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Neutral gas temperature estimates and metastable resonance energy transfer for argon-nitrogen discharges

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Rovibrational spectroscopy band fitting of the nitrogen (N_2) second positive system is a technique used to estimate the neutral gas temperature of N_2 discharges, or atomic discharges with trace amounts of a N_2 added. For mixtures involving argon and N_2 , resonant energy transfer between argon metastable atoms (Ar^*) and N_2 molecules may affect gas temperature estimates made using the second positive system. The effect of Ar^* resonance energy transfer is investigated here by analyzing neutral gas temperatures of argon- N_2 mixtures, for N_2 percentages from 1% to 100%. Neutral gas temperature estimates are higher than expected for mixtures involving greater than 5% N_2 addition, but are reasonable for argon with less than 5% N_2 addition when compared with an analytic model for ion-neutral charge exchange collisional heating. Additional spatiotemporal investigations into neutral gas temperature estimates with 10% N_2 addition demonstrate that although absolute temperature values may be affected by Ar^* resonant energy transfer, spatiotemporal trends may still be used to accurately diagnose the discharge. © 2016 AIP Publishing LLC.
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I. INTRODUCTION

Low temperature plasma discharges are used for a variety of functions across many disciplines including materials processing, biomedical and propulsion applications.^{1,2} In many applications, it is important to determine the neutral gas temperature of the discharge to within a reasonable degree of accuracy. For example, electrothermal plasma thruster performance depends directly on the neutral gas temperature,³ and biomedical applications where a plasma jet is applied directly to biomaterials requires carefully controlled gas temperatures to avoid thermal damage.⁴

Due to the natural light emission from plasma discharges, non-invasive emission spectroscopy techniques are often used for temperature determination of low temperature discharges.^{2,5,6} In this work, the focus is on neutral gas temperature determination using rovibrational spectroscopy band fitting. Rovibrational spectroscopy involves the study of diatomic or molecular species with excited rotational and vibrational states. Rotational and vibrational states within a molecule add additional excitation channels for electrons, and the resulting spectra consist of a series of moderately spaced vibrational bands, each with a series of tightly spaced rotational bands within it.

For certain rovibrational band systems, it is possible to simulate the intensity profile of a band using well published equations and constants.^{7,8} The relative intensities of the vibrational and rotational bands are dependant on the distribution of particles within the vibrational and rotational states, and hence the vibrational temperature (T_v) and rotational temperature (T_r). So estimates for T_v and T_r of an experimental discharge can be found using rovibrational

spectroscopy band fitting, by iteratively comparing experimentally recorded spectra with simulated spectra of known T_r and T_v until a good fit is found. The temperatures used in the fitted simulated spectra are then approximately T_r and T_v of the experimental discharge.⁷

Under certain conditions, rovibrational band fitting can be extended to estimate neutral gas temperature (T_g) as well as T_r and T_v . Having higher energy level separation, excitation energy for vibrational modes is higher than for rotation and translation, and T_v is often much higher than T_g , but T_r and T_g may be in thermal equilibrium. For T_r and T_g to be in equilibrium, the lifetime of the ground rotational state must be longer than the time between collisions² allowing for molecules in the rotational ground state to thermalise. Additionally, during rovibrational spectroscopy experiments, the light analyzed is the emission from an upper rotational state, not the ground state, so it is also a requirement that the upper and ground rotational states are in thermal equilibrium. Assuming that the ground state is a single Boltzmann distribution, the excited state of interest must also be a single Boltzmann distribution.^{2,9} This can be safely assumed if the lifetime of the excited state is shorter than the time between heavy particle collisions, such that the excited state is created mainly from electron collisions. Electrons having low mass do not significantly alter the molecular rotational moment during a collision and the ground states distribution effectively maps onto the upper state distribution.¹⁰

A variety of rovibrational bands within a variety of molecules in various discharges have been used previously for gas temperature determination from rovibrational band fitting. The temperature of an atmospheric pressure air plasma was estimated using oxygen (O_2) and nitrogen ion (N_2^+) bands, and in agreement with each other within 2.4%.¹¹ Temperature of an inductively coupled CF_4 plasma was

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found to range from 1250 K to 1800 K using C_2 , CF, CN, and CO bands.¹² The Swann bands of carbon (C_2) have been used to determine a neutral gas temperature of a high power transformer coupled fluorocarbon plasma,⁸ and hydroxyl (OH) bands have been used to estimate temperatures in a 10 kV gliding arc discharge at atmospheric pressure.¹³

Nitrogen gas (N_2) is widely used for temperature estimates from rovibrational band fitting. The N_2 first positive system has been used for temperature estimates in a low pressure helicon plasma,^{14,15} for a high pressure direct current (DC) slot discharge,¹⁶ an RF ICP at low pressure,¹⁷ and a high power, low pressure microwave discharge.¹⁸ The N_2^+ first negative system has been used to find gas temperature in a gliding arc discharge at atmospheric pressure,¹³ a pulsed DC hollow cathode discharge,¹⁹ and a low pressure dual frequency CCP.²⁰

The N_2 second positive system ($C^3\Pi_u \rightarrow B^3\Pi_g$) is the most common band used, with gas temperature estimates made for capacitively coupled and inductively coupled plasma discharges,^{5,10,20–22} a radio-frequency (RF) helicon discharge,²³ and low pressure glow or positive column discharges.^{24,25} Temperatures of higher pressure and atmospheric pressure discharges have also been analysed with the N_2 second positive system,^{4,26,27} and also temperatures during the first 400 ns of spark breakdown for an N_2 discharge.⁷ The popularity of the N_2 second positive system is perhaps due to the simplicity in creating the synthetic spectrum, the strength, and highly distinctive shape of the rovibrational spectrum, and wide historical usage.

Addition of trace amounts of a diatomic gas to an atomic element discharge allows for rovibrational spectroscopy band fitting technique to be expanded to estimate the atomic neutral gas temperature. This has been previously done with trace amounts of N_2 in chlorine gas (Cl_2),^{5,21} hydrogen gas (H_2),^{28,29} and for noble gas discharges of helium^{4,24} neon (Ne),²⁶ argon,^{4,8–10,16,22,30} and krypton (Kr).¹⁰

Rovibrational band fitting to determine T_g from T_r of a diatomic molecule is only relevant if the single excitation channel to the upper measured state (here the $C^3\Pi_u$ state) is from electron impact. Being very low mass in comparison to N_2 molecules an electron collision has little effect on the rotational distribution, and the upper rotational distribution can be considered to be identical to the ground state rotational distribution, giving correct values for T_r and hence T_g .

For discharges involving mixtures of N_2 and argon, resonance energy transfer between argon metastable atoms (Ar^*) and N_2 molecules introduces a second excitation channel that does not necessarily map the ground rotational state onto the $C^3\Pi_u$ state and enhances high rotational levels of the $C^3\Pi_u$ state.^{31,32} Deactivation of Ar^* by an N_2 molecule has a cross-section 100 times larger than for deactivation by another argon atom,³¹ making it a significant process within argon- N_2 discharges. Resulting T_r estimated using the rovibrational spectroscopy method on the second positive system may be too high, therefore any resultant estimates of T_g will also be too high.

The resonant energy transfer between Ar^* and N_2 is confined to the second positive system because of the similarity in excitation potentials. The excitation energy

of the N_2 first positive system is 3–4 eV below the argon metastable energy, so the transfer is not resonant and is much slower than electron impact excitation. The N_2^+ first negative system (first negative system) has an excitation energy of 18.7 eV, significantly higher than the argon metastable energy. Therefore, both the N_2 first positive system and N_2^+ first negative system are potential alternatives to use for rovibrational band fitting to estimate T_g .

The initial reaction is therefore to avoid using the N_2 second positive system for gas temperature estimates in argon, and instead to look at the N_2^+ first negative system or the N_2 first positive system. When using the N_2^+ first negative system, it is required that the ion and neutral temperatures are in thermal equilibrium, which is reasonable in a highly collisional discharges as the ion-neutral mean free path is small.³³ Previous rovibrational experiments have used the N_2^+ first negative system as an indication of T_g .^{19,20,24} However, for a 1 Torr positive column discharge enclosed in an oven to provide limits for T_g estimates, values for T_g using the N_2^+ FNS were consistently 150 K too high and outside the limit range.²⁴ Comparatively, values for T_g using the N_2 second positive system were found to lie within the bounds given by the oven temperature. Similarly, for a dual frequency CCP at 20 mTorr, the N_2^+ first negative system gave 493 K whereas the N_2 second positive system gave a lower temperature of 379 K.²⁰

The N_2 first positive system has previously been shown to produce estimates for gas temperature with good agreement to the N_2 second positive system for a 1.0 Torr microwave discharge at 600 W.¹⁸ Excitation channels for the N_2 first positive system are from electron impact excitation of the ground state ($N_2(X^1\Sigma_g)$) or the $N_2(A^3\Sigma_u)$ metastable state, and radiative decay from the $N_2(C^3\Pi_u)$ state.³⁴ The rate coefficient for population through radiative decay is an order of magnitude lower than from electron impact excitation, and $T_r \approx T_g$.

However, when simulating a first positive system rovibrational band spectrum for fitting, the triplet state fine structure must be resolved, a change from Hund's case (a) to (b) at high rotational states must be considered, and alternating intensities from nuclear spin degeneracy must be correctly simulated.^{15,18} Calculated wavelengths may have up to 0.04 nm errors which is significant in relation to the wavelength separation of the fine structure of the triplet states,¹⁴ and experimentally predetermined wavelengths are required to be used instead. This introduces additional complexity and potential sources of error when compared to simulating the N_2 second positive system.

For this work, neutral gas temperature estimates using rovibrational band fitting of the N_2 second positive system for an argon discharge are investigated, to determine under what conditions the simpler N_2 second positive system can be used with confidence on argon discharges. This is achieved by adding various amounts of N_2 gas to an argon discharge and comparing the results with an analytic model for gas temperature. Mixtures involving between 1% and 100% N_2 are investigated.

II. APPARATUS

The experimental discharges analyzed are low temperature radio frequency discharges created in the previously described in depth “Pocket Rocket” electrothermal plasma thruster experimental setup.^{35,36} The device, shown in Figure 1, consists of a 18 mm long, 4.2 mm inner diameter alumina tube. RF power at 13.56 MHz and a few tens of Watts, coupled to the system through a 5 mm wide, 12 mm outer diameter copper electrode placed at the axial midpoint of the alumina tube, creates a weakly ionized plasma within the tube. Two 3 mm wide aluminium grounded electrodes located at each end of the tube join onto a 60 mm diameter solid aluminium experiment housing. The powered and grounded electrodes are separated by a 3–4 mm thick insulating Macor housing in two parts surrounding the powered electrode.

Power is supplied from an ENI ACG-10 RF generator through a large variable capacitance π -matching network, although recent work has miniaturized the matching network to be suitable for micro-satellite operation.³⁷ Argon-nitrogen gas mixtures are introduced through an upstream plenum chamber. Plenum pressure is measured using a convectron gauge and is held constant at a total pressure of 1.5 Torr for all mixtures tested. The percentage of N_2 added to argon is given by the partial pressures in the plenum and ranges from 1% to 100%. The plenum chamber contains a viewport located on the rear wall, providing optical access to the plasma volume within the alumina tube. Downstream the plume expands into a 50 mm diameter evacuated glass tube connected to a vacuum chamber fitted with a rotary pump giving a pressure gradient of four between the plenum and chamber.

Computational fluid dynamics (CFD) simulations have shown the discharge operates in a gamma mode and is driven by ion-induced secondary electrons ejected from the inner alumina tube walls.³⁸ The large asymmetry of the device creates a DC self bias on the alumina tube in the vicinity of the powered electrode, acting to accelerate the ion-induced secondary electrons into the center of the discharge bulk. This

results in a peak ion density within the center of the tube, both axially and radially, which has also been observed in experiments.³⁵

Emission spectra are captured using a 4 mm diameter fused silica fibre optic cable positioned to capture light emitted through the plenum window and direct it into a SPEX 500M monochromator with 500 mm focal length, 50 μm entrance slit width and 1200 groove mm^{-1} grating. An Ames Photonics Garry 3000S CCD array is placed at the exit plane of the monochromator. The CCD array is 21 mm long with 3000 pixels which when combined with a dispersion of 1.6 nm/mm in the monochromator simultaneously captures a 34 nm wavelength range spectra with a resolution of 0.02 nm.

The discharge is turned on and left to run for 20 to 30 s prior to starting the first integration to ensure steady state operation has been reached. Integration times range from 1000 ms for argon with 1% N_2 to 60 ms for pure N_2 , decreasing as the percentage of N_2 increases and the rovibrational signal intensity increases. To assist in reducing noise while ensuring a sufficient rovibrational signal is captured, 30 spectra are recorded and averaged.

For this work, the wavelength region from 365 nm to 381 nm is used, capturing the persistent strong bands of N_2 at 380.5 nm, 375.5 nm, and 371.1 nm corresponding to the (0,2), (1,3), (2,4) vibrational transitions, as well as the slightly weaker (3,5) band at 367.2 nm. Additionally, this region contains only a few weak argon lines³⁹ to minimise argon interference. To account for the few weak argon lines, pure argon spectra are captured to subtract from the argon-nitrogen mixture spectra during processing. The final spectra are also smoothed using a Golay smoothing function to reduce any remaining background argon and noise effects.

III. ROVIBRATIONAL BAND FITTING METHOD

To artificially create the spectra required for fitting to the experimental data, the wavelengths and intensities for each possible transition between the various rotational, vibrational, and electronic states must be calculated. This is achieved by first calculating the energy of each rotational and vibrational state of interest (denoted by J and v , respectively) by analyzing the molecule as an anharmonic oscillating, non-rigid rotor. Below is a summary of the main equations and theory used here. For full treatment, refer to Refs. 7, 40, and 41, for example.

The vibration of a diatomic molecule comes from the repelling force of the positively charged nuclei and the attracting force of the electron swarm causing oscillatory motion of the two atoms, analogous to two point masses connected by a spring. The bounds for diatomic vibration are given by the limits of the molecular potential energy curve, representing the balance between the repulsion of the nuclei and the attraction of the electron swarm. The wavefunction of each vibrational mode must form a standing wave within the bounds of the curve, otherwise the wavefunction annihilates and the vibrational mode cannot exist. Solving for the associated allowed energies for vibrational modes (E_v) gives Equation (1),⁴⁰ where $\bar{\omega}_e$ and $\bar{\omega}_e x_e$ are molecular constants found in References 40 and 42, for example,

FIG. 1. The “Pocket Rocket” device and experimental housing.

$$E_v = \bar{\omega}_e \left(v + \frac{1}{2} \right) - \bar{\omega}_e x_e \left(v + \frac{1}{2} \right)^2. \quad (1)$$

Rotational motion of a molecule is approximated as a non-rigid rotor, as the changing bond length from vibration can affect the rotational modes. The allowed rotational energies (E_J) of a non-rigid rotor are given by Equation (2), where B_e and D_e are rotational constants, found in References 40 and 42, for example,

$$E_J = B_e J(J+1) - D_e J^2(J+1)^2. \quad (2)$$

The intensity (I) of an electronic transition from an upper state ($n'v'J'$) to a lower state ($n''v''J''$) with wavelength λ is given by Equation (3), where h is Planck's constant, c is the speed of light, $N_{n'v'J'}$ is the number of molecules in the upper state, and $A_{n''v'',J''}^{n'v'J'}$ is the transition probability,

$$I_{n''v'',J''}^{n'v'J'} = \frac{hc^2}{\lambda} N_{n'v'J'} A_{n''v'',J''}^{n'v'J'}. \quad (3)$$

The number of molecules in the upper state can be estimated using a Maxwell-Boltzmann distribution as the temperature is significantly higher than the difference between vibrational and rotational energy levels. Hence, the number of molecules in the upper vibrational state (v') is given by Equation (4), where N_{v0} is the number of molecules in the vibrational ground state and T_v is vibrational temperature. The number of molecules in the upper rotational state (J') is given by Equation (5), where N_{J0} is the number of molecules in the rotational ground state and T_r is the rotational temperature

$$N_{v'} \approx N_{v0} e^{-\frac{E_{v'}}{kT_v}}, \quad (4)$$

$$N_{J'} \approx N_{J0} e^{-\frac{E_{J'}}{kT_r}}. \quad (5)$$

The probability of a vibrational transition is dependent on the overlap of the wavefunctions of the upper and lower vibrational levels.⁴³ The internuclear separation of a diatomic molecule immediately after an electronic transition is the same as immediately prior to the transition.⁴⁴ However, often this no longer is the equilibrium position for the new vibrational level and the molecule will begin to vibrate more. The most probable transitions, therefore, involve a minimum change in equilibrium internuclear distance. The resulting vibrational transition probabilities are known as Franck Condon factors ($q_{v',v''}$)^{40,41} and are always constant for a given transition.⁴⁵ For this work, values for $q_{v',v''}$ are taken from Zare *et al.*⁴⁶

Transition probabilities for rotation depend on the selection rules for allowed rotational transitions, given by Equation (6),

$$\Delta J = J' - J'' = 0, \pm 1. \quad (6)$$

This results in three branches: the $\Delta J = +1$ or R branch, the $\Delta J = -1$ or P branch, and the $\Delta J = 0$ or Q branch. The transition probabilities, hence relative line strengths between the three branches, are determined by Hönl-London factors ($S_{J',J''}$). Calculation of $S_{J',J''}$ depends on the coupling of the angular momentum of rotational and electronic motion. The

type of coupling is given by the Hund's coupling case, of which there are five possible cases in total ((a)–(e)),⁴⁰ two of which are relevant to the N_2 second positive system and will be discussed here.

Hund's case (a) occurs when the angular momentum of nuclear rotation interacts only weakly with electron angular momentum effects, so electron motion occurs mostly on the axis joining the nuclei. The treatment of a molecule in Hund's case (a) is that of a simple vibrating rotator (as described above). For Hund's case (b), spin is only weakly or not at all coupled to the internuclear axis in which case total orbital angular momentum excluding spin may become slightly magnetically coupled leading to a slight splitting into triplet states occurring.

The Hund's case selection depends on the ratio of the spin-orbit constant (A_v) to the rotational constant, which are approximately 38 cm^{-1} and 1.8 cm^{-1} , respectively, for the (2,0) and (1,3) band of the N_2 second positive system.⁴⁷ This gives a ratio $Y = \frac{A_v}{B_e} \approx 21$. Therefore, the N_2 second positive system is Hund's case (a) for low J values, transitioning to Hund's case (b) for higher J values.⁷ However, at high J values the difference between the (a) and (b) cases is negligible, and case (a) can be assumed throughout.

Nuclear spin degeneracy (Λ -Doubling) is less than 0.004 nm for the N_2 second positive system,⁷ which is smaller than the rotational separation and hence is neglected here. The separation of triplet splitting decreases with increasing J values,⁴⁸ and is less than 0.08 nm which is also smaller than the rotational separation except for low J values (near the bandhead).⁷ Although there may be some effect from triplet splitting noticeable for rotational levels near the band head, in general the effect will be negligible and it is also neglected here.

Assuming Hund's case (a), the relevant equations to calculate the Hönl-London factors for the N_2 second positive system are shown in Equations (7)–(9), where Λ is the component of total angular momentum along the internuclear axis⁴⁰

$$S_J^R = \frac{(J' + \Lambda')(J' - \Lambda')}{J'}, \quad (7)$$

$$S_J^Q = \frac{(2J' + 1)\Lambda'^2}{J'(J' + 1)}, \quad (8)$$

$$S_J^P = \frac{(J' + 1 + \Lambda')(J' + 1 - \Lambda')}{J' + 1}. \quad (9)$$

Substituting the Hönl-London factors (Equations (7)–(9)), the Franck-Condon factors ($q_{v',v''}$) and Maxwell-Boltzmann population distributions (Equations (4) and (5)) into Equation (3), give Equation (10), the intensity of a spectral line in the N_2 second positive system, where D is an arbitrary scaling constant accounting for constants collected throughout the analysis and experimental equipment sensitivity

$$I_{n''v'',J''}^{n'v'J'} = \frac{D}{\lambda^4} q_{v',v''} e^{-\frac{E_{v'}}{kT_v}} S_{J',J''} e^{-\frac{E_{J'}}{kT_r}}. \quad (10)$$

The wavelength (λ) for a transitions from an upper state ($n'v'J'$) to lower state ($n''v''J''$) in a diatomic molecule is given by Equation (11)⁷

$$\lambda_{n''v''J''}^{n'v'J'} = \left[n_a \sum_{pq} Y_{pq}^{n''} \left(v' + \frac{1}{2} \right)^p [J'(J' + 1)]^q - Y_{pq}^{n''} \left(v'' + \frac{1}{2} \right)^p [J''(J'' + 1)]^q \right]^{-1}. \quad (11)$$

In Equation (11), n_a is the refractive index of air included to convert the calculated wavelength from the vacuum state to the adjusted wavelength for propagation in air, and Y_{pq} are Dunham coefficients⁴⁹ with subscripts p and q referring to the powers of the vibrational and rotational quantum numbers, respectively. Dunham coefficients are essentially reduced versions of various combinations of ω_e , $\omega_e x_e$, B_e , and D_e to simplify the wavelength equation, taken for this work for values of p from 0 to 5 and q from 0 to 2 from equations published in Dunham.⁴⁹

Using Equation (11) for wavelength and Equation (10) for intensity, the rovibrational spectrum of a diatomic molecule can be simulated. The final step before fitting the theoretical and experimental spectra is to artificially broaden the simulated lines to match the natural experimental broadening effects. Here, a Gaussian convolution kernel, described in Equation (12), is used on λ to match the experimental broadening. The value of σ determines the magnitude of the broadening and is chosen based on the shape of the sharp mercury 546 nm line, produced by a mercury lamp and recorded using the same equipment as described above

$$g(\lambda) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(\Delta\lambda)^2}{2\sigma^2}}. \quad (12)$$

The iterative fitting procedure between the experimental and simulated spectra is performed using Monte Carlo Markov Chains (MCMC) over 50 000 iterations, with the first 10 000 iterations binned. This results in a range of credible values output for T_r and T_v from which a 95% confidence range for the temperature is stated. Example fits between the experimental data and corresponding simulated spectrum for a 10 W, 1.5 Torr plasma in N_2 , and argon with 1% N_2 addition are shown in Figure 2. The error between the experimental data and simulated spectra is also included in Figure 2 as an indication as to the quality of the fit. The visibility of the rotational band oscillations in the error shows that slight improvements could be made to the wavelength calculations to reduce overall uncertainties.

IV. RESULTS

Results for T_g measured in argon with varying percentages of N_2 added are shown in Figure 3, with error bars based on a 95% confidence interval from the fitting procedure. Errors bars are larger for lower N_2 percentages as the reduced rovibrational signal results in a lower signal to noise ratio. Also, overlaid in Figure 3 as bold red crosses are theoretical estimates for T_g for pure argon and pure nitrogen discharges, made using an analytic model previously presented by Greig *et al.*³ The analytic model analyzed heating through ion-neutral charge exchange collisions, verifying that a pure argon discharge is expected to be hotter than a pure N_2

FIG. 2. Example rovibrational band fitting for a 10 W, 1.5 Torr plasma in (a) N_2 and (b) argon with 1% N_2 . The experimental spectra are shown as dotted black lines with the simulated spectra overlaid as solid grey lines. The errors between the experimental and simulated spectra are shown as a thin grey line as an indication to the quality of the fit.

discharge due to a lower ionization percent for N_2 and additional degrees of freedom for N_2 compared to argon. During an ion-neutral charge exchange collision, the kinetic energy (KE) transfer is related to the change in T_g through $\Delta KE = \frac{n}{2} k \Delta T_g$, where n is the degrees of freedom of the molecule. Argon, as an atomic element, has only three translational degrees of freedom ($n=3$) for energy to be distributed between during an ion neutral collision, whereas a diatomic N_2 molecule has two rotational and one vibrational mode in addition to three translational modes ($n=6$) for the energy to be distributed between, resulting in a lower temperature gain.

FIG. 3. Measured gas temperature estimates using rovibrational band matching of the N_2 second positive system with varying N_2 percent in an argon discharge.

For 1% N₂ addition, the lowest percent addition of N₂ tested, T_g is 1030 K. Previously, the temperature of an argon with 1% N₂ discharge at 10 W and 1.5 Torr in Pocket Rocket was reported as 1090 K.³ At 100% N₂, T_g has decreased to 400 K, in agreement with a previous estimate of neutral gas temperature in Pocket Rocket of 430 K at 10 W and 1.5 Torr.³ The intermediate percentages tested form an asymmetric inverted parabolic trend, with a maximum gas temperature of 1360 K at 20% N₂ addition. Previous works have shown increases in gas temperature for increasing percentages of N₂ added to argon, with addition of 0%, 3%, and 45% N₂ giving temperatures of 400–700 K in a 100 W CCP using a combination of Doppler broadening and N₂ second positive system rovibrational band fitting.²²

It has previously been noted that the intensity of an argon-N₂ spectrum is highest with 10% N₂,^{31,50} roughly corresponding to the highest measured T_g here at between 10% and 20% N₂. Additionally, above ~10% N₂ the density of N₂⁺ does not significantly change, but below 10% N₂, density of N₂⁺ is significantly lower and is almost negligible below 5%.⁵¹ These results suggest that the increased temperatures measured between ~5% N₂ and 50% N₂ are enhanced by metastable quenching. This may be caused by the enhanced tail region affecting the fitting and producing artificially high temperatures, the temperature of the discharge actually being higher than pure argon or pure N₂ discharges or a combination of both. It has been previously noted in an RF hollow cathode discharge that low percentage N₂ addition in argon produces enhanced thermionic emission from a titanium nozzle caused by a small population of hot N₂ in the discharge created Ar* quenching.⁵²

V. DISCUSSION

The Ar* states, ³P₂ and ³P₀, have lifetimes in the order of seconds,⁵³ due to the spin and rotation selection rules (ΔS = 0 and ΔJ = 0, ±1, respectively) preventing spontaneous radiative transitions to the ground state. The long lifetimes denote that Ar* density can become a significant proportion of the neutral density population. Excitation energies for the ³P₂ and ³P₀ states are 11.72 eV and 11.54 eV, respectively,^{15,52} similar to the threshold excitation energy for the N₂ second positive system of 11.1 eV.⁵⁴ Collisions between Ar* and N₂ results in deactivation of the metastable atom with resonance energy transfer to the N₂ C³Π_u state through the process shown in Equation (13), where N₂(X¹Σ_g) is the ground state

The rate of reaction for resonant energy transfer (r_{N_2,Ar^*}) is given by Equation (14),²² where n_{Ar^*} is the metastable argon density and n_{N_2} is the N₂ density. The rate of reaction for electron impact excitation of the C³Π_u state ($r_{N_2,e}$) is given by Equation (15), where T_e is electron temperature and n_e is the electron density²²

$$r_{N_2,Ar^*} = 2.9 \times 10^{-14} \sqrt{\frac{T_g}{300}} n_{Ar^*} n_{N_2} \text{ cm}^{-3} \text{ s}^{-1}, \quad (14)$$

$$r_{N_2,e} = 1.36 \times 10^{-8} T_e^{0.138} e^{\frac{-11.03}{T_e}} n_e n_{N_2} \text{ cm}^{-3} \text{ s}^{-1}. \quad (15)$$

To identify the dominant excitation process in Pocket Rocket, Equations (14) and (15) are used to calculate r_{N_2,Ar^*} and $r_{N_2,e}$ for varying percents of N₂ in a 1.5 Torr total pressure argon discharge. Electron temperature (T_e) is estimated as 2.5 eV based on previous experimental and global model results for Pocket Rocket.³⁵ Electron density (n_e) is estimated as $2 \times 10^{12} \text{ cm}^{-3}$ for pure argon and $1 \times 10^{12} \text{ cm}^{-3}$ for pure N₂ based on ion saturation current measurements of 10 W discharges.³ A linear decrease in n_e was assumed between pure argon and pure N₂.^{17,51}

In the absence of experimental data for Ar* density, a value of $2 \times 10^{13} \text{ cm}^{-3}$ is used for pure argon, based on previous works demonstrating Ar* density can be up to an order of magnitude higher than n_e .^{51,53} Density of Ar* is assumed to decrease by two orders of magnitude by 90% N₂ addition.⁵¹ Using these approximations, estimates for $r_{N_2,e}$ and r_{N_2,Ar^*} for both 300 K and 1000 K with varying percent N₂ in argon are as shown in Figure 4.

The electron impact excitation rate is consistently two orders of magnitude higher than excitation from quenching of Ar*, supported by previous findings.^{2,10} However, electron impact excitation may be from the ground state (Equation (16)) or from the N₂(A³Σ_u) and metastable state (Equation (17)), with excitation from the metastable state usually dominant over excitation from the ground state

In discharges where the N₂(X¹Σ_g) density is significantly higher than the N₂(A³Σ_u) density, the excitation through Ar* quenching may become dominant over electron impact excitation. Even if that is not the case, the enhanced rotational tail from Ar* quenching may still affect T_g estimated by rovibrational band matching of the N₂ second positive system. Based on the results in Figure 3, trace amounts (~1%–2%) of N₂ added to an argon discharge do not significantly affect estimates for T_g, and the second positive system can be safely used for neutral gas temperature estimates of argon-nitrogen discharges.

FIG. 4. Reaction rates for excitation of N₂ C³Π_u state by quenching of Ar* at 300 K (dashed blue line) and 1000 K (solid blue line) calculated from Equation (14) and electron impact (solid red line) calculated from Equation (15).

Despite higher percentages of N_2 creating neutral gas temperature estimates that are potentially higher than the actual neutral gas temperature, the second positive system may still prove useful for some applications where the temperature trend is of interest and not necessarily the absolute value. For example, the temporal evolution of temperature can be used to identify heating mechanisms present within a discharge.⁵⁵ Recording the change in temperature, the fitting lines of the form are shown in Equation (18) where T_0 is the initial temperature and ΔT is the total temperature change, allows for extraction of the time constant of heating (τ). Each different heating mechanism will have a different time constant; hence, the time constants found can be used in the identification of heating processes

$$T = T_0 + \Delta T(1 - e^{-t/\tau}). \quad (18)$$

The temporal evolution of a 60 W, 1.5 Torr N_2 discharge over the first 300 s of operation has previously been analyzed and used to identify three distinct heating mechanisms in Pocket Rocket with time constants of 80 μ s, 8 s, and 100 s.⁵⁵ The heating mechanisms were identified as fast heating from ion-neutral collisions, intermediate heating from ion bombardment of the thruster walls creating wall heating, and slow heating from the thruster housing increasing in temperature over time.⁵⁶

The same experiment is repeated here using a 60 W, 1.5 Torr total plenum pressure argon discharge with 10% N_2 added, as 1% N_2 does not give sufficient rovibrational signal for rovibrational band fitting. Temporal evolution of gas temperature spanning seven orders of magnitude from 70 μ s to 300 s is captured through the use of a specially written Labview program to simultaneously control the RF power generator and CCD array and synchronize the initiation and duration of the discharge with the integration timing of the CCD array. Comparison of the time constants of heating for the pure N_2 discharge with the argon-nitrogen mixture will show if the temporal method to identify heating mechanisms is valid with the second positive system in argon.

Results for the temporal evolution of T_g in argon with 10% N_2 are shown in Figure 5 with error bars estimated from a 95% confidence interval from the fitting procedure and repeatability of experimental results in terms of variation in the percentage of N_2 added. A decrease in temperature from 1000 K to around 700 K occurs within the first millisecond, followed by a slow increase in T_g to reach the final temperature measured after 300 s of 790 K.

Although the decrease in T_g within the first millisecond is a repeatable experimental result, no logical explanation can be provided as to why this might be physically occurring, and instead it is assumed to be an aberration of the rovibrational band fitting method, possibly related to a settling time for electron impact and metastable resonant energy transfer balance. A spike in impedance, hence post-match voltage, is observed during breakdown for argon with 10% N_2 , but this is insufficient by itself to account for the reversal in trend for T_g in the first millisecond.

The time constant fit line for T_g in argon with 10% N_2 is given in Equation (19) and is overlaid on the data in Figure 5

FIG. 5. Temporal evolution of T_g for a 60 W, 1.5 Torr argon with 10% N_2 discharge. Overlaid on the data are fit lines given in Equation (19) (solid black line) and Equation (20) (dashed grey line).

as a solid black line. The initial temperature of 690 K (first term on the RHS of Equation (19)) is chosen arbitrarily to allow for the initial decrease in temperature to be fitted, and the second term on the RHS accounts for the initial decrease in T_g

$$T_g = 690 + 380e^{-\frac{t}{1 \times 10^{-4}}} + 40(1 - e^{-\frac{t}{10}}) + 60(1 - e^{-\frac{t}{100}}). \quad (19)$$

A second time constant fit line for T_g in argon with 10% N_2 ignoring the initial increase in temperature in the first millisecond is given in Equation (20) and is overlaid on the data in Figure 5 as a dashed grey line. Here, the initial temperature is assumed to be ambient $T_0 = 300$ K (first term on the RHS) with a fast increase in temperature with a time constant of 80 μ s. This time constant has been chosen to be the same as that found in the N_2 study⁵⁵ and found to be from collisional heating,⁵⁶

$$T_g = 300 + 390(1 - e^{-\frac{t}{8 \times 10^{-5}}}) + 40(1 - e^{-\frac{t}{10}}) + 60(1 - e^{-\frac{t}{100}}). \quad (20)$$

Regardless of the treatment of the initial settling period, T_g in argon with 10% N_2 has two distinct heating periods with time constants $\tau_2 = 10$ s and $\tau_3 = 100$ s, respectively (last two terms in Equations (19) and (20)). These are similar to the time constants of $\tau_2 = 8$ s and $\tau_3 = 100$ s in pure N_2 , demonstrating the same heating mechanisms are present. Therefore, although the absolute values of temperature may not be exactly accurate, the temporal trend of neutral gas temperature estimates from the second positive system of N_2 is not affected by Ar^* resonant energy transfer, and this method may be used to identify heating mechanisms present.

Similarly, a spatiotemporal study of neutral gas temperature can identify locations where gas heating is more prominent, to further aid in the identification of heating mechanisms within a discharge, for example.⁵⁶ A previously performed spatiotemporal profile of a 60 W, 1.5 Torr N_2 discharge in Pocket Rocket over the first 100 s of operation confirmed three distinct heating mechanisms with time constants of 80 μ s, 10 s, and 100 s from collisional heating, discharge

tube wall heating, and experimental housing heating, respectively.⁵⁶ Being surface heating effects, the intermediate and slow heating mechanisms with time constants of 10 s and 100 s were observed to be more pronounced in the vicinity of the walls, whereas the fast heating from collisions with time constant $80 \mu\text{s}$ was evenly distributed across the discharge volume.

The spatiotemporal profile of gas temperature in a 60 W, 1.5 Torr total plenum pressure argon discharge with 10% N_2 added, is analyzed to confirm if Ar^* resonance energy transfer affects the spatial distribution of neutral gas temperature estimates. The experimental setup used is the same as previously described in Greig *et al.*⁵⁶ The first 100 s of discharge operation is recorded with a temporal resolution of 1 s. A set of baffles used to restrict the optical image and separate heating mechanisms occurring in the central bulk discharge region and near the thruster walls.

Using the convention of the axial centerline of the thruster as $r=0 \text{ mm}$, the three regions of interest analyzed are the center of the discharge ($r_1=0\text{--}1.1 \text{ mm}$), a broad annular region near the walls encompassing the sheath and some of the plasma bulk ($r_2=0.8\text{--}2.1 \text{ mm}$), and a narrow annular region near the walls ($r_3=1.4\text{--}2.1 \text{ mm}$) encompassing just the sheath region based on previous estimates for sheath width of up to 0.6 mm .⁵⁷ The broad wall region is used as well as the narrow region for comparison, as the brightness of the discharge in the sheath region is significantly lower than in the plasma bulk, and noise in the rovibrational spectra may introduce errors in the temperature estimates.

Spatiotemporal results for neutral gas temperature in argon with 10% nitrogen added are given in Figure 6. Measured temperatures at each spatial and temporal coordinate recorded are shown as filled circles, with corresponding error bars based on a 95% confidence interval from the fitting procedure shown as thin black lines. Colours indicating temperature and an extrapolated grid connecting the measurement points are also included as visual aids.

During the first 1 s of operation, the temperature has increased to between 790 K and 860 K across the entire

radius. After 100 s, the temperature near the walls has risen to 1060 K, while the temperature in the center of the discharge has increased to a lower value of 910 K. These results are in agreement with the pure N_2 results, showing the fast heating within the first second was uniform across the discharge radius and the slower surface heating effects were more pronounced at later time in the vicinity of the walls where the heating mechanisms are localized.⁵⁶

Time constant fitting lines of the form given in Equation (18) applied to the spatiotemporal data for each of the three regions of interest are shown in Equation (21), and are overlaid on the experimental data in Figure 6 as dashed black lines. $T_{g1-\text{Ar}}$ is the gas temperature in region r_1 , $T_{g2-\text{Ar}}$ is the gas temperature in region r_2 , and $T_{g3-\text{Ar}}$ is the gas temperature in region r_3 . Again, fast heating below 1 s is not directly resolved here, and $\tau_{1\text{Ar}} = 80 \mu\text{s}$ is approximated for all three spatial regions, based on the previous results in N_2 .⁵⁵

$$T_{g1-\text{Ar}} = 300 + 480(1 - e^{-\frac{t}{8 \times 10^{-5}}}) + 80(1 - e^{-\frac{t}{10}}) + 90(1 - e^{-\frac{t}{100}}), \quad (21a)$$

$$T_{g2-\text{Ar}} = 300 + 540(1 - e^{-\frac{t}{8 \times 10^{-5}}}) + 120(1 - e^{-\frac{t}{10}}) + 100(1 - e^{-\frac{t}{100}}), \quad (21b)$$

$$T_{g3-\text{Ar}} = 300 + 540(1 - e^{-\frac{t}{8 \times 10^{-5}}}) + 120(1 - e^{-\frac{t}{10}}) + 130(1 - e^{-\frac{t}{100}}). \quad (21c)$$

The time constants are the same for all spatial coordinates as expected, as the same three dominant heating mechanisms are present throughout the volume. The time constants are also the same as those identified in the volume average temporal study, further validating that the metastable energy transfer does not affect the trend of the temperature, but only the absolute value.

Unlike the volume averaged steady-state and temporal studies, the spatial distribution of metastable argon atoms within the discharge may affect the spatial trend of temperature. Spatial regions with a higher population of metastable atoms may result in increased over-estimation of temperature when compared to regions with lower metastable populations. The spatially resolved metastable population density is estimated through imaging of the 811 nm argon spectral emission line. This line is not produced directly through spontaneous emission of a metastable state as the selection rules forbid this, but is rather the decay from the $2p_9$ state. The $2p_9$ state is predominantly populated by electron collisions from the $1s_3$ and $1s_5$ metastable states,⁵⁸ hence emission from the $2p_9$ states gives an indication of the metastable population density within the discharge.

Figure 7 shows the normalized emission line intensity profile across the discharge tube radius for 488 nm (Ar^+) and 811 nm (Ar^*), captured using an ICCD camera looking through the rear plenum view port. These profiles show that both the argon ions (plasma density) and argon metastable atom density peak on the centerline of the discharge tube, decreasing with the radial distance towards the walls at -2.1 mm and $+2.1 \text{ mm}$. A similar profile for electron density

FIG. 6. Spatiotemporal profile T_g in argon with 10% N_2 , during the first 100 s of operation at 60 W and 1.5 Torr. Measured temperatures are filled circles with colouring indicative of temperature. Error bars are shown as thin black lines and an extrapolated grid is included for clearer visualisation of the data. Thicker dashed black lines represent fit lines for T_g given in Equations (19).

FIG. 7. Normalized, phase averaged Ar^+ 488 nm (blue circles) and Ar^* 811 nm (red diamonds) emission line intensity imaged with an ICCD camera viewed through the rear plenum viewport, for a 40 W, 1.5 Torr argon plasma. The intensity profiles are indicative of the density of argon ions and argon metastable atoms radially within the discharge.

within the Pocket Rocket discharge was also previously identified.³⁵

Hence, it is highly unlikely that the increased temperature near the walls is enhanced purely due to the metastable influence, which is also supported by the fact the temperature near the walls increases more for a pure N_2 discharge when metastable energy transfer effects are not in effect. Also, as the plasma density and metastable argon density follow similar profiles, the spatiotemporal trend is not likely highly affected by the spatial distribution of metastable argon within the discharge. Therefore, spatiotemporal studies of gas temperature can be performed with the N_2 second positive system for argon-nitrogen discharges as an indication of heating locations for heating mechanism identifications, despite the absolute gas temperatures potentially being overestimated.

VI. CONCLUSIONS

Rovibrational spectroscopy band fitting is a technique for estimating neutral gas temperature of molecular discharges, or atomic discharges with trace amounts of a diatomic molecule added. The nitrogen second positive system ($\text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g$) is one of the most commonly used bands based on the simplicity of simulating the spectra for fitting. However, resonant energy transfer between Ar^* and N_2 molecules may affect temperature measurements made using the second positive system for argon- N_2 mixtures.

The effect of Ar^* resonance energy transfer was investigated by analyzing neutral gas temperatures of argon- N_2 mixtures estimated using rovibrational band fitting of the N_2 second positive system, for N_2 percentages from 1% to 100%. Results showed neutral gas temperature estimates were higher than expected for greater than 5% N_2 addition in argon. Neutral gas temperature estimates for argon with less than 5% N_2 addition gave reasonable values compared with an analytic model for charge exchange collisional heating,³ and can therefore be considered reliable estimates.

Volume averaged temporal and spatiotemporal studies of argon with 10% N_2 discharges demonstrated similar

findings to studies performed with pure N_2 discharges. Therefore, although the absolute gas temperature values may not be accurate with higher percentages of N_2 addition, temporal and spatial trends can still be used to identify aspects of the discharge such as heating mechanisms, in cases when the simplicity of the N_2 second positive system is preferred over the N_2 first positive system.

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