Effects of helium upon electron beam excitation of N_2^+ at 391.4 and 427.8 nm

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Relativistic electron beam interactions with very small ratios of nitrogen to helium (10^{-1}–10^{-4}) have been found to produce extremely large N_2^+ ($B\,^2\Sigma_u^+$–$X\,^2\Sigma_g^+$) intensities at 391.4 and 427.8 nm, compared to line intensities originating from helium. These results occurred in the total pressure regime of 0.1–500 Torr. The pressure scaling results presented here are inconsistent with previously proposed kinetic mechanisms for the N_2^+ laser pumped by helium. With a simple model of the chemical kinetics, we show that this effect is due to the collisional transfer of energy between excited states of helium atoms and the ground state of N_2^+.

It is well known that population inversions of the $B\,^2\Sigma_u^+$–$X\,^2\Sigma_g^+$ electronic transition of N_2^+ can be achieved in the presence of helium.[1] Two possible mechanisms have been used to describe the pumping process. Collins[1] believes the upper laser level is pumped by charge transfer from He_2^+ to N_2. Kokawa *et al.*[2] believe that electron impact excitation is the dominant pump mechanism. Most of the research performed on the N_2^+ laser has involved large overall He–N_2 discharge pressures (1–36 atm)[1,2] where the presence of He_2^+ may be feasible. Investigations of lower (<50 Torr) overall pressures, however, have observed population inversions in atomic nitrogen[3,4] rather than in molecular nitrogen. Population mechanisms proposed for atomic nitrogen lasers range from excitation of nitrogen atoms by collisions between metastable excited atoms of helium (2^3S) and nitrogen molecules[3] to the recombination of electron-ion pairs.[4] In this letter, we present intensity measurements for a wide range of helium to nitrogen ratios for relativistic electron beam pumped gases in the intermediate pressure range of 0.1–500 Torr and show that these results are inconsistent with the above mentioned mechanisms. We also present a simple chemical kinetic model which is consistent with our experimental observations.

The experimental apparatus has been described previously.[5] The experiment consisted of a relativistic electron beam at a peak voltage of 300 keV, a peak current of 1 kA, and a pulse width of 300 ns. The diode consisted of a 2.5-cm-diam carbon brush cathode and a 0.025-mm titanium anode foil. The beam was injected into an aluminum vacuum vessel with lucite windows on the sides and end. The emitted light at several helium partial pressures each with nitrogen partial pressures of 0.1, 1, and 10 Torr was sampled axially. The light was analyzed by a 0.275-m spectrograph coupled to an optical multichannel analyzer (OMA). The OMA was gated with pulses of 50 and 500 ns.

For all experiments where helium was present with small to large amounts of nitrogen, two very intense lines were observed at 391.4 and 427.8 nm. These lines correspond to the (0–0) and (0–1) vibrational transitions in the first negative band of N_2^+, $B\,^2\Sigma_u^+$–$X\,^2\Sigma_g^+$. Lines originating from atomic or molecular helium had negligible intensities for these cases. When no nitrogen was present, the major lines were attributed to neutral atomic helium at 388.8, 447.1, 501.5, and 587.5 nm. In time-resolved studies performed with OMA gates of 50 ns delayed by 20 ns for each pulse, the N_2^+ light emission was found to follow the beam voltage after the initial rise time (see Fig. 1). During the time-resolved studies, no other lines were observed except for the 391.4- and 427.8-nm nitrogen lines. Figure 2 shows the relative intensity of the 391.4-nm band as a function of helium to nitrogen ratio for nitrogen partial pressures of 0.1, 1, and 10 Torr. Figure 3 shows similar results for the 427.8-nm band.

As seen in Figs. 2 and 3, the largest light intensities at 391.4 and 427.8 nm for a given pressure of nitrogen occur for the largest ratio of He/N_2. That is, the more helium present, the more light is produced up to total pressures of about 300 Torr where the intensity levels off. The linear portion of the curves corresponds to a slope of about 1 for the range of total

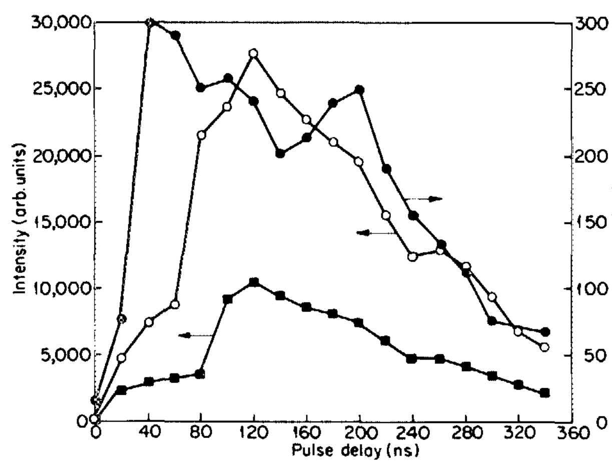

FIG. 1. Beam voltage (●) and 391.4 nm (○) and 427.8 nm (■) emission band intensities as a function of time. The partial pressures of N_2 and helium were 0.5 and 100 Torr. Optical multichannel analyzer gates were 50 ns and times plotted are for the center of the gate.

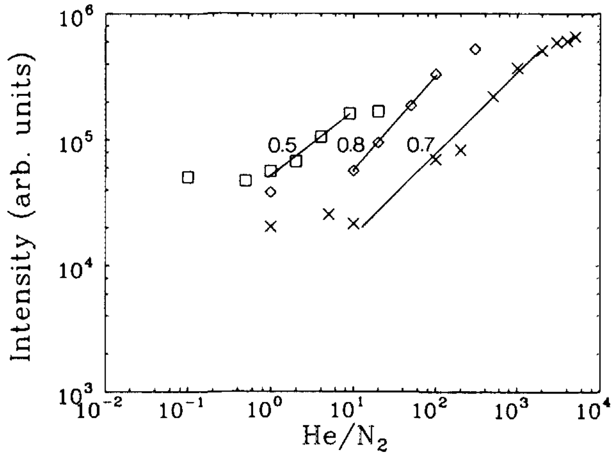

FIG. 2. Intensity of the 391.4-nm emission band as a function of He/N_2 ratio for N_2 pressures of 0.1 Torr (×), 1 Torr (◇), and 10 Torr (□). The slopes of the linear portions of the curves are as indicated.

pressure 10–300 Torr for the cases where the N_2 partial pressure was 1 and 0.1 Torr. The slope was 0.5 when the partial pressure of N_2 was 10 Torr. For cases where the helium partial pressure is smaller or about the same as the nitrogen partial pressure, there is very little increase in the intensity of the N_2^+ lines compared to the case of nitrogen alone.

As mentioned previously, the largest intensity lines observed when no added nitrogen was present were 388.8, 447.1, 501.5, and 587.5 nm. In the case of the 388.8-nm line, the energy of this transition is very close to that of the N_2^+ 391.4-nm band. Therefore, a possible mechanism for the excitation of this band is

$$N_2^+ (X\,^2\Sigma) + \mathrm{He}(3^3P) \xrightarrow{k_1} N_2^+ (B\,^2\Sigma) + \mathrm{He}(2^3P), \quad (1)$$

where k_1 is the reaction rate constant. Since the slope of the log of the intensity as a function of the log of He/N_2 is close to 1 for the small N_2 partial pressure cases, there appears to be a one to one correspondence between the number of photons emitted for the given bands and the number of helium atoms present, above a particular helium to nitrogen threshold. This one to one correspondence is consistent with reaction (1) as illustrated by a simple kinetic model. Assume that the electron beam excites the helium from the ground state to the 3^3S state as follows:

$$\mathrm{He}(1^1S) + e_b \xrightarrow{k_2} \mathrm{He}(3^3P) + e, \quad (2)$$

where k_2 is the rate constant for reaction (2) and is a function of the electron beam energy. At low pressures, the main deactivation mechanism of He(3^3P) and N_2^+ ($B\,^2\Sigma$) is radiative decay.

$$\mathrm{He}(3^3P) \xrightarrow{k_3} \mathrm{He}(2^3S) + h\nu_{388.8\,\mathrm{nm}}, \quad (3)$$

$$N_2^+ (B\,^2\Sigma) \xrightarrow{k_4} N_2^+ (X\,^2\Sigma) + h\nu_{391.4\,\mathrm{nm}}. \quad (4)$$

Note that He(2^3S) is a metastable state. We also make the following assumptions: all back reactions are negligible, collisional decay of He(3^3P) is unimportant because the exchange reaction $\mathrm{He}(3^3P) + \mathrm{He}(2^3S) \rightarrow \mathrm{He}(2^3S) + \mathrm{He}(3^3P)$ does not alter the He(3^3P) concentration, the collisional quenching of N_2^+ ($B\,^2\Sigma$) is unimportant for low pressures (although this assumption is discussed later), and that the electron beam density can be approximated by an exponential of the form $[e_b] = [e_b]^0(e^{-w_1 t} - e^{-w_2 t})$ where $[e_b]^0$ is some constant characteristic of the beam density and w_1 and w_2 are constants which describe the beam current temporal profile. We now write a differential equation for He(3^3P) as

$$\frac{d\,[\mathrm{He}(3^3P)]}{dt} = k_2[\mathrm{He}(1^1S)]\,[e_b]^0(e^{-w_1 t} - e^{-w_2 t}) - k_3[\mathrm{He}(3^3P)] - k_1[\mathrm{He}(3^3P)]\,[N_2^+ (X\,^2\Sigma)]. \quad (5)$$

Now assume that the ground-state populations He(1^1S) and N_2^+ ($X\,^2\Sigma$) stay approximately constant. Then a linear, homogeneous, ordinary differential equation exists for [He(3^3P)] and can be solved using standard techniques. The solution is

$$[\mathrm{He}(3^3P)] = A\left(\frac{e^{-w_1 t} - e^{-kt}}{k - w_1} - \frac{e^{-w_2 t} - e^{-kt}}{k - w_2}\right), \quad (6)$$

where $k = k_1[N_2^+ (X\,^2\Sigma)] + k_3$ and $A = k_2[\mathrm{He}(1^1S)] \times [e_b]^0$. We can also write the rate equation for $[N_2^+ (\mathrm{B}\,^2\Sigma)]$.

$$\frac{d\,[N_2^+ (B\,^2\Sigma)]}{dt} = k_1[N_2^+ (X\,^2\Sigma)]\,[\mathrm{He}(3^3P)] - k_4[N_2^+ (B\,^2\Sigma)]. \quad (7)$$

Substituting [He(3^3P)] from Eq. (6) and solving for $[N_2^+ (B\,^2\Sigma)]$ gives

$$[N_2^+ (B\,^2\Sigma)] = k_1[N_2^+ (X\,^2\Sigma)]\,[\mathrm{He}(1^1S)]\,[e_b]^0 \times\left(\frac{(w_2 - w_1)(e^{-kt} - e^{-k_4 t})}{(k - w_2)(k - w_1)(k_4 - k)} + \frac{e^{-w_1 t} - e^{-k_4 t}}{(k - w_1)(k_4 - w_1)} - \frac{e^{-w_2 t} - e^{-k_4 t}}{(k - w_2)(k_4 - w_2)}\right). \quad (8)$$

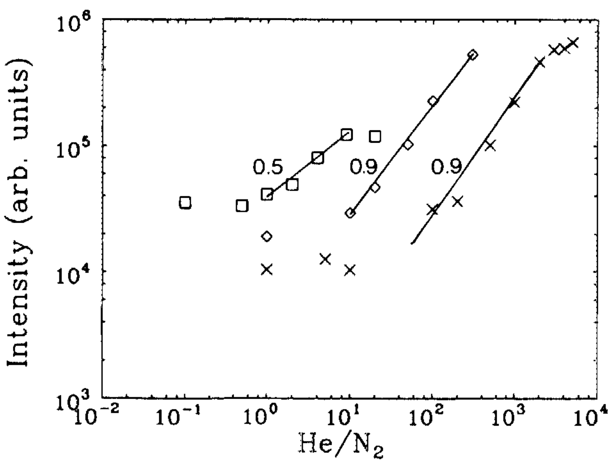

FIG. 3. Intensity of the 427.8-nm band emission as a function of He/N_2 ratio for N_2 pressures of 0.1 Torr (×), 1 Torr (◇), and 10 Torr (□). The slopes of the linear portions of the curves are as indicated.

A rate equation for the time rate of change of the photon emission at 391.4 nm can be written as

$$\frac{d\,[h\nu_{391.4\,\mathrm{nm}}]}{dt} = k_4[N_2^+ (B\,^2\Sigma)]. \tag{9}$$

Substituting the results of Eq. (8) gives

$$\frac{d\,[h\nu_{391.4\,\mathrm{nm}}]}{dt} = k_2k_4k_1[N_2^+ (X\,^2\Sigma)][\mathrm{He}(1\,^1S)][e_b]^0 \times\left(\frac{(w_2 - w_1)(e^{-kt} - e^{-k_4t})}{(k - w_2)(k - w_1)(k_4 - k)} + \frac{e^{-w_1t} - e^{-k_4t}}{(k - w_1)(k_4 - w_1)} - \frac{e^{-w_2t} - e^{-k_4t}}{(k - w_2)(k_4 - w_2)}\right). \tag{10}$$

Thus, the emission rate for $N_2^+ (B\,^2\Sigma\text{–}X\,^2\Sigma)$ is linearly proportional to the He ground-state concentration, the electron beam density, and the ground-state population of N_2^+. If collisional quenching of $N_2^+ (B\,^2\Sigma)$ is included as

$$N_2^+ (B\,^2\Sigma) + M \xrightarrow{k_{4'}} N_2^+ (X\,^2\Sigma) + M, \tag{11}$$

then k_4 in Eq. (10) would be replaced by $k' = k_4 + k_{4'}[M]$, where M is any collisional partner such as He or N_2. Equation (10) would then have a more complicated dependence upon helium concentration than the simple linear one shown here. Obviously, to best investigate the effects of collisional de-excitation and to remove the assumption that $N_2^+ (X\,^2\Sigma)$ and He$(1\,^1S)$ remain constant would require accurate rate constants and a computer solution of the differential equations.

Another important result of the data shown in Figs. 2 and 3 is that as the nitrogen partial pressure increases, the overall amount of line enhancement decreases, as well as the slope of the linear part of the intensity versus pressure ratio curves. For nitrogen partial pressures of 0.1 Torr, the emitted intensity increases by almost a factor of 100 whereas for nitrogen partial pressures of 10 Torr, the overall increase is less than a factor of 10 compared to the no helium case. It appears that a very important collisional depopulating mechanism of $N_2^+ (B\,^2\Sigma)$ is collisions with other nitrogen molecules.

Never at any time was emission due to He_2 or postulated He_2^+ (see Ref. 6) observed. This, in addition to the fact that the highest overall pressure examined was 500 Torr, leads to the conclusion that charge transfer between He_2^+ was probably negligible, also since for example the 388.8-nm helium line which populates the metastable state of helium was not observed to increase or decrease with the 391.4-nm band, in contrast to the results of Atkinson and Sanders.[3] Instead, the 388.8-nm helium line was observed only in the absence of nitrogen, thus it is doubtful that direct transfer between the metastable state of helium (2^2S) and the $N_2^+ (B\,^2\Sigma)$ was significant. Kokowa *et al.*,[2] claim that electron impact ionization is the major pumping process and that the presence of helium only helps to raise the electron temperature rather than supplying reactants for the pumping process. The results presented here show a definite helium dependency, particularly since we have shown previously[5] that the electron temperature is pressure insensitive for our *e*-beam produced discharges.

Relativistic electron beam produced plasmas in helium-nitrogen mixtures produce very large intensity lines at 391.4 and 427.8 nm. These lines originate from the vibrational transition of (0–0) and (0–1) in the first negative system of N_2^+. The line intensities increase as the ratio of helium to nitrogen increases. The greatest increase is seen for the lowest nitrogen concentrations. The increased intensity is linear with helium pressure between the total pressure of 10–300 Torr for small partial pressures (0.1–1.0 Torr) of nitrogen. This increase is believed to be due to collisional transfer of energy between helium excited states and the N_2^+ ground state as shown by the agreement between our simple kinetic model and experimental results.

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[1]C. Collins, IEEE J. Quantum Electron. **QE-20**, 47 (1984).
[2]M. Kokawa, M. Saito, S. Horiguchi, and T. Nakaya, J. Phys. D **18**, 177 (1985).
[3]J. Atkinsen and J. Sanders, J. Phys. B (Proc. Phys. Soc.) Ser. 2, **1**, 1171 (1968).
[4]G. Cooper and J. Verdeyen, J. Appl. Phys. **48**, 1170 (1977).
[5]M. Brake, T. Repetti, K. Pearce, and R. F. Lucey, Jr., J. Appl. Phys. **60**, 99 (1986).
[6]J. Tucker, M. Brake, and R. Gilgenbach, J. Appl. Phys. **59**, 2251 (1986).