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Population inversion of molecular nitrogen in an Ar: N₂ mixture by selective resonance-enhanced multiphoton ionization

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Resonance-enhanced multiphoton ionization (REMPI) is shown to offer an attractive strategy for population inversion of molecular nitrogen in an Ar: N₂ gas mixture. We present a detailed analysis of the key processes leading to a population inversion of molecular nitrogen in a REMPI-pumped Ar: N₂ gas mixture, including a (3 + 1) REMPI of argon atoms, conversion of the REMPI-generated atomic argon ions into molecular ions, and generation of long-lived metastable excited-state argon atoms through dissociative recombination, populating the C³π_u states of molecular nitrogen. Population inversion achieved for the second-positive-band laser transitions of molecular nitrogen enables stimulated emission of ultraviolet radiation at 337 nm. A high selectivity of the REMPI process helps to radically reduce the depletion of the working medium through the ionization of N₂, providing a pump mechanism that is ideally suited for the creation of a new type of a highly efficient nitrogen laser. © 2011 American Institute of Physics. [doi:10.1063/1.3646478]

I. INTRODUCTION

Lasing action in nitrogen is known for almost half a century.¹,² Still, interesting physics behind population inversion in molecular nitrogen, an unusual mechanism of lasing, and numerous potential applications of this cost-efficient laser system continue to attract growing attention. The most important lasing transition in nitrogen molecules couples the C³π_u and B³π_g electronic states and gives rise to the emission of ultraviolet radiation at 337.1 nm. In a standard scheme of an N₂ laser, population inversion of these states is created by an electron impact in a fast discharge.³ Since the minimum of the potential curve of the B³π_g state is shifted toward larger internucleus distances relative to the minimum of the potential curve of the C³π_u state, the Franck–Condon principle dictates a much higher population efficiency for the C³π_u state. The gain provided by the C³π_u – B³π_g transition is so high that a transverse-electric-discharge N₂ laser can operate with the atmospheric air as an active medium.⁴ The question as to whether N₂ molecules can lase under conditions of optically excited atmospheric air has been a subject of intense studies through the past years.⁵ Such an optically pumped N₂ laser in the atmosphere would provide a powerful tool for laser-based remote sensing and standoff detection. The utility of a UV N₂ laser for atmosphere sensing using Raman scattering has been known for more than four decades.⁶ Modern laser technologies offer unique possibilities for the delivery of ultrashort high-power laser pulses over large distances in the filamentation regime,⁶–⁸ enabling a remote optical excitation of the atmosphere.⁹ A lasing-like emission of molecular nitrogen at 357 nm has been reported by the Laval group.¹⁰ Recent experimental demonstration of lasing by two-photon-excited oxygen atoms in the atmosphere,¹¹,¹² on the other hand, suggests that narrowband laser excitation may often be advantageous as a method of optical pumping for lasing by atmospheric constituents.

In this paper, we examine a new optical method for the population inversion of the laser C³π_u and B³π_g states of molecular nitrogen in a gas mixture. Our method is based on resonance-enhanced multiphoton ionization (REMPI) of argon in an Ar: N₂ gas mixture, leading to an efficient population transfer to the C³π_u states of molecular nitrogen. A high selectivity of the REMPI process helps to radically reduce the depletion of the working medium through the ionization of N₂, providing a pump mechanism that is ideally suited for the creation of a new type of a highly efficient nitrogen laser.

II. MODEL

The population inversion scenario considered in this work involves the following key processes. The REMPI of an Ar: N₂ gas mixture with an ultraviolet optical pump provides a highly selective ionization of argon without producing any noticeable ionization of nitrogen. Atomic argon ions Ar⁺ generated as a result of the REMPI process are converted into molecular argon ions,

\[ Ar^+ + Ar + Ar \rightarrow Ar^+_2 + Ar. \]  (1)

Dissociative recombination of these ions,

\[ Ar^+_2 + e \rightarrow Ar^+ (4^3P_2) + Ar, \]  (2)

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gives rise to long-lived metastable excited-state argon atoms, which efficiently populate the \( C^3\pi_u \) states of molecular nitrogen,

\[
Ar^\ast(4^3P_2) + N_2 \rightarrow N_2(C^3\pi_u) + Ar,
\]

inverting the population of these states with respect to the \( B^3\pi_g \) state. This population inversion enables lasing at the wavelengths of 337 and 357 nm in the second positive band of molecular nitrogen, \( N_2\left(C^3\pi_u\right) \rightarrow N_2\left(B^3\pi_g\right)\), \( \nu=0,1,2,3, \ldots + \hbar\nu \). In the earlier work, the sequence of processes, Eqs. (1) – (3), has been identified as a mechanism of population inversion of the \( C^3\pi_u \) and \( B^3\pi_g \) states of molecular nitrogen in Ar: N\(_2\) gas mixture pumped by an electric discharge,\(^{15}\) giving rise to high-efficiency lasing at 337 nm. Lasing through other transitions of the second positive band of molecular nitrogen is also possible, but these lasing lines are typically much less intense and will be neglected here. Vibrational excitation of excited-state nitrogen \( N_2\left(B^3\pi_g\right) \) is also neglected.

The REMPI pump requires a laser pulse with a sufficiently narrowband, which, however, does not need to have a high intensity, which allows the impact ionization of the gas mixture to be readily avoided. We consider a two-step single-frequency \((3+1)\) REMPI of argon by picosecond laser pulses with a central wavelength of 261.27 nm, where the first step involves a three-photon excitation of argon atoms to the \( 3p^5\ 3d\ [5/2]^3 \) \((J = 3)\) intermediate level, followed by a one-photon ionization from this intermediate state in the second step.

The rate of three-photon excitation in the first step of our REMPI process is given by\(^{16,17}\)

\[
W_{f,i}^{(3)} = (2\pi a F \omega_{0L})^3 \sum_{|p|} \sum_{|g|} \langle f | p | 2 \rangle \langle 2 | p | 1 \rangle \frac{\sqrt{\omega_{0L}^2 - 2 \omega_{0L}^2 + \gamma_i^2/4}}{\gamma_i^2 \sqrt{\omega_{0L}^2 - 2 \omega_{0L}^2 + \gamma_i^2/4}} G(\omega_L)^2_{Gf}
\]

where \(f\) and \(i\) stand for the ground \((3p^6\ 1S)\) and final \((3p^5\ 3d\ [5/2]_j J = 3)\) states of the three-photon excitation process, \(\gamma_i\) is the frequency difference between the intermediate \((i = 1, 2)\) and ground states, \(\alpha\) is the fine-structure constant \((1/\lambda_{\text{C67.036}})\), \(F\) is the total photon flux measured in number of photons per meter-squared per second, \(F(r,t) = I_L(r,t)/\omega_{0L}\), \(I_L(r,t)\) is the laser intensity, \(r\) is the radial coordinate, \(\omega_{0L}\) is the laser radiation frequency, \(\langle p | r | q \rangle\) are the dipole matrix elements for a transition the \(p\) and \(q\) states, \(\gamma_i\) is the linewidth of the \(i\)th intermediate state, and \(G\) is the line shape profile. The laser pump is assumed to have a Gaussian temporal envelope and a Gaussian beam profile. \(I_L(r,t) = I_0(t) \exp(-r^2/r_0^2)\), with the beam-waist radius \(r_0\) assumed to be large enough to neglect all the radial gradients. \(B\) The factor \(G\) is defined as a convolution of the Lorentzian, Doppler, and laser line profiles, yielding a contour that is strongly confined to the frequency of the three-photon resonance.

The cross section of one-photon ionization in the second step of the REMPI process, we use the quantum-defect approximation, which is exact for hydrogen-like atoms and provides an adequate accuracy for the Rydberg states of rare gases:\(^{18}\)

\[
\sigma_{pi} = \frac{8 \times 10^{-22}}{Z(U_i/R)^{1/2} (\hbar\omega_L/|U_i|)} [m^2]
\]

Here, \(Z\) is the charge of the resulting ion, \(U_i\) is the ionization potential of the excited-state atom, \(R\) is the Rydberg constant, and \(\hbar\omega_L\) is the photon energy.

The model of plasma dynamics for the REMPI-pumped Ar: N\(_2\) mixture is based on the rate equation for the local density of excited-state argon atoms,

\[
\frac{dN^*}{dt} = N_{Ar} \sigma_{(3)} F^3 - N^* \sigma_{pi} F^3 - \left( \frac{1}{\tau} + k_1 N_{Ar} + k_3 N_{Ar}^2 + k_e n_e \right) N^*
\]

where \(N^*\) is the number density of argon atoms in the \(3p^5\ 3d\ [5/2]^3\) state, \(N_{Ar}(t) = N_{Ar}(0) - n_{Ar^+} - n_{Ar^2} - N^* - N^{**}\) is the number density of ground-state argon atoms, \(n_{Ar^+}\) and \(n_{Ar^2}\) are the number densities of atomic and molecular argon ions, \(N^{**}\) is the number density of argon atoms in the metastable state \(4^3P_2\), \(\sigma_{(3)}\) is the three-photon excitation cross section, defined as \(W_{f,i}^{(3)} = \sigma_{(3)} F^3\), \(\tau\) is the spontaneous relaxation time of the \(3p^5\ 3d\ [5/2]^3\) state, \(k_1\) is the quenching collision rate coefficient of the \(3p^5\ 3d\ [5/2]^3\) state, \(k_3\) is the rate of three-body collisions of ground- and excited-state atoms, and \(k_e\) is the rate of collisions of electrons and excited-state atoms. Equation (6) is subject to the initial condition \(N^*(t = 0) = 0\).

The quenching collision and three-body collisions rates appearing in Eq. (6) are taken equal to \(k_1 = 2.3 \times 10^{-21} [m^6/s]\) and \(k_3 = 1.4 \times 10^{-24} [m^6/s]\) in accordance with Refs.\(^ {19,20}\). The spontaneous relaxation time is estimated as \(\tau = 10^{-7} \approx 6.6 \times 10^{-8} s\). The effective lifetime of the metastable state \(4^3P_2\) meets the inequality \(21\) \(\tau^{**} > 1.3 s\). The rate of conversion of atomic argon ions to molecular argon ions through the process, Eq. (1), is \(k_{\text{com}} = 2.5 \times 10^{-43} (T_0/T)^{3/4} [m^6/s]\) (Refs.\(^ {21,22}\)).

The balance equations for Ar: N\(_2\) plasma components are written as

\[
\frac{d[n_e]}{dt} = |G_s| - |L_s|
\]

where \(n_e\) stands for electrons \((e)\), Ar\(^{+}\), Ar\(_2^{+}\), N\(^{+}\), N\(_2^{+}\), N\(_3^{+}\), N\(_4^{+}\), N, N\(_2\) (A), N\(_2\) (B), N\(_3\) (C), N\(_4\), N\(_5\), and \(G_s\) and \(L_s\) are the relevant generation and loss rates.

The rate of recombination of electrons with Ar\(^{+}\) ions is given by \(\beta_{eff} = 5 \times 10^{-39} T_0^{-1/5} n_e + 2.7 \times 10^{-19} T_x^{0.75} [m^3/s]\), where \(T_e\) is in eV and \(n_e\) is in m\(^{-3}\). The first term in Eq. (7) accounts for recombination in three-body collisions,\(^ {18}\) while the second term includes photorecombination.\(^ {21}\) The cross-sections of three-photon excitation, \(\sigma_{(3)}\), and one-photon ionization, \(\sigma_{pi}\), are estimated as \(\sigma_{(3)} = 2.81 \times 10^{-22} m^6/s^3\) and \(\sigma_{pi} = 7.67 \times 10^{-23} m^2\), in agreement with Ref.\(^ {16}\).
The electron temperature $T_e$ is found from the hydrodynamic equation, \(^{16,21}\)

$$
\frac{3}{2} k \frac{d}{dt} (n_e T_e) = J_L - \frac{3}{2} n_e k (T_e - T_i) \nu_{eN} - \frac{3}{2} n_e k (T_e - T) \\
\times \left[ \delta N_e (\nu_{eN} + \nu_{eN_2} + \frac{1}{2} \nu_{eN_2}^2) \\
+ \delta_{Ar} (\nu_{eAr} + \nu_{eAr_2} + \frac{1}{2} \nu_{eAr_2}^2) \\
+ N^+ \sigma_{ph} F e_{ph} + k_e n_e (N^+I_m^+ + N^{++}I_m^{++}) \right]
$$

(8)

where $T_e$ is the vibrational temperature, $T_i$ is the translational gas temperature, $\delta N_e = 2m_2/M_{N_e}$, and $\delta_{Ar} = 2m_2/M_{Ar}$, and

$$
J_L = e^2 n_e L(t) \sum \nu_{es/N_e} \left[ \omega_e^2 + \left( \sum \nu_{es} \right)^2 \right]
$$

is the Joule heat, with the sum

$$
\sum \nu_{es}
$$

taken overall the electron-neutral and Coulomb elastic collisions, which change the electron momentum. The first term on the right-hand side of Eq. (8) describes the transfer of electron energy to the vibrations of nitrogen molecules. The second term of this equation accounts for the transfer of electron energy transfer to the translational energy of nitrogen and argon molecules, atoms and ions through elastic and Coulomb collisions. The last two terms include gas heating due to the generation of photoelectrons with energies $e_{ph}$ through the REMPI process and electron gas heating in superelastic collisions with $3p^5(3d^2p_1/2)[3d^2(5s2)]$ (excitation

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**TABLE I.** Processes included in the model of plasma dynamics with the relevant rate constants.

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate Constant</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ar^+ + Ar + Ar \rightarrow Ar^+_2 + Ar$</td>
<td>$2.5 \times 10^{-11} (300/T_{eK})^{0.75}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$Ar^+_2 + e \rightarrow Ar(4^3P_2) + Ar$</td>
<td>$9.1 \times 10^{-13} (300/T_{eK})^{0.6}$</td>
<td>[m$^6$/s$^3$]</td>
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<tr>
<td>$e + N_2 \rightarrow N + N$</td>
<td>$2 \times 10^{-13} (300/T_{eK})^{0.5}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + e \rightarrow N + N$</td>
<td>$2 \times 10^{-13} \exp(300/T_{eK})$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + N \rightarrow N + N_2$</td>
<td>$6.6 \times 10^{-18}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + N \rightarrow N + N_2$</td>
<td>$10^{-15}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + N \rightarrow N + N_2$</td>
<td>$2.1 \times 10^{-22} \exp(T_{eK}/121)$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + e \rightarrow N + N$</td>
<td>$6 \times 10^{-39} \exp(300/T_{eK})$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + e \rightarrow N + e$</td>
<td>$7 \times 10^{-32} \exp(300/T_{eK})$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + e \rightarrow N + h\nu$</td>
<td>$7 \times 10^{-18}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + N \rightarrow N + N_2$</td>
<td>$10^{-19}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2^+ + N \rightarrow N + N_2$</td>
<td>$1.7 \times 10^{-41} (300/T_{eK})^{2.1}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$e + Ar(4^3P_2) \rightarrow Ar^+ + e + e$</td>
<td>$6.8 \times 10^{-15}[e^{-0.67}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$e + e + e \rightarrow Ar(4^3P_2) + e$</td>
<td>$5 \times 10^{-39}T_e^{-4.5}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$Ar(4^3P_2) + Ar(4^3P_2) \rightarrow Ar^+ + e + Ar$</td>
<td>$5 \times 10^{-16}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$Ar(4^3P_2) + N_2 \rightarrow Ar + N_2(C)$</td>
<td>$3 \times 10^{-17}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$Ar(4^3P_2) + N_2 \rightarrow Ar + N_2(B)$</td>
<td>$9.8 \times 10^{-18}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$Ar(4^3P_2) + N_2 \rightarrow Ar + N + N$</td>
<td>$1.6 \times 10^{-17}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2(A) \rightarrow N_2(C) \rightarrow N_2(C)$</td>
<td>$1.5 \times 10^{-16}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2(A) \rightarrow N_2(B) \rightarrow N_2(B)$</td>
<td>$7 \times 10^{-17}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2(A) \rightarrow N_2(N) + N_2 + N_2$</td>
<td>$3 \times 10^{-22}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2(A) \rightarrow N + N + N_2$</td>
<td>$9.6 \times 10^{-17}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$e + N_2 \rightarrow N_2(X) + N_2(X)$</td>
<td>$2 \times 10^{-12} (300/T_{eK})^{0.5}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2(C) \rightarrow Ar + N_2(B) + Ar$</td>
<td>$8.16 \times 10^{-19}$</td>
<td>[m$^6$/s$^3$]</td>
</tr>
<tr>
<td>$N_2(C) \rightarrow N_2(B) + h\nu$</td>
<td>$2.74 \times 10^7$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2(B) \rightarrow N_2(A) + h\nu$</td>
<td>$2 \times 10^5$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2(B) \rightarrow N + e + Ar$</td>
<td>$8 \times 10^{-18}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2(B) \rightarrow N + N + N_2$</td>
<td>$3 \times 10^{-17}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2(C) \rightarrow N + N + N_2$</td>
<td>$1.4 \times 10^{-17}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$Ar^+ + N_2 \rightarrow Ar^+ + N_2^+$</td>
<td>$4.5 \times 10^{-16}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$e + N_2 \rightarrow N + N$</td>
<td>$2 \times 10^{-11} (300/T_{eK})^{0.5}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2^+ + N + M \rightarrow N_2^+ + M + M \rightarrow N_2 + Ar$</td>
<td>$5.24 \times 10^{-41} (300/T_{eK})^{2.2}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2^+ + N + M \rightarrow N_2^+ + M + M \rightarrow N_2 + Ar$</td>
<td>$8.3 \times 10^{-46} \exp(500/T_{eK})$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2^+ + N + N \rightarrow N_2^+ + N_2$</td>
<td>$0.9 \times 10^{-41} \exp(400/T_{eK})$</td>
<td>[s$^{-1}$]</td>
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<tr>
<td>$N_2^+ + N \rightarrow N_2^+ + N_2$</td>
<td>$7.2 \times 10^{-19} \exp(300/T_{eK})$</td>
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<tr>
<td>$N_2^+ + N \rightarrow N_2^+ + N_2$</td>
<td>$10^{-17}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2^+ + N \rightarrow N_2^+ + N_2$</td>
<td>$5.5 \times 10^{-18}$</td>
<td>[s$^{-1}$]</td>
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<tr>
<td>$N_2^+ + N_2 \rightarrow N_2^+ + N_2$</td>
<td>$1.2 \times 10^{-17}$</td>
<td>[s$^{-1}$]</td>
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<tr>
<td>$N_2^+ + N_2 \rightarrow N_2^+ + N_2$</td>
<td>$3 \times 10^{-16}$</td>
<td>[s$^{-1}$]</td>
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<tr>
<td>$N_2^+ + N_2 \rightarrow N_2^+ + N_2$</td>
<td>$4 \times 10^{-16}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2^+ + N_2 \rightarrow N_2^+ + N_2$</td>
<td>$6 \times 10^{-16}$</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$N_2^+ + N_2 \rightarrow N_2^+ + N_2$</td>
<td>$6 \times 10^{-16}$</td>
<td>[s$^{-1}$]</td>
</tr>
</tbody>
</table>
energy $I_m' \approx 14.1$ eV) and 4 $^{3}P_2$ (excitation energy $I_m^0 \approx 11.6$ eV) metastable states. The frequency $\nu_{ev}(T_e)$ of collisions of electrons with nitrogen molecules was calculated from the electron inelastic energy loss function:  

$$\nu_{ev} = 3.87 \times 10^{-14} N_{N_2} \exp(-1.5/T_e) \text{ for } T_e \leq 1 \text{ eV}$$

$$\nu_{ev} = [A + 7.5 \times 10^{-15}(1 - 0.036T_e)]N_{N_2}/T_e \text{ for } T_e > 1 \text{ eV}$$

$$A = 2.13 \times 10^{-13} T_e^{1/2}[1 - 0.05(T_e - 4)] \exp(-7.86/T_e)$$

The electron-ion Coulomb collision frequency is given by $\nu_{e,n_3}$ except the optical processes (population loss from the $\text{N}_2(4\text{~P}_3)$ state through spontaneous transitions to $\text{N}_2(2\text{~S}_1)$), $\nu_{e,N_2}$, $\nu_{e,Ar}$ collisions in Eq. (9) were estimated using the Landau-Teller approximation:  

$$\nu_{e,n_3} = 2.91 \times 10^{-12} n_{+} T_e^{-3/2} \text{ in } \Lambda, \text{ where } n_{+}, n_{-} \text{ are the densities of } \text{Ar}^{+}, \text{Ar}^{-}, \text{N}_2^{+}. \text{ and } \text{N}_2^{-} \text{ ions; in } \Lambda \text{ is the Coulomb logarithm. The transport collision frequencies (all frequencies are in sec)}^{-1}$, $\nu_{e,N_2}$, $\nu_{e,Ar}$ were estimated from the relevant mobilities, calculated with the relevant drift velocities and temperatures as listed in Ref. 24.

The equation for the vibrational temperature is written as

$$\frac{dT_v}{dt} = \left( n_e/N_{N_2} \right) (T_e - T_v) \nu_{ev} - (T_v - T_v) [1/\tau_{VT,N_2} + (N_{Ar}/N_{N_2})/\tau_{VT,Ar}] \quad (9)$$

The times of vibrational relaxation through $\text{N}_2$-$\text{N}_2$ and $\text{N}_2$-$\text{Ar}$ collisions in Eq. (9) were estimated using the Landau-Teller approximation:  

$$\tau_{VT,N_2} = 3.98 \times 10^6 \exp(221.46/T_e^{1/3})/N_{N_2} \text{ and}$$

$$\tau_{VT,Ar} = 1.73 \times 10^6 \exp(239.5/T_e^{1/3})/N_{Ar}$$

The translational gas temperature remains almost constant for the above-specified conditions and time intervals. The dissociative recombination rate for the process, Eq. (2), is $\beta_{Ar^+} = 9.1 \times 10^{-13} (T/T_e)^{0.61} \text{ [m/sec]}$ (Ref. 26). The other processes included in the model along with their rate constants and the relevant references are listed in Table I.

Kinetic equations are solved in our model jointly with the rate equations for the populations in the lasing states:

$$\frac{dn_1}{dt} = S_1 + n_2 (A_{21} + \sigma_{21} n_{ph}) - n_1 \sigma_{12} n_{ph} \quad (10)$$

$$\frac{dn_2}{dt} = S_2 - n_2 (A_{21} + \sigma_{21} n_{ph}) + n_1 \sigma_{12} n_{ph} \quad (11)$$

$$\frac{dn_{ph}}{dt} = \sigma_{21} (n_2 - n_1) n_{ph} c \frac{n_{ph}}{1 + I_c/I_c} - \frac{n_{ph}}{\tau_{ph}} \quad (12)$$

where $n_1$ is the population of the $B^1\Pi_u$ state, $n_2$ is the population of the $C^3\Pi_u$ state, $n_{ph}$ is the photon density, $A_{21}$ are the Einstein coefficients, $I_c = n_{ph} h \nu / c$ is the laser intensity, $\nu = c/\lambda_L$, $\lambda_L$ is the lasing wavelength, $S_1$ and $S_2$ are the rates of processes populating the laser states via all channels except the optical processes (population loss from the $N_2(B)$ state through spontaneous transitions to $N_2(A)$ is included into $S_1$), $\tau_{ph}$ is the laser photon lifetime, $\sigma_{21}$ is the stimulated emission cross section, $I_c = h \nu / (\sigma_{21} \tau_s)$ is the saturation intensity, and $\tau_s \approx A_{21}^{-1}$.

The $\sigma_{21}$ cross section is calculated as $\sigma_{21} = A_{21} (8\pi)^{-1} n^{-2} \lambda_L^2 g(\nu)$, where $g(\nu)$ is the spectral line shape.

To include pressure-induced line broadening, we take $g(\nu) \approx g_0(\nu)\nu/\nu_{500}/p_{Ar} + p_{N_2}$, where $g_0(\nu)$ is the spectral line shape at the gas pressure $p = 1$ atm and $T = 300$ K and $p_{Ar}$ and $p_{N_2}$ are the partial pressures of argon and molecular nitrogen. We set $g(\nu) \approx \Delta \nu^{-1}$, where $\Delta \nu = \Delta \nu_L^2/\lambda^2$ and $\Delta \lambda$ is the linewidth. For conditions typical of a TEA $N_2$ laser, $\lambda_L \approx 337.1$ nm, we have $\Delta \lambda \approx 0.1$ nm, $g \approx 3.66 \times 10^{-12}$ s, and $s_{21} \approx 4.96 \times 10^{-19}$ m$^2$. Assuming that the plasma is induced within a laser beam waist region with a length $L$,

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**FIG. 1.** (Color online) Kinetics of the densities of gas-mixture components (a), electron and vibrational temperatures (b), and populations of the $C^3\Pi_u$ and $B^1\Pi_u$ states of molecular nitrogen (c) for a gas mixture with initial partial pressures of argon and nitrogen of 500 and 100 Torr, respectively. The pump laser has a central wavelength of 261.27 nm and a bandwidth of 0.2 nm.
we estimate the laser photon lifetime as $\tau_{ph} = L/c$. In simulations presented below $L$ is taken equal to 5 cm.

III. RESULTS AND DISCUSSION

Results of simulations performed for a laser pulse with a pulse width of 200 ps, a central wavelength of 261.27 nm, an energy of 0.5 mJ, and a beam radius of 25 $\mu$m are presented in Figs. 1 and 2. As can be seen from Figs. 1(a) and 2(a), the REMPI process gives rise to a fast buildup of the electron density, as well as the densities of argon ions and argon atoms in the $3p^5 3d [5/2]^3$ state. Results of calculations presented in these figures also show that the density of molecular nitrogen ions remains much lower than the density of argon ions, indicating that the high selectivity of the REMPI process helps to minimize the depletion of the working medium through the ionization of $N_2$, thus providing favorable conditions for efficient lasing.

The kinetic energy of photoelectrons produced by REMPI is $E_{ph} = h\omega - U_I \approx 3.2$ eV. REMPI-induced plasmas are generally nonequilibrium, with the electron temperature $T_e$, the vibrational temperature of $N_2$ molecules $T_v$, the translational temperature $T$ and the temperatures of atomic, and molecular ions $T_+$ and $T_{2+}$ meeting the relations [Figs. 1(b) and 2(b)] $T_e \geq T_v = T_+ = T_{2+}$. Due to the low intensity of the laser pulse, no impact ionization occurs within the laser pulse, as indicated by the kinetics of the electron density in Figs. 1(a) and 1(b), providing optimal conditions for population transfer to the upper lasing level.

Population inversion of the lasing $C^3\Pi_u$ and $B^3\Pi_g$ states of molecular nitrogen is achieved through the conversion of atomic argon ions into molecular ions through the process, Eq. (1), followed by the dissociative recombination of these ions, Eq. (2), giving rise to long-lived metastable excited-state argon atoms, which efficiently populate the $C^3\Pi_u$ through collisions with nitrogen molecules, Eq. (3).

Figures 1(c) and 2(c) illustrate the buildup of inverted population in the $C^3\Pi_u$ and $B^3\Pi_g$ states of molecular nitrogen. Since the lifetime of the $C^3\Pi_u$ state is limited by spontaneous and stimulated emission, as well as by collisional quenching, the populations of the $C^3\Pi_u$ and $B^3\Pi_g$ states remain inverted.

**FIG. 2.** (Color online) Kinetics of the densities of gas-mixture components (a), electron and vibrational temperatures (b), and populations of the $C^3\Pi_u$ and $B^3\Pi_g$ states of molecular nitrogen (c) for a gas mixture with initial partial pressures of argon and nitrogen of 100 Torr. The pump laser has a central wavelength of 261.27 nm and a bandwidth of 0.2 nm.

**FIG. 3.** (Color online) Dynamics of the intensity $I_p(t) = n_{ph}(t)hc/\lambda_0$ of stimulated emission from the REMPI induced region of 10 cm length for a gas mixture with initial partial pressures of argon and nitrogen of 500:100 and 100:100 Torr. The pump laser has a central wavelength of 261.27 nm and a bandwidth of 0.2 nm.
within a finite interval of time, thus limiting the laser pulse width. Both the magnitude of population inversion and the time interval within which the populations of the lasing levels are inverted are highly sensitive to the content of argon in the gas mixture. Higher concentrations of argon [Figs. 1(a)–1(c)] provide larger magnitudes of population inversion and keep the populations of the $C^3\Pi_u$ and $B^3\Pi_g$ states inverted for longer time intervals [cf. Figures 1(c) and 2(c)], giving rise to more intense and longer laser pulses (Figs. 3 and 4), due to the higher concentrations of argon ions generated by the REMPI process, converted by processes, Eqs. (1) and (2), to the populations of $C^3\Pi_u$ and $B^3\Pi_g$ states over a period of time of about 50 ns, providing ideal conditions for highly efficient lasing (Fig. 3).

The intensity of laser radiation from a REMPI-pumped Ar: $N_2$ mixture is a nonmonotonic function of the partial pressure of $N_2$. While for low pressures of $N_2$, larger amounts of nitrogen lead to higher lasing intensities because of a larger number of molecules in the laser levels, for higher pressures of $N_2$, quenching of the $C^3\Pi_u$ state through the $N_2(C) + N_2 \rightarrow N_2(B) + N_2$ process starts to play a noticeable role, reducing the lasing intensity.

IV. CONCLUSION

We have shown that resonance-enhanced multiphoton ionization offers an attractive strategy for population inversion of molecular nitrogen in an Ar: $N_2$ gas mixture. A high selectivity of the REMPI process helps to radically reduce the depletion of the working medium through the ionization of $N_2$, providing a pump mechanism that is ideally suited for the creation of a new type of a highly efficient nitrogen laser. The high concentration of argon required for lasing in a REMPI-excited Ar: $N_2$ gas mixture the implementation suggests no straightforward extension of this lasing mechanism to the standoff detection mode, where several promising options, including lasing by molecular nitrogen and atomic oxygen, have been demonstrated. While the motivation for a REMPI-pumped nitrogen laser is certainly not limited to standoff detection applications, as outlined in the Introduction, it is worth noting here that, according to our simulations, the gain provided by REMPI excitation for a properly chosen gas mixture is several orders of magnitude higher than the gain accessible with the mechanisms enabling atmospheric-air lasers. We anticipate that the existing atmospheric laser schemes could be enhanced by REMPI-type processes, although the specific REMPI excitation pathways pertinent to lasing in the atmosphere are still not clear. The work on this concept is in progress.

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