Natural population inversion in a gaseous molecular filament

See Leang Chin (陈瑞良)[1], Huailiang Xu (徐淮良)[2*], Ya Cheng (程 亚)[3], Zhizhan Xu (徐至展)[3], and Kaoru Yamanouchi[4]**

[1]*Department of Physics and Center for Optics, Photonics and Laser, Laval University, Québec, G1V 0A6, Canada*

[2]*State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China*

[3]*State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China*

[4]*Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan*

[*]*Corresponding author: huailiang@jlu.edu.cn;* [**]*corresponding author: slchin@phy.ulaval.ca*

Received September 14, 2012; accepted November 16, 2012; posted online January 6, 2013

We propose a new mechanism/scheme to explain the ultrafast population inversion of molecular ions which takes place in a time scale comparable to the femtosecond laser pulse. The nonlinear pumping process including the pump photons and the self-generated harmonic photons of the pump laser would be responsible for building up population inversion to realize remote molecule lasers in femtosecond laser filaments in gases. It is shown that the remote laser emissions in molecular ions of gases may be a universal process in the femtosecond laser filament.

OCIS codes: 320.0320, 190.0190, 140.0140, 300.0300.
doi: 10.3788/COL201311.013201.

Lasing action in gaseous filaments of intense femtosecond laser pulses has attracted a lot of attention in recent years[1−6] since the first observation in air in 2003[7]. In the latter work, amplified spontaneous emission from N_2 and N_2^+ was measured. Several recent works also observed gain in N_2 and N_2^+ in air[8,9]. However, the mechanism of population inversion in N_2^+ has not been completely understood. Indeed, it is not clear why the natural population inversion is achieved between the vibrational levels of the excited $B^2\Sigma_u^+$ and the ground $X^2\Sigma_g^+$ states of the molecular ion N_2^+.

These two electronic states of N_2^+ are prepared by the excitation from the electronic ground state of neutral N_2 through multiphoton/tunnel ionization inside the filament. The first qualitative explanation of the population inversion was given by Luo *et al.*[7] as being due to the faster decay time of the ground state as compared to that of the excited state of N_2^+ through recombination with electrons. Such decay times would have been rather slow, of the order of hundreds of picosecond or nanosecond.

However, recently, using femtosecond infrared (IR) laser pulses (∼1 900 nm), 'instantaneous' pumping of population inversion between the vibrational levels of the excited $B^2\Sigma_u^+$ and ground $X^2\Sigma_g^+$ states of N_2^+ was observed[8]. The tentative explanation in that paper was the following. The excited state of N_2^+ was formed due to the removal of the inner valence electron while the ground state ion came from the ejection of an electron from the highest occupies molecular orbital. In Ref. [8], the authors argued that the two electrons being different, the excited state resulting from the removal of the inner valence electron was considered a distinct channel. Hence, this excited state created by the removal of an inner valence electron would immediately be in a state of population inversion.

Unfortunately, these two channels have to be considered as a whole in the gain medium and the two electrons in the electronic configurations of the ground state neutral molecule are indistinguishable when they are ionized. Thus, one could not distinguish the two pathways and hence could not explain the instantaneous population inversion. Although in that paper the authors also discussed the effect of single-photon absorption of the fifth harmonics by N_2^+ ion from its ground state to the excited state resulting in population inversion, a clear physical picture is still lacking.

In this letter, we propose a new mechanism to explain the instantaneous population inversion in N_2^+ inside a filament of a femtosecond laser pulse. This mechanism, in principle, is universal in many molecules that could satisfy the conditions similar to N_2. The whole idea is based upon the high (clamped) intensity inside a filament. We shall look at the N_2 molecule in air first.

During filamentation of a Ti-sapphire laser pulse with the wavelength around 800 nm, the clamped intensity is reached when the self-focusing action is balanced by the defocusing action of the self-induced plasma. The latter is created through multiphoton/tunnel ionization of the air molecules. In particular, nitrogen molecules are ionized into the states including the ionic ground $X^2\Sigma_g^+$ and excited $B^2\Sigma_u^+$ states. According to Becker's calculation[10] of the transition between the excited and ground states of the N_2^+ ion, $B^2\Sigma_u^+(v') \rightarrow X^2\Sigma_g^+(v)$ for $B(v' = 1, 2, 3, \cdots) \rightarrow X(v = 2, 3, 4, \cdots)$ (cf: table 1, ref. 10), the transitions from higher vibrational states $(v' > 1) \rightarrow (v > 2)$ seems to be slightly inverted, but not $(0 \rightarrow 0)$ or $(0 \rightarrow 1)$. However, the $(v' > 1) \rightarrow (v > 2)$

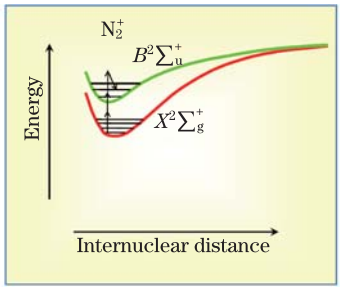

Fig. 1. Schematic diagram of a typical nonlinear process for the population inversion of N_2^+.

transitions are weak lines. Experimentally, the strongest lines are from the $(0 \rightarrow 0)$ and $(0 \rightarrow 1)$ transitions and they exhibit gain[3,7,8]; i.e. population inversion.

We note that the clamped intensity is relatively high, of the order of 5×10^{13} W/cm^2, being able to induce the absorption of about 10 photons for the inner valence electron ionization of N_2. Thus, inside the filament, any other nonlinear physical process requiring fewer photons (less than or equal to 10) could directly or indirectly pump the ground state ion into the excited state with high efficiency instantaneously because of the high intensity. This is what could have happened for N_2. For example, an additional channel of 3 photon-absorption from the ground $X^2\Sigma_g^+$ state to the excited $B^2\Sigma_u^+$ state in the (clamped) intense laser field would probably be one of those lower order processes, pumping the electrons from the ground to the excited state giving rise to gain. This sequential 3-photon transition always exists and would be very strong because the clamped intensity is relatively high. Thus, any ground state ion created by the pump from the ground neutral state would be immediately excited to the excited ionic state through sequential 3-photon absorption resulting in an inversion. Another possible lower order process is a four-photon process, which could pump most of the ground state population into the higher vibrational levels of the excited state instantaneously (Fig. 1). The consequence is the observation of gain in the emission $B^2\Sigma_u^+(v') \rightarrow X^2\Sigma_g^+(v)$[7−9]. This type of nonlinear pumping with intense broad bandwidth (femtosecond) pulses should be universal and applicable to other molecules in a similar situation.

In the case of using femtosecond IR pulses with the central wavelength $\lambda \approx 1\,900$ nm, third and fifth harmonics might also contribute to pumping the ground state of N_2^+ into the excited state. At this longer wavelength, the clamped intensity is of the order of 10^{14} W/cm^2 in air[8] higher than that using 800-nm pulses. This is a situation in which the lower order nonlinear process (third harmonic generation (THG) and fifth harmonic generation (FHG)) takes place with high efficiency because of the high intensity inside the filament. Therefore, these harmonics could immediately (instantaneously) pump the ground state ion into the excited states. Simultaneously, a multiphoton (about 6) absorption (pumping) with high efficiency could also have taken place similar to what is shown in Fig. 1. Therefore, it is not surprising that there is population inversion as reported in Ref. [8].

These nonlinear processes are sensitive to the intensity of the laser pulse in the interaction zone. In order to examine the effect of the intensity, we measured in the forward direction in air the spectrum of nitrogen emissions and the fifth harmonics of a 1 900-nm, 200-fs laser pulse, as shown in Fig. 2. The mid-infrared (MIR) laser pulses was generated from an optical parametric amplifier (HE-TOPAS, Light Conversion, Inc.) pumped by a commercial Ti:Sapphire laser system (Legend Elite-Duo, Coherent, Inc.). The laser beam was focused into air directly by a lens of 36 mm, and a grating spectrometer (Shamrock 303i, Andor) with a 1 200 grooves/mm grating was used to record the spectra. For details of this experimental setup, the readers are referred to Ref. [8]. It can be seen that the amplification of the fifth harmonic at 391 nm does not start when the input energy of the laser pulse is lower (18 and 23 μJ) even if the seeding fifth harmonic is already there. It should be pointed out that the calculated intensity is 3.4×10^{13} W/cm^2 for the value of 30 μJ if we assume that the pulse is focused into vacuum; however, it has not reached the filamentation clamped intensity yet. Therefore, the intensity in the interaction zone becomes stronger as the energy increases from 18 to 30 μJ. Instead of observing the amplification, absorption can be observed when the laser power is 18 and 23 μJ (see the solid arrows shown in Fig. 2), which gives a clear evidence of no population inversion in these two situations. But when the laser energy is 30 μJ, a strong narrow band emission at 391 nm appears in the forward direction of the filament (see the dash arrow shown in Fig. 2), showing the strong dependence of the amplification on the laser intensity.

The fundamental reason why the excited ionic state of N_2^+ could be pumped from the neutral ground state resulting in a population inversion is because the ionization potentials of the outer and inner valence electrons are energetically close to each other[10]. Thus, molecules possessing an excited ionic state not far from the ground state could be ionized in a similar way as N_2. An example is the CO_2 molecule. Indeed, gain was observed when filamentation was induced in a CO_2 gas using IR femtosecond pulses around $\lambda \approx 1\,285$ nm[11]. The population inversion between the excited and ground states of CO_2^+ could have been prepared in a similar way as that described in the case of N_2. Since the excited state of CO_2^+ is energetically not far from the ground state, it could be pumped by the strong field inside the filament directly. In this case, several scenarios of lower order pumping (compared to ionization) could occur. First of all, because of the high intensity inside the filament, efficient

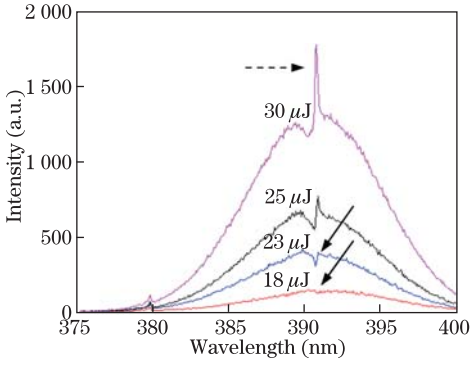

Fig. 2. Spectra obtained in the forward direction of the laser beam by the excitation of femtosecond laser pulses with different laser energies.

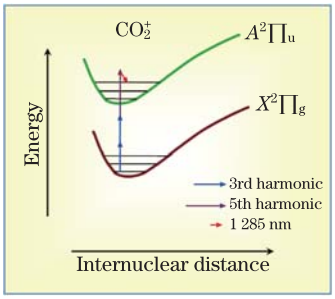

Fig. 3. Schematic diagram of a four-wave type pumping process for the population inversion of CO_2^+.

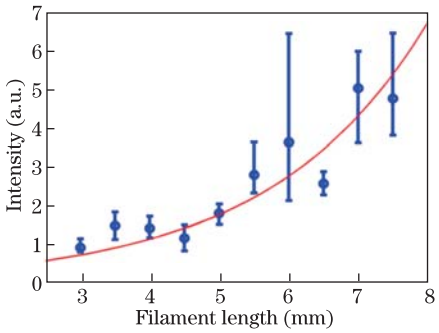

Fig. 4. 337-nm signal intensity measured in the forward direction as a function of filament length in CO_2 gas (circle dot). The signal is obtained by integrating the spectral flux over a narrow window from 336 to 337.5 nm. The exponential fit (solid line) gives a gain coefficient of 4.4 cm^{-1}.

third harmonic generation (THG) and fifth harmonic generation (FHG) were generated and measured. These harmonics as well as the fundamental could have contributed to pumping the ground ionic state into the excited state in many wave mixing scenarios. For example, a four-wave type pumping (Fig. 3) could include one photon of the fifth harmonic, two photons of the third harmonic, and one photon of the fundamental laser pulse. The consequence is again the manifestation of gain along the filament direction as shown in Fig. 4.

In conclusion, any small molecule possessing excited ionic states which are energetically not far from the ionic ground state could be pumped inside a femtosecond laser filament into a population-inverted system so long as this molecule is not yet fragmented.

This work was supported by the financial supports from NSERC, Canada Research Chairs, CIPI, CFI, FQRNT, the National Natural Science Foundation of China (Nos. 11074098, 11134010, 60825406, and 10974213), NCET-09-0429, the fundamental research funds of Jilin University, and two grants from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan; the Grant-in-Aid for Specially Promoted Research on Ultrafast Hydrogen Migration (No. 19002006), and the Grant-in-Aid for Global COE Program for Chemistry Innovation.

References

1. A. Dogariu, J.B. Michael, M. O. Scully, and R. B. Miles, Science **331,** 442 (2011).
2. V. Kocharovsky, S. Cameron, K. Lehmann, R. Lucht, R. Miles, Y. Rostovtsev, W. Warren, G. R. Welch, and M. O. Scully, Proc. Natl. Acad. Sci. **102,** 7806 (2005).
3. M. N. Shneider, A. Baltuska, and A. M. Zheltikov, J. Appl. Phys. **110,** 083112 (2011).
4. P. R. Hemmer, R. B. Miles, P. Polynkin, T. Siebert, A. V. Sokolov, P. Sprangle, and M. O. Scully, Proc. Natl. Acad. Sci. **108,** 3130 (2011).
5. J. Penano, P. Sprangle, B. Hafizi, D. Gordon, R. Fernsler, and M. Scully, J. Appl. Phys. **111,** 033105 (2012).
6. L. Q. Yuan, K. E. Dorfman, A. M. Zheltikov, and M. O. Scully, Opt. Lett. **37,** 987 (2012).
7. Q. Luo, W. Liu, and S. L. Chin, Appl. Phys. B **76,** 337 (2003).
8. J. Yao, B. Zeng, H. L. Xu, G. Li, W. Chu, J. Ni, H. Zhang, S. L. Chin, Y. Cheng, and Z. Z. Xu, Phys. Rev. A **84,** 051802(R) (2011).
9. D. Kartashov, S. Ališauskas, A. Pugzlys, A. Baltuška, M. Shneider, and A. Zheltikov, Research in Optical Sciences, OSA Technical Digest, HW3C.2 (2012).
10. A. Becker, A. D. Bandrauk, and S. L. Chin, Chem. Phys. Lett. **343,** 345 (2001).
11. W. Chu, B. Zeng, J. Yao, H. L. Xu, J. Ni, G. Li, H. Zhang, F. He, C. Jing, Y. Cheng, and Z. Z. Xu, EPL **97,** 64004 (2012).