Influence of Ar and O₂ atmospheres on the Li atom concentration in the plasma produced by laser ablation of LiNbO₃

F. J. Gordillo-Vázquez and C. N. Afonso

Citation: *J. Appl. Phys.* **92**, 7651 (2002); doi: 10.1063/1.1524023

View online: <http://dx.doi.org/10.1063/1.1524023>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v92/i12>

Published by the [American Institute of Physics](#).

Related Articles

Production and acceleration of ion beams by laser ablation

Rev. Sci. Instrum. **83**, 02B717 (2012)

Proton emission from a laser ion source

Rev. Sci. Instrum. **83**, 02B310 (2012)

Optical diagnosis and theoretical simulation of laser induced lead plasma spectrum

Phys. Plasmas **19**, 013302 (2012)

Saturation effects in femtosecond laser ablation of silicon-on-insulator

Appl. Phys. Lett. **99**, 231108 (2011)

Effect of air breakdown with a focusing lens on ultrashort laser ablation

Appl. Phys. Lett. **99**, 234104 (2011)

Additional information on J. Appl. Phys.

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>

ADVERTISEMENT

Working @ low temperatures? Contact Janis for Cryogenic Research Equipment Click here to browse our site at www.janis.com
---	---	---

Influence of Ar and O₂ atmospheres on the Li atom concentration in the plasma produced by laser ablation of LiNbO₃

F. J. Gordillo-Vázquez^{a)} and C. N. Afonso

Instituto de Óptica, CSIC, Serrano 121, 28006 Madrid, Spain

(Received 15 May 2002; accepted 4 October 2002)

An analytic kinetic model is elaborated to determine the spatial evolution of the concentration of ground and excited Li atoms (up to the 3^2D level) present in the plasma generated by pulsed laser ablation of a LiNbO₃ crystal in gas atmospheres (at 1 Torr) of different nature, both reactive (O₂) and inert (Ar). Whereas the Li atom population densities in the plasma produced in gas are, in general, higher than those found in vacuum, the concentration of ground Li atoms close to the substrate is similar in vacuum and Ar, though lower than in O₂. It is suggested that the reabsorption of radiation by the plasma is more important within O₂ than in Ar since the absorber (ground Li) concentration is higher in O₂ environments. A very reasonable qualitative agreement is found when comparing the Li I-670.8 nm spectral line emission intensity predicted by the model with that obtained experimentally in Ar and O₂ atmospheres. © 2002 American Institute of Physics.
[DOI: 10.1063/1.1524023]

I. INTRODUCTION

Lithium niobate (LiNbO₃) is a well-known material with excellent nonlinear properties of interest for many applications in optoelectronics and photonics that normally require the production of high quality thin films.^{1,2} Although the use of pulsed laser deposition (PLD) has proven to be one of the most successful techniques in growing complex oxide materials,³ the films deposited by ablation of LiNbO₃ in vacuum or low pressure (<1 Torr) atmospheres are often found to be Li deficient.^{4,5} However, when the growth is carried out at a pressure of about 1 Torr, independently of the nature of the used ambient atmosphere (either inert, Ar, or reactive, O₂), the LiNbO₃ films grow stoichiometrically.⁶ This latter result has been understood in the frame of the blast-wave model which accurately describes the plasma expansion dynamics in a gas atmosphere at a sufficiently high pressure.^{7,8} Under these conditions, the leading edge of the plasma pushes the gas environment ahead creating a transient period in which the central region of the expanding plasma is at pressures lower than the surrounding gas.⁹ Thus, slow or late ejected species from the same laser pulse would be scattered towards the plasma center by collisions with the gas boundary, becoming focused towards the central part of the plasma and the deposit.⁹

The objective of this work is to build a collisional-radiative kinetic model of the nonequilibrium lithium-like plasma generated from the laser ablation of LiNbO₃ targets in gas environments at 1 Torr. The present model is a generalization of the one reported earlier,¹⁰ hereafter referred to as article I, for laser-generated lithium-like plasmas in vacuum which was based on a diagnostic method originally proposed by Suckewer¹¹ and Kunc.¹²

The comparison between the concentration of Li atoms predicted by the model under vacuum conditions and in Ar and O₂ atmospheres at 1 Torr will provide: (i) quantitative information on the spatial evolution of ground and excited Li atom concentrations in vacuum, and in Ar and O₂ atmospheres at 1 Torr by simply introducing the previously reported N_e and T_e values^{13,14} into the model equations, (ii) qualitative agreement with the spatial evolution of available experimental emission intensities from excited Li atoms in Ar and O₂ environments at 1 Torr, and (iii) quantitative information on the relative loss and gain electron-impact rate coefficients contributing to, respectively, population and depopulation of the different energy levels of Li atoms present in the laser-produced plasmas of interest here.

The results above could also be useful for improving the hydrodynamic models presently available for simulating the plasma plume expansion dynamics in different gas atmospheres.

II. KINETIC MODEL

The plasmas typically found in PLD experiments are not stationary but rather in transient conditions. However, with the N_e and T_e values commonly measured in the laser-produced plasmas during PLD of LiNbO₃ in vacuum,¹³ these transients are, in general, much longer than the relaxation times of the different excited levels of Li atoms (see article I) but, often, they are shorter than the relaxation times of ground state Li. However, for plasmas produced by lasers with a pulse duration of several nanoseconds, as in our case, it happens to be that the relaxation time of electrons¹⁵ (the thermalization time) is much shorter than any characteristic time scale of the laser-produced plasma. The above considerations also apply to the plasma produced after laser ablation of LiNbO₃ in Ar and O₂ atmospheres at 1 Torr since the measured N_e and T_e are of the same order ($\sim 10^{16}$ cm⁻³ and ~ 0.6 – 0.9 eV, respectively¹⁴) as those obtained in vacuum.¹³

^{a)} Author to whom correspondence should be addressed; electronic mail: vazquez@io.cfmac.csic.es

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. Therefore, we can study the kinetics driven by electrons in our plasmas (produced in vacuum, Ar, and O₂ environments) by applying a steady-state collisional-radiative model not only to levels $i=2, 3, 4$ and 5 but also to the case of the plasma electrons. In consequence, the concentration of ground Li atoms can be approximately derived from the rate equation for the plasma electrons.

A. Vacuum

The laser-generated plasma by ablation of a LiNbO₃ crystal in vacuum is mainly composed of Nb atoms, O atoms, O₂ molecules, possibly some NbO and LiO molecules and, due to its low ionization and excitation energy thresholds, ground Li⁺ ions and Li atoms in their ground and several excited levels. However, in this work we focused our attention in the kinetics of Li atoms driven by electron-atom collisions, which are the most probable processes underlying the observed emission pattern of Li.

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, following article I, the net production rates of Li atoms excited to the i th level can be obtained from the steady-state balance given by equations

$$N_{\text{Li}(i)} \left(\sum_{j<i} A_{ij} \kappa_{ij} + N_e \sum_{j<i} R_{ij} \right) = \sum_{j<i} N_e N_{\text{Li}(j)} C_{ji} \quad (1)$$

and the net production rate of plasma electrons can be approximated by a steady-state ionization-recombination balance given by

$$N_e N_{\text{Li}(1)} S_{1c}^{\text{Li}} = N_e^3 \beta_{c1}^{\text{Li}}, \quad (2)$$

where $N_{\text{Li}(i), i \neq 1}$ and $N_{\text{Li}(1)}$ are the population densities of, respectively, 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_{ji} is the rate coefficient for electron-impact excitation of the i th atomic level from the lower level j ; R_{ij} is the rate coefficient for electron-impact de-excitation of level i into a lower level j ; S_{1c}^{Li} is the rate coefficient for ionizing collisions of an electron with a Li atom in its ground level; β_{c1}^{Li} is the rate coefficient for three-body recombination leading to a ground Li atom; A_{ij} is the transition probability for the $i \rightarrow j$ ($i > j$) spontaneous emission, and κ_{ij} is a radiation escape factor for the radiation emitted in bound-bound transitions in the plasma which is optically thin ($\kappa_{ij}=1$) for all the dipole-allowed radiative transitions considered in vacuum.

In order to study the kinetics of lithium atoms and ions, we need to consider their basic energy level structure. We show in Fig. 1 a diagram corresponding to the five lower energy levels (up to the 3²D level corresponding to ~ 4 eV) of the Li atom including the continuum of energy (from 5.4

FIG. 1. Diagram of the lower energy levels for Li atoms. The arrows indicate the dipole-allowed transitions.

eV). The electric dipole-allowed transition probabilities¹⁶ and the statistical weights of the energy levels considered are also indicated in Fig. 1 (see also Table I).

The concentrations of the Li atoms excited to the i th energy level (with $i=2, 3, 4, 5$) can be obtained from Eq. (1) as

$$N_{\text{Li}(i)} = \frac{N_e \sum_{j<i} N_{\text{Li}(j)} C_{ji}}{\sum_{j<i} A_{ij} \kappa_{ij} + N_e \sum_{j<i} R_{ij}}, \quad (3)$$

where only rate coefficients for collisional electronic excitations and de-excitations, and spontaneous emission are required.

From Eq. (2) it is straightforward to derive the ground ($i=1$)-Li atom concentration in vacuum

$$N_{\text{Li}(1)} = \frac{N_e^2 \beta_{c1}^{\text{Li}}}{S_{1c}^{\text{Li}}}. \quad (4)$$

Concerning rate coefficients for the electron-impact excitation and de-excitation processes, we use here the collisional rate coefficients proposed by Kunc and Zgorzelski¹⁷ for alkali metal atoms based on the classical binary-encounter theory by Gryzinski.¹⁸ The collisional rate coefficient C_{ji} is obtained by assuming a Maxwellian electron energy distribution, and the principle of detailed balance is used to evaluate the corresponding electron-impact de-excitation rate coefficients R_{ij} .

TABLE I. Transition probabilities A_{ij} (in 10^7 s^{-1}) and corresponding wavelengths λ_{ij} (in nm) for dipole-allowed transitions between the lower electronic levels of Li atoms.

$i \rightarrow j$	Transition	$A_{ij} (10^7 \text{ s}^{-1})$	$\lambda_{ij} \text{ (nm)}$
2 → 1	2 ² P → 2 ² S	3.720	670.8
3 → 2	3 ² S → 2 ² P	3.490	812.6
4 → 1	3 ² P → 2 ² S	0.117	323.2
4 → 3	3 ² P → 3 ² S	0.377	2687.7
5 → 2	3 ² D → 2 ² P	7.160	610.3
5 → 4	3 ² D → 3 ² P	0.000 381	27 949.0

On the other hand, the electron-impact ionization rate coefficient from the ground level of lithium, S_{1c}^{Li} , is taken from Drawin,¹⁹ while the three-body electron recombination rate coefficient, β_{c1}^{Li} , is deduced by applying the principle of detailed balance. The reader is referred to article I for details on the calculation procedure of C_{ji} , R_{ij} , and S_{1c}^{Li} , β_{c1}^{Li} , together with that of the coefficients l_{ij} , g_{ji} that allow us to evaluate the relative contribution of the different kinetic mechanisms considered for populating (g_{ji}) and depopulating (l_{ij}) the ground and excited energy levels of Li atoms.

B. Oxygen atmosphere

When an O₂ environment at 1 Torr is used, we can still use most of the assumptions made for the calculation of the concentration of Li atoms in the case of vacuum. In particular, since we are not considering atom–atom collisions as a possible excitation channel of Li atoms (its efficiency is, in general, much less than that of the electron-atom processes^{20,21}), we can keep Eq. (1) to evaluate the concentration of excited Li atoms. Apart from atom–atom collisions, ion-atom collisions are also possible but of relatively small importance in a first approximation. Reactions involving negative ions are negligible because the electron affinities of the neutrals (Li, Ar, Nb) are small and, in the case of oxygen (the most electronegative), the reactions leading to ground O[−](²P) have small²² rate coefficients when compared to other electron-atom processes considered here.¹⁷ In addition, although, in general, symmetric charge-transfer reactions, that is, those between a neutral and its positive ion (Li⁺ and Li, Ar⁺ and Ar, or O⁺ and O), have relatively high cross sections,²³ we have not considered them because the concentrations of Ar⁺ and O⁺ are assumed small (they have a high ionization energy). The reaction between fast Li⁺ and Li is quite possible but its cross section is roughly constant¹⁹ and similar in value (sometimes even smaller) to the other electron-Li excitation and ionization cross sections, although the latter ones are more accurately known (both experimentally and theoretically). Therefore, due to the above considerations and in order to simplify the calculations, we can also neglect in a first approach the charge-transfer reaction between Li⁺ and Li. On the other hand, the possible asymmetric charge-transfer reactions, that is, those between the unlike systems Li⁺ and Ar or Li⁺ and O, have a small cross section ($\sim 10^{-18}$ cm² for the reaction between Li⁺ and Ar),²⁴ or they have not been investigated very much (to the best of our knowledge) which is the case of the collisions between Li⁺ and O.

In order to evaluate the concentration of ground Li atoms, we need to re-define the steady-state balance equation for the plasma electrons so that it includes ionization and recombination of, respectively, oxygen atoms and ions since both of them are presumably more abundant than any of the other components (Nb atoms or molecules of NbO, LiO) from the ablated LiNbO₃ target. The steady-state kinetic equation for the plasma electrons would now be

$$\frac{dN_e}{dt} = 0 = N_e N_{\text{Li}(1)}^{\text{O}} S_{1c}^{\text{Li(O)}} + N_e (N_{\text{O}(1)} S_{1c}^{\text{O}} + N_{\text{O}(2)} S_{2c}^{\text{O}}) - N_e^2 N_{\text{Li}(+)}^{\text{O}} \beta_{c1}^{\text{Li(O)}} - N_e^2 N_{\text{O}(+)} (\beta_{c1}^{\text{O}} + \beta_{c2}^{\text{O}}), \quad (5)$$

where $N_{\text{Li}(1)}^{\text{O}}$, $N_{\text{O}(1)}$ and $N_{\text{O}(2)}$ stand for the population densities, in an O₂ environment, of, respectively, ground Li atoms, and O atoms in their ground and first excited state; and $N_{\text{Li}(+)}^{\text{O}}$ and $N_{\text{O}(+)}$ are, respectively, the concentrations of lithium and oxygen ions in their ground state. Moreover, $S_{1c}^{\text{Li(O)}}$ and $\beta_{c1}^{\text{Li(O)}}$ represent, respectively, the ionization and recombination rate coefficients of ground Li atoms and ions, and they are calculated as S_{1c}^{Li} and β_{c1}^{Li} in article I. The magnitudes S_{1c}^{O} , S_{2c}^{O} are the ionization rate coefficients from, respectively, oxygen atoms in their ground and first excited state taken from Soon and Kunc,²² and β_{c1}^{O} and β_{c2}^{O} are the rate coefficients for three-body recombination to, respectively, ground and first excited oxygen atoms which expressions are from Kunc and Soon.²⁵

The concentration of ground Li atoms in a laser-generated plasma formed after the ablation of a LiNbO₃ crystal in 1 Torr of O₂ is then deduced from Eq. (5), that is, from an electronically driven ionization-recombination balance of the most abundant atoms and ions in the plasma. Thus, we have that

$$N_{\text{Li}(1)}^{\text{O}} \cong \frac{0.6 N_e^2 \beta_{c1}^{\text{Li}} + 0.4 N_e^2 (\beta_{c1}^{\text{O}} + \beta_{c2}^{\text{O}}) - N_{\text{O}(1)} S_{1c}^{\text{O}} - N_{\text{O}(2)} S_{2c}^{\text{O}}}{S_{1c}^{\text{Li(O)}}}, \quad (6)$$

where, considering on one side the reasonable expected relative amounts of O and Li in the plasma and, on the other, their corresponding ionization potentials, 5.4 eV for Li and 13.6 eV for O, we have assumed that $N_{\text{Li}(+)}^{\text{O}} = 0.6 \times N_e$ and $N_{\text{O}(+)} = 0.4 \times N_e$, so that the plasma remains electrically neutral. Therefore, the numbers 0.6 and 0.4 [and 0.8 and 0.2 in Eq. (9)] can simply be considered as “reasonable parameters.” We must note that the fact of changing the relative amounts of Li and O or Ar ions, that is, use, for example, 0.7 and 0.3 instead of the assigned numbers 0.6 and 0.4 in the case of using an O₂ environment, hardly changes (maximum 7%) the final Li atom concentrations obtained with expressions (6) and (9). The latter is a consequence of the fact that $N_{\text{Li}(1)}^{\text{O}}$ and $N_{\text{Li}(1)}^{\text{Ar}}$ [see Eq. (9)] depend only linearly on, respectively, $N_{\text{Li}(+)}^{\text{O}}$, $N_{\text{O}(+)}$ and $N_{\text{Li}(+)}^{\text{Ar}}$, $N_{\text{Ar}(+)}$.

In order to use Eq. (6) we first need to determine the concentration of oxygen atoms in their ground and first excited state. These population densities are obtained by assuming that the electron properties (N_e and T_e) in a parent plasma (our laser-produced plasma) can be studied using a kinetic model of an equivalent plasma which contains a mixture of electrons, oxygen atoms, and ions under the same physical conditions as the parent plasma under consideration.²² This parent plasma usually contains several neutral components each consisting of one kind of atom or molecule but with a “basic” component, oxygen in our case, with a concentration greater than 10% of all heavy particles and where the ionization degree (η) of the plasma is greater

FIG. 2. Diagram representing the conditions under which the laser-produced "parent" plasma can be substituted by an equivalent plasma to estimate the concentration of oxygen atoms in their ground and two lower ($i=2,3$) excited states.

than $10^{-3}-10^{-2}$ so that the energy distribution of free electrons is close to a Maxwellian distribution. If the total density (N_T) of the heavy particles in such plasmas is less than approximately 10^{18} cm^{-3} , then the impact of inelastic collisions of the oxygen atoms with the other heavy particles on the distribution of the electronic energies of the atoms can be neglected when compared to the impact of the inelastic collisions of the electrons and photons with oxygen atoms.

The conditions summarized above are generally accomplished at the T_e and N_e values measured in the laser-generated plasmas found in PLD experiments of LiNbO₃ thin films performed in 1 Torr of O₂.¹⁴ Consequently, as it is shown in Fig. 2, in order to derive $N_{O(1)}$ and $N_{O(2)}$ we can now use an equivalent atomic oxygen plasma containing O, O⁺, and electrons [O₂ is probably very much dissociated due to its relatively low dissociation energy ($\sim 5.1 \text{ eV}$)] instead of the original parent plasma containing a complex mixture of ablated species from the target (Li, Nb, O, LiO, NbO, O₂, Li⁺, Nb⁺, O⁺, e⁻) plus the more abundant oxygen species from the O₂ environment (O, O₂, O⁺, e⁻).

Therefore, since we have measurements of the spatial evolution of N_e and T_e in our laser-produced parent plasma,¹⁴ we can introduce them in the collisional-radiative model for atomic oxygen proposed by Soon and Kunc²² to estimate the ground and excited state concentrations of oxygen atoms in our parent plasma. According to this model, the populations of the three lower energy levels of an oxygen atom almost always follow a Boltzmann distribution with $N_{O(1)} \cong 0.90 \times N_O$ where N_O is the total amount (ground and excited) of oxygen atoms in the plasma (see Fig. 6 of Ref. 22). Assuming a gas temperature of 300 K and since there is an oxygen pressure of 1 Torr ($N_O = 3.22 \times 10^{16} \text{ cm}^{-3}$) in the ablation chamber, we have $N_{O(1)} = 2.9 \times 10^{16} \text{ cm}^{-3}$ and

$$N_{O(2)} = \frac{5}{9} N_{O(1)} e^{-(E_2 - E_1)/KTe} \quad \text{and} \quad N_{O(3)} = \frac{1}{9} N_{O(1)} e^{-(E_3 - E_1)/KTe}, \quad (7)$$

where $E_1 = 0 \text{ eV}$, $E_2 = 1.97 \text{ eV}$, and $E_3 = 4.19 \text{ eV}$ are the energies corresponding to the ground, first, and second excited energy levels of oxygen atoms, respectively.

C. Argon atmosphere

In order to evaluate the concentration of excited Li atoms when using 1 Torr of Ar we can also use expression (1). However, we reformulate the kinetic equation controlling the generation of plasma electrons so as to include the influence of electron ionization of Ar atoms together with the three-body and radiative recombination of Ar ions. Thus, we have that

$$\frac{dN_e}{dt} = 0 = N_e N_{\text{Li}(1)}^{\text{Ar}} S_{1c}^{\text{Li(Ar)}} + N_e N_{\text{Ar}(1)} S_{1c}^{\text{Ar}} - N_e^2 N_{\text{Li}(+)}^{\text{Ar}} \beta_{c1}^{\text{Li(Ar)}} - N_e N_{\text{Ar}(+)} (N_e \beta_{c1}^{\text{Ar}} + A_{c1}^{ef(\text{Ar})}), \quad (8)$$

where $N_{\text{Li}(1)}^{\text{Ar}}$ and $N_{\text{Ar}(1)}$ stand for the population densities, in 1 Torr of Ar, of, respectively, the ground Li atoms, and ground Ar atoms; and $N_{\text{Li}(+)}^{\text{Ar}}$ and $N_{\text{Ar}(+)}$ are, respectively, the concentrations of positive lithium and argon ions in their ground state; S_{1c}^{Ar} , β_{c1}^{Ar} and $A_{c1}^{ef(\text{Ar})}$ are the ionization, three-body recombination, and radiative recombination rate coefficients of ground Ar atoms and ions, respectively, and they are taken from Braun and Kunc.²⁶ In addition, $S_{1c}^{\text{Li(Ar)}}$ and $\beta_{c1}^{\text{Li(Ar)}}$ represent, respectively, the ionization and three-body recombination rate coefficients of ground Li atoms and positive ions, and are calculated as in article I.

The concentration of ground Li atoms in a laser-generated plasma formed after the ablation of a LiNbO₃ target in an atmosphere of Ar at 1 Torr is then straightforward derived from Eq. (8) as

$$N_{\text{Li}(1)}^{\text{Ar}} \cong \frac{0.8 N_e^2 \beta_{c1}^{\text{Li(Ar)}} + 0.2 N_e^2 \beta_{c1}^{\text{Ar}} + 0.2 N_e A_{c1}^{ef(\text{Ar})} - N_{\text{Ar}(1)} S_{1c}^{\text{Ar}}}{S_{1c}^{\text{Li(Ar)}}}, \quad (9)$$

where, considering on one side the reasonable relative amount of Ar and Li in the plasma and, on the other, their corresponding ionization potentials, 5.4 eV for Li and 15.6 eV for Ar, we have assumed that $N_{\text{Li}(+)}^{\text{Ar}} = 0.8 \times N_e$ and $N_{\text{Ar}(+)} = 0.2 \times N_e$, so that the plasma keeps its electrical neutrality. Also, assuming a gas temperature of 300 K and, since there is an Ar pressure of 1 Torr ($N_{\text{Ar}} = 3.22 \times 10^{16} \text{ cm}^{-3}$) in the ablation chamber and Ar is difficult to excite (its first excited levels is 11.6 eV above the ground state), we can approximately assume that $N_{\text{Ar}(1)} \cong N_{\text{Ar}} = 3.22 \times 10^{16} \text{ cm}^{-3}$.

III. RESULTS AND DISCUSSION

In this section we will describe and discuss the main predictions from the kinetic model presented, as well as their comparison with some experimental results available from studies of the plasma produced by laser ablation of a LiNbO₃ crystal in gas atmospheres of O₂ and Ar at 1 Torr where stoichiometric LiNbO₃ are obtained.

The model proposed in this work gives us the concentration of Li atoms excited or de-excited by the plasma electrons. In vacuum, these kinetically produced Li atoms correspond to most of the Li reaching the growing LiNbO₃ film since the delayed release ($2-20 \mu\text{s}$ after the laser pulse) Li atoms, detected in absorption spectroscopy experiments,²⁷

FIG. 3. Predicted population densities for Li atoms in their (a) ground, $N_{Li(1)}$, and (b) first excited level, $N_{Li(2)}$, as a function of the distance from the target in vacuum (■) and in 1 Torr of Ar (○) and O_2 (△). The laser fluence is 1.2 J cm^{-2} . The solid lines are a guide for the eye.

expand within a broader solid angle and thus contribute very little to maintain the stoichiometry of Li along the direction perpendicular to the LiNbO_3 target.

On the other hand, emission spectroscopy experiments, also performed in vacuum conditions, reveal that the time evolution of the electron density (N_e) in the plasma has a maximum at around 0.3 or 0.4 μs after the laser pulse and that, after 2 μs , the N_e has decreased to much smaller values.¹³ This suggests that: (a) the delayed Li atoms cannot be electronically activated because of the different time scales of electrons and delayed Li atoms, and (b) that the electrons in the plasma primarily come from the target and/or from ionization events of the nondelayed release ablated species (mainly Li due its low ionization potential). These nondelayed release Li atoms in the plasma are then kinetically excited and ionized by electron collisions, and a significant part of them reach the substrate although not in the proportion needed to keep the stoichiometry of the target.

However, when a gas environment of O_2 and Ar at 1 Torr is used, the slow or late ejected Li atoms from the same laser pulse (but 2–300 μs after it, as in the case of gas atmospheres of Ar and O_2 ²⁸) would contribute to the stoichiometric growth of LiNbO_3 thin films,^{20,29} due to the particular expansion dynamics of the plasma.⁹ In this case, the emitting species are mainly located at the plasma edge.

Figures 3(a) and 3(b) show the predicted spatial evolution (at a laser fluence of 1.2 J cm^{-2}) of the concentrations of ground Li atoms and of their first excited level (the concentration of the upper levels follow similar trends) under the influence of a gas atmosphere (O_2 and Ar at 1 Torr) and in vacuum. As the electron density increases (see Ref. 14), the Li ions in the plasma recombine to ground Li and, consequently, their concentration tends to grow [see Fig. 3(a)]; however, the behavior of the concentration of ground Li at-

FIG. 4. Predicted population densities for Li atoms in their ground, $N_{Li(1)}$, and upper excited levels ($i=2,3,4,5$) at 7 mm from the target in vacuum (■) and in 1 Torr of Ar (○) and O_2 (△). The laser fluence is 1.2 J cm^{-2} . The solid lines are a guide for the eye.

oms always represents a more complex balance between the different ionization and recombination trends of Li, O, and Ar atoms and their ions.

A straightforward result from Fig. 3 is the fact that the concentrations of ground and excited Li atoms obtained within Ar and O_2 environments are, in general, higher than in vacuum. Moreover, whereas the population density of (ground and excited) Li atoms found in O_2 is always higher than in Ar, the concentrations of excited Li atoms in vacuum and close (2–5 mm) to the target are slightly higher than in Ar.

Figure 4 represents the calculated concentrations of ground and excited (up to level $i=5$) Li atoms at 7 mm from the target. A remarkable feature in Fig. 4 is the fact that the concentrations of levels $i=3$, $i=4$, and $i=5$ are inverted, that is, $N_{Li(5)} > N_{Li(4)} > N_{Li(3)}$. The latter happens since, according to our model, the ratio $\gamma_i = G_i/L_i$ as defined in article I (balance between gain, G_i , and loss, L_i , electron kinetic mechanisms for populating or depopulating a particular level i) remains practically constant as the distance to the target is increased for the five energy levels of Li considered and it is higher for $i=5$ ($\gamma_5=1.33$) and $i=4$ ($\gamma_4=0.75$) than for $i=3$ ($\gamma_3=0.36$). The constant values of γ_i are directly connected to the fact that the available spatial measurements of the electron temperature, in vacuum and O_2 and Ar atmospheres, are approximately constant and similar within experimental error.^{13,14}

The measured and calculated maxima of the emission intensity associated with the 670.8 nm line from the excited Li atoms in Ar and O_2 environments (at 1 Torr) are shown, respectively, in Figs. 5(a) and 5(b) as a function of the distance to the target.

In order to understand the results shown in Figs. 5(a) and 5(b) we have to consider, on one hand, that the maximum of the line intensities plotted corresponds to the emission from level $i=2$, that is, from the first excited level of Li atoms to ground state $i=1$. On the other hand, that the emission intensity of the $2 \rightarrow 1$ spectral line in a homogeneous plasma (which is assumed here as our case) is $I_{21} = h\nu_{21} A_{21} N_{Li(2)} \kappa_{21}$, where $h\nu_{21} \approx 1.9 \text{ eV}$ is the energy gap between levels $i=2$ and $i=1$, A_{21} is the Einstein emission probability, $N_{Li(2)}$ is the concentration of Li atoms excited to level $i=2$, and κ_{21} is the radiation escape factor controlling the amount of radiation that is reabsorbed in the

FIG. 5. Spatial evolution of (a) the experimental values of the maximum of the emission intensity (I_{21}^{Exp}) corresponding to the dipole-allowed radiative transition $2 \rightarrow 1$ (670.8 nm) in Li I, and (b) the calculated emission intensity (I_{21}^{Theo}) from the present model. The measurements and calculations were performed for a laser fluence of 1.2 J cm^{-2} and in 1 Torr of Ar (○) and O_2 (△). The solid lines are a guide for the eye.

plasma (for $\kappa_{21}=0$ all the radiation is reabsorbed and for $\kappa_{21}=1$ all the radiation from this radiative transition leaves the plasma).

Figure 5(a) shows the spatial evolution of the measured I_{21}^{Exp} in O_2 and Ar, both exhibit a maximum peaking around 4 and 6 mm, respectively. These peaks almost coincide with the maxima of the spatial profiles of N_e determined in O_2 and Ar atmospheres under the same conditions (see Fig. 1 of Ref. 14). However, when looking at Fig. 3(b) we have obtained that $N_{\text{Li}(2)}$ in Ar is lower than in O_2 , which, since level $i=2$ is electronically excited from ground Li ($i=1$), is consistent with the fact that N_e is lower in Ar than in O_2 as reported in a previous work.¹⁴ This might suggest that, contrary to the experimental result shown in Fig. 5(a), the intensities predicted by the present kinetic model would be such that I_{21}^{Theo} (Ar) is lower than I_{21}^{Theo} (O_2). The latter, however, is not that straightforward since we first would need to properly evaluate the radiation escape factor κ_{21} in the laser-produced plasma in vacuum and under the action of O_2 and Ar atmospheres at 1 Torr. This is a not trivial issue since, rigorously speaking, it would require solving the radiative transport problem in a transient and nonuniform plasma. However, in the first-order approximation, the escape factors can be treated as constants and, in a more realistic case, they depend on plasma conditions. For example, it is found that the ability of the plasma to reabsorb the dipole-allowed lines increases monotonally with the plasma density when the reabsorption involves the lowest energy levels of the emitting atom as absorbers,²² which are usually the most populated ones.

We have assumed that $\kappa_{21}=1$ in vacuum and in Ar since the ground Li atom density is quite similar in both cases.

FIG. 6. Most relevant electron-impact kinetic mechanisms responsible for (a) populating (g_{ji}) and depopulating (l_{ij}) levels $i=1, 4, 5$, and (b) populating (g_{ji}) and depopulating (l_{ij}) levels $i=2, 3$ of Li atoms in the laser-generated plasma after ablation of a LiNbO_3 crystal in vacuum (without superscript), and in atmospheres of Ar and O_2 at 1 Torr. The numerical intervals in some (g_{ji})^{Ar,O} and (l_{ij})^{Ar,O} correspond to their variation with distance as we go away from the target.

However, for an O_2 environment, we have assumed that $\kappa_{21} \approx 0.5$ since here $N_{\text{Li}(1)}$ is almost twice (except close to the target) its value in vacuum and Ar and, consequently, the ability of the ground level of Li to reabsorb the radiation from the $2 \rightarrow 1$ transition is more important in O_2 than in Ar or vacuum. Following the above considerations, the I_{21}^{Theo} calculated with our model is plotted in Fig. 5(b) where we can clearly see a qualitative agreement when comparing with its experimental value shown in Fig. 5(a).

Finally, we have obtained that, for Ar and O_2 environments, both the relative loss, l_{ij} [see Eq. (20) in article I], and gain rate coefficients, g_{ji} [Eq. (21) in article I] remain almost constant, as in vacuum, as we go away from the target. Figure 6 represents the partial contribution of each of these electron-atom rate coefficients to the population and depopulation of the considered energy levels of Li atoms. As can be seen in Fig. 6(a), the collisional excitation and de-excitation processes from, respectively, level 4–5, and 5–4 are the same and they are the most important for populating and depopulating these two upper energy levels. In addition,

whereas collisional de-excitation mechanisms from levels 2 ($\sim 60\%$) and 3 ($\sim 32\%$, $\sim 33\% \rightarrow 34\%$ in Ar, $\sim 32\% \rightarrow 34\%$ in O_2) are responsible for populating the ground level of Li atoms, collisional excitation ($\sim 98\%$) from level 1 to level 2 is the main mechanism for depopulating the ground level. Regarding Fig. 6(b), we see that collisional de-excitation from levels 4 ($\sim 33\%$) and 5 ($\sim 64\%$) are the principal populating mechanisms of level 3, while collisional excitation to levels 4 ($\sim 20\%$) and 5 ($\sim 55\%$) together with de-excitation processes to level 2 ($\sim 25\%$) are the most important depopulating mechanisms of level 3. Moreover, the collisional de-excitation ($\sim 85\%$) from level 3 is the principal populating process for level 2, while its collisional decay ($\sim 65\%$, $66\% \rightarrow 68\%$ in Ar, $\sim 63\% \rightarrow 70\%$ in O_2) to the ground level and collisional excitation ($\sim 27\%$, $\sim 25\%$ in Ar, $\sim 28\% \rightarrow 23\%$ in O_2) to level 3 are the main kinetic mechanisms depopulating level 2.

IV. CONCLUSIONS

We have studied the spatial electron kinetics of the non-equilibrium plasma generated by laser ablation of a $LiNbO_3$ crystal under the influence of Ar and O_2 atmospheres at 1 Torr. The results obtained have been compared with those previously reported in vacuum. An analytic quasistationary kinetic model for studying the laser-generated plasma has allowed us to predict the spatial behavior of the concentration of ground and excited Li atoms in Ar and O_2 , as well as the underlying electron collisional excitation and de-excitation mechanisms leading to the predicted Li population densities which are always higher in O_2 than in Ar and vacuum. The model considered here uses as input parameters the experimental values of the N_e and T_e previously obtained from optical (atomic) emission measurements. In addition, the predicted emission intensity from level 2 to 1 of Li agrees reasonably well with its experimental value in Ar and O_2 . It is found that, in the latter case, the reabsorption of radiation by the plasma is more important since the absorber (ground Li) concentration is higher in O_2 atmospheres.

ACKNOWLEDGMENTS

This work was funded by CICYT (Spain) under Project No. TIC99-0866. F.J.G.V. acknowledges a Ramón y Cajal

contract from the Spanish Ministry of Science and Technology (MCYT). The authors thank Dr. J. A. Chaos, Dr. J. Gonzalo, and Dr. A. Perea (I. Óptica, CSIC) for kindly supplying the experimental data on emission intensities.

- ¹*Pulsed Laser Deposition*, edited by D. B. Chrisey and G. K. Hubler (Wiley, New York, 1994).
- ²T. H. Lin and S. H. Lee, in *Properties of Lithium Niobate*, EMIS Data Review Ser. 5 (Inspect, London, 1989).
- ³C. N. Afonso, in *Materials for Optoelectronics: New Developments*, edited by F. Agulló-López (World Scientific, Singapore, 1995), Chap. 1, and references therein.
- ⁴S. B. Ogale, R. Nawathey-Dikshit, S. J. Dikshit, and S. M. Kanetkar, J. Appl. Phys. **71**, 5718 (1992).
- ⁵Y. Shibata, Y. Kanno, K. Kaya, M. Knai, and T. Kawai, Jpn. J. Appl. Phys., Part 1 **34**, L320 (1995).
- ⁶J. A. Chaos, J. Gonzalo, C. N. Afonso, J. Perrière, and M. T. García-González, Appl. Phys. A: Mater. Sci. Process. **72**, 705 (2001).
- ⁷W. K. A. Kummuduni, Y. Nakayama, Y. Nakata, T. Okada, and M. Maeda, J. Appl. Phys. **74**, 7510 (1993).
- ⁸P. E. Dyer, A. Issa, and P. H. Key, Appl. Phys. Lett. **57**, 186 (1990).
- ⁹D. J. Lichtenwalner, O. Auciello, R. Dat, and A. I. Kingon, J. Appl. Phys. **74**, 7497 (1993).
- ¹⁰F. J. Gordillo-Vázquez, J. Appl. Phys. **90**, 599 (2001).
- ¹¹S. Suckewer, Phys. Rev. **170**, 239 (1968).
- ¹²J. A. Kunc, J. Appl. Phys. **63**, 656 (1988).
- ¹³F. J. Gordillo-Vázquez, A. Perea, J. A. Chaos, J. Gonzalo, and C. N. Afonso, Appl. Phys. Lett. **78**, 7 (2001).
- ¹⁴F. J. Gordillo-Vázquez, A. Perea, and C. N. Afonso, Appl. Spectrosc. **56**, 381 (2002).
- ¹⁵J. A. Kunc, Phys. Rev. A **40**, 1507 (1989).
- ¹⁶W. L. Wiese, M. W. Smith, and B. M. Glennon, NBS Report No. NSRDS-NBS 4, 1966, Vol. 1.
- ¹⁷J. A. Kunc and M. Zgorzelski, At. Data Nucl. Data Tables **19**, 1 (1977).
- ¹⁸M. Gryzinski, Phys. Rev. A **138**, 322 (1965).
- ¹⁹H. W. Drawin, Report No. EUR-CEA-FC 383 (revised), 1967.
- ²⁰H. P. Gu, Q. H. Lou, N. H. Cheung, S. C. Chen, Z. Y. Wang, and P. K. Liu, Appl. Phys. B: Lasers Opt. **58**, 143 (1994).
- ²¹C. Timmer, S. K. Srivastava, T. E. Hall, and A. Fucaloro, J. Appl. Phys. **70**, 1888 (1991).
- ²²W. H. Soon and J. A. Kunc, Phys. Rev. A **41**, 825 (1990).
- ²³J. B. Hasted, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, New York, 1962), Chap. 18, and references therein.
- ²⁴S. Kita and N. Shimakura, Phys. Rev. A **55**, 3504 (1997).
- ²⁵J. A. Kunc and W. H. Soon, Phys. Rev. A **40**, 5822 (1989).
- ²⁶C. G. Braun and J. A. Kunc, Phys. Fluids **31**, 671 (1988).
- ²⁷J. A. Chaos, R. W. Dreyfus, A. Perea, R. Serna, J. Gonzalo, and C. N. Afonso, Appl. Phys. Lett. **76**, 649 (2000).
- ²⁸J. A. Chaos, Ph.D. thesis, Universidad Autónoma de Madrid, Madrid, Spain, 2001.
- ²⁹H. F. Sakeek, T. Morrow, W. G. Graham, and D. G. Walmsley, J. Appl. Phys. **75**, 1140 (1994).