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Controlled production of atomic oxygen and nitrogen in a pulsed radio-frequency atmospheric-pressure plasma

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Abstract

Radio-frequency driven atmospheric pressure plasmas are efficient sources for the production of reactive species at ambient pressure and close to room temperature. Pulsing the radio-frequency power input provides additional control over species production and gas temperature. Here, we demonstrate the controlled production of highly reactive atomic oxygen and nitrogen in a pulsed radio-frequency (13.56 MHz) atmospheric-pressure plasma, operated with a small 0.1 % air-like admixture (N_2/O_2 at 4 : 1) through variations in the duty cycle. Absolute densities of atomic oxygen and nitrogen are determined through vacuum-ultraviolet absorption spectroscopy using the DESIRS beamline at the SOLEIL synchrotron coupled with a high resolution Fourier-transform spectrometer. The neutral-gas temperature is measured using nitrogen molecular optical emission spectroscopy. For a fixed applied-voltage amplitude (234 V), varying the pulse duty cycle from 10 % to 100 % at a fixed 10 kHz pulse frequency enables us to regulate the densities of atomic oxygen and nitrogen over the ranges of $(0.18 \pm 0.03) - (3.7 \pm 0.1) \times 10^{20} \text{ m}^{-3}$ and $(0.2 \pm 0.06) - (4.4 \pm 0.8) \times 10^{19} \text{ m}^{-3}$, respectively. The corresponding 11 K increase in the neutral-gas temperature with increased duty cycle, up to a maximum of $(314 \pm 4) \text{ K}$, is relatively small. This additional degree of control, achieved through regulation of the pulse duty cycle and time-averaged power, could be of particular interest for prospective biomedical applications.

1 Introduction

Non-thermal atmospheric-pressure plasma jets (APPJs) enable efficient, non-aqueous delivery of chemically reactive species to temperature-sensitive materials¹. Prospective applications in materials processing include the surface modification of polymers^{2,3} and photoresist removal⁴, and substantial progress has also been made with respect to a variety of biomedical applications^{5,6}, such as cancer therapy⁷ and antimicrobial treatments⁸. A key feature is the capability to efficiently generate highly reactive neutral particles, including atomic oxygen and nitrogen, which are important to the surface interaction that occurs during material processing and also as precursors to longer-lived solvated reactive species that can play a key role in biological systems^{9,10}.

Low-voltage (\sim hundreds of Volts) radio-frequency (rf, \sim tens of MHz) APPJs are typically operated with a feed gas of helium (selected to minimise thermal instabilities through its relatively high thermal conductivity) with a small molecular admixture of oxygen and nitrogen (in the order of \sim 0.1 - 1%) to produce a spatially homogeneous discharge and reproducible fluxes of reactive species including atomic oxygen and nitrogen. Their stable operating range, between ignition and an uncontrolled constricted mode, typically spans about an order of magnitude in terms of the rf power dissipated in the plasma¹¹. There is therefore a limited range of power that can be dissipated in the plasma, which limits the control over reactive species production and the neutral-gas temperature.

Enhanced control of time-averaged power dissipation is highly desirable, in particular for temperature sensitive applications such as biomedical technologies. Pulse modulation (\sim kHz) techniques have proven to be very useful strategies for

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6 low pressure rf plasmas and are broadly applied in industrial applications¹²⁻¹⁴.
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8 They have also been investigated at atmospheric pressure¹⁵⁻²⁰, and specifically
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10 to plasma sources that generate reactive species. Results to date, which have
11
12 focused upon plasma sources operating with pure helium or helium-oxygen gas
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14 mixtures in the plasma core, highlight the promise of pulse modulation techniques
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16 for achieving additional control over reactive species production and the neutral-
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18 gas temperature, and in particular for enabling stable discharge operation at low
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20 average powers²¹⁻²⁵.

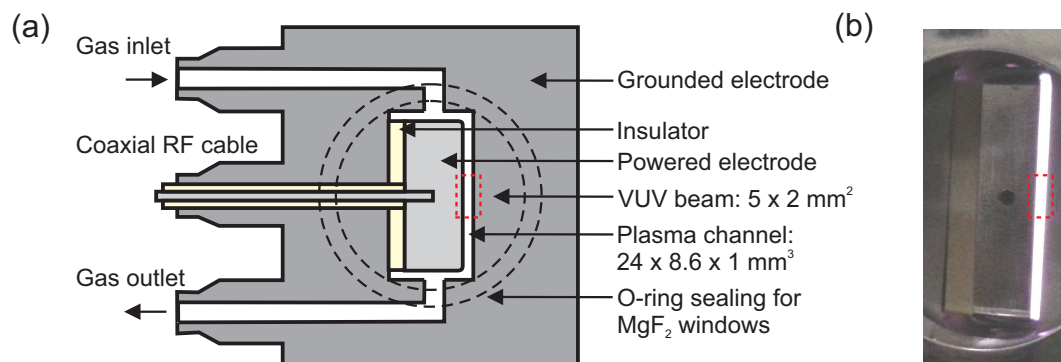
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22 Gas mixtures that include oxygen and nitrogen, in particular those using an air-
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24 like ratio of 4:1, are especially important for applications requiring the production
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26 of reactive oxygen and nitrogen species in ambient air, for example biomedical
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28 technologies. Atomic oxygen and nitrogen have been shown to play key roles
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30 in the chemical kinetics of these systems²⁶⁻³¹. In this study, we have therefore
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32 combined the use of rf pulse modulation with an air-like admixture (0.1 % N₂/O₂
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34 at 4:1) to a helium-fed APPJ to more closely match the conditions of prospective
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36 applications.

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38 In contrast to one-photon and two-photon laser induced fluorescence, which
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40 are widely used for the measurement of atomic species densities, absorption spec-
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42 troscopy is insensitive to quenching. It is therefore well suited to the highly col-
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44 lisional conditions and complex gas mixtures that are most relevant to applica-
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46 tions in ambient air. The time-honoured technique of resonance absorption spec-
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48 troscopy has previously been applied in the experimentally challenging vacuum-
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50 ultraviolet (VUV) wavelength range for absolute density measurements of atomic
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52 oxygen and nitrogen in low-pressure plasmas³²⁻³⁶. It has also recently enabled the
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54 direct and absolute measurement of these densities in atmospheric-pressure plas-
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 6 mas using synchrotron radiation with a high-resolution Fourier-transform spec-
 7 trometer³⁷. This technique is experimentally complex and limited to specialised
 8 plasma sources that provide high vacuum compatibility. While it is important to
 9 note that absorption measurements are spatially integrated and are hence unable
 10 to detect the influence of spatial gradients across the beam cross-section and ab-
 11 sorption length, the results of previous investigations combining experiments and
 12 simulations suggest that the atomic oxygen density remains relatively flat between
 13 the electrodes²⁶. Here, we use this technique to quantify the influence of pulse
 14 modulation on the densities of atomic oxygen and nitrogen.
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2 Experimental setup

Experiments are undertaken using the plasma source shown in Figure 1.



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 45 Figure 1: (a) Schematic cross-section and (b) photograph of the plasma source:
 46 The perpendicular orientation of the synchrotron vacuum ultraviolet (VUV) beam
 47 with respect to the plasma channel is indicated by the dashed rectangle.
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51 This plasma source was designed to operate within the DESIRS (*Dichroïsme*
 52 *Et Spectroscopie par Interaction avec le Rayonnement Synchrotron*) beamline³⁸ at
 53 the SOLEIL synchrotron facility. The coupling of the VUV DESIRS beamline and
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6 a unique Fourier transform spectrometer (VUV-FTS)³⁹ simultaneously enables
7 high spectral resolution (resolving power $\lambda/\Delta\lambda$ up to $\approx 1 \times 10^6$) and broadband
8 coverage over the full VUV spectral range⁴⁰.
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11 The electrode material (stainless steel), length (24 mm) and spacing (1 mm) are
12 selected to approach that of the well-characterised COST reference microplasma (μ APPJ)
13 that operates in ambient air⁴¹. For vacuum compatibility, the electrode width is
14 8.6 mm and hence the surface-to-volume ratio of the channel (2.2 mm^{-1}) is smaller
15 than that of the μ APPJ (4 mm^{-1}). To contain the gas within the vacuum chamber
16 while allowing optical access, MgF_2 windows (1 mm thick) are installed on either
17 side of the channel.
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26 RF power at 13.56 MHz is coupled to the powered electrode using an arbitrary
27 waveform generator (Tabor WS8352, 350 MHz), broadband amplifier (IFI
28 SCCX100, 220 MHz) and matching network (Coaxial Power Systems MMN150).
29 The housing of the plasma source forms the other electrode and is electrically
30 grounded. For continuous operation, 9 W is coupled (amplifier reading: forward
31 minus reflected power) to generate a homogeneous-glow-like α -mode discharge.
32 This is lower than the 115 W applied in the previous measurement campaign of
33 Ref. 37, and is a result of improved coupling efficiency and reduced flow of air-like
34 admixture (N_2/O_2 at 4:1) to the 10 slm helium feed gas. The plasma properties
35 are however considered to be comparable, as confirmed using measurements
36 of the atomic oxygen and nitrogen densities for continuous power coupling to be
37 described later. Here, an admixture of 0.1 % is used (on the low end of typical
38 admixtures in these types of plasmas), which requires less rf power due to lower
39 molecular dissociation, and minimizes neutral-gas heating at the same time.
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55 A high-voltage probe (PMK, 14 KV_{rms} , 100 MHz) and oscilloscope (Lecroy Wave-

jet 354A, 500 MHz) are used to measure the applied voltage. The peak voltage amplitude is held constant at 234 V as shown in Figure 2. The pulse rise-time and fall-time, which are defined as the time for the voltage to increase or decrease between 10-90 % of its peak value (excluding overshoot), are 2.4 μs and 3.1 μs , respectively.

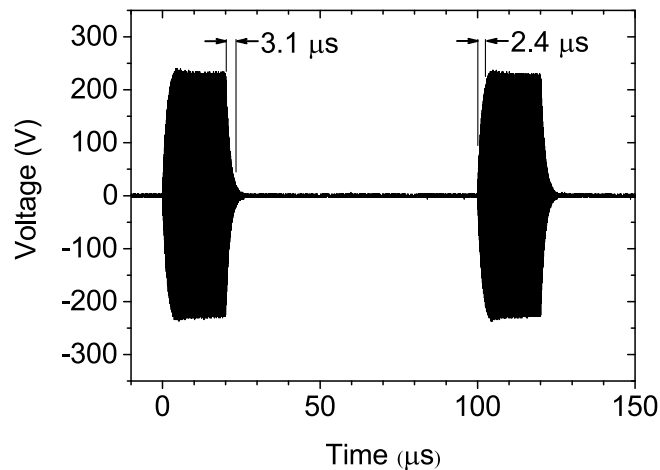


Figure 2: Representative rf voltage pulses applied to the plasma channel: 10 kHz modulation frequency with a duty cycle of 20 %. Helium flux 10 slm, N_2/O_2 (4:1) admixture 0.1 %.

To investigate the impact of pulse modulation on the production of atomic oxygen and nitrogen, two cases are considered: (1) variation of the pulse duty cycle over 10 - 100 % at a fixed modulation frequency of 10 kHz, and (2) variation of the pulse-modulation frequency over 1 - 50 kHz at a fixed duty cycle of 50 %.

To measure changes in gas heating, the neutral-gas temperature is determined using nitrogen molecular optical emission spectroscopy. A Czerny-Turner spectrograph (Andor SR500i, 0.5 m focal length, 2400 grooves/mm) with an attached non-intensified charge coupled device camera (Andor Newton DU940P-BU2, 2048×512 array of $13.5 \mu\text{m}^2$ pixels) is used to measure the optical emission spectrum of the N_2

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6 second-positive system ($C^3\Pi \rightarrow B^3\Pi, \nu = 0 \rightarrow 2$). Simulated spectra are fitted to
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8 the measurements to determine the gas temperature, by assuming that the rota-
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10 tional distribution is in thermal equilibrium with the neutral-gas temperature^{42,43}
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12 as previously undertaken in high-pressure discharges for applications including,
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14 e.g. combustion⁴⁴, electric propulsion⁴⁵ and biomedicine^{46–48}. Our spectrum sim-
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16 ulation is based on molecular constants from Ref. 49 and line strength expressions
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18 from Ref. 50 for intermediate coupling of upper and lower state between Hund's
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20 case (a) and (b). The first rotational lines are treated according to Ref. 51, and
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22 Lambda-doubling is omitted. A Gaussian apparatus function is used in the anal-
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24 ysis, and the spectral fitting routine is estimated to be accurate within ± 4 K.
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26 However, results of the overall diagnostic technique should be treated conserva-
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28 tively⁴³ and for these conditions we consider the overall systematic uncertainty to
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30 be ± 10 K.
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33 Absolute densities of atomic oxygen and nitrogen, spatially averaged over the
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35 1 mm electrode gap at the longitudinal midpoint of the plasma channel (VUV
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37 beam cross-section $\sim 5 \times 2$ mm²), are determined using VUV-FTS transmission
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39 spectra as described in Ref. 37. The O-atom and N-atom Doppler widths are
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41 $\Delta\sigma_D(308\text{ K}) = 0.24\text{ cm}^{-1}$ and $\Delta\sigma_D^N(308\text{ K}) = 0.28\text{ cm}^{-1}$, respectively, for a
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43 neutral-gas temperature of 308 K, representing the mean value found across all
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45 of our measurements. Representative transmission spectra for atomic oxygen and
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47 nitrogen are shown in Figure 3 and Figure 4, respectively, for a 10 kHz pulse-
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49 modulation frequency and duty cycle of 20 %.
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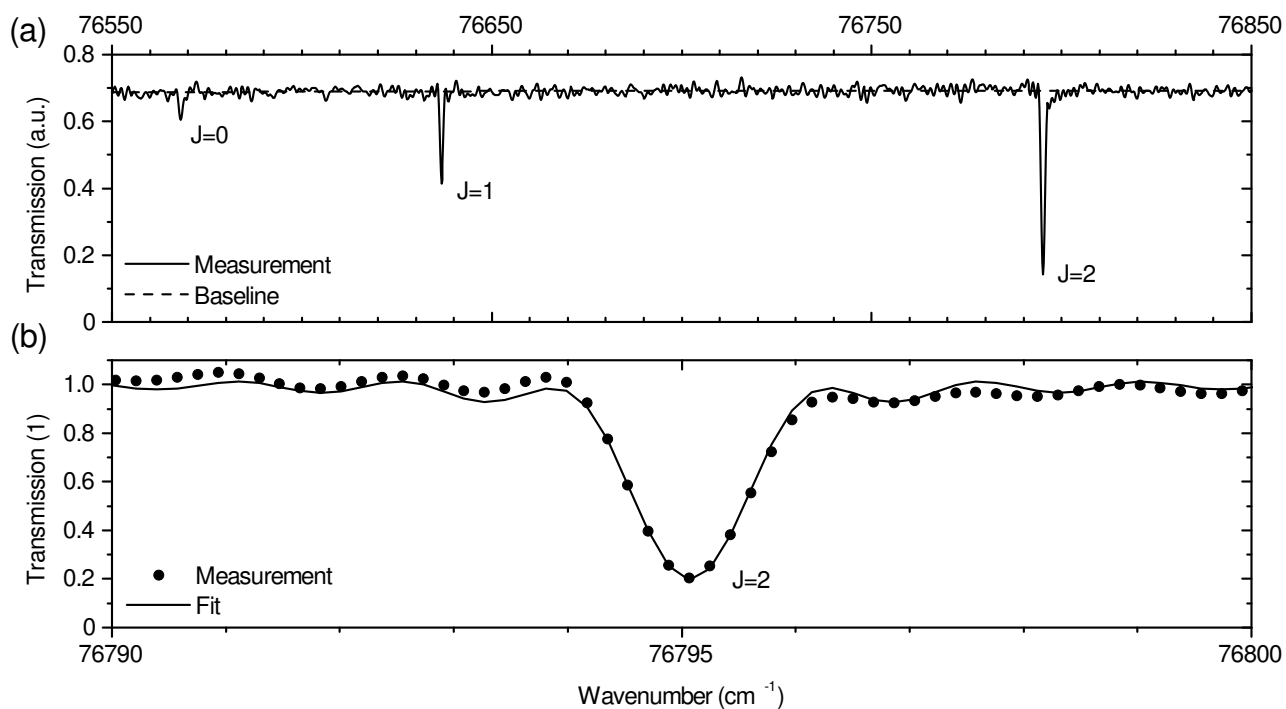


Figure 3: (a) Measured spectrum (not normalized or deconvoluted) and (b) normalized spectrum ($J = 2$ component) used to determine the density of atomic oxygen, $\text{O}(2p^4 \ ^3P_J \rightarrow 3s \ ^3S^*_1)$. Helium flux 10 slm, N_2/O_2 (4:1) admixture 0.1 %, pulse voltage 234 V, pulse duty cycle 20 %, pulse frequency 10 kHz.

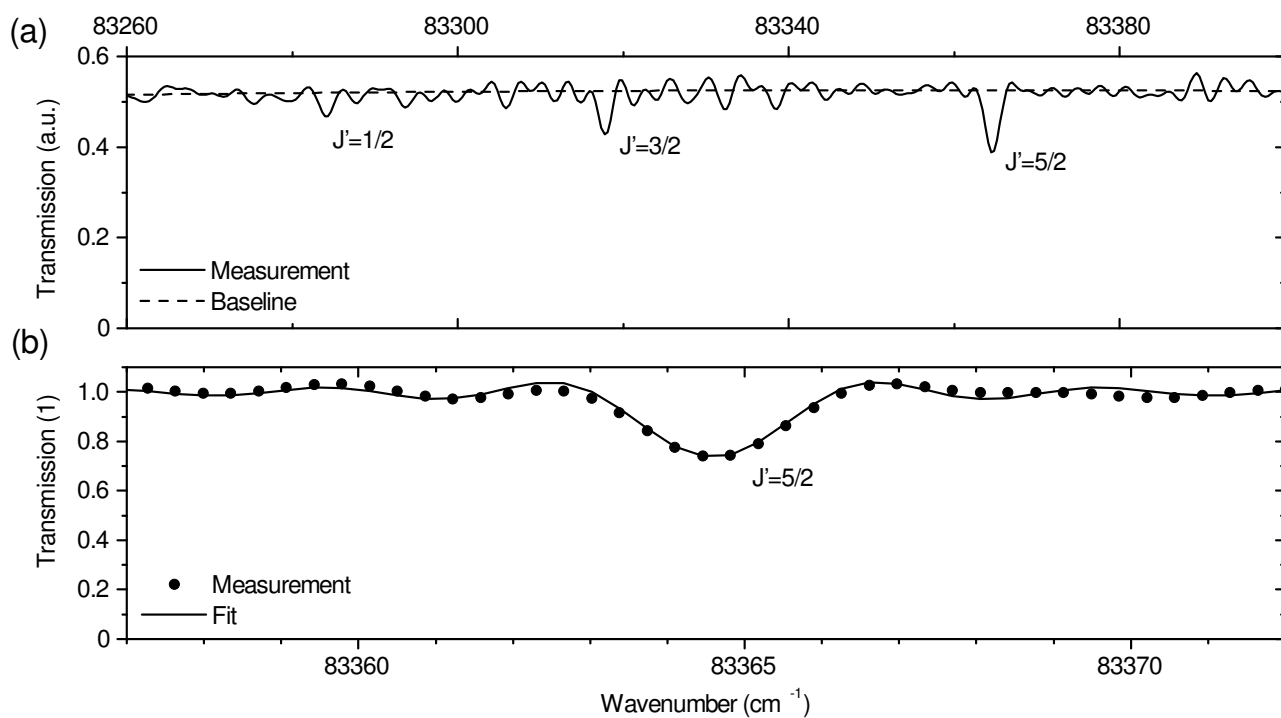


Figure 4: (a) Measured spectrum (not normalized or deconvoluted) and (b) normalized spectrum ($J' = 5/2$ component) used to determine the density of atomic nitrogen, $\text{N}(2p^3 \ ^4\text{S}_{3/2}^* \rightarrow 3s \ ^4\text{P}_{J'})$. Helium flux 10 slm, N_2/O_2 (4:1) admixture 0.1 %, pulse voltage 234 V, pulse duty cycle 20 %, pulse frequency 10 kHz.

3 Results

The variation of the atomic oxygen and nitrogen densities and neutral-gas temperature are shown in Figure 5 as a function of the pulse duty cycle. To confirm repeatability, two measurements were undertaken for the atomic oxygen density at a representative duty cycle of 20 %. Similarly, the density of atomic nitrogen was measured three times at a duty cycle of 90 %. The displayed data points represent average values. It is important to note that the expected decay time of the atomic densities, previously observed to be \sim ms^{26,31}, is significantly longer than the time interval between pulses.

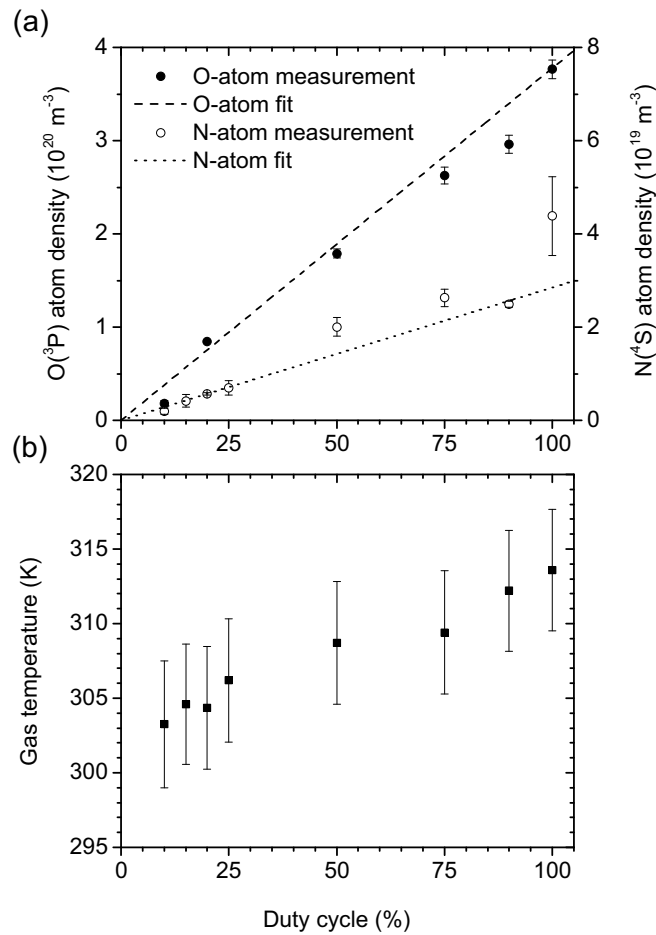


Figure 5: (a) Densities of atomic oxygen and atomic nitrogen, and (b) neutral-gas temperature with respect to pulse duty cycle. Helium flux 10 slm, N_2/O_2 (4:1) admixture 0.1 %, pulse voltage 234 V, pulse frequency 10 kHz.

The densities of atomic oxygen and nitrogen, shown in Figure 5 (a), were first measured for continuous power coupling (100 % duty cycle). They are observed to agree reasonably well (17 % increase and 23 % decrease, respectively) with that of Ref. 37 for the same gas mixture and low power, homogeneous-glow-like α -mode of operation.

In our previous investigation using continuous power coupling, we observed the densities of atomic oxygen and nitrogen to be maximal at 0.35 % and 0.1 % dry-

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6 air admixture, respectively³⁷. Therefore, in this work at a dry-air admixture of
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8 0.1 %, we operate the source under a condition of maximal production of atomic
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10 nitrogen, while the maximal production of atomic oxygen is expected to occur at
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12 a slightly higher dry-air admixture.

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14 When the plasma is pulsed, the densities of atomic oxygen and nitrogen are
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16 observed to increase linearly with duty cycle, varying between $(0.18 \pm 0.03) -$
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18 $(3.7 \pm 0.1) \times 10^{20} \text{ m}^{-3}$ and $(0.2 \pm 0.06) - (4.4 \pm 0.8) \times 10^{19} \text{ m}^{-3}$, respectively, for
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20 duty cycles of 10 - 100 %. A linear increase in both densities with respect to the
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22 pulse duty cycle is consistent with the linearly increasing time-averaged rf power.
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24 It is important to note that the control in atomic-species density can be achieved in
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26 addition to that obtainable by changing the on-phase power level (not undertaken
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28 here), extending the range down to lower fluxes while ensuring stable plasma
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30 operation. The neutral-gas temperature, shown in Figure 5 (b), also exhibits a
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32 linear increase with duty cycle, where the gas temperature is measured to vary
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34 from $(303 \pm 4) - (314 \pm 4) \text{ K}$ for duty cycles of 10 - 100 %. These values are of
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36 significant interest as they can be used to benchmark future plasma chemistry
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38 models that incorporate both oxygen and nitrogen species.

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40 The results as the pulse-frequency is varied for a fixed duty cycle of 50 % are
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42 shown in Figure 6 for (a) densities of atomic oxygen and nitrogen and (b) neutral-
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44 gas temperature.
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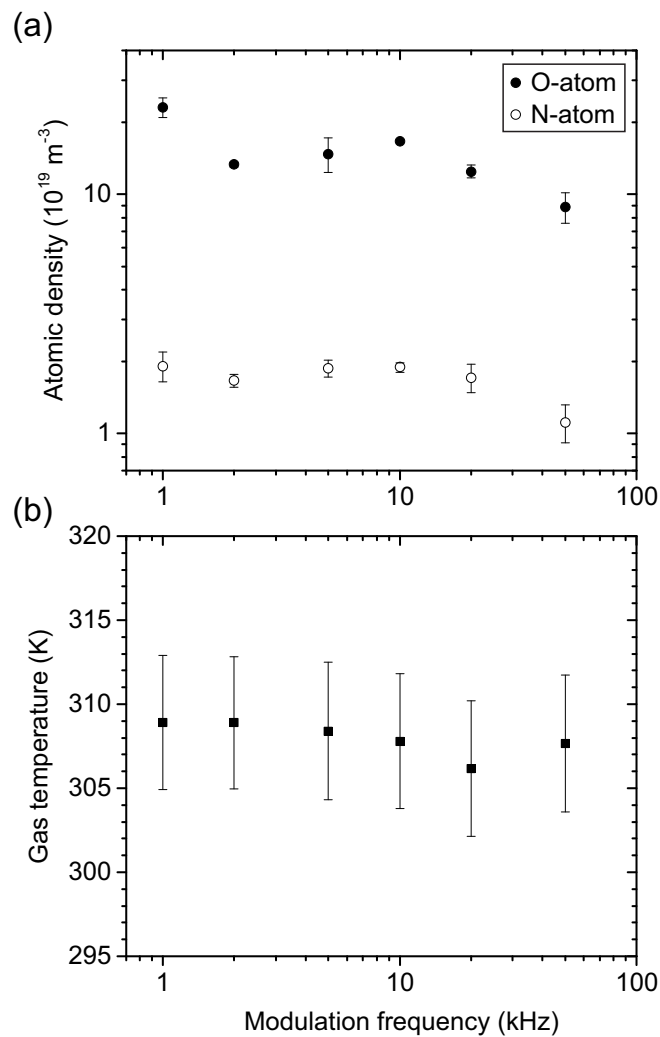


Figure 6: (a) Densities of atomic oxygen and atomic nitrogen, and (b) neutral-gas temperature with respect to pulse-modulation frequency. Helium flux 10 slm, N_2/O_2 (4:1) admixture 0.1 %, pulse voltage 234 V, pulse duty cycle 50 %.

In this case, the time-averaged power remains constant, independent of pulse frequency. Consistent with this, the neutral-gas temperature is observed to remain relatively constant for pulse frequencies of 1 - 50 kHz. The density of atomic oxygen is observed to be relatively independent of the pulse frequency, except above 20 kHz, where a small decrease is seen as shown in Figure 6 (a). This

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6 agrees qualitatively with the results of recent fluid simulations of a capacitively
7 coupled atmospheric-pressure plasma source (2 mm electrode separation) operating
8 in helium with oxygen admixtures of 0 - 1 %²³.
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12 The observed decrease in the atomic densities measured for a modulation fre-
13 quency of 50 kHz could be attributed to the relatively large pulse rise-time com-
14 pared to its duration (2.4 μs and 10 μs , respectively). However, as this is partially
15 compensated by the pulse fall-time (3.1 μs) a more detailed experimental inves-
16 tigation of the temporal evolution in the afterglow remains the subject of future
17 work.
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27 4 Conclusion

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31 The absolute densities of atomic oxygen and nitrogen have been measured in an rf-
32 driven and pulse-modulated atmospheric-pressure plasma jet operating in helium
33 with a small 0.1 % air-like admixture (N_2/O_2 at 4:1). The atomic densities were de-
34 termined by vacuum-ultraviolet absorption spectroscopy using the DESIRS beam-
35 line at the SOLEIL synchrotron coupled with a high resolution Fourier-transform
36 spectrometer. The neutral-gas temperature was measured using nitrogen molec-
37 ular optical emission spectroscopy. The densities of atomic oxygen and nitrogen
38 increase linearly with respect to pulse duty cycle, which is consistent with linear
39 increases in the time-averaged power and neutral-gas temperature. Pulse mod-
40 ulation of the driving voltage enables stable operation of the discharge at lower
41 average power compared to continuous operation, providing a lower neutral-gas
42 temperature and densities of atomic oxygen and nitrogen. The direct and abso-
43 lute measurement of reactive atomic species densities, without assumptions about
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6 the ambient quenching conditions, provides valuable information for the ongoing
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8 development of plasma chemistry models. This will in-turn drive the development
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10 of experimental techniques for achieving enhanced precision in the production of
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12 reactive gas chemistry for prospective technological and biomedical applications.
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19
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