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Optical emission study of nonthermal plasma confirms reaction mechanisms involving neutral rather than charged species

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Charge transfer reactions are commonly used to explain NO_x conversion in nonthermal plasma. An analysis of optical emission spectra induced by pulsed corona discharge in NO_x-containing argon suggests that, in fact, the contribution of charge transfer reactions to NO_x conversion in nonthermal plasma is negligible. During electrical discharge in such gas mixtures, NO(*B*), an electronic excited state of NO formed due to the dissociative recombination reactions of NO₂⁺ and N₂O⁺ and the optical emission of NO(*B*) could be a proof that cations are responsible for NO_x conversion. However, the optical emission of NO(*B*) is not observed, leading to the conclusion that cations are not involved to any measurable degree. Therefore, charge transfer reactions cannot play a significant role in nonthermal plasma largely because the cations are neutralized with electrons before any charge transfer reactions can occur and concentrations of radicals are far higher than those of cations, which inhibits charged particle reactions. Instead, neutral active species, such as atoms, molecular fragments, and excited molecules, are the major active species contributing to nonthermal plasma reactions. © 2007 American Institute of Physics. [DOI: 10.1063/1.2434002]

I. INTRODUCTION

Short-duration high-voltage pulses in a wire-cylinder reactor produce nonhomogeneous electric fields that induce nonthermal plasma used for conversion of nitrogen oxides (NO_x). When the wire electrode is positively charged, the induced plasma channels are positive streamers that propagate from the wire anode to the cylinder cathode; the discharge pulse itself is then called a positive corona discharge. The pulse duration of the corona discharge is less than 100 ns,^{1–3} and is defined as the pulse-on period. The energetic electrons in the streamer excite gas molecules and produce three kinds of chemically active species, metastable excited states, radicals, and cations, through the following reactions:

where the asterisk denotes an excited molecule. These active species contribute to the conversion of nitrogen oxides in between discharge pulses (the pulse-off periods).

The ions produced from (3) mainly react with molecules through charge transfer reactions, for example,

The cations CD⁺ formed from charge transfer reactions can be dissociated through dissociative recombination reactions with electrons

Extensive experimental and theoretical work^{4–6} has shown that the rate constant of dissociative recombination reaction (5) is at least on the order of 10¹⁷ cm³ mol^{−1} s^{−1}, which is more than three orders of magnitude higher than the rate constants of radical reactions and reactions of neutral species in electronic excited states, that is, about 10¹⁴ cm³ mol^{−1} s^{−1}, based on the kinetic limit of these active species at room temperature. Therefore, NO_x may be converted through two reaction pathways: (I) charge transfer reaction (4) and subsequent dissociative recombination (5) involving positive ions and (II) reaction with neutral active species, including atoms, molecular fragments, and excited molecules, which are produced from direct electron collision reactions (1) and (2).

The contribution of ions to NO_x conversion has been debated in the literature. For example, Chang⁷ compared the rate constants of charge transfer reactions and radical reactions and found that the probabilities of charge transfer reactions are a few orders of magnitude larger than radical reactions. He concluded that charge transfer reactions (path I) play an important role in the NO_x decomposition processes. In contrast, on the basis of abundant experimental and theoretical experience, Kogelschatz⁸ proposed that charged particle reactions are negligible in nonthermal plasmas at atmospheric pressure and that neutral active species, such as atoms, molecular fragments, and excited molecules, are the major active species contributing to nonthermal plasma reactions (path II). van Veldhuizen *et al.*⁹ analyzed the relative

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importance of ions and radicals for NO conversion in a pulsed corona reactor and concluded that the ion contribution to NO conversion (path I) is approximately 10%–20% of the radical contribution (path II). However, their theoretical calculation of NO conversion based on this conclusion was 10–100 times lower than the experimentally observed values. Recently, Hu *et al.*¹⁰ proposed that cations N_2^+ and atomic N radicals are responsible for NO_x (NO, NO_2 , and N_2O) conversion in nonthermal N_2 plasma. However, this reaction mechanism was unable to account for byproduct concentrations as a function of power input, e.g., N_2O in reactant mixtures of NO and N_2 or NO in reactant mixtures of NO_2 and N_2 . Later, Zhao *et al.*^{11,12} found that only two active species, $N_2(A^3\Sigma_u^+)$, which is the first electronic excited state of molecular N_2 , and N radicals, are responsible for NO_x conversion in nonthermal N_2 plasma and that N_2^+ is not involved. Using a reaction mechanism that includes only $N_2(A^3\Sigma_u^+)$ and N radicals, while excluding cations such as N_2^+ , Zhao *et al.*^{11,12} predicted all experimental data in the paper of Hu *et al.*,¹⁰ which further confirms that N_2^+ does not contribute to NO_x conversion. A similar reaction mechanism involving only the neutral active species can also predict the effect of CO, O_2 , and CO_2 on NO_x conversion in nonthermal nitrogen plasmas.^{11,13–15} More recently, however, Hu *et al.*¹ proposed that Ar^+ is the only active species responsible for NO_x conversion in low (ppm) concentrations of NO_x in Ar, but was unable to demonstrate that such a reaction mechanism can predict the effect of CO on NO_x conversion in nonthermal Ar plasma.

Although the reaction mechanism involving ions could not explain the experimental results, no reports with direct experimental evidence exclude the contribution of ions. The products of dissociative recombination reaction (5) depend on the reactant ions. For atomic ions such as Ar^+ , electron-ion reaction produces both ground state argon atoms ($\sim 65\%$) and metastable atomic excited states ($\sim 35\%$).¹⁶ For diatomic ions, the main products of electron-ion reactions are dissociated atoms and atomic excited states.⁶ For example, NO^+ is dissociated by electrons into ground state atomic O and N and excited state $N(^2D)$;^{17,18} N_2^+ is dissociated into ground state N and excited states $N(^2D)$ and $N(^2P)$;^{19,20} and O_2^+ is dissociated into ground state O and excited states $O(^1D)$ and $O(^1S)$.^{21,22} For polyatomic ions, the main products of electron-ion reaction are dissociated atoms, polyatomic radicals, molecules, and their excited states.⁴ Others^{23,24} found that NO_2^+ and N_2O^+ can be dissociated into the excited states of NO such as NO(B) and NO(A) by dissociative recombination reactions with electrons. Therefore, almost all cations can be dissociated into atomic or molecular excited states, which can emit photons through radiative emission to their respective ground state, if these excited states have short enough natural radiative lifetimes. For example, the optical emissions of $N(^2D)$, $N(^2P)$, $O(^1D)$, and $O(^1S)$ are not observed at atmospheric pressure because their natural radiative lifetimes are longer than 0.7 s.²⁵ However, the optical emission of NO(B) and NO(A) can be observed because their natural radiative lifetimes are short enough ($< 2 \mu s$).^{26,27} These facts led us to explore the importance of charge transfer reactions in nonthermal plasma

using optical emission measurements. The optical emission of NO(B) and NO(A) resulting from dissociative recombination reactions of NO_2^+ and N_2O^+ should be observable if charge transfer reactions are important for NO_x conversion in nonthermal plasma (path I).

The goal of this work is to evaluate the importance of ionic reactions (mainly charge transfer reactions) in nonthermal plasma with argon as a background gas by optical emission measurements. Although most NO_x containing gases are combustion exhaust gases that contain predominantly nitrogen, oxygen, water, and CO_2 ,^{9,28} argon is chosen as a background gas for two reasons. First, argon has a very low dielectric strength (0.18) that is just higher than that of helium (0.15), which has the lowest dielectric strength of any gas.²⁹ This implies that argon is one of the most easily ionized species in nonthermal plasma. Although the first ionization energy of argon (15.76 eV) is larger than most diatomic and polyatomic molecules, including N_2 (15.58 eV), O_2 (12.06 eV), NO (9.25 eV), CO_2 (13.77 eV), NO_2 (9.79 eV), and N_2O (12.89 eV),³⁰ the rotational and vibrational degrees of freedom offered by diatomic and polyatomic molecules effectively deactivate energetic electrons within one mean free path length, resulting in greater energy dissipation compared to monoatomic gases.³¹ Therefore, in the same electric field, electrons can build up more energy in argon than in diatomic and polyatomic gases because the electrons do not lose as much energy during elastic collisions with neutral argon. The higher energy electrons that form in argon plasma then ionize argon to a greater degree compared to other diatomic and polyatomic molecules under similar reaction conditions. If ionic reactions in argon nonthermal plasmas are shown to be unimportant, the ion concentrations in other gases are expected to be even lower and result in similarly negligible ionic reactions. Therefore, argon should provide general results. The second reason for selecting argon is the simplicity of the analysis. The active species formed from electron collision reactions with argon are relatively simple because no molecular dissociation reaction (2) occurs. Since molecular argon species, such as Ar_2^+ , are not formed from direct electron collision reactions,³² the only possible active species are Ar^+ and the excited atomic states of argon.

II. EXPERIMENTAL SECTION

Figure 1 shows the experimental setup. A similar pulsed corona discharge reactor (PCDR) has been described in detail previously.^{2,3,11–15,33} In brief overview, the PCDR consists of a high-voltage power supply, control unit, and pulser/reactor assembly. The high-voltage supply controls the pulsed power delivered to the reactor. The pulser/reactor assembly contains the pulsed power generator and the pulsed corona discharge reaction chambers. These two subassemblies are connected by a high-voltage cable for charging the capacitors in the pulsed power system and by high-pressure gas lines for controlling the voltage delivered to the reactor. Electrical and switch gas supplies are connected to the control unit; the reactor gas supply and exhaust lines are connected directly to the reactor. The reactor, consisting of two parallel reaction tubes, is fitted with UV-grade quartz win-

FIG. 1. Experimental setup.

dows for diagnostics and plasma observation. The stainless steel wire has a diameter of 0.58 mm and each tube is 93 cm long and 2.3 cm in diameter. The design permits variation and measurement of the applied voltage and its frequency, reactor current, and voltage, and discharge power and energy. The energy delivered to the reactor per pulse can be calculated from $\frac{1}{2}CV_c^2$, where C is the pulse forming capacitance (800 pF) and V_c is the constant charge voltage before discharge. The power consumed, W (J s^{-1}), is calculated as the product of the input energy per pulse and the pulse frequency.

Plasma-induced optical emissions are observed through the quartz window located 49 cm from the reactor inlet and are imaged onto the entrance slit of a 0.3 m focal length monochromator (SpectraPro-300i model). This monochromator includes a triple grating turret for 1, 2, or 3 gratings, an imaging optical system, 32 bit microprocessor controlled scanning, and micrometer controlled entrance slit. An intensified charge coupled device (ICCD) camera with a detection range of 220 to 1000 nm is mounted on the spectrometer to detect luminescence. The exposure time, entrance-slit width of the spectrometer (10 μm for these experiments), and camera gain were carefully manipulated to obtain the data.

The experimental test matrix is shown in Table I. The four reactant gas mixtures shown in Table I, including ultra-high purity (UHP) 99.999% Ar, 290 ppm N_2O in UHP Ar, 566 ppm NO in UHP Ar, and 408 ppm N_2O in UHP N_2 , are used as obtained from the manufacturer (US Airgas). The test

gas mixture is introduced into the PCDR at ambient temperature, around 300 K, and at a flow rate of $1.98 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$ (at the reactor inlet conditions). The PCDR pressure is maintained at 141 kPa by control valves on the outlet gas lines. Feed and reactor effluent samples are captured in small stainless steel cylinders and analyzed using a Spectrum 2000 Perkin Elmer Fourier transform infrared (FTIR) spectrometer with a narrow band mercury cadmium telluride (MCT) detector. All experimental data are reproducible within a $\pm 10\%$ error limit including the FTIR and flow measurement uncertainties.

III. RESULTS AND DISCUSSION

A. Optical emission

Excited active molecules (e.g., AB^*) can return to lower excited energy levels or ground states through two processes:

- (1) natural radiation of light, which sometimes produces optical emission (fluorescence) as excited electrons return to lower energy levels,

- (2) quenching by interaction with other atoms or molecules,

(6) and (7) are parallel reactions. In these chemical equations, k_0 and k_q are the rate constants of natural radiation and quenching, respectively, C is the mole concentration of the respective species, and R is the reaction rate. The rate constant of natural radiation is inversely proportional to the natural lifetime of the excited molecules. If there are n kinds of molecules in the gas mixture which can quench AB^* , the selectivity of natural radiation, S_0 , can be defined as

TABLE I. Experimental matrix.

System	Flow rate ($\text{m}^3 \text{ s}^{-1}$)	Pressure (kPa)
UHP Ar	1.98×10^{-4}	141
290 ppm N_2O in Ar	1.98×10^{-4}	141
566 ppm NO in Ar	1.98×10^{-4}	141
408 ppm N_2O in N_2	1.98×10^{-4}	141

FIG. 2. Energy level diagram of argon electronic excited states.

$$S_0 = \frac{R_0}{R_0 + \sum_{i=1}^n R_{q,i}} = \frac{k_0}{k_0 + \sum_{i=1}^n k_{q,i} C_i} 100\%, \quad (8)$$

where C_i is the concentration of species i .

From our previous experimental observations,¹¹ fluorescence is easily detected if S_0 is larger than 0.02% and if there are sufficient quantities of the excited species. The minimum detectable concentration of a species by fluorescence may be estimated from the detection limit of the instrument, which can be calculated using the SBR-RSDB approach,³⁴

$$DL = 0.03RSDB \frac{C_0}{SBR}, \quad (9)$$

where DL is the detection limit of the instrument, RSDB is the relative standard deviation of the background signal, C_0 is the analyte concentration, and SBR is the signal to background ratio. Previous experiments³⁵ in the same reactor under similar reaction conditions showed that the NO(A) intensity is 7200 counts in 150 ppm NO in N_2 , while the intensity of the background and the relative standard deviation are 120 and 20 counts, respectively. Thus, SBR is 60 and RSDB is 20 for this condition. The corresponding concentration of NO(A) calculated from a reliable reaction model¹⁴ is 3.5×10^{-6} ppm (1.42×10^{-16} mol cm^{-3}). Substituting these values into Eq. (9), results in an estimated fluorescence detection limit of about 3.5×10^{-8} ppm. Therefore, if optical emission of an excited species is not detected and S_0 for that species is larger than 0.02%, the concentration of that species is expected to be less than $\sim 3.5 \times 10^{-8}$ ppm (1.42×10^{-18} mol cm^{-3}).

B. Optical emission of UHP argon

Argon is an inert atomic gas with the ground state electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$. When highly energetic electrons collide with argon, one electron in the $3p$ orbital can be excited to a higher energy level orbital. Figure 2 shows an energy level diagram with seven groups of excited states of argon,³⁶ which correspond to one $3p$ electron ex-

cited into $4s$, $4p$, $3d$, $5s$, $5p$, $4d$, and $6s$ orbitals, as labeled in the figure. Selectivity rules based on electron spin and resonance dictate allowed transitions and energy levels. For example, a $3p$ electron may be excited to any of 4 excited states within each $4s$, $5s$, and $6s$ orbital, 10 excited states within each $4p$ and $5p$ orbital, and 12 excited states in each $3d$ and $4d$ orbital.^{36,37} The excited states in Fig. 2 are labeled with the Paschen notation,³⁸ which corresponds to the more common term symbol notation (e.g., the four $3p^5 4s$ states, in order of increasing energy, are $1s_5$, $1s_4$, $1s_3$, and $1s_2$ in the Paschen notation, which are equivalent to the term symbols 3P_2 , 3P_1 , 3P_0 , and 1P_1).

Figure 3(a) shows the optical emission of UHP argon measured between 220 and 1000 nm at a pulse frequency of 200 Hz. Similar optical emission spectra are observed at other pulse frequencies. No significant fluorescence is observed from 220 to 680 nm and from 880 to 1000 nm. Strong fluorescence is observed in the wavelength range from 680 to 880 nm, as shown in Fig. 3(b). The excited states of Ar in the PCDR were deduced by comparison of the observed optical emission spectra with the standard optical spectra of argon.³⁷

1. Optical emission from the 5p level

The excited states of Ar with an electron in the $5p$ level radiatively decay by three pathways,^{36,37,39}

The transitions from $5p$ to $3d$ and $5s$ mainly produce infrared radiation, as shown in Fig. 2, which falls outside the detection range of our apparatus. The transitions from $5p$ to $4s$ produce blue light, as shown in Fig. 2, which is within our detection range. Investigations by Inoue *et al.*³⁶ showed that about 20% of the $\text{Ar}(5p)$ radiative decay process is associated with the $\text{Ar}(5p \rightarrow 4s)$ blue transition. Table II shows the radiation emission data for the $\text{Ar}(5p \rightarrow 4s)$ transition and quenching rate constants of excited states of $\text{Ar}(5p)$ levels. Argon is the only quench atom in these experiments. The mole concentration of argon is 5.64×10^{-5} mol cm^{-3} at 141 kPa and 300 K. Using this argon concentration and published rate constants³⁶ for radiative emission and quenching by argon, the selectivities of natural radiation from the $\text{Ar}(5p)$ level are calculated from Eq. (8). As shown in Table II, S_0 for all $\text{Ar}(5p \rightarrow 4s)$ transitions are larger than 0.02%. Therefore, if electron collision reactions with argon produce appreciable $\text{Ar}(5p)$ excited states ($> \sim 3.5 \times 10^{-8}$ ppm), all blue lines corresponding to the $\text{Ar}(5p \rightarrow 4s)$ transition from 394–471 nm should be observed. However, no blue lines in this wavelength range are observed, as shown in Fig. 3, which indicates that the $\text{Ar}(5p)$ excited states are negligible in our nonthermal plasma reactor.

2. Optical emission from 3d and 5s levels

Nearly all argon $3d$ and $5s$ excited states relax into $\text{Ar}(4p)$ excited states.³⁷ Due to the close energy level spacing

FIG. 3. Optical emission spectra of UHP Ar at the pulse frequency of 200 Hz.

between $\text{Ar}(3d,5s)$ and $\text{Ar}(4p)$, the wavelengths of most of the numerous emission lines between these levels are larger than 1000 nm (Ref. 37) and fall outside the detection range of our apparatus. However, four lines with wavelengths of 887.5 and 934.1 nm [$\text{Ar}(3d \rightarrow 4p)$ transitions] and 919.5 and 929.2 nm [$\text{Ar}(5s \rightarrow 4p)$ transitions] could be detected, if present. The natural radiation lifetimes of each $\text{Ar}(3d)$ and $\text{Ar}(5s)$ states are about 50 ns.^{36,40} There are no reports on the quenching rate constants of the $\text{Ar}(3d)$ and $\text{Ar}(5s)$ states by argon. However, the energy level of the $\text{Ar}(3d)$ and $\text{Ar}(5s)$ states are between the $\text{Ar}(5p)$ and $\text{Ar}(4p)$, as shown in Fig. 2. The quenching rate constants of the $\text{Ar}(3d)$ and $\text{Ar}(5s)$ states by argon should be on order of the quenching rate constants of the $\text{Ar}(5p)$ and $\text{Ar}(4p)$ levels, which are $\sim 10^{13} - 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, as shown in Tables II and III.^{36,38,41} For the upper limit of $10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as the quenching rate constant for $\text{Ar}(3d)$ and $\text{Ar}(5s)$ states, which is approximately the kinetic limit of the quenching reaction at room temperature, S_0 from Eq. (8) for the $\text{Ar}(3d)$ and $\text{Ar}(5s)$ states is about 0.35%, which is much larger than the limit of 0.02%. Therefore, if electron collision reactions with argon produce appreciable $\text{Ar}(3d)$ and $\text{Ar}(5s)$ excited states, these four lines should be detected between 880 and 940 nm. Again, these lines are not observed, as shown in Fig. 3. Therefore, no appreciable quantities of $\text{Ar}(3d)$ or $\text{Ar}(5s)$ excited states appear to be formed.

3. Optical emission from 4p levels

Deactivation of $\text{Ar}(4p)$ to the ground state is improbable and does not appreciably occur.³⁸ Therefore, the $\text{Ar}(4p)$ states can only relax into $\text{Ar}(4s)$ states by radiative emission, which mainly produce light at red wavelengths, as shown in Fig. 2. Using the known argon concentration and published rate constants^{38,41} of radiative emission and quenching of $\text{Ar}(4p)$ by argon as shown in Table III, S_0 can be calculated

from Eq. (8). S_0 for all the $\text{Ar}(4p \rightarrow 4s)$ transition are 1.3%–5.2% (Table III), which is roughly two orders of magnitude larger than 0.02%. As shown in Fig. 3(b) and Table III, the principle optical emission peaks of all the $\text{Ar}(4p)$ excited states except $\text{Ar}(2p_{10})$ are detected, which indicates that the $\text{Ar}(4p)$ excited states are formed in our nonthermal plasma reactor in appreciable amounts.

The principal products of $\text{Ar}(4p)$ quenched by argon are $\text{Ar}(4s)$ level excited states.^{38,42} Tachibana⁴³ showed that 25–40% of the total excitation of the $\text{Ar}(4p)$ levels cascades to each of the $1s_5$, $1s_4$, and $1s_2$ levels, while the contribution to the $1s_3$ level only amounts to about 7% because the number of allowed transitions to this level is small.

4. Optical emission from 4s levels

The four excited states of the $\text{Ar}(4s)$ level can be quenched by argon through both two-body and three-body quenching reactions.^{44,45} Table IV shows radiative emission data for the $\text{Ar}(4s \rightarrow \text{ground state})$ transition and quenching rate constants of $\text{Ar}(4s)$ levels. Two excited states, $\text{Ar}(1s_4)$ and $\text{Ar}(1s_2)$, have a natural radiation lifetime of less than 10 ns. For these states, S_0 calculated from Eq. (8) are higher than 90%. However, both of them emit light at ~ 100 nm, beyond the minimum detection limit of 220 nm for our detector. The other two excited states, $\text{Ar}(1s_5)$ and $\text{Ar}(1s_3)$, are predominantly quenched by argon because of long natural radiation lifetimes (38–45 s).^{46–49} Although the $\text{Ar}(4s)$ levels are undetectable with our apparatus, we suspect excited $\text{Ar}(4s)$ atoms are produced in large quantities from direct electron collision reactions with argon because the excitation rate coefficient of the $\text{Ar}(4s)$ levels are about twice as large as the $\text{Ar}(4p)$ levels when the electric field to gas density (E/N) ratio is $5 \times 10^{-17} - 5 \times 10^{-15} \text{ V cm}^2$,⁴³ which is a typical operation range of nonthermal plasma reactors.⁵⁰ Therefore, in addition to the $\text{Ar}(4s)$ formed from the $\text{Ar}(4p)$ decay,

TABLE II. Radiative emission data for Ar($5p \rightarrow 4s$) transitions and quenching of Ar($5p$) levels.

Upper level	Lower level	Transition branch ratio (%) ^a	Wavelength (nm) ^b	Natural lifetime (ns) ^a	k_q by Ar (cm ³ mol ⁻¹ s ⁻¹) ^a	S ₀ (%)	Obs. ^c
3p ₁	1s ₂	100	425.9	251	...	...	N
3p ₂	1s ₂	23	433.4	100	1.63 × 10 ¹⁴	0.109	N
	1s ₃	34	418.2				N
	1s ₄	4	404.4				N
	1s ₅	39	394.8				N
3p ₃	1s ₂	52	433.5	123	2.53 × 10 ¹⁴	0.057	N
	1s ₄	39	404.6				N
	1s ₅	9	394.9				N
3p ₄	1s ₂	34	434.5	145	3.37 × 10 ¹⁴	0.036	N
	1s ₃	64	419.1				N
	1s ₄	2	405.5				N
3p ₅	1s ₂	26	451.1	100	1.63 × 10 ¹⁴	0.109	N
	1s ₄	74	419.8				N
3p ₆	1s ₄	18	426.6	106	2.05 × 10 ¹⁴	0.082	N
	1s ₅	82	415.9				N
3p ₇	1s ₂	8	459.6	128	2.23 × 10 ¹⁴	0.062	N
	1s ₄	71	427.2				N
	1s ₅	21	416.4				N
3p ₈	1s ₂	6	462.8	118	2.29 × 10 ¹⁴	0.066	N
	1s ₄	64	430.0				N
	1s ₅	30	419.1				N
3p ₉	1s ₅	100	420.1	132	7.22 × 10 ¹³	0.186	N
3p ₁₀	1s ₂	34	470.2	141	3.01 × 10 ¹⁴	0.042	N
	1s ₃	26	452.2				N
	1s ₄	4	436.4				N
	1s ₅	36	425.1				N

^aReference ³⁶.^bReference ³⁷.^cLine observability. N means line not observed.

Ar($4s$), as the lowest energy excited states of argon, are expected to be formed directly by electron collision reactions even more easily than the Ar($4p$) states that are clearly detected.

Therefore, we conclude that only the Ar($4p$) and Ar($4s$) levels are formed in nonthermal argon plasma. The higher energy excited states of argon are not formed in appreciable amounts. The Ar($4p$) and Ar($4s$) excited states can be produced from two sources:

- (1) electron collision reaction [see (1)],

- (2) ionization reactions and subsequent collision-radiative recombination reactions

$$k = 1.09 \times 10^{17} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \quad (\text{Ref. 51}), \quad (12)$$

$$k = 1.81 \times 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 52}), \quad (13)$$

$$k = 5.48 \times 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 53}). \quad (14)$$

For example, Skrzypkowski *et al.*¹⁶ investigated the electron recombination reaction of Ar⁺ and detected intense near-infrared Ar lines between 700 and 850 nm originating from Ar($4p \rightarrow 4s$) transitions. However, Bultel *et al.*³² proposed that the products of the electron recombination reaction of Ar⁺ are mainly Ar($4s$) states with negligible amounts of Ar($4p$). Shiu and Biondi⁵⁴ and Kuo and Keto⁵⁵ observed appreciable optical emission of Ar($4p$) from dissociative recombination reaction of Ar₂⁺. Therefore, using only optical emission measurements with UHP argon, no conclusions can be drawn on whether the Ar($4p$) and Ar($4s$) levels shown in Fig. 3 are from direct electron collision reaction (10) or ionic recombination reactions (11)–(14).

TABLE III. Radiative emission data for Ar ($4p \rightarrow 4s$) transitions and quenching of Ar ($4p$) levels.

Upper level	Lower level	Transition branch ratio (%) ^a	Wavelength (nm) ^b	Natural lifetime (ns) ^c	k_q by Ar ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) ^d	S_o (%)	Obs. ^e
$2p_1$	$1s_2$	100	750.4	21.7	2.41×10^{13}	3.51	Y
	$1s_4$	~ 0	667.7				N
$2p_2$	$1s_2$	42.6	826.5	28.3	1.14×10^{13}	2.91	Y
	$1s_3$	33.1	772.4				Y
	$1s_4$	5.1	727.3				Y
	$1s_5$	19.2	696.5				Y
$2p_3$	$1s_2$	63.0	840.8	29.0	1.87×10^{13}	2.92	Y
	$1s_4$	24.3	738.4				Y
	$1s_5$	12.7	706.7				Y
$2p_4$	$1s_2$	43.1	852.1	29.3	2.11×10^{13}	1.25	Y
	$1s_3$	54.8	794.8				Y
	$1s_4$	0.07	747.2				N
	$1s_5$	2.1	714.7				Y
$2p_5$	$1s_2$	0	857.8	24.4	2.83×10^{13}	2.71	N
	$1s_4$	100	751.5				Y
$2p_6$	$1s_2$	13.3	922.5	29.4	2.17×10^{13}	2.50	N
	$1s_4$	11.3	800.6				Y
	$1s_5$	75.4	763.5				Y
$2p_7$	$1s_2$	3.0	935.4	30.2	4.64×10^{13}	2.79	N
	$1s_3$	7.8	866.8				N
	$1s_4$	74.4	810.4				Y
	$1s_5$	14.8	772.4				Y
$2p_8$	$1s_2$	4.5	978.5	30.6	1.93×10^{13}	3.17	N
	$1s_4$	65.7	842.5				Y
	$1s_5$	29.8	801.5				Y
$2p_9$	$1s_5$	100	811.5	30.7	1.93×10^{13}	5.19	Y
$2p_{10}$	$1s_2$	0.6	1148.8	40.5	1.20×10^{13}	3.28	N
	$1s_3$	3.6	1047.0				N
	$1s_4$	21.8	965.8				N
	$1s_5$	74.0	912.3				N

^aReference 38.^bReference 37.^cReference 39.^dReferences 38 and 41.^eLine observability. N means line not observed. Y means line observed.TABLE IV. Radiative emission data for Ar($4s \rightarrow$ Ar ground state) transitions and quenching of Ar ($4s$) levels.

Ar ($4s$) level	$1s_5$ (3P_2)	$1s_4$ (3P_1)	$1s_3$ (3P_0)	$1s_2$ (1P_1)
Natural radiation lifetime ^a	38 s	9.5 ns	44.9 s	2.5 ns
Fluorescence wavelength (nm) ^b	...	106.67	...	104.82
Two-body k_q by Ar ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) ^c	1.26×10^9	2.41×10^{10}	3.19×10^9	3.07×10^{10}
Three-body k_q by Ar ($\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$) ^c	2.17×10^{15}	2.54×10^{15}	3.01×10^{15}	9.42×10^{14}
S_o (%)	~ 0	91.7	~ 0	98.8

^aReferences 46–49.^bReference 83.^cReferences 44 and 45.

FIG. 4. Optical emission of N_2O in Ar at the pulse frequency of 200 Hz.

Recent investigations^{23,24} on the dissociative recombination of NO_2^+ and N_2O^+ with electrons showed that $NO(B)$ is formed and detected in the optical emission spectra. Therefore, if Ar^+ or Ar_2^+ are the principal active species contributing to NO_x conversion through path I in nonthermal argon plasma, NO_2^+ and N_2O^+ should be produced from charge transfer reactions of Ar^+ or Ar_2^+ with NO_2 or N_2O , with concomitant optical emission from the $NO(B)$ produced from dissociative recombination reactions of NO_2^+ or N_2O^+ . This hypothesis leads to the examination of NO_2 and N_2O decomposition in nonthermal argon plasma.

C. Optical emission of N_2O in Ar

Figure 4(a) shows the optical emission spectra from 290 ppm N_2O in Ar at a pulse frequency of 200 Hz with a power input of 31.0 W. The observed optical emissions arise from excited states of three species: NO [$NO(A)$], N_2 [$N_2(C)$ and $N_2(B)$], and argon [$Ar(4p)$]. The excited states of $Ar(4p)$ are also detected, as expected when argon is the balance gas (Fig. 3).

For N_2O conversion in Ar plasma, the principal species in the reactor are N_2 , O_2 , unconverted N_2O , and Ar. Other by-products should be less than 5 ppm, as determined from FTIR measurements. The concentration of N_2O at the reactor

outlet quantified by FTIR is 60 ppm. From a previously published lumped kinetic model¹² and reaction mechanism,³³ the calculated N_2O concentration in the reactor at the window used for optical emission detection is 125 ppm. From mass balance, the concentrations of N_2 and O_2 at the window are 165 and 82.5 ppm. Therefore, the mole concentrations of Ar, N_2O , N_2 , and O_2 at the window at 300 K and 141 kPa are 5.64×10^{-5} , 7.05×10^{-9} , 9.31×10^{-9} , 4.65×10^{-9} mol cm^{-3} , respectively. If, as many investigators have reported,^{1,7,9,10,35} positive ions are the major active species contributing to plasma reactions, the following reactions should occur

$$k = 1.09 \times 10^{17} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \quad (\text{Ref. 51}), \quad (12')$$

$$k = 1.75 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 56}), \quad (15)$$

$$k = 6.62 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 56}), \quad (16)$$

$$k = 2.77 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 56}). \quad (17)$$

Using these reactant concentrations and the rate constants for parallel reactions (12) and (15)–(17), the Ar selectivities of (12) and (15)–(17) are estimated to be 99.6%, 0.4%, 0%, and 0%, respectively, which implies that Ar^+ is predominantly converted into Ar_2^+ without significant reactions with N_2O , N_2 , or O_2 . However, Ar_2^+ can further react with N_2O , N_2 , and O_2 in the following charge transfer reactions:

$$k = 4.94 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 57}), \quad (18)$$

$$k = 1.32 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 58}), \quad (19)$$

$$k = 4.45 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 56}). \quad (20)$$

The calculated selectivities of (18)–(20) are 70.8%, 25.0%, and 4.2%, respectively. Therefore, most (70.8%) of Ar_2^+ (derived from Ar^+) should contribute to the N_2O^+ formation through reaction (18). Johnsen *et al.*^{23,24} found that the dissociative recombination reactions of N_2O^+ produce the strongest fluorescence from $\text{NO}(B)$, the weaker fluorescence from $\text{NO}(A)$, and the weakest fluorescence from $\text{N}_2(C)$. Therefore, if Ar_2^+ (derived from Ar^+) is responsible for N_2O conversion, N_2O^+ should be generated and optical emission from $\text{NO}(B)$, $\text{NO}(A)$, and $\text{N}_2(C)$ should be detected.

Figures 4(b) and 4(c) show the amplified optical emission detected at 220–290 and 290–360 nm, respectively. By comparing with the standard molecular spectra⁵⁹ of $\text{NO}(B)$, $\text{NO}(A)$, and $\text{N}_2(C)$, strong fluorescences from $\text{NO}(A)$ and $\text{N}_2(C)$ are observed. Three vibrational states of $\text{NO}(A)$, with $v=0, 1, 2$, are observed. The optical emission intensity increases with decreasing vibrational state, which implies that $\text{NO}(A)$ with $v=0$ is predominantly formed in the PCDR. The strongest optical emission lines for $\text{NO}(B)$, if present, should therefore appear at wavelengths of 304.3, 320.7, 338.6, and 358.4 nm, as reported by many investigators.^{27,59–61} However, Fig. 4(c) shows no optical emission at these wavelengths. One reason that $\text{NO}(B)$ might not be observed is due to quenching by Ar, N_2O , N_2 , and O_2 . However, this possibility can be discounted by the consideration of the following quenching and radiative emission reactions:

$$k = 1.15 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 62}), \quad (21)$$

$$k = 8.25 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 63}), \quad (22)$$

$$k = 2.89 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 64}), \quad (23)$$

$$k = 1.11 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 64}), \quad (24)$$

$$k = 5.00 \times 10^5 \text{ s}^{-1} \quad (\text{Ref. 27}). \quad (25)$$

Using the previously calculated reactant concentrations with the rate constants in parallel reactions (21)–(25), S_0 of $\text{NO}(B)$ is estimated from Eq. (8) to be 7%, which is sufficient for optical emission detection, if present. Similarly, $\text{NO}(A)$ is deactivated by the following processes:

$$k = 2.36 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 65}), \quad (26)$$

$$k = 2.84 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 14}), \quad (27)$$

$$k = 4.70 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 14}), \quad (28)$$

$$k = 9.09 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 14}), \quad (29)$$

$$k = 4.59 \times 10^6 \text{ s}^{-1} \quad (\text{Ref. 14}). \quad (30)$$

The selectivity of the natural radiation of $\text{NO}(A)$ is estimated from Eq. (8) to be 22%, which is about three times S_0 for $\text{NO}(B)$. Therefore, if N_2O^+ is formed from Ar_2^+ (and indirectly from Ar^+), which results in $\text{NO}(A)$ formation and detection, $\text{NO}(B)$ should also be formed and detected. Undetectable $\text{NO}(B)$ suggests that Ar^+ and Ar_2^+ do not contribute to N_2O conversion. However, the observed optical emissions from $\text{NO}(A)$ and $\text{N}_2(C)$ must still be explained.

As discussed previously, the major excited states of argon formed in nonthermal Ar plasmas are $\text{Ar}(4p)$ and $\text{Ar}(4s)$. The reaction rate constant of $\text{Ar}(4p)$ with N_2O has not been reported, but it is estimated in this work to be on order of $10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.⁴² Due to the short radiation lifetimes (20–40 ns) and large quenching rate constants (on the order of $10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) of $\text{Ar}(4p)$ excited states by Ar (Table III), the $\text{Ar}(4p)$ excited states are not expected to react appreciably with N_2O , N_2 , and O_2 at the high prevailing concentration of argon. More than 95% of $\text{Ar}(4p)$ excited

FIG. 5. Optical emission of 566 ppm NO in Ar at the pulse frequency of 200 Hz.

states are quenched to Ar(4s) levels, as shown in Table III. Therefore, only Ar(4s) excited states appear to contribute to N₂O conversion in argon nonthermal plasma. Both Ar(1s₄) and Ar(1s₂) are not expected to contribute to any reactions with N₂O, N₂, and O₂ because of their very short radiation lifetimes (<10 ns, as shown in Table IV). Therefore, only the two long-life excited states of argon, Ar(1s₅) and Ar(1s₃), appear to contribute to reactions with N₂O, N₂, and O₂, with the result that the following well-established reactions contribute to the observed optical emission shown in Fig. 4:

$$k = 2.65 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 66}), \quad (31)$$

$$k = 2.17 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 67}), \quad (32)$$

$$k = 2.73 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 68}), \quad (33)$$

$$k = 2.00 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 68}), \quad (34)$$

$$k = 1.69 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 69}), \quad (35)$$

$$k = 3.85 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \quad (\text{Ref. 70}), \quad (36)$$

D. Optical emission of NO in Ar

Similar experimental conditions and optical emission measurements were conducted for NO in Ar. Figure 5(a) shows the optical emission spectra from 566 ppm NO in Ar at a pulse frequency of 200 Hz with a power input of 31.0 W. The observed optical emissions belong to the same species identified in Fig. 4: NO [NO(A)], N₂ [N₂(C) and N₂(B)], and argon [Ar(4p)].

For NO conversion in Ar plasma, the species in the reactor are N₂, O₂, NO₂, and unconverted NO and Ar. Other products are negligible, as determined from previous FTIR measurements.¹ The concentrations of NO and NO₂ at the

FIG. 6. Optical emission of 408 ppm N_2O in N_2 at the pulse frequency of 200 Hz.

reactor outlet measured by FTIR are 336 and 67 ppm, respectively. From a previously published lumped kinetic model and reaction mechanism,³⁵ the calculated concentrations of NO and NO_2 at the window used for optical emission detection are 425 and 53 ppm, respectively. From mass balance, the concentrations of N_2 and O_2 at the window are 44 and 17 ppm, respectively. Therefore, the concentrations of Ar, NO, NO_2 , N_2 , and O_2 at the window at 300 K and 141 kPa are 5.64×10^{-5} , 2.40×10^{-8} , 2.99×10^{-9} , 2.48×10^{-9} , and 9.59×10^{-10} mol cm^{-3} , respectively.

Through similar reasoning used for N_2O conversion in Ar, if Ar^+ or Ar_2^+ is the major active species contributing to NO_x conversion, the optical emission of $\text{NO}(B)$ formed during the dissociative recombination reaction of NO_2^+ should again be observed. However, the results in Figs. 5(b) and 5(c) show that no optical emission from $\text{NO}(B)$ is observed, which discounts the contribution of the Ar^+ or Ar_2^+ to NO_x conversion in nonthermal argon plasma.

E. Optical emission of N_2O in N_2

Similar optical emission measurements were made for 408 ppm N_2O in N_2 at a pulse frequency of 200 Hz to explore the contribution of N_2^+ in N_2O conversion. Hu *et al.*¹⁰ proposed that N_2^+ was responsible for N_2O conversion in nonthermal N_2 plasma through the following reactions:

If this mechanism is correct, optical emission of $\text{NO}(B)$ from dissociative recombination of N_2O^+ in (39) should be observed. However, the results in Fig. 6 again show no optical emissions from $\text{NO}(B)$, which discounts the contribution of N_2^+ to N_2O conversion in nonthermal nitrogen plasma. Those observations and results can be explained by examining the mechanism of streamer formation and propagation in corona discharges.

F. Streamer mechanism of corona discharge

Nonthermal plasma is a weakly ionized gas in which ions are present.⁷¹ The insignificance of charge transfer reactions in nonthermal plasma and the key role of radicals and

excited molecules with long lifetimes in the observed reactions can be explained on the basis of nonthermal plasma discharges.

The accepted mechanism of nonthermal plasma discharge is the streamer theory, proposed by Leob and Meek in 1940.^{72,73} A filamentlike streamer is a narrow-channel current that emits light and rapidly bridges and short-circuits overvolted discharge gaps in gases near atmospheric pressure.⁷⁴ From an electrostatic point of view, a streamer may be thought of as an elongated conductive needle from anode to cathode which transports potential from the anode into discharge gap.

Figure 7 illustrates the formation and development of a streamer. When the high voltage is applied to a wire-cylinder reactor, an external nonhomogeneous electric field between anode and cathode is established. The field strength can be calculated from⁷⁵

$$E_e(r) = \frac{U}{r \ln R_1/R_2}, \quad (40)$$

where E_e is the external electric field, r is the distance from the wire center to the point of concern, U is the voltage applied between wire and tube, and R_1 and R_2 are the radius of the tube and the radius of the wire, respectively. From Eq. (40), the field near the wire is much stronger than that away from the wire. For our reactor, U is about 20 kV.¹ The electric field at the surface of the wire is about 187 kV cm^{-1} , which is high enough to ionize the gas.⁷⁶ Once the gas molecules are ionized, the electrons expelled from the molecules are accelerated quickly in the strong external field from a position close to the wire to the anode. Due to the displacement of electrons with respect to positive ions, a polarization space charge field E_c that can be as high as 100 kV cm^{-1} arises.⁷⁷ Thus, the net electric field is weakened in the direction of the anode by the reverse space charge field that opposes the external electric field, and hence is strengthened in

FIG. 7. Schematic diagram showing formation and development of streamer.

TABLE V. Basic parameters for streamer discharge of nonthermal plasma at atmospheric pressure and ambient temperature.

Item	Streamer head	Ref.	Streamer channel	Ref.
Electron concentration	$10^{14} - 10^{15} \text{ cm}^{-3}$	Williams and Peterkin (Ref. 79)	...	...
Electrical resistance	...	...	6 k Ω	Williams and Peterkin (Ref. 79)
Electric field	100 kV cm $^{-1}$	Kulikovsky (Ref. 77)	$\sim 5 \text{ kV cm}^{-1}$	Morrow and Lowke (Ref. 84)
Electron drift velocity	$\sim 10^8 \text{ cm s}^{-1}$	Namihira <i>et al.</i> (Ref. 85)	...	...
Mean electron energy	$\sim 10 \text{ eV}$	van Veldhuizen (Ref. 9)	0.5–1 eV	van Veldhuizen (Ref. 9)
Diameter	10^{-2} cm	Kulikovsky (Ref. 80)	$10^{-2} - 10^{-1} \text{ cm}$	Kulikovsky (Ref. 86)
Total streamer volume fraction	...	...	$10^{-4} - 10^{-3}$	van Veldhuizen (Ref. 9)
Streamer density	...	...	$\leq 25 \text{ streamers/mm}$	Simek <i>et al.</i> (Ref. 87)

the direction of the cathode. This leads to further ionization of gas near the space charge in the direction of the cathode. This way, the streamer propagates from the anode to the cathode, while electron drift is in the reverse direction. The streamer tip is called the streamer head (ionization region), while the streamer tail is called the streamer channel (electron drift region),⁷⁸ as shown in Fig. 7.

The streamer dynamics have been extensively studied both theoretically and experimentally. The basic parameters of streamer dynamics^{9,77,79,80} are summarized in Table V. The following conclusions can be drawn from these parameters.

- (1) The degree of ionization in the streamer is low. The electron concentration in the streamer head is $10^{14} - 10^{15} \text{ e cm}^{-3}$, corresponding to $\sim 15 \text{ ppm}$ at 300 K and 141 kPa at the upper limit.
- (2) The major electron collision reactions occur in the streamer head. The high electric field in the streamer head accelerates the electrons from the ionized gas. The mean electron energy in the streamer head is $\sim 10 \text{ eV}$, which is high enough to initiate molecular dissociation and excitation, but not high enough to initiate ionization processes. The electron energy in the streamer channel is too low to contribute significantly to the excitation processes.⁹
- (3) The electron drift velocity in the streamer head is the streamer propagation velocity. The streamer velocity of $\sim 10^8 \text{ cm s}^{-1}$ across a 1–2 cm gap implies that the electrical discharge should be complete in 10–20 ns, which is consistent with our experimental data.¹
- (4) The streamer diameter is small, and hence the total volume fraction of the streamers within the reactor volume is low.

Because of the low degree of ionization, the probability of direct electron-ion collision reactions is small compared to the probability of direct electron-molecule collision reactions in the streamer head. The direct electron-molecule collision reactions in the streamer head produce the radicals and excited states. The excited molecules with short lifetimes emit light when they transfer lower energy excited states, which is observed as fluorescence of the filamentlike streamer. The electron drift velocity ($\sim 10^8 \text{ cm s}^{-1}$) in the streamer head is

around three orders of magnitude higher than the thermal velocity (about $3.5 \times 10^4 \text{ cm s}^{-1}$) of the molecules, radicals, excited states, and positive ions. Due to the high streamer head velocity, essentially no reactions among molecules, radicals, excited states, and ions can occur in the streamer head. In other words, the streamer head passes and the streamer channel is formed before any significant reactions among molecules, radicals, excited states, and ions occur. Instead, the reactions among molecules, radicals, excited states, ions, and electrons occur in the streamer channel, where the electron velocity has been considerably reduced due to the energy transfer processes in the electron collision reactions. For example, all probable ion reactions in the streamer channel for 290 ppm N_2O in argon are listed below.

$$k = 1.09 \times 10^{17} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \quad (\text{Ref. 51}), \quad (12'')$$

$$k = 1.75 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 56}), \quad (15')$$

$$k = 1.81 \times 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 52}), \quad (13')$$

$$k = 5.48 \times 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 53}), \quad (14')$$

$$k = 4.94 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Ref. 57}). \quad (18')$$

Using the calculated reactant concentrations and the rate constants listed above, the selectivities of Ar^+ consumption for reactions (12), (15), and (13) are estimated to be 69.4%, 0.6%, and 30.0%, respectively. The selectivities of Ar_2^+ consumption for reactions (14) and (18) are estimated to be 98.3% and 1.7%, respectively. Therefore, the net selectivity of the Ar^+ contribution to charge transfer reaction with N_2O is only about 1.8%. Even at NO_x concentrations as high as 1000 ppm, only around 5.8% of Ar^+ and Ar_2^+ contributes to

charge transfer reactions with N_2O . In brief, the positive ions significantly contribute only to the recombination reactions with electrons to form the radicals and the excited states before any charge transfer reactions occur.

By contrast, since the drift velocity of electrons in the streamer head is very high, the electrons experience many collisions with gas molecules and produce much more radicals and excited states than ions. This has been demonstrated by Eliasson and Kogelschatz.^{71,81,82} They found that the concentrations of radicals and excited states is about two orders of magnitude higher than that of ions. These studies confirm that the major active species contributing to the NO_x conversion in nonthermal plasma are radicals and the excited states of atoms or molecules, and they support the conclusion of the present work that the contribution of ions to plasma reactions through charge transfer reactions is negligible.

IV. CONCLUSIONS

On the basis of pulsed electrical discharge-induced optical emission spectra, the major active species produced from pulsed electrical discharge in argon are found to be the $Ar(4s)$ excited states. By contrast, Ar^+ and N_2^+ and their charge transfer reactions are found not to contribute to NO_x conversion in nonthermal argon plasma and nitrogen plasma, respectively, as determined from a detailed analysis of optical emission spectra induced by pulsed electrical discharge in argon, 290 ppm N_2O in argon, 566 ppm NO in argon, and 408 ppm N_2O in nitrogen. If positive ions are responsible for NO_x conversion in such mixtures, the optical emission of $NO(B)$ should be observed due to the dissociative recombination reactions of NO_2^+ and N_2O^+ . However, the optical emission of $NO(B)$ is not observed. In general, charge transfer reactions are insignificant because (1) the cations formed from direct electron collision reactions are predominantly neutralized with electrons before any charge transfer reactions can occur and (2) concentrations of radicals in the streamer are far higher than that of cations, which results in negligible charged particle reactions. This means that neutral active species, such as atoms, molecular fragments, and excited molecules, are largely responsible for NO_x conversion in nonthermal plasma.

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