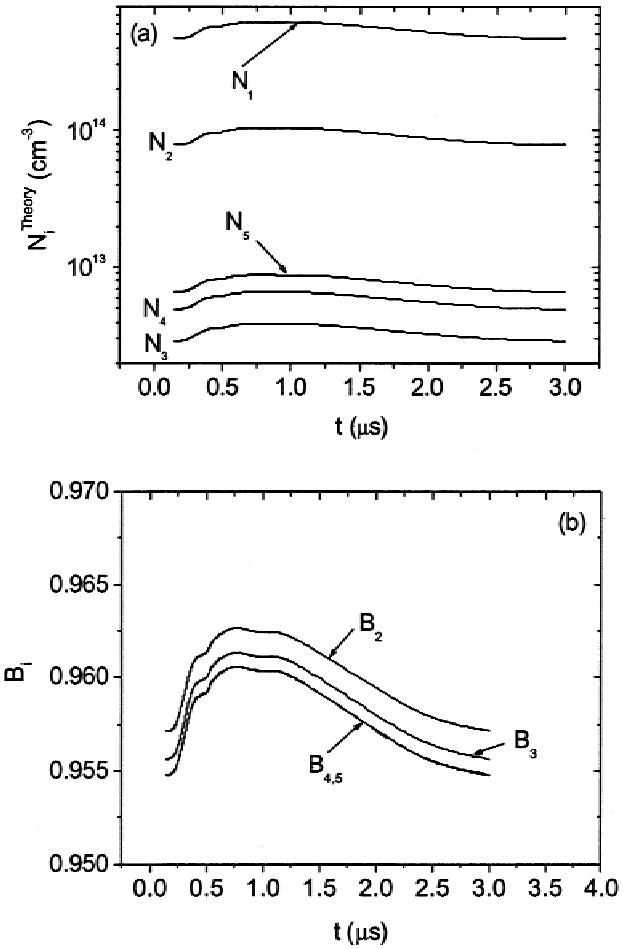

Fig. 2. Predicted (a) population densities for the ground (N_1) and excited (N_i, $i > 1$) Li atoms, and (b) their deviation (B_i, $i > 1$) from their LTE values at 11 mm from the target as a function of the time after the laser pulse is off. The laser fluence used for ablation of the $LiNbO_3$ target was 1.2 J cm^{-2}.

Li atoms, and the coefficients B_i accounting for the deviation of the population density of Li atoms in the plasma from their local thermodynamic equilibrium (LTE) values. The most remarkable feature in Figure 2a is the presence of a slight maximum and the inversion of the concentrations of levels $i = 3$, $i = 4$, and $i = 5$. The latter is a consequence of having higher gain/loss mechanism ratios for $i = 5$ and $i = 4$ than for $i = 3$ (Gordillo-Vázquez, 2001). Since $B_i = 1$ when LTE occurs, the results shown in Figure 2b indicate that the laser generated plasma almost preserves LTE when working with a laser fluence of 1.2 J cm^{-2}.

In Figure 3, we present a comparison, at a distance of 11 mm to the target, between the theoretical temporal evolution of the population density of ground Li atoms (N_1^{Theo}) predicted by the kinetic model [Eq. (9)] at a laser fluence of 1.2 J cm^{-2} and the experimental values of N_1^{Exp} (at 0.06 J cm^{-2}) obtained from Eq. (12) using the measured optical (atomic) absorption transients (at the 670.8 nm resonance line of Li I) of the laser-generated plasma. We see in Figure 3 that there is a fairly good qualitative agreement between N_1^{Theo} (1.2 J cm^{-2}) and N_1^{Exp} (0.06 J cm^{-2}), the most significant different being the fact that the maximum observed at both energies happens earlier (as is expected) the higher the laser fluence.

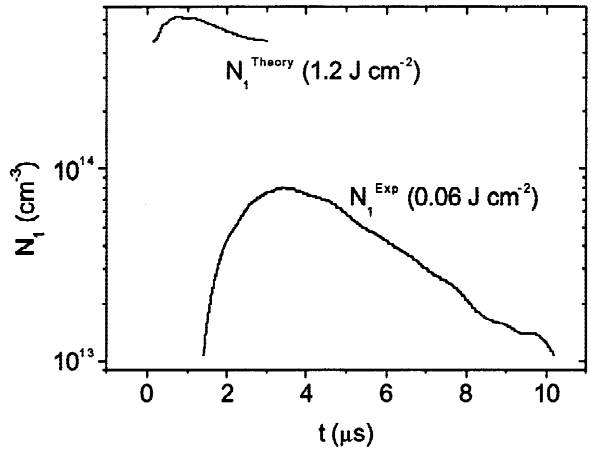

Fig. 3. Comparison between the temporal evolution of the theoretically predicted population density of ground Li atoms (N_1^{Theo}) obtained at a laser fluence of 1.2 J cm^{-2}, and the experimental values N_1^{Exp} obtained at a laser fluence of 0.06 J cm^{-2} from expression (12). The distance to the target is 11 mm in both cases. The solid lines are the best fits.

We show in Figure 4 a comparison between the temporal evolution of the ionization degrees obtained with the electron densities measured at 11 mm (at constant $T_e \cong 0.67$ eV) to the target and with either the concentration of ground Li atoms obtained from experiments performed with a fluence of 0.06 J cm^{-2} (ρ^{Exp}) or with that predicted by the kinetic model (ρ^{Theo}) when using 1.2 J cm^{-2}. The fact that ρ^{Exp} is higher than ρ^{Theo} is a consequence of using [in Eq. (11)] the N_e measured at 1.2 J cm^{-2} instead of at 0.06 J cm^{-2}. No emission could be detected at 0.06 J cm^{-2}, so that the electron density at such low fluence is not available.

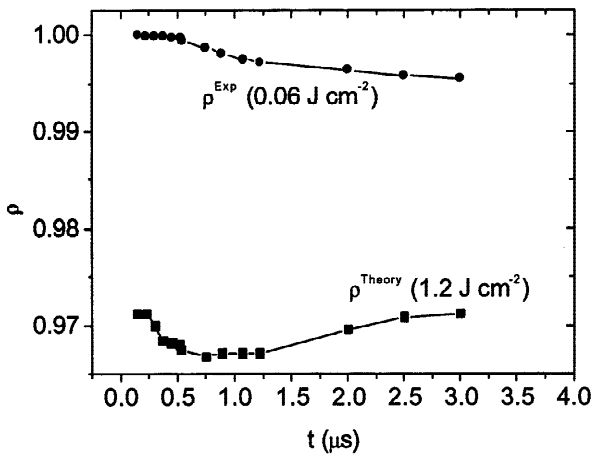

Fig. 4. Comparison between the temporal evolution of the theoretically predicted degree of ionization (ρ^{Theo}), at a laser fluence of 1.2 J cm^{-2}, and the experimental value (ρ^{Exp}) obtained at 0.06 J cm^{-2}. The distance to the target is 11 mm in both cases. The solid lines are the best fits.

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Figure 4 shows that both the experimental and the predicted values of the degree of ionization are close to 1. To achieve such a high degree of ionization in, for example, a monoatomic gas of Li at thermal equilibrium ($T \cong T_e$), we would have to assume an unreasonably high gas temperature (atom temperature) close to approximately 8000 K. This temperature is too high, especially considering the fact that a laser fluence of 0.06 J cm^{-2} causes a temperature rise of the target of ~2000 K that is enough to melt and even vaporize $LiNbO_3$ (Chaos *et al.*, 2000). At higher fluences (like 1.2 J cm^{-2}), the atoms of the vaporized target can only increase their temperature by collisions with electrons and/or with other atoms or ions. However, the energy transfer in elastic electron–atom collisions is quite inefficient because of their mass difference, so that the electron and gas temperatures would remain different. In addition, the cross sections for atom–atom collisions are in general much lower than electron–atom collisions (Griem, 1997). Therefore, at 1.2 J cm^{-2}, the gas temperature might slightly increase above 2000 K, but it will not reach T_e.

It is then possible that the electron and atom temperatures differ even if their individual energy distributions are close to Maxwellian (which is the basic LTE assumption) because the electron–electron energy transfer rates are much larger than electron–atom/ion rates (Griem, 1997). Therefore, only nonthermal (electronic) ionization mechanisms can produce such high electron densities and ionization degree. Consequently, the ejection of Li atoms from the $LiNbO_3$ target would probably be caused by an electronic rather than a thermal ejection mechanism. The existence of an electronic ejection mechanism is further supported by the predictions of the kinetic model regarding the presence in the plasma of nonnegligible (and close to their LTE values) concentrations of excited Li atoms due to electron–Li collisions. Moreover, recent experimental results on the delayed release of Li atoms reported an ejection velocity of $\sim 6 \times 10^5$ cm s^{-1}, which is also consistent with an electronic ejection mechanism (Chaos *et al.*, 2000).

In the electronic ejection mechanism, the UV laser light absorption by the target results in excitations of weakly bound or repulsive electronic states (Dreyfus *et al.*, 1986) that can lead to an extensive removal of seed electrons from the target that ionize the gas atoms previously vaporized. This process increases the production of electrons in the vaporized cloud, which further causes a runaway breakdown of the entire ablated plume. The latter explains the high N_e and ionization degree found in the plasma.

5. CONCLUSIONS

A very convenient analytic and quasi-stationary kinetic model has been used to study the temporal electron kinetics of Li atoms present in the plasma generated by ablation with an ArF laser of a $LiNbO_3$ target in vacuum. A reasonable agreement is found between the predicted and measured degrees of ionization being both close to 1. This ionization would require an unreasonably high gas temperature (~8000 K), which is unlikely due to the low efficiency of the electron–atom energy transfer rates compared to that of the electron–electron rates. Therefore, the high degree of ionization (predicted and measured) together with the high electron density measured and the fact that the concentrations of electronically excited Li atoms predicted by the model are also high provide an indirect support for an electronic rather than thermal ejection mechanism of Li from $LiNbO_3$ targets ablated by a pulsed ArF laser.

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