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Optical gain in rotationally excited nitrogen molecular ions

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We pump low-pressure nitrogen gas with ionizing femtosecond laser pulses at 1.5 μm wavelength. The resulting rotationally excited N$_2^+$ molecular ions generate directional, forward-propagating stimulated and isotropic spontaneous emissions at 428 nm wavelength. Through high-resolution spectroscopy of these emissions, we quantify rotational population distributions in the upper and lower emission levels. We show that these distributions are shifted with respect to each other, which has a strong influence on the transient optical gain in this system. Although we find that electronic population inversion exists in our particular experiment, we show that sufficient dissimilarity of rotational distributions in the upper and lower emission levels could, in principle, lead to gain without net electronic population inversion.

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Studies of stimulated emission in the constituents of air are motivated by potential applications in air lasing [1], a concept, the realization of which would enable efficient single-ended remote sensing in the atmosphere [2]. Various schemes of turning air into an active laser medium are being investigated [3–6]. One of the most promising approaches is based on pumping atmospheric nitrogen by ultra-intense femtosecond laser pulses propagating in the filamentation regime in air [7]. Intensity inside the core of the femtosecond laser filament is on the order of 100 TW/cm$^2$, which is sufficient to partially ionize oxygen and nitrogen molecules, producing, in particular, singly-ionized molecular nitrogen ions N$_2^+$.

It has been suggested that air ionization may result in the optical gain on the electronic transitions of N$_2^+$ at 391 nm and 428 nm emission wavelengths, as well as on several weaker transitions [8]. However, the gain mechanism responsible for those emissions has been controversial. Apart from its practical potential, air lasing in N$_2^+$ presents an intriguing problem in intense AMO physics. Indeed, it is counter-intuitive that strong-field ionization of the nitrogen molecule appears to preferentially create a molecular ion in the upper, not the lower emission state X$^2\Sigma_u^+$ of N$_2^+$ (Figure 1, see Supplementary Material for details). These emissions occur at the wavelengths around 428 nm. To disentangle filamentation and gain, we conduct our experiments at low gas pressure and with very tight focusing of the pump beam. Under these conditions, the geometry of the interaction zone is determined by the linear propagation of the focused pump. Although we still probe the gain medium with a co-propagating, spectrally broadened third harmonic of the pump, as we will show below, we are able to estimate the absolute value of optical gain using the well-known spin statistics of nitrogen molecules and the associated degeneracies of different rotational transitions in the N$_2^+$ molecular ions.

We pump low-pressure nitrogen gas with an intense ultrashort laser pulses at 1,500 nm. The pumping wavelength is chosen to reduce single-photon coupling between the lower emission state X$^2\Sigma_u^+$ and the intermediate state A$^2\Pi_u$ (not shown in Figure 1). In the case of 800 nm pumping, it has been argued that X$^2\Sigma_u^+$ to A$^2\Pi_u$ coupling enables stimulated emission in N$_2^+$ via population transfer [10, 11]. If A$^2\Pi_u$-state population transfer were key, our use of the 1,500 nm driver would inhibit lasing. Our results show otherwise.

In our experimental setup, 60 fs pulses with an energy of 2 mJ per pulse at 1,500 nm wavelength are generated by an Optical Parametric Amplifier (OPA) pumped by 15 mJ, 60 fs laser pulses at 800 nm. The pulse repetition frequency is 10 Hz. The N$_2^+$ lasing takes place in a gas cell filled with pure nitrogen gas at a variable pressure. The 15 mm-diameter pump beam is tightly focused inside the gas cell, using a lens with the focal length of 15 cm.

No directional nitrogen lasing is detected in the backward direction (i.e. in the direction opposite to that of the pump beam). In the forward direction, lasing is detected at both 391 nm and 428 nm emission bands of N$_2^+$, corresponding to the transitions B$^2\Sigma_u^+$(0) → X$^2\Sigma_u^+$ (0) and B$^2\Sigma_u^+$(0) → X$^2\Sigma_u^+$ (1), respectively, where the number in parentheses designates the vibrational level within the...
electronic state of \( \text{N}_2^+ \).

The interaction between the 391 nm and 428 nm transitions that share a common upper emission state is beyond the scope of this paper. Here we choose to study the 428 nm emission because of the availability of a Krypton calibration light source with several tabulated spectral lines near the lasing wavelength. The forward-propagating optical signal at 428 nm is directional and linearly polarized in the same way as the pumping beam, indicating that this emission is stimulated and self-seeded by the spectrally broadened third-harmonic of the pump.

Under our experimental conditions, the total energy of the forward-propagating 428 nm emission grows approximately linearly with the gas pressure. For the data shown here, the pressure is set to 4 Torr. Under these conditions, the propagation of the pumping laser beam is unaffected by its nonlinear interaction with the nitrogen in the gas cell. To quantify the parameters of the pump beam in the interaction zone, we have conducted multiple knife-edge measurements of the beam size, inside the low-pressure chamber, at different transverse planes along the propagation path. Thus measured minimum waist radius of the beam at the 1/2\(e^2\) intensity level is about 60 \(\mu\text{m}\), and the length of the interaction zone is about 1 mm. The peak intensity of the pump beam at the beam waist, inferred from the knife-edge measurements, is about 600 TW/cm\(^2\), which is close to the saturation intensity for the complete single ionization of nitrogen molecules. Using a 1/4 m spectrometer equipped with a 3,600 lines per mm grating, we record spectra of radiation from \( \text{N}_2^+ \) in the gas cell in the forward direction (self-seeded stimulated emission) and from the side (spontaneous emission). The spectrometer we use has resolution of 9 picometers (0.5 cm\(^{-1}\)) in the spectral range of interest around 428 nm wavelength. As we will show below, measuring the spectra of stimulated and spontaneous emissions separately allows us to approximately quantify rotational population distributions of \( \text{N}_2^+ \) ions in the upper and lower emission levels. The side- and forward-emitted spectra are integrated over 1000 and 100 laser shots, respectively.

The measured spectrum of side emission is shown in Figure 2. The spectrum of spontaneous emission of \( \text{N}_2^+ \) comprises the so-called P and R branches, which consist of lines with the change of the rotational quantum number \( N \) (lower minus upper emission state) of +1 and -1, respectively [12]. The peak value of the P-branch emission is stronger than that of the R-branch, because the P-branch is composed of multiple overlapping emission lines, while the R-branch lines are well separated.

Everywhere in this paper, as well as in the Supplementary Material, we index emission lines in the P and R emission branches by the \( N'' \) value of the lower emission state of the corresponding transition. For example, the R-branch emission line indexed with \( N'' = 6 \) corresponds to the transition from the \( N' = 7 \) state of the upper electronic energy manifold \( B^2 \Sigma_u^+ (0) \) to the \( N'' = 6 \) state of the lower electronic energy manifold \( X^2 \Sigma_g^+ (1) \).

The R-branch of the side emission peaks at the \( N'' \) value of 6. The placements of the individual spectral lines in the R branch follow their tabulated values [13], shown in Figure 2 with the vertical dashed lines. The amplitudes of the neighboring peaks in the R-branch are different by a factor of 2, which is a consequence of different nuclear-spin multiplicity of states involved in the emissions on the adjacent spectral lines (see the Supplementary Material for details).
The spectrum of the forward-propagating (stimulated) emission, for the same experimental conditions as those used to measure the spontaneous emission spectrum, is shown in Figure 3. The spectrum of the R-branch emission is shown in the main figure; the complete spectrum including both P- and R-branch emissions is shown in the inset. In contrast to the case of the spontaneous emission spectrum, the amplitudes of the neighboring emission peaks in the R-branch no longer differ by a factor of two, which is a consequence of the emission process being stimulated.

Due to different nuclear-spin multiplicities of even and odd N-states, the ratio of the values of the exponential gain constants (in the units of cm$^{-1}$) on the adjacent lines equals 2. Therefore, if the exponential gain constant for the weaker line near the overall peak of the spectral curve is $\alpha$, the ratio of the amplitudes of the two adjacent stronger and weaker lines equals $e^{2\alpha l} / e^{\alpha l} = G$, where $l$ is the total gain length (which is the same for both the weaker and the stronger lines) and $G$ is the total value of gain on the weaker line. The amplitude ratio for the adjacent spectral peaks, inferred from the measured spectrum, is about 8. Therefore the total value of gain, on the strongest line, can be estimated as 64. The upper estimate of the gain length $l$ is 1 mm, which is the total length of the interaction zone inferred from the knife-edge experiments. Accordingly, the lower-bound estimate of the peak exponential gain per unit length, on the strongest line, is about 40 cm$^{-1}$. The above estimate is based on the assumption that the overall spectral widths of both the R-branch emission and of the spectrally broadened third harmonic of the pump light, that seeds it, are much larger than the separation between the adjacent spectral lines.

Note that in contrast to the previous studies, e.g., [5] the broad-band pedestal due to the third-harmonic emission that seeds stimulated emission at 428 nm is not visible in the spectrum. That is because our spectrometer has a much higher resolution compared to the spectrometers used in the earlier studies. Generally, if an optical spectrum consists of a broad pedestal and narrow spectral lines that have spectral width much less than the resolution bandwidth of the spectrometer, the detected spectrally broad radiation will be artificially enhanced relative to the narrow spectral lines approximately in proportion to the ratio between the resolution bandwidth and the spectral width of the narrow lines.

Our key experimental observation is that spontaneous emission peaks at the value of the rotational quantum number $N''$ of about 6, while stimulated emission peaks at a higher value of 12. This experimentally observed difference indicates that the rotational systems in the B$^2\Sigma_u^+(0)$ and X$^2\Sigma_g^+(1)$ states are populated differently. Combined with the $\Delta N = \pm 1$ selection rules, the difference in the rotational population distributions in the two states has a profound effect on the optical gain in this system, as we discuss below. The rotational degree of freedom of $N_2^+$ is a key physical ingredient of this problem.

We point out that high-resolution measurements of rotational spectra of stimulated emission in $N_2^+$ under ultrafast laser pumping have been reported previously [14], but not in the connection with the gain mechanism in the $N_2^+$ ions. The focus of Ref. [14] was on stimulated emission and no spectra of spontaneous emission were reported. Only the difference between stimulated and spontaneous emission spectra is indicative of the rotational effect on the optical gain in $N_2^+$ that we discuss below.

To fit our experimental data, we parametrize the rotational probability distributions $f'[N']$ and $f''[N'']$, in the upper and lower emission levels B$^2\Sigma_u^+(0)$ and X$^2\Sigma_g^+(1)$, respectively, as follows:

$$f'[N'] \propto \exp \left( \frac{-E'[N' - N_B]}{k_B T_0} \right)$$

$$f''[N''] \propto \exp \left( \frac{-E''[N'' - N_X]}{k_B T_0} \right)$$

In the above equations, $k_B$ is the Boltzmann constant and $T_0 = 300$ K is the room temperature. The rotational energies in the upper and lower emission levels are sums of two terms:

$$E'[N'] = B_0 N' \cdot (N' + 1) - D_0 (N' \cdot (N' + 1))^2,$$

$$E''[N''] = B_1 N'' \cdot (N'' + 1) - D_1 (N'' \cdot (N'' + 1))^2.$$
where $B_{0.1}$ and $D_{0.1}$ are the N$_2^+$ ion’s rigid and non-rigid rotor constants, respectively, in the upper and lower electronic emission levels. Numerical values for these constants are given in the Supplementary Material [17]. The individual emission peaks are assumed to have the same spectral FWHMs, that are different in the cases of spontaneous and stimulated emission spectra.

Formulas (1),(2) represent Boltzmann-like probability distributions that are coherently shifted in the space of the rotational quantum number by constant values $N_B$ and $N_X$, which are different for the upper and lower emission states. These shifts are imposed by an impulsive excitation of nitrogen molecular ions by the driver pulse with the duration much shorter than the rotational period of the ions. Shifted Boltzmann distributions in the form (1),(2) have been used previously to describe velocity distributions in ensembles of particles that move, as a whole, with constant speeds (see, for example, [18]).

Needless to say, the ansatz (1),(2) is oversimplified. It is not intended to supplement rigorous analysis that has to account for the interaction of the high intensity laser pulse with the neutral nitrogen molecules [15], the directional dependence of ionization [16] for each electronic state of the ion and the subsequent interaction of the laser field with the ions in X$^2\Sigma^+_g$, A$^2\Pi_u$ and B$^2\Sigma^+_u$ states. Alternative parametrizations can be used, e.g. Boltzmann distributions with different rotational temperatures in the upper and lower emission levels.

The spectrum of the side (spontaneous) emission is representative of the rotational population distribution in the upper electronic emission level B$^2\Sigma^+_u(0)$. It is independent of the rotational distribution in the lower level X$^2\Sigma^+_g(1)$. Treating $N_B$, the overall shift of the Boltzmann rotational distribution (1) in the level B$^2\Sigma^+_u(0)$, the FWHM linewidth of the Lorentzian spectral peaks and the overall normalization constant of the spectral curve, as adjustable parameters, we achieve an excellent fit to the experimental data simultaneously for both P and R branches of the spontaneous emission spectrum. The best fit, shown in Figure 2, is obtained with $N_B$ equal to $+2.5$. In the calculation of the fit, we took into account the selection rules for the transitions between different N' and N'' states, as well as the nuclear spin multiplicity and the degeneracy with respect to the projection of the nuclear angular momentum in different rotational energy states. The relative root-mean-square deviation between the experimental data and the fit is 0.016.

After having determined the rotational distribution in the upper emission level B$^2\Sigma^+_u(0)$ and the Lorentz FWHM linewidth of the individual spectral peaks $\Delta \nu$, we fit the spectrum of stimulated emission, by varying: (i) the ratio of the total populations in the upper B$^2\Sigma^+_u(0)$ and lower X$^2\Sigma^+_g(1)$ electronic levels of N$_2^+$, summed over all rotational states within the two levels, (ii) $N_X$, the net shift of the rotational distribution (2) in the lower emission level X$^2\Sigma^+_g(1)$, (iii) the effective dimensionless gain length $l_{\text{eff}}$ and (iv) the overall normalization factor of the spectral curve. The details of the fitting procedures for both spontaneous and stimulated emission spectra are given in the Supplementary Material. We found that the ratio of the total populations in the B$^2\Sigma^+_u(0)$ and X$^2\Sigma^+_g(1)$ states is predominantly responsible for the relative strengths of the P and R branches in the stimulated emission spectrum, while the shift of the rotational distribution in the lower lasing level, $N_X$ predominantly controls the position of the maximum of the R-branch. The best fit is obtained for the case with net population inversion, with the ratio of populations in the upper and the lower lasing levels equal to 1.35. The best-fit value of the shift of the rotational population in the X$^2\Sigma^+_g(1)$ state is $N_X = -1.3$. As in the case of spontaneous emission spectrum, the agreement between the experimentally recorded stimulated emission spectrum and the fit is very good. The relative root-mean-square deviation between the experimental data and the fit is 0.030.

Note that the detected spontaneous emission with the spectrum shown in Figure 2 may have occurred on the time scale longer than the time-scale for the thermalization of the rotational population distribution in the B$^2\Sigma^+_u(0)$ state. Consequently, we could have measured an effectively lower value of the distribution shift $N_B$, in our parametrization (1), than what it was immediately after the impulsive excitation by the ultrashort driver pulse. In order to match the spectrum of stimulated emission shown in Figure 3, we had to correspondingly reduce the value of $N_X$, the distribution shift in the lower emission state, resulting in the negative value of $N_X$. Thus parametrized rotational distribution in the X$^2\Sigma^+_g(1)$ state turned out to be colder than Boltzmann room-temperature distribution, which may appear to be unphysical.

Although the experimentally measured spectra indicate that an overall electronic population inversion exists between the upper lasing level B$^2\Sigma^+_u(0)$ and the lower lasing level X$^2\Sigma^+_g(1)$, the net gain involves an additional rotational contribution, which is essential for quantitative description of the experimental data. Figure 4(A) shows the rotational population distributions in the upper and lower emission levels that have been inferred from fitting of the measured spectra. The two allowed transitions that produce strongest spontaneous emission originate from the most populated rotational state in the upper emission level B$^2\Sigma^+_u(0)$. These transitions are marked with dashed arrows terminating at the baseline (zero population), indicating that spontaneous emission empties the upper emission state entirely, independently of the population of the lower emission state. The two allowed transitions that produce strongest stimulated emission originate from a different rotational state within the B$^2\Sigma^+_u(0)$ level. The solid arrows that mark these transitions terminate not at the baseline but at the populations of the corresponding lower emission states, to indicate that stimulated emission requires population inversion.

In Figure 4(B), we show what would happen if the net
The rotational quantum number $N$ still exist on a subset of rotational transitions with large values of the $N^2$ molecular ion. The particular mechanism responsible for the generation of dissimilar rotational population distributions in the upper and lower emission levels of the $N^2$ molecular ion remains to be found. We show that gain could, in principle, exist even if the net electronic population inversion was negative, provided that rotational population distributions in the upper and lower emission levels were sufficiently dissimilar. Our results suggest the feasibility of the optimization of gain in this system through temporal shaping of the pump pulse.

In conclusion, we have reported the results of high-resolution spectroscopic studies of spontaneous and stimulated emissions in singly ionized nitrogen molecules under intense femtosecond pumping at 1,500 nm wavelength. The propagation aspect for the intense pump field was disentangled from the effects involved in the generation of stimulated emission through conducting the experiment at low pressure and using tight focusing for the pump beam. Our results point to a contribution to the gain that is due to a shift between rotational population distributions in the upper and lower emission levels of the $N^2$ molecular ion. The particular mechanism responsible for the generation of dissimilar rotational population distributions in the $B^2Σ_u^+(0)$ and $X^2Σ_u^+(1)$ states remains to be found. We show that gain could, in principle, exist even if the net electronic population inversion was negative, provided that rotational population distributions in the upper and lower emission levels were sufficiently dissimilar. Our results suggest the feasibility of the optimization of gain in this system through temporal shaping of the pump pulse.

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**References**


