

Supplementary Material for

Enhanced Coherent Emission from Ionized Nitrogen Molecules by Femtosecond Laser Pulses

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1. Experimental method

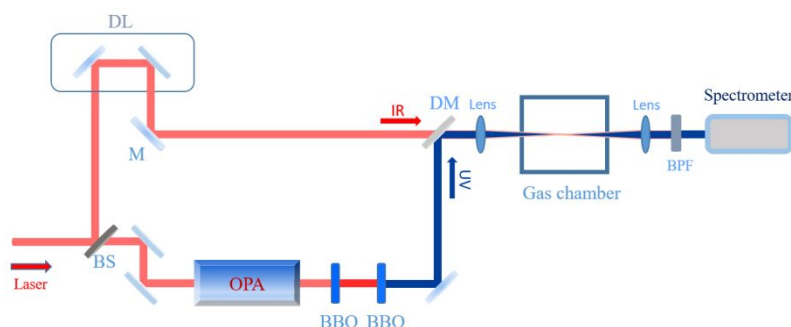


Figure S1: Experimental setup. DL: delay line; BBO: β -barium borate crystal; BPF: Band-pass filter; DM: dichroic mirror; BS: beam splitter; M: reflective mirror; Lens: 300-mm fused silica lenses.

Figure S1 shows the experimental setup. The experiments were carried out using a commercial Ti:sapphire laser amplifier, which delivers linearly polarized femtosecond laser pulses with a central wavelength of 800 nm, pulse duration of 35 fs, and pulse energy of 6 mJ. The 800-nm laser beam was split into three beams by two beam splitters. The first 800-nm laser beam with a single pulse energy of about 2 mJ was utilized as a pump laser to ionize neutral nitrogen molecules. The second 800-nm laser beam with a single pulse energy of about 3 mJ was introduced into an optical parametric amplifier system to generate a tunable mid-infrared laser source. Its fourth harmonics was generated by two BBO crystals and utilized as an external seed. The third weak 800-nm laser beam was utilized to generate the sum frequency signal with the enhanced coherent emission from ionized nitrogen molecules in a BBO crystal. In

the experiment, the pump laser and the seed were recombined collinearly by a dichroic mirror with high reflectivity around 320–470 nm and high transmission around 680–900 nm. Then they were focused by an $f = 300$ mm convex lens into a gas chamber filled with pure nitrogen gas. After filtering the 800-nm pump laser by another pair of dichroic mirrors, the forward emission was focused into a fiber spectrometer. The intensity of the forward emission from ionized nitrogen molecules was measured as a function of the time delay between the 800-nm pump laser and the external seed. Figure S2 shows the experimental setup for measuring the temporal profile of the enhanced coherent emission from ionized nitrogen molecules, which was obtained by combining the enhance coherent emission with the third 800-nm laser beam to measure their sum frequency signal.

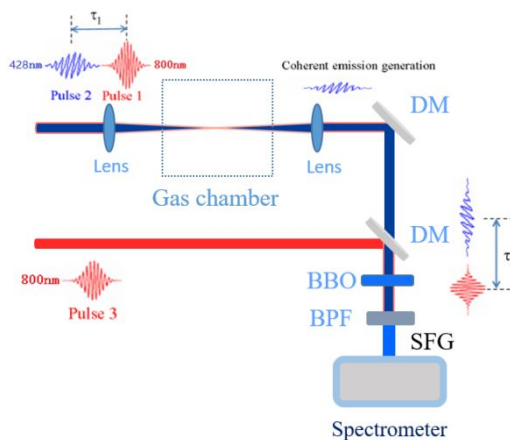


Figure S2: Experimental setup for measuring the sum frequency signal. BBO: β -barium borate crystal; BPF: Band-pass filter; DM: dichroic mirror; Lens: 300-mm fused silica lenses.

2. Population distribution determined by genetic algorithm

Throughout this supplement and the paper we will use the prime symbol ' to mark quantities associated with the upper emission states and the blank symbol to mark quantities associated with the lower emission states. The enhanced emission around 391 nm and 428 nm are composed of rotational lines of N_2^+ , which can be assigned to the transition of $B^2\Sigma_u^+ (v'=0, J') \rightarrow X^2\Sigma_g^+ (v=0, J)$ and $B^2\Sigma_u^+ (v'=0, J') \rightarrow X^2\Sigma_g^+ (v=1, J)$. The intensity of the emission line is related with the population of corresponding quantum states. In the present manuscript, three vibrational states of N_2^+ are involved. They are $X^2\Sigma_g^+ (v=0)$, $X^2\Sigma_g^+ (v=1)$, and $B^2\Sigma_u^+ (v'=0)$. It is known that the total energy of N_2^+ in unit of cm^{-1} can be expressed as:

$$E[v, J] = \omega_e \left(v + \frac{1}{2} \right) - X_e \omega_e \left(v + \frac{1}{2} \right)^2 + Y_e \omega_e \left(v + \frac{1}{2} \right)^3 + Z_e \omega_e \left(v + \frac{1}{2} \right)^4 + B_v J(J+1) - D_e J^2(J+1)^2 + T_e, \quad (1a)$$

$$T_e = T_0 - \frac{\omega_e}{2} + \frac{X_e \omega_e}{4} - \frac{Y_e \omega_e}{8} - \frac{Z_e \omega_e}{16} - \frac{\alpha_e \omega_e}{32}, \quad (1b)$$

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) + \gamma_e \left(v + \frac{1}{2} \right)^2 + \delta_e \left(v + \frac{1}{2} \right)^3 + \epsilon_e \left(v + \frac{1}{2} \right)^4. \quad (1c)$$

The rotational and vibrational constants can be obtained from the literature [1]. Here we assume that Boltzmann distribution is satisfied for each vibrational state, thus the relative rotational population can be described by rotational temperature [2]. Considering the fine structure of electron spin degeneracy and the multiplicities of the nuclear-spin states within the hyperfine structure of the energy spectrum, the total populations of three states, summed over all degenerate states within those states, are:

$$F^{x0}[J^{x0}] = 2g_{J^{x0}}(2J^{x0} + 1)f^{x0}[J^{x0}] \propto 2g_{J^{x0}}(2J^{x0} + 1)\exp\left(-\frac{E^{x0}[J^{x0}]}{K_b * T1}\right) \quad (2a)$$

$$F^{x1}[J^{x1}] = 2g_{J^{x1}}(2J^{x1} + 1)f^{x1}[J^{x1}] \propto 2g_{J^{x1}}(2J^{x1} + 1)\exp\left(-\frac{E^{x1}[J^{x1}]}{K_b * T2}\right) \quad (2b)$$

$$F^{b0}[J^{b0}] = 2g_{J^{b0}}(2J^{b0} + 1)f^{b0}[J^{b0}] \propto 2g_{J^{b0}}(2J^{b0} + 1)\exp\left(-\frac{E^{b0}[J^{b0}]}{K_b * T3}\right) \quad (2c)$$

Square brackets will be used for arguments of functions, while round brackets will be reserved for the designation of vibrational quantum numbers and for regular algebra. T1, T2 and T3 represent the rotational temperature of $X^2\Sigma_g^+$ ($v=0$), $X^2\Sigma_g^+$ ($v=1$) and $B^2\Sigma_u^+$ ($v'=0$), respectively. J^{x0} , J^{x1} and J^{b0} represent the rotational quantum number of $X^2\Sigma_g^+$ ($v=0$), $X^2\Sigma_g^+$ ($v=1$) and $B^2\Sigma_u^+$ ($v'=0$), respectively. $g_{J^{x0}}$, $g_{J^{x1}}$ and $g_{J^{b0}}$ represent the nuclear spin weight of $X^2\Sigma_g^+$ ($v=0$), $X^2\Sigma_g^+$ ($v=1$) and $B^2\Sigma_u^+$ ($v'=0$), respectively. For even J^{x0} (odd J^{x0}), even J^{x1} (odd J^{x1}) and even J^{b0} (odd J^{b0}), we can get that $g_{J^{x0}} = 6$ (3), $g_{J^{x1}} = 6$ (3) and $g_{J^{b0}} = 3$ (6). The total populations of $X^2\Sigma_g^+$ ($v=0$), $X^2\Sigma_g^+$ ($v=1$) and $B^2\Sigma_u^+$ ($v'=0$) are:

$$P_{X0} = \sum_{J=0}^{\infty} F^{x0}[J^{x0}] \quad (3a)$$

$$P_{X1} = \sum_{J=0}^{\infty} F^{x1}[J^{x1}] \quad (3b)$$

$$P_{B0} = \sum_{J'=0}^{\infty} F^{b0}[J^{b0}] \quad (3c)$$

In the case of enhanced emission, assumed to be not saturated by the signal, amplitudes of individual spectral lines are given by:

$$I_{P,R}^{(stim)}[J] = I_0 e^{\alpha_{P,R}[J]l_{eff}} \quad (4)$$

where the seed signal I_0 is assumed to be spectrally much broader than the entire spectral interval covering both P- branch and R-branch emissions that we study. l_{eff} is the effective interaction length, assumed to be the same for all spectral lines. The gain constants $\alpha_{P,R}[J]$ depend on the rotational population distributions in both upper and lower emission manifolds [2]:

For R-branch ($J = J' - 1$)

$$\alpha_R[J] \propto (J+1)g_J(f'[J+1] - f[J]) \propto \frac{J+1}{2J+3}(F'[J+1] - \frac{2J+3}{2J+1}F[J]) \quad (5)$$

The following is about the calculation of genetic algorithm.

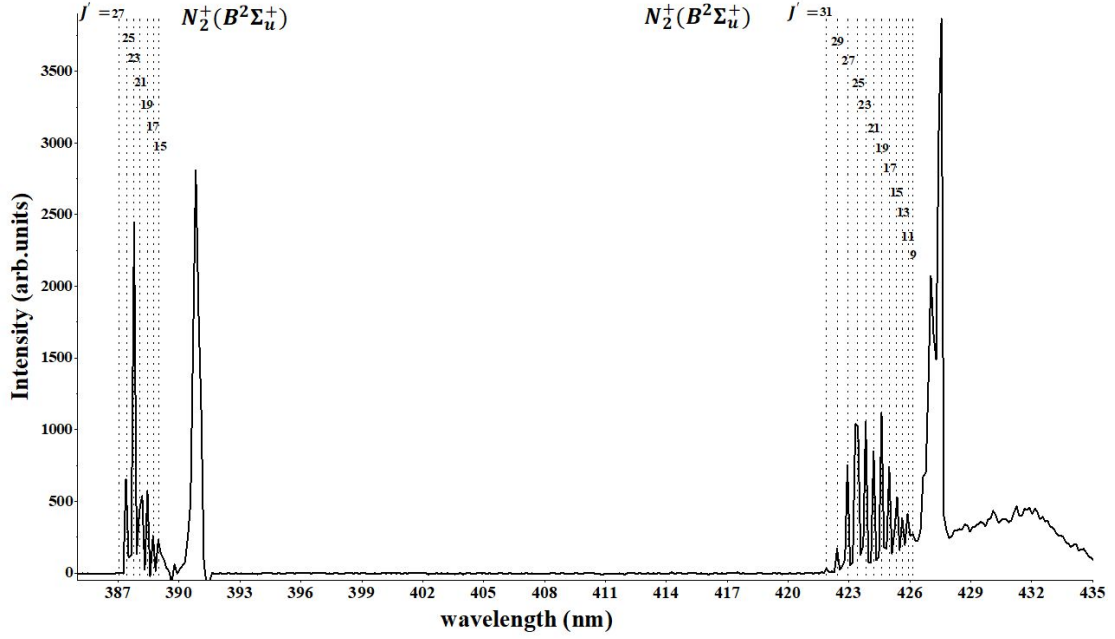


Figure S3: Forward emission spectrum in the presence of an external 428-nm seed with optimized time delay. The signal intensity around 391 nm is magnified by 10 for visual convenience.

There are five variables involved. Here, b_2 and b_3 represent the vibrational population of $X^2\Sigma_g^+(v=1)$ and $B^2\Sigma_u^+(v'=0)$ relative to that of $X^2\Sigma_g^+(v=0)$. T_1 , T_2 and T_3 represent the rotational temperature of $X^2\Sigma_g^+(v=0)$, $X^2\Sigma_g^+(v=1)$ and $B^2\Sigma_u^+(v'=0)$, respectively. The scope of the variable is limited as follows: $300K \leq T_1 \leq 1000K$, $300K \leq T_2 \leq 1000K$, $300K \leq T_3 \leq 3000K$, $0 \leq b_2 \leq 2$, $0 \leq b_3 \leq 2$.

The first step of the genetic algorithm is initialization. This step is to get the system to generate a bunch of individuals that satisfy the conditions. In the case of initial rotational temperatures T_1 , T_2 and T_3 , we can get two ratios from all the previous formulas: the ratio of the total populations of the $X^2\Sigma_g^+(v=1)$ to the total populations of the $X^2\Sigma_g^+(v=0)$ is bb_2 and the ratio of the total populations of the $B^2\Sigma_u^+(v'=0)$ to the total populations of the $X^2\Sigma_g^+(v=0)$ is bb_3 . If you multiply the population distribution of the $X^2\Sigma_g^+(v=1)$ by b_2/bb_2 , you get a new population distribution of the $X^2\Sigma_g^+(v=1)$. If you multiply the population distribution of the $B^2\Sigma_u^+(v'=0)$ by b_3/bb_3 , you get a new population distribution of the $B^2\Sigma_u^+(v'=0)$. By doing this, the total populations of three energy manifolds satisfy initial conditions: b_2 is the ratio of the total populations of the $X^2\Sigma_g^+(v=1)$ to the total populations of the $X^2\Sigma_g^+(v=0)$. b_3 is the ratio of the total populations of the $B^2\Sigma_u^+(v'=0)$ to the total populations of the $X^2\Sigma_g^+(v=0)$. You can see that formulas (2a) and (2b) and (2c) use direct proportions instead of equals. Our first step is to determine the appropriate proportionality coefficients, which are b_2/bb_2 and b_3/bb_3 here.

The second step of the genetic algorithm is to set the fitness function. It mainly includes the following five parts: k_1 , k_2 , k_3 , k_4 and k_5 . The greater the fitness function value, the lower the individual's survival ability, and the easier it is to be eliminated. According to the formula (4) and the 428-nm and 391-nm fast Fourier transform spectrum and forward emission spectrum, if a rotational modulated signal can be observed by the spectrometer under different delay conditions, which indicates that the exponential part of the enhanced radiation expression of the corresponding rotational

state is greater than or equal to zero. If the exponential part is less than zero, the signal will decay exponentially as the transmission distance increases and will not be detected by the spectrometer. According to the formula (2a), formula (2b) and formula (5), we can get the 428-nm gain constant $\alpha_{R,428nm}$. According to the formula (2a), formula (2c) and formula (5), we can get the 391-nm gain constant $\alpha_{R,391nm}$.

With the 428-nm data information provided in Figure 4 and Figure S3, we can do the following. When J value changes from 6 to 30, calculate the value of $\alpha_{R,428nm}[J]$. If $\alpha_{R,428nm}[J]$ is less than zero, then let $k1$ be assigned a very large value. Instead, let $k1=0$. When J value changes from 1 to 60, calculate the value of $\alpha_{R,428nm}[J]$. And also calculate to get a J_{max} where $\alpha_{R,428nm}[J_{max}]$ gets its maximum. Considering that $J=6$ is the boundary of the 428-nm spectrum, we calculate an initial boundary $J2$ where $\alpha_{R,428nm}[J]$ is positive. We use $k2$ to measure the difference between $J2$ and 6. With the 391-nm data information provided in Figure 4 and Figure S3, we can do the following. When J value changes from 14 to 26, calculate the value of $\alpha_{R,391nm}[J]$. If $\alpha_{R,391nm}[J]$ is less than zero, then let $k3$ be assigned a very large value. Instead, let $k3=0$. When J value changes from 1 to 60, calculate the value of $\alpha_{R,391nm}[J]$. Considering that $J=14$ is the boundary of the 391-nm spectrum, we calculate an initial boundary $J3$ where $\alpha_{R,391nm}[J]$ is positive. We use $k4$ to measure the difference between $J3$ and 14.

Considering that 391-nm signal is converted from 428-nm signal through vibrational Raman process, the converted 391-nm signal is also the strongest when the 428-nm signal is the strongest. In the spectrum of 391 nm, the rotational modulation signal with the rotational quantum number 22 is the strongest. So we use $k5$ to measure the difference between J_{max} and 22.

We use Roulette Wheel Selection method to select fit chromosomes from our population which can mate and create their off-springs. Here we select a random crossover point and the tails of both the chromosomes are swapped to produce a new off-springs. We set the mutation probability of the population to 0.5 for a quick global search. A thousand generations later, then we can reach our best possible solution. The genetic algorithm results will fluctuate somewhat, but the general results are as follows: $T1=310K$, $T2=345K$, $T3=2654K$, $b2=0.25$, $b3=1.6$.

Finally, the model is further verified. Considering that the fluorescence spectrum can reflect the information of the upper state, at the same time we assume that the rotational population distributions in the upper state $B^2\Sigma_u^+$ ($v'=0$) satisfy the Maxwell Boltzmann distribution.

$$\text{Population} \propto (2J + 1) \exp\left(-\frac{E_J}{K_b T}\right) \propto (2J + 1) \exp\left(-\frac{BhcJ(J+1)}{K_b T}\right) \quad (6)$$

When formula (6) reaches the maximum value, the expression of the rotational quantum number J_{peak} is

$$J_{peak} = \sqrt{\frac{K_b T}{2hcB}} - 1/2 \quad (7)$$

According to the results of recent fluorescence experiment [3], the rotation temperature T can be deduced by using the obtained J_{peak} .

$$T = \frac{\left(J_{peak} + \frac{1}{2}\right)^2 * 2 * B * h * c}{K_b} \approx 2700K \quad (8)$$

This value is close to T3 predicted by our model calculation. Meanwhile, according to the LIF experiment in literature [4], the ratio of total populations between $X^2\Sigma_g^+$ ($v=1$) and $X^2\Sigma_g^+$ ($v=0$) is about 0.27, which is in good agreement with $b_2=0.25$. These agreements indicate the reliability of our calculation.

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