Remote creation of coherent emissions in air with two-color ultrafast laser pulses

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Abstract. We experimentally demonstrate the generation of narrow-bandwidth emissions with excellent coherent properties at ~391 and ~428 nm from N₂⁺ (B²Σ_u⁺(v' = 0) → X²Σ_g⁺(v = 0, 1)) inside a femtosecond filament in air by an orthogonally polarized two-color driver field (i.e. 800 nm laser pulse and its second harmonic). The durations of the coherent emissions at 391 and 428 nm are measured to be ~2.4 and ~7.8 ps, respectively, both of which are much longer than the duration of the pump and its second harmonic pulses. Furthermore,
the measured temporal decay characteristics of the excited molecular systems suggest an ‘instantaneous’ population inversion mechanism that may be achieved in molecular nitrogen ions at an ultrafast time scale comparable to the 800 nm pump pulse.

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1. Introduction

In recent years, lasing actions created remotely in air have attracted increasing interest due to their promising applications in remote detection of multiple pollutants based on nonlinear spectroscopy [1–10]. Early experiments demonstrated remote amplified spontaneous emission (ASE)-based lasers, which have enabled operation either at ~391 and 337 nm using molecular nitrogen [3–5] or at ~845 nm using molecular oxygen [6] as the gain medium. The generation of population inversion was ascribed to the recombination of free electrons with molecular nitrogen ions (N$_2^+$) [3–5] and resonant two-photon excitation of atomic oxygen fragments [6]. For the backward 845 nm ASE from atomic oxygen and the 337 nm ASE laser from neutral molecular nitrogen, the population inversion mechanisms are well understood [3–5, 11]. However, the mechanism responsible for the 391 nm ASE from N$_2^+$ is not totally clear; that is, the question of how the population inversion in the ASE of the 391 nm is established is still open [4].

Remarkably, a series of recent experiments showed that coherent multi-wavelength emissions with perfectly linear polarization (i.e. different from the random polarization of ASE) could be realized in nitrogen (N$_2^+$) and carbon dioxide (CO$_2^+$) gases using a wavelength-tunable optical parametric amplifier (OPA) laser system with wavelengths in the range of 1.2–2.4 μm, which can produce the third and fifth harmonics in air with spectral ranges overlapping the fluorescence lines of N$_2^+$ and CO$_2^+$ [7–9]. These emissions in N$_2^+$ (330, 357, 391, 428, 471 nm) and CO$_2^+$ (315, 326, 337, 351 nm) are found to be generated in an unexpected femtosecond time scale comparable to that of the pump lasers, indicating that population inversion in N$_2^+$ and CO$_2^+$ could have been achieved only with intense ultrafast driver pulses. This observation challenges the previous conjecture on the population inversion mechanism based on the recombination of free electrons with the molecular ions because such a process occurs on a time scale of a few nanoseconds [6]. To shed more light on the mechanisms underlying the ultrafast population inversion as well as on the coherent emissions themselves, which are both now under hot debate, temporal characterizations of these phenomena based on the concept of pump–probe measurement are important.

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The fact that the ultrafast coherent emissions observed in previous experiments employing mid-infrared driver pulses always show a linear polarization parallel to that of the harmonic or supercontinuum indicates that a seeding effect may exist [7–9]. However, with the mid-infrared pump pulses, it is difficult to separate the self-generated harmonics or supercontinua from the driver pulses, making it difficult to vary the delay between the driver pulses and the seeding pulses. In this paper, we will address this problem by remote generation of coherent emissions in air with an orthogonally polarized two-color laser field. In this new scheme, the driver pulses are provided by a 40 fs, 800 nm laser amplifier, whereas the 400 nm seed pulses are externally produced by a second harmonic generation process with a nonlinear crystal.

2. Experimental setup

The pump–probe experiment scheme is illustrated in figure 1. A commercial Ti:sapphire laser system (Legend Elite-Duo, Coherent, Inc.), operated at a repetition rate of 1 kHz, provides ~40 fs (full-width at half-maximum (FWHM) intensity profile) Fourier-transform-limited laser pulses with a central wavelength at ~800 nm and a single pulse energy of ~6 mJ. The laser
beam is first split into two arms using a 1 : 1 beam splitter with a variable delay: one is used as the pump beam (Pulse 1) and the other will pass through a 0.2 mm-thickness BBO crystal to produce the second harmonic probe pulse at 400 nm wavelength (Pulse 2) whose polarization is perpendicular to that of the pump pulses. The pump pulses have a pulse energy of \( \sim 1.9 \text{ mJ} \) and a diameter of \( \sim 11 \text{ mm} \), whereas the probe pulses have a pulse energy of \( \sim 3 \mu \text{J} \) and a diameter of \( \sim 6 \text{ mm} \), which are much weaker than the pump pulses. We have confirmed that the narrow-bandwidth emissions at 391 and 428 nm cannot be generated with the probe pulses alone. The pump and probe pulses are combined using a dichroic mirror (DM) with high reflectivity at 400 nm and high transmission at 800 nm and then are collinearly focused by an \( f = 40 \text{ cm} \) lens into a chamber filled with 180 mbar of nitrogen gas to generate a \( \sim 1 \text{ cm-long} \) filament and coherent emission. A small portion of the 800 nm beam split from the output beam of the laser system with an energy of 440 \( \mu \text{J} \) (indicated as Pulse 3 in figure 1) is used for performing a cross-correlation measurement of the coherent emissions generated from the gas chamber. After passing through the gas cell, the 400 nm probe pulses containing coherent emissions are combined with Pulse 3 by another DM and then are launched into a 2 mm-thick BBO crystal. The sum frequency generation (SFG) signal of the 800 nm and the coherent emission is produced and recorded by a grating spectrometer (Shamrock 303i, Andor) with a 1200 grooves mm\(^{-1}\) grating. The time-resolved SFG signal provides temporal information on the coherent emissions generated in \( \text{N}_2 \).

3. Experimental results

3.1. Coherent emissions driven by a two-color laser field

Figures 2(a) and (b) show two typical spectra measured in the forward propagation direction with the narrow-bandwidth emissions generated, respectively, at the wavelengths of \( \sim 391 \) and \( \sim 428 \text{ nm} \) in \( \text{N}_2 \). The emissions at the \( \sim 391 \) and \( \sim 428 \text{ nm} \) correspond, respectively, to the transitions \((0, 0)\) and \((0, 1)\) between the vibrational levels of the excited state \( \Sigma^+_u \) and ground state \( \Sigma^+_g \) of \( \text{N}_2 \), as indicated by the inset of figure 1. In these two measurements, the BBO crystal for generating the second harmonic 400 nm laser light was finely tuned to optimize the \( \sim 391 \) or \( \sim 428 \text{ nm} \) emissions, and the temporal and spatial overlap between the 800 and 400 nm pulses are optimized by maximizing the intensities of the coherent emissions. It is also confirmed that when either the 800 nm pump beam or the 400 nm probe beam is blocked, the line emissions will disappear, indicating that both the pump and probe pulses are important for their creation. Furthermore, by placing a Glan–Taylor polarizer in front of the spectrometer, we examine the polarization of the line emissions at the \( \sim 391 \) and \( \sim 428 \text{ nm} \) wavelengths. As indicated in the insets of figures 2(a) and (b), when the transmitted polarization direction is parallel to that of the 400 nm pulse, which is defined as \( 0^\circ \), both the \( \sim 391 \) and \( \sim 428 \text{ nm} \) emissions are the strongest. In contrast, when the polarizer is rotated by \( \pm 90^\circ \), the emissions become too weak to be detected. The polarization contrast of coherent emissions at both \( \sim 391 \) and \( \sim 428 \text{ nm} \) is measured to be \( \sim 10^3 \). Therefore, the line emissions at \( \sim 391 \) and \( \sim 428 \text{ nm} \) are confirmed to have a nearly perfect linear polarization parallel to that of the second harmonic probe pulses. This important fact indicates that the weak second harmonic pulses play a role as a seed to activate the coherent emissions. Furthermore, we fitted the experimental curves with theoretical ones calculated using the Malus law, as shown in the insets of figures 2(a) and (b). The deviation between experimental and theoretical results is mainly due to the intensity

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Figure 2. Typical forward emission spectra with the coherent emission at (a) ∼391 nm and (b) ∼428 nm. Polarization property of coherent emissions at ∼391 nm (inset in (a)) and ∼428 nm (right-hand side inset in (b)). The left-hand side inset in (b): the original spectrum of the 400 nm probe pulses.

fluctuation of the measured signals. Specifically, the original spectrum of the 400 nm probe pulses is shown in the left-hand side inset of figure 2(b). Although the spectral intensities at both ∼391 and ∼428 nm are very low for the probe pulses, the weak signals are necessary for the creation of the laser-like coherent emissions in figures 2(a) and (b). Once the probe pulses are blocked, we observe that the coherent emissions at both ∼391 and ∼428 nm disappear.

3.2. The dependence of coherent emissions on the time delay

To gain a deeper insight, we investigate the intensities of the coherent emissions at both ∼391 and ∼428 nm as functions of the time delay between the pump and the probe pulses ($\tau_1$), as shown in figures 3(a) and (b), respectively. Here, the zero time delay is indicated by the green arrows in both figures 3(a) and (b) and the positive delay means that the second harmonic 400 nm probe pulse is behind the fundamental 800 nm pump pulse. As shown in figure 3(a), the emission at ∼391 nm first increases rapidly on the time scale of ∼400 fs (see the inset of figure 3(a)), which reflects the long pulse duration of the second harmonic (∼700 fs, see later), and then shows a slow exponential decay with a decay constant $\tau \approx 46.2$ ps, as indicated by the red dashed line. It is noteworthy that when the time delay is above ∼1 ps, the pump
Figure 3. The coherent emission at (a) ∼391 nm and (b) ∼428 nm as a function of time delay of the 800 nm pump and the 400 nm probe pulses. The zero delay is indicated by green arrows. Inset in (a): a higher-resolution picture in the range from −1 to 13 ps.

pulses at 800 nm and the second harmonic probe pulses are essentially temporally separated, because the pulse durations of both the pump and probe pulses are significantly shorter than ∼1 ps. However, even when the pump and probe pulses are temporally separated, the line emission at ∼391 nm can still be generated with perfectly linear polarization parallel to the 400 nm probe light. Not surprisingly, like most strong field molecular phenomena which are sensitive to molecular alignment and revival, we observe in this pump–probe experiment the modulation of the line emission at the times $1/2 T_{\text{rot}}$, $T_{\text{rot}}$ and $3/2 T_{\text{rot}}$ ($T_{\text{rot}}$ is the revival period of nitrogen molecules) [12, 13] as indicated in the inset of figure 3(a). The mechanism behind this might be due to the modulation of the intensity of the probe pulses owing to the periodic focusing and defocusing in the filament due to the dynamic change of the alignment degree of the N$_2$ molecules [14, 15]. Figure 3(b) shows a similar decay behavior of the line emission at ∼428 nm, but with a much shorter decay time of ∼2 ps.

3.3. Temporal structures of coherent emissions

Lastly, by introducing the third laser beam at 800 nm (Pulse 3), a cross-correlation measurement is carried out to obtain the temporal information on the coherent line emissions at both ∼391
Figure 4. Frequency- and time-resolved SFG signals of (a) 800 nm and the 400 nm probe pulse, (b) 800 nm and the coherent emission at $\sim 391$ nm and (c) 800 nm and the coherent emission at $\sim 428$ nm. (d) Time-resolved SFG signals distributed on black dashed lines in figures (a)–(c). (e) Schematic diagram of the pumping mechanism for generating population inversion.

and $\sim 428$ nm. Figures 4(a)–(c) show the frequency- and time-resolved SFG signals of the 800 and 400 nm probe pulses at $\sim 267$ nm, the 800 nm and the $\sim 391$ nm line emission at $\sim 263$ nm and the 800 nm and the $\sim 428$ nm line emission at $\sim 279$ nm, respectively. We confirm that the narrow-bandwidth signals at $\sim 263$ and $\sim 279$ nm are unambiguously from the SFG of coherent line emissions and 800 nm pulses on the basis of the following two points. Firstly, in comparison with the SFG signal of the 800 and 400 nm probe pulses as shown in figure 4(a), both the SFG signal of 800 nm and the coherent emission at $\sim 391$ nm and the SFG signal of 800 nm and the coherent emission at $\sim 428$ nm, as shown in figures 4(b) and (c), respectively, have much narrower spectra, because the coherent emissions of $\sim 391$ and $\sim 428$ nm have narrower bandwidths than the second harmonic 400 nm pulses. Secondly, the SFG signals at $\sim 263$ and $\sim 279$ nm cannot be observed in vacuum or argon. Here, the zero point of the time delay $\tau_2$ is defined as the point at which 800 and 400 nm probe pulses are well overlapped and the positive delay indicates that the second harmonic 400 nm probe pulse is behind the fundamental 800 nm pump pulse. It should also be pointed out that to obtain the three afore-mentioned SFG signals, we have carefully adjusted the phase-matched angle $\phi$ of the nonlinear crystal to optimize each SFG signal. Figure 4(d) presents the SFG signals distributed on the black dashed lines in figures 4(a)–(c) (i.e. 267.2, 263.1 and 278.9 nm). It can be seen in figure 4(d)
that the SFG signals centered at 263.1 and 278.9 nm, which reflect the temporal profiles of the line emissions at 391 and 428 nm, start to rise gradually after the SFG signal centered at 267.2 nm (i.e. the contribution from the broad bandwidth 400 nm probe pulses and the 800 nm pulse). From the SFG signal centered at 267.2 nm, the pulse duration of 400 nm (FWHM) at the crystal is obtained to be \( \sim 700 \) fs due to the positive chirp induced by the dispersion in the windows, crystals, etc and the cross-phase modulation during filamentation. In contrast, the pulse durations of coherent emissions at \( \sim 391 \) and \( \sim 428 \) nm (FWHM) are \( \sim 2.4 \) and \( \sim 7.8 \) ps, respectively, which are much longer than that of the 400 nm probe pulses.

4. Discussion

The mechanism responsible for coherent forward emissions is yet to be clarified. Noting that the polarization of the line emissions is determined by the polarization of the 400 nm probe pulses despite their completely different pulse durations, a possible scheme for the seed amplification that can be enabled by generation of population inversion in \( \text{N}_2^+ \) is considered. In this situation, the population inversion has to be established within an ultrashort time period for initiating the amplification of the second harmonics, which are resonant with the transitions of electronic states in \( \text{N}_2^+ \). This finding suggests an ‘instantaneous’ population inversion mechanism in molecular nitrogen ions. It is noteworthy that here, the word ‘instantaneous’ is used as a counterpart of the relatively slow pumping processes in the previously demonstrated ASE-based remote lasing experiments \([3–6]\), in which the build-up of population inversion occurs at the nanosecond time scale. As shown in figures 3(a) and (b), the instantaneous creation of population inversion is evidenced by pump–probe characterization of the coherent emissions generation, i.e. the amplification of the probe pulses is achieved within an ultrashort time scale after the pump and probe pulses begin to temporally overlap.

It is known that the ejection of an inner-valence electron (HOMO-2) of \( \text{N}_2 \) leaves the ion \( \text{N}_2^+ \) in the excited \( \text{B}^2\Sigma_u^+ \) state, whereas the ionization of an outer-valence electron (HOMO) leads to \( \text{N}_2^+ \) lying on the ground \( \text{X}^2\Sigma_g^+ \) state \([16]\). Although it has been observed experimentally that the lower-lying orbitals such as HOMO-1, HOMO-2, etc indeed can participate in the ionization process \([17, 18]\), numerical calculations \([19–22]\) have shown that the ionization probability of HOMO-2 is about one to two orders of magnitude lower than that of HOMO in an intense laser field of similar parameters as our experiment. Thus, the population inversion in nitrogen molecular ion system cannot be achieved merely by the photoionization of nitrogen molecules from their neutral ground state. There must be some other mechanisms for achieving the population inversion between the upper and lower levels if the seed-amplification scheme works. Because of the high laser intensity inside the filament, a nonlinear absorption process in \( \text{N}_2^+ \) ions in the ground state, as shown in figure 4(e), could occur, which induces the absorption of a few photons to deplete the population of \( \text{N}_2^+ \) in the lower vibrational levels of the ground state, and enhances the upper level of the B state with a Raman-type scheme, thus achieving the population inversion between B(0)–X(0) and B(0)–X(1).

With this population inversion scheme, the faster decay of the 428 nm emission than that of the 391 nm emission shown in figure 3 can be well understood. The vibrational relaxations, as indicated by the shortest green arrows in figure 4(e), first lead to an increase of the population on X(1) and then that on X(0) \([23]\). Thus, the cascade vibrational relaxation process makes the lifetime of the population inversion of B(0)–X(1) significantly shorter than that of B(0)–X(0), giving rise to the faster decay observed in figure 3(b) than that in figure 3(a).
Last but not least, it should be pointed out that other than the temporal characteristics, the intensity dependence of the coherent emissions is also an important aspect for examination as such a dependence will provide valuable information on understanding the physical mechanism of observation reported here. Indeed, our previous work has shown that the signal intensity of coherent emission at 391 nm critically depended on the intensities of the pump and the seed (probe) pulses [9]. However, in the current experiment, to accurately characterize the temporal behaviors of the coherent emissions, first of all, the energy of the pump pulses was finely adjusted and fixed at a value at which a single filament with a good spatial property was obtained. Secondly, the probe pulse at 400 nm remained sufficiently weak to avoid its participation in the process of population inversion. The intensity dependence of the coherent emission will be systematically investigated in the future.

5. Conclusions

In conclusion, we have observed coherent emissions at $\sim$391 and $\sim$428 nm from nitrogen in an orthogonally polarized two-color laser field and measured their temporal profiles with cross-correlation measurements. We found that the pulse durations of the line emissions at both $\sim$391 and $\sim$428 nm are much longer than the 400 nm seed pulse, which is mainly due to the narrow bandwidths of the two line emissions. The results suggest that the coherent line emissions could originate from seed-injected amplification enabled by the remotely generated population-inverted molecular systems in air.

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