

Article

Optical Emission Spectroscopic Investigation of CN-Related Emission Behavior and C-N-O Coupling in CO₂/N₂ Plasmas

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Abstract

Optical emission spectroscopy was used to investigate CN-related emission in atmospheric-pressure microsecond-pulsed spark discharges of pure N₂, pure CO₂, and CO₂/N₂ mixtures. This study examines how gas composition and pulse repetition frequency affect the relative evolution of C-, N-, O-, and CN-containing emitting species in plasma-assisted CO₂/N₂ carbon–nitrogen coupling. Pure N₂ discharge was dominated by N₂ second positive bands and N atomic lines, whereas pure CO₂ discharge mainly showed C- and O-related emissions. In mixed gases, the CN violet band was observed together with C, N, and O emissions, indicating the coexistence of carbon- and nitrogen-containing reactive species. CN band fitting and atomic-line analysis indicated a non-equilibrium plasma state, with T_{vib} and T_{rot} of approximately 7850 and 2150 K, an excitation temperature of 0.8–1.0 eV, and an electron density on the order of 10^{15} cm^{-3} . An emission-based CN characterization index was introduced to compare the relative variation in CN-related emission. Changes in gas composition and pulse frequency modified the relative CN-, N-, and O-related emission responses, consistent with competition between C–N coupling and oxygen-related pathways. The index is a semi-quantitative spectral descriptor, not a direct measure of CN concentration or formation efficiency.

Keywords: CN radicals; pulsed discharge; CO₂/N₂ plasma; optical emission spectroscopy

1. Introduction

CN is an important transient species in carbon–nitrogen coupling chemistry because it contains a direct C–N bond and can connect carbon-containing and nitrogen-containing reactive species in plasma environments. In CO₂/N₂ plasmas, CN-related emission is influenced by the relative availability of carbon-containing fragments, nitrogen-containing species, and oxygen-containing reactive particles. Therefore, CN can serve as a useful spectroscopic probe for examining the relative balance among C-, N-, and O-related reaction channels. The CN violet system also exhibits well-resolved rovibrational structures, making it suitable for optical emission spectroscopic diagnostics in non-equilibrium plasmas [1–6]. However, CN emission intensity does not directly represent the absolute CN concentration, formation rate, or formation efficiency.

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Previous studies of CN radicals have mainly focused on laser-induced plasmas, thermal plasmas, low-pressure discharges, and plasma-assisted deposition systems [7–12]. These studies have provided important information on CN spectroscopy and excitation behavior. However, many of these systems involve solid carbon targets, hydrocarbon precursors, low-pressure operation, or localized high-temperature environments. Such conditions differ substantially from atmospheric-pressure CO₂/N₂ plasmas, where CO₂ simultaneously acts as a carbon source and an oxygen source.

CO₂ and N₂ are abundant carbon- and nitrogen-containing feedstocks, respectively, and their activation in non-equilibrium plasmas is relevant to plasma-assisted carbon–nitrogen coupling chemistry. Electron-impact processes can generate carbon-, nitrogen-, and oxygen-containing reactive species from CO₂ and N₂. The resulting oxygen-containing species may further modify the relative reaction environment through competitive conversion and oxidation processes. Although plasma-assisted CO₂ conversion and carbon–nitrogen coupling have received increasing attention, the coupled evolution of CN-, C-, N-, and O-related emission features in atmospheric-pressure pulsed CO₂/N₂ discharges remains insufficiently understood. In particular, the effects of gas composition and pulse repetition frequency on the relative competition between CN-associated emission and oxygen-related emission channels require further clarification [13–15].

Optical emission spectroscopy is well suited for this purpose because it enables non-intrusive detection of multiple emitting species and can provide information on vibrational temperature, rotational temperature, excitation temperature, and electron density [13,16,17]. Nevertheless, emission intensity is affected by excitation processes, transition probabilities, collisional quenching, and plasma parameters. Therefore, intensity-based quantities should be interpreted as relative spectroscopic descriptors rather than direct measurements of species concentration, reaction rate, or chemical yield.

In this work, optical emission spectroscopy was used to compare pure N₂, pure CO₂, and CO₂/N₂ mixtures under atmospheric-pressure microsecond-pulsed spark discharge conditions. The originality of this study lies in the condition-resolved comparison of the coupled C-, N-, O-, and CN-related emission responses across the three gas systems, with gas composition and pulse repetition frequency considered as two independent discharge variables. The spectral analysis was further combined with CN rovibrational fitting and atomic-line-based plasma diagnostics to examine the non-equilibrium characteristics associated with the observed emission behavior. An emission-based CN characterization index (CFI) was introduced to compare the relative variation in CN-related emission under different discharge conditions. The CFI is used only as a semi-quantitative descriptor and is not interpreted as an absolute CN formation efficiency, concentration, or reaction rate. This study aims to provide an OES-based characterization of the relative C–N–O emission behavior in pulsed CO₂/N₂ discharges and to establish experimental constraints for future plasma-chemical kinetic modeling and particle-balance analysis.

2. Materials and Methods

2.1. Experimental Setup

Figure 1a presents a schematic overview of the experimental apparatus. The system consists of three main components, namely the input section, the reactor section, and the diagnostic section. These components operate in coordination to ensure stable discharge and reliable parameter measurement. The input section primarily includes a microsecond-pulsed power supply (USPS80140-700W, Nanjing Tech University, Nanjing, China), a gas supply system, and mass flow controllers. The microsecond-pulsed power supply provides a stable high-voltage pulse, which enables gas breakdown and sustains the discharge process. Regarding the gas supply, high-purity CO₂ and N₂ gases (both with a purity of 99.999%) are independently regulated by two mass flow controllers. The outlets of

the two mass flow controllers are connected to a common gas line upstream of the reactor inlet, where the gas streams are combined before entering the reactor. No separate mixing chamber is used in the present system. The premixed CO_2/N_2 gas enters the reactor from the top through the central channel of the hollow high-voltage electrode, passes through the interelectrode discharge region, and is exhausted from the outlet located at the lower side of the reactor. This top-to-bottom flow configuration establishes a defined one-pass gas flow through the active discharge zone, continuously supplies fresh feed gas to the electrode gap, and helps to reduce gas recirculation in the reaction region. The reactor was operated as a gas-tight continuous-flow system at atmospheric pressure. Before each experiment, the sealing performance of the reactor and gas connections was checked. After setting the desired gas composition, the CO_2/N_2 mixture was continuously introduced for 5 min before ignition to purge residual air from the gas line and reactor volume. Optical emission spectra were collected only after the discharge had operated for 3 min, ensuring that stable discharge conditions were established before spectral acquisition.

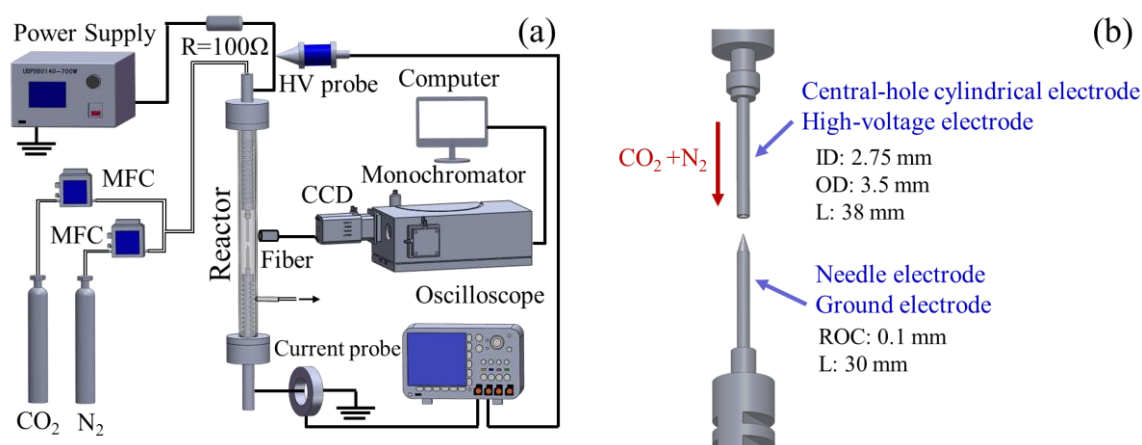


Figure 1. (a) Schematic diagram of the experimental setup and (b) the electrode configuration of the reactor. The arrow indicates the downward flow direction of the premixed CO_2/N_2 gas through the central channel of the hollow high-voltage electrode.

In the reactor section, a needle–tube electrode configuration is employed for the discharge structure. The high-voltage electrode is a hollow stainless-steel cylinder with an inner diameter of 2.75 mm, an outer diameter of 3.5 mm, and a length of 38 mm. The grounded electrode is a stainless-steel needle with a tip curvature radius of 0.1 mm and a length of 30 mm. A magnified view of the corresponding electrode configuration is shown in Figure 1b. In addition, a 100 Ω resistor is connected in series in the external circuit between the microsecond-pulsed power supply and the reactor, in order to limit the discharge current and enhance discharge stability.

The diagnostic section mainly consists of two measurement approaches, namely optical emission spectroscopy (OES) and electrical parameter diagnostics (EPD). On the one hand, the voltage and current waveforms during the discharge process are recorded in real time using an oscilloscope (MDO34, Tektronix, Beaverton, Oregon, USA; 350 MHz, 2.5 GS/s), which is employed to analyze the discharge characteristics and energy input. The applied voltage across the reactor and the current in the circuit are monitored using a high-voltage probe (HV-P60, IWATSU Electric Co., Ltd., Tokyo, Japan; 2000:1, 1000 MΩ, 5 pF) and a current probe (Model 6600, Pearson Electronics Inc., Palo Alto, CA, USA; 0.1 V/A), respectively. On the other hand, optical diagnostics are performed using optical emission spectroscopy to detect active species in the plasma region during the discharge process. The measurement system consists of a grating spectrometer, an intensified charge-coupled device (ICCD), a fiber optic probe, an optical fiber transmission line, and

a computer. The spectrometer used in this study is an Andor 750i equipped with gratings of 2400 lines/mm (blaze wavelength: 300 nm) and 1200 lines/mm (blaze wavelength: 500 nm).

2.2. Parameter Definition

To compare the relative evolution of selected emission features under different discharge conditions, an emission intensity ratio (R) and an emission-based CN characterization index (CFI) were introduced. All intensities used in the analysis were extracted from the same response-corrected full-range spectrum acquired under identical discharge conditions. The selected spectral features were C I (247.8 nm, integrated over (247.4–248.1) nm), the CN violet band (near 388 nm, integrated over (380.4–389.5) nm), N I (746.8 nm, integrated over (746.3–747.3) nm), and O I (777.2 nm, integrated over (774.6–779.7) nm). For each feature, the baseline-subtracted integrated intensity was calculated using the same wavelength interval under all operating conditions.

The emission intensity ratio is defined as follows:

$$R = \frac{I_1}{I_2} \quad (1)$$

where I_1 and I_2 represent the baseline-subtracted integrated intensities of the selected spectral features. The intensity ratio is used to compare the relative variation in two emission signals under different discharge conditions.

The emission-based CN characterization index is defined as follows:

$$\text{CFI} = \frac{I_{\text{CN}}}{I_{\text{CN}} + I_{\text{C}} + I_{\text{N}} + I_{\text{O}}} \quad (2)$$

where I_{CN} , I_{C} , I_{N} , and I_{O} represent the integrated intensities of the CN violet band, C I, N I, and O I spectral features, respectively. The CFI is introduced as a semi-quantitative descriptor of the relative CN-related emission response within the selected spectral signals. Because the CFI combines molecular CN-band emission with atomic C, N, and O emissions, its value can be influenced by differences in excitation mechanisms, radiative transition probabilities, collisional quenching, electron density, and electron excitation conditions. No separate correction was applied for these species-dependent population effects. Accordingly, the CFI is used only for internal comparison of relative spectral trends under the present experimental conditions and is not interpreted as a direct measure of CN concentration, formation rate, yield, or formation efficiency.

3. Analysis and Discussion

3.1. Full Spectral Characteristics Analysis

As shown in Figure 2, this study first performs an overall comparative analysis of the emission spectra of pure N_2 , pure CO_2 , and CO_2/N_2 mixed gas systems in order to clarify the influence of different gas compositions on plasma emission characteristics. The results show that, in the pure N_2 system, the emission lines are mainly composed of N_2 (C-B) bands, N^+ lines, and atomic nitrogen (N I) lines, which indicates that N_2 molecules undergo excitation and partial dissociation under electron-impact processes, thereby forming abundant excited N_2 molecular states and atomic nitrogen species. In this system, the N_2 ($\text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g$) transition serves as the dominant molecular-band emission, which further indicates that electron excitation processes govern the discharge behavior. In contrast, the pure CO_2 system is primarily characterized by CO (B-A)-band emissions, C_2 Swan bands, atomic oxygen lines, and atomic carbon lines. These spectral features demonstrate that CO_2 molecules undergo significant dissociation under high-energy electron bombardment, resulting in the formation of multiple reactive carbon- and oxygen-containing species:



Furthermore, this study observes that a portion of CO molecules and carbon-containing fragments undergo further dissociation and recombination reactions, leading to the formation of carbon cluster species such as C₂. As a result, a distinct C₂ Swan band emission appears in the wavelength range of 500–520 nm. In addition, the appearance of a large number of atomic oxygen lines indicates that the dissociation of CO₂ proceeds extensively. This observation also suggests that the discharge system exhibits a strong oxidative characteristic due to the high concentration of oxygen-containing reactive species.

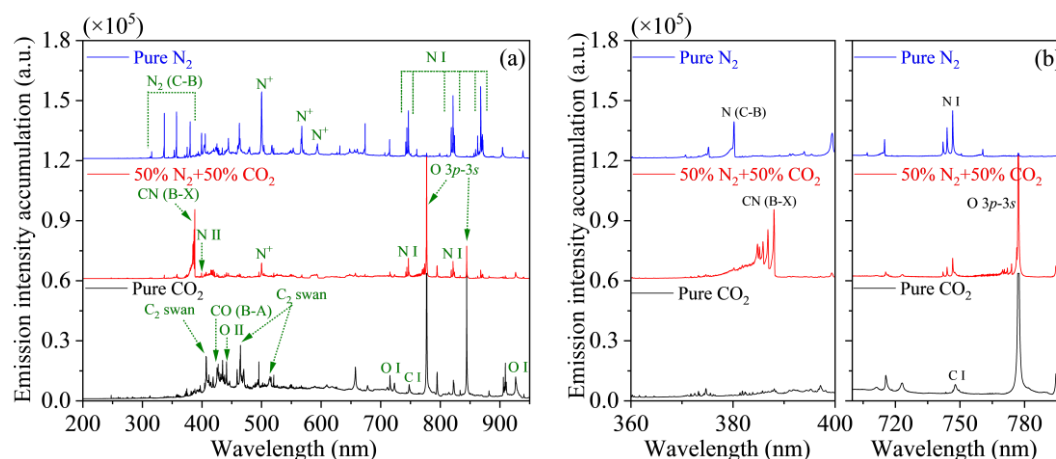


Figure 2. Typical optical emission spectra of spark discharge in three gas systems, namely pure N₂, N₂/CO₂ mixture (50% N₂), and pure CO₂: (a) full-range spectra recorded from 200 to 950 nm using a single spectral acquisition; (b) enlarged wavelength regions extracted from the corresponding full-range spectra.

In contrast, in the N₂/CO₂ mixed gas system, this study observes not only O atoms, N⁺ ions, and atomic nitrogen (N I), but also a distinct CN violet-band emission. Figure 3 further presents the typical emission spectral features of N I (3p–3s), O (3p–3s), C I, and CN (B²Σ⁺ → X²Σ⁺) in the mixed system. These results indicate that both carbon-containing species and nitrogen-containing species coexist in the mixed plasma, which provides the necessary conditions for CN radical formation. This observation further demonstrates that CN production depends on the synergistic interaction between carbon- and nitrogen-reactive species. During the discharge process, carbon-containing species such as C atoms and CO fragments generated from CO₂ dissociation react with atomic nitrogen or excited nitrogen molecules, thereby promoting the formation of CN radicals. On the other hand, the large amount of oxygen atoms produced from CO₂ dissociation participates in competitive reaction pathways with carbon-containing species in the system, for example



Previous plasma-chemical studies have identified CO₂ dissociation, N₂ activation, carbon–nitrogen coupling, and oxygen-related conversion processes as possible contributors to the chemistry of CO₂/N₂ plasmas [13–15]. In the present work, the simultaneous variation in C-, N-, O-, and CN-related emission features is qualitatively interpreted using these literature-supported representative pathways. For example, oxygen-related conversion of carbon-containing species may reduce the availability of carbon precursors for CN-associated channels.

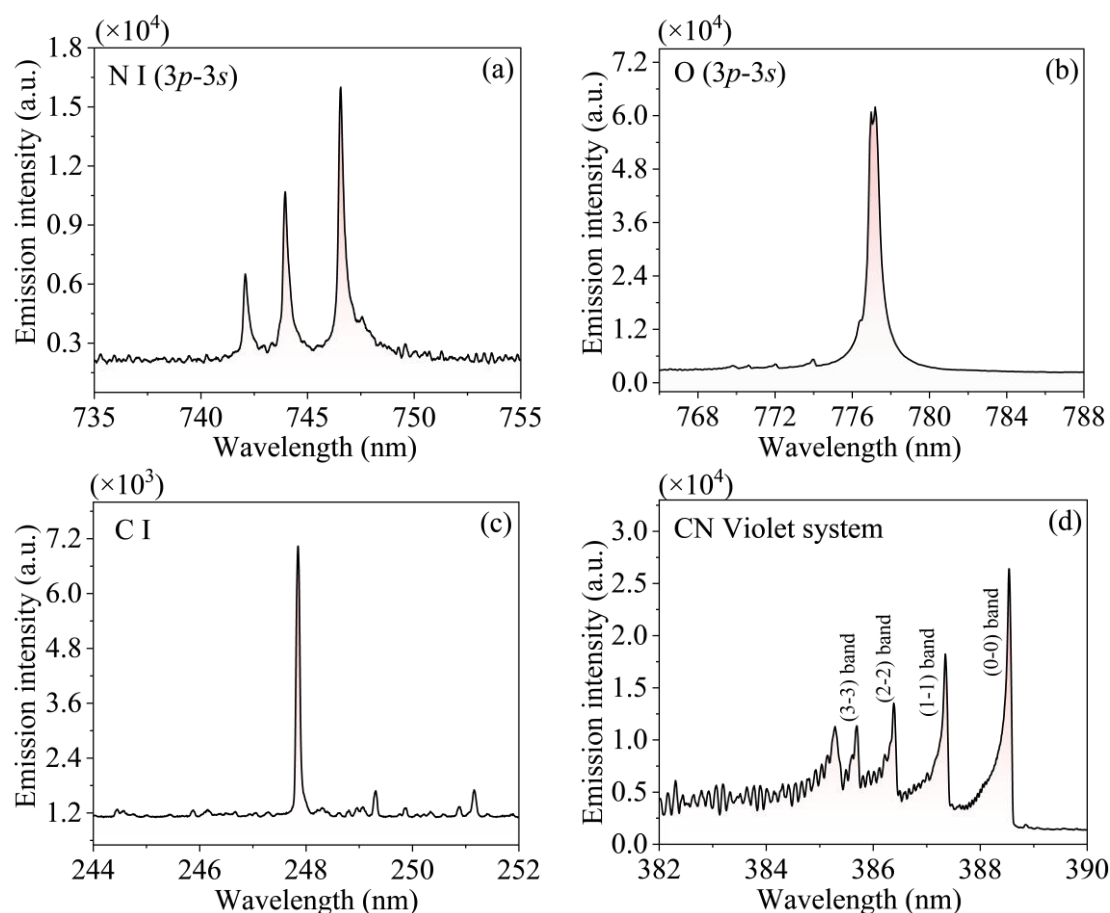


Figure 3. Typical emission spectra obtained in the N_2/CO_2 gas mixture (50% N_2 + 50% CO_2): (a) N I (3p–3s) emission spectrum; (b) O I (3p–3s) emission spectrum; (c) C I emission spectrum; (d) CN violet-system emission spectrum corresponding to the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition.

To compare the relative spectral responses of the selected emitting features, the response-corrected and baseline-subtracted integrated intensities of CN, C I, N I, and O I were normalized at each operating condition, as shown in Figure 4. The normalized contribution of each feature was calculated by dividing its integrated intensity by the sum of the integrated intensities of the four selected features (CN, C I, N I, and O I). Therefore, the percentages in Figure 4 represent normalized relative emission contributions within the selected spectral signals. They do not represent gas mixing ratios, absolute species concentrations, reaction rates, or product yields. Because atomic and molecular emission intensities can be influenced by excitation processes, transition probabilities, collisional quenching, and plasma parameters, the normalized values are used only to compare relative spectroscopic trends under the present experimental conditions. The results show that, as the CO_2/N_2 ratio increases gradually from 1:3 to 3:1, the species distribution in the plasma exhibits a clear evolutionary trend. The normalized fraction of CN radicals decreases from 36% to 24%, while the proportion of atomic nitrogen decreases from 27% to 15%. In contrast, the proportion of atomic oxygen increases continuously from 35% to 60%, whereas atomic carbon remains at a consistently low level of approximately 1%. These results indicate that the plasma environment gradually transforms from a nitrogen-rich condition to an oxygen-rich condition with increasing CO_2 content. This evolution reflects a significant shift in the dominant reaction pathways. In addition, free carbon atoms tend to be rapidly converted into molecular species such as CO or C_2 , which results in a relatively weak atomic carbon emission intensity throughout all conditions.

The changes in the normalized species distribution reflect, from an overall perspective, the competitive relationships among the dominant reaction channels in the system. On the one hand, the reduction in the proportion of atomic nitrogen directly limits reaction pathways that depend on nitrogen participation. On the other hand, the increase in atomic oxygen influences the conversion processes of both carbon- and nitrogen-containing species through oxidation reactions, thereby exerting a significant effect on CN radical formation. Therefore, under conditions with a higher CO₂ fraction, although the source of carbon-containing species in the plasma increases, the simultaneous rise in oxygen atom concentration leads to a reduced relative formation capability of CN radicals. Overall, different gas compositions modify the distribution of the main reactive atoms and molecules in the plasma, which directly affects the emission spectral characteristics and further determines the formation behavior of CN radicals.

Based on the full-spectrum analysis, this study identifies atomic carbon (C), atomic nitrogen (N), atomic oxygen (O), and CN radicals as the most dominant and most significantly varying reactive species in the N₂/CO₂ mixed system. In comparison, the emission intensities of other species remain relatively weak or provide limited diagnostic relevance to the CN formation process. Therefore, this study selects these four species, namely C, N, O, and CN, to construct the composite formation index (CFI) in Section 2.2, which is used to characterize the relative variation trend of CN formation under different discharge conditions. This selection strategy ensures that the principal reaction pathways are adequately represented while minimizing uncertainties introduced by minor or less relevant species.

Although full-spectrum analysis can identify the dominant emitting species and their relative intensity characteristics in different gas systems, the distribution of spectral lines alone is insufficient to quantitatively describe the internal energy distribution and electron states of the plasma. Therefore, it is necessary to further combine plasma diagnostic methods to analyze the key physical parameters governing the discharge process.

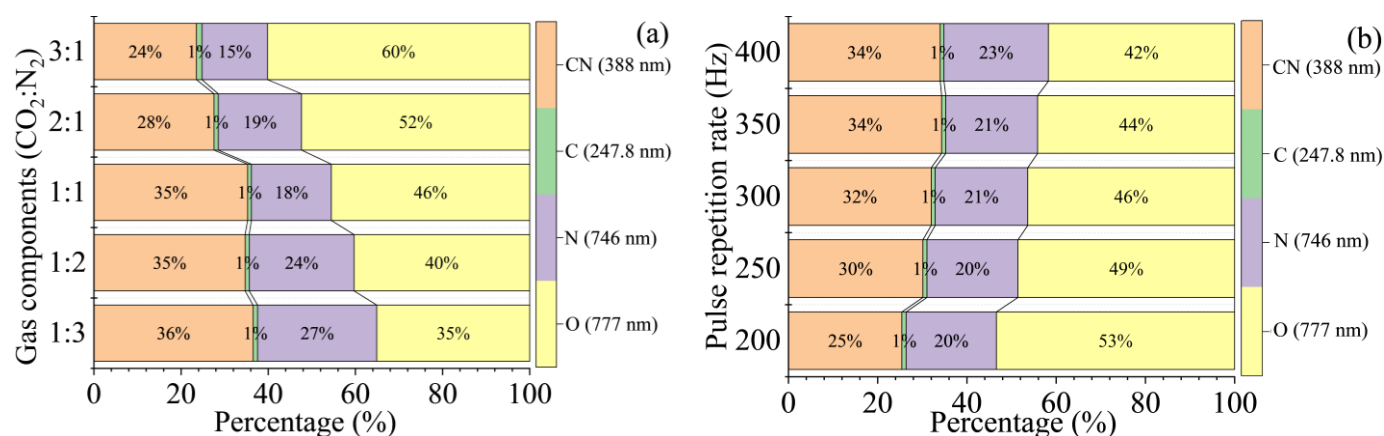


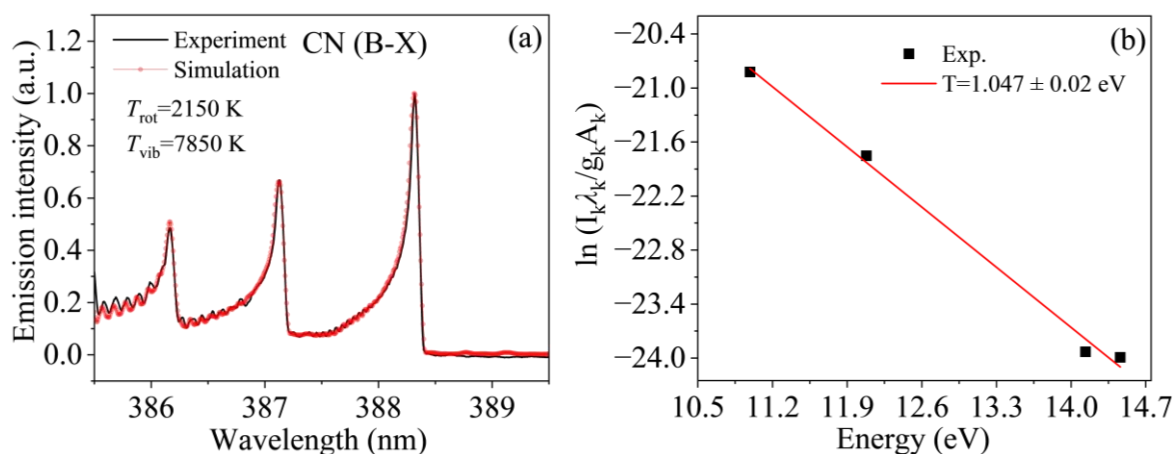
Figure 4. Normalized relative contributions of the response-corrected integrated emission signals of CN, C I, N I, and O I under different gas compositions (a) and pulse repetition frequencies (b).

3.2. Plasma Parameter Diagnostics

Based on the full spectral characteristics analysis, this section further performs a systematic diagnosis of key plasma parameters to characterize the plasma state during the discharge process, including the vibrational temperature (T_{vib}), rotational temperature (T_{rot}), O I excitation temperature (T_{exc}), and electron density (n_e). The CN violet system corresponding to the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition exhibits well-resolved rovibrational structures near 388 nm and is therefore suitable for molecular spectral fitting [9]. In the present work, the CN violet band was simulated using Specair, a radiative-spectrum calculation

program for plasma diagnostics. Specair calculates molecular emission spectra on the basis of the energy-level structure, radiative transition probabilities, and selection rules of the selected species. For molecular spectra, Specair allows the electronic, vibrational, rotational, and translational energy modes to be described by separate characteristic temperatures. The populations associated with each energy mode are prescribed using the corresponding Boltzmann distribution. Therefore, the simulation can represent a non-equilibrium molecular population distribution in which the vibrational and rotational temperatures are different. In this study, the experimental CN violet spectrum was imported into Specair, and the CN $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition was selected for spectral simulation. The vibrational and rotational temperatures were varied iteratively to reproduce the measured rovibrational band structure and relative intensity distribution. The fitted values of T_{vib} and T_{rot} were obtained from the best agreement between the calculated and experimental spectra. These fitted parameters should be regarded as effective vibrational and rotational population temperatures of the emitting CN molecules, rather than direct evidence that the entire discharge plasma is in local thermodynamic equilibrium. Figure 5a presents a comparison between the experimental spectrum and the simulated results, and the two show good agreement. The best-fit values were $T_{\text{vib}} = 7850$ K and $T_{\text{rot}} = 2150$ K. The substantial difference between T_{vib} and T_{rot} indicates a non-equilibrium rovibrational population distribution of the emitting CN molecules. This result supports non-equilibrium energy partitioning in the discharge, but it does not imply that all plasma species or all energy modes are characterized by a common thermodynamic temperature. Similar non-equilibrium temperature distributions have also been reported in plasma systems generated by pulsed discharges, dielectric barrier discharges (DBDs), and spark discharges [18–22]. In these systems, high-energy electron-molecule collisions preferentially excite vibrational degrees of freedom, which leads to a relatively elevated vibrational temperature. In contrast, rotational degrees of freedom are more strongly coupled to heavy-particle collisions, and therefore the rotational temperature is generally closer to the actual gas temperature. These results indicate that, in microsecond-pulsed spark discharges, the plasma receives substantial electron energy input; however, the neutral gas does not reach full thermal equilibrium during the discharge process. Previous studies have also reported the transient evolution and diagnostic characterization of spark-discharge plasmas, including streamer-to-spark transitions and electron-density behavior [23–25].

Because the CN spectral fit is based on rovibrational band-shape matching, it does not provide a direct estimate of the excitation state of atomic species. Therefore, the excitation state of selected atomic oxygen levels was further evaluated using the Boltzmann plot method [18–20].



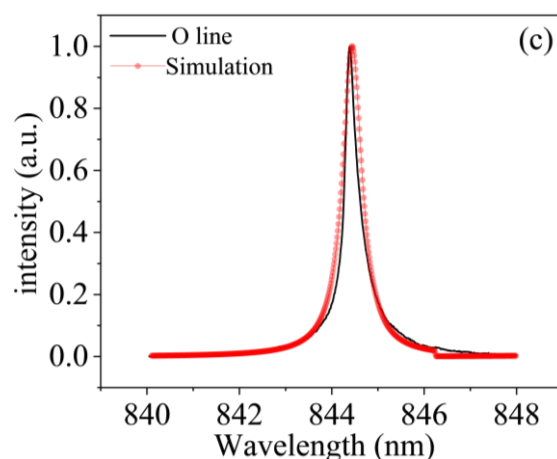


Figure 5. (a) Comparison between experimental and fitted spectra of CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, 388 nm); (b) Boltzmann plot of the selected O I emission lines used to determine the apparent O I excitation temperature, T_{exc} ; (c) instrument-corrected Voigt-profile fitting of the O I 844.6 nm line for electron-density determination.

The Boltzmann plot method was used to derive an apparent excitation parameter from the relative populations of the selected O I emission levels. The parameter obtained from the fit is referred to here as the apparent O I excitation temperature, T_{exc} . Because the present microsecond-pulsed spark discharge is strongly non-equilibrium, T_{exc} is not interpreted as a direct measurement of electron temperature T_e or as evidence that the complete discharge plasma satisfies local thermodynamic equilibrium. Instead, T_{exc} is used only to compare the relative excitation-state distribution of the selected O I emission levels under different discharge conditions.

For a spontaneous radiative transition from an upper level k to a lower level i , the integrated line intensity can be expressed as [18–20]:

$$I_{ki} = N_k A_{ki} \nu_{ki} = N_k A_{ki} \frac{hc}{\lambda_{ki}} \quad (5)$$

where N_k denotes the population density of particles in the upper level k , A_{ki} is the spontaneous transition probability, λ is the wavelength of the spectral line, and h and c represent the Planck constant and the speed of light, respectively. When the relative populations of the selected O I upper levels are represented by an effective Boltzmann-type distribution over the examined energy interval, the population density N_k can be written as

$$N_k = N_a \frac{g_k}{Q_a(T_{\text{exc}})} \exp\left(-\frac{\Delta E_k}{k_B T_{\text{exc}}}\right) \quad (6)$$

where N_a is the total number density of the emitted atomic species, g_k is the statistical weight of the upper level, E_k is the upper-level excitation energy, $Q_a(T_{\text{exc}})$ is the partition function, and k_B is the Boltzmann constant. Substituting Equation (6) into Equation (5) gives

$$I_{ki} = N_a \frac{g_k}{Q_a(T_{\text{exc}})} A_{ki} \frac{hc}{\lambda_{ki}} \exp\left(-\frac{\Delta E_k}{k_B T_{\text{exc}}}\right) \quad (7)$$

After rearrangement and logarithmic transformation, Equation (7) can be written in the linear form

$$\ln\left(\frac{I_{ki} \lambda_{ki}}{g_k A_{ki}}\right) = -\frac{\Delta E_k}{k_B T_{\text{exc}}} + \ln\left(\frac{N_a hc}{Q_a(T_{\text{exc}})}\right) \quad (8)$$

Accordingly, the independent variable of the Boltzmann plot was defined as $x = E_k$, and the dependent variable was defined as $y = \ln(I_{ki}\lambda_{ki}/g_k A_{ki})$. Within the effective Boltzmann-type representation adopted for the selected O I upper levels, the slope of the linear regression is given by $m = -1/(k_B T_{\text{exc}})$. Therefore, the apparent O I excitation temperature was calculated from the fitted slope according to $T_{\text{exc}} = -1/(k_B m)$.

Four O I lines at 715.6, 844.6, 882.0, and 926.6 nm were selected because they showed sufficiently high signal-to-noise ratios and acceptable spectral separation in the measured spectra. Before constructing the Boltzmann plot, the integrated intensities of the selected lines were corrected for the wavelength-dependent response of the optical system. The air wavelengths, upper-level excitation energies, statistical weights, and transition probabilities used in the calculation are listed in Table 1 and were obtained from the NIST Atomic Spectra Database [26].

Figure 5b shows the Boltzmann plot obtained from the four selected O I lines. The fitted slope and the corresponding apparent O I excitation temperature, T_{exc} , are indicated in the figure.

To assess the applicability of the local thermodynamic equilibrium (LTE) assumption, the McWhirter criterion was evaluated as $n_{\text{e,crit}} = 1.6 \times 10^{12} T^{1/2}(\Delta E)^3$, where $n_{\text{e,crit}}$ is expressed in cm^{-3} , T is expressed in K, and ΔE is the maximum energy separation between the selected upper levels in eV. For the selected O I lines, $\Delta E = 3.471 \text{ eV}$ (Table 1). Using the measured T_{exc} range of 9900–11,200 K as a characteristic temperature, the calculated electron-density threshold is $(6.66\text{--}7.08) \times 10^{15} \text{ cm}^{-3}$. This value is higher than the measured electron-density range of $(1.91\text{--}2.37) \times 10^{15} \text{ cm}^{-3}$. Therefore, the necessary McWhirter condition for global LTE is not satisfied in the present discharge [27].

Accordingly, the approximate linearity of the selected O I data points is not regarded as proof of global LTE or partial LTE. T_{exc} is retained only as an apparent excitation parameter describing the relative population distribution of the selected O I emitting levels, rather than as a direct measurement of electron temperature or the electron energy distribution function. The uncertainty of T_{exc} was obtained from the standard error of the fitted slope, with the ordinate uncertainty propagated from the uncertainty of the integrated line intensity. The reported uncertainty therefore represents the statistical uncertainty of the Boltzmann fit. Possible systematic uncertainties associated with spectral-response correction and adopted transition-probability data are not fully quantified and constitute limitations of the present diagnostic method.

Table 1. Spectroscopic constants of the selected O I lines used for the apparent O I excitation-temperature analysis [26].

λ_{ki} (nm)	A_{ki} (s^{-1})	E_k (eV)	g_k
715.6	5.05×10^7	14.460	2
844.6	3.22×10^7	10.989	2
882.0	2.93×10^7	14.134	3
926.6	4.45×10^7	12.079	4

The electron density was estimated from the Stark broadening of the O I 844.6 nm line. The observed line profile contains contributions from instrumental, Doppler, van der Waals, natural, resonance, and Stark broadening mechanisms. Therefore, the instrumental line-spread function was determined using a narrow spectral line from a Hg–Ar calibration lamp recorded under the same grating, slit-width, ICCD, fiber-coupling, and optical-collection conditions as those used for the plasma measurement. The instrumental full width at half maximum in the spectral region near 844.6 nm was determined to be 0.02 nm. The measured O I 844.6 nm profile was fitted using an instrument-corrected Voigt function. The Gaussian contribution included Doppler and instrumental broadening,

whereas the Lorentzian contribution included Stark and van der Waals broadening. The Stark width was obtained after subtracting the calculated van der Waals contribution from the fitted Lorentzian width. Natural and resonance broadening were evaluated to be negligible compared with the fitted line width under the present conditions. The corrected Stark width was then substituted into Equation (9) to calculate the electron density. In this study, their values are taken as 5.28×10^{-2} nm and 0.032 according to Ref. [28]. The uncertainty in n_e was evaluated by propagating the uncertainties of the fitted Lorentzian width, instrumental broadening, van der Waals correction, and Stark-broadening parameters. The reported uncertainty range corresponds to the 95% confidence interval of the calculated electron density.

$$\Delta\lambda_{\text{Stark}} (\text{nm}) = 2\omega_e (T_e) \times \left[1 + 1.75 \left(1 - 0.75 \times \left(8.99 \times 10^{-2} n_e^{\frac{1}{6}} T_e^{-\frac{1}{2}} \right) a_e (T_e) \right) \right] \times 10^{-16} n_e \quad (9)$$

$$\Delta\lambda_{\text{Lorentz}} = \Delta\lambda_{\text{Stark}} + \Delta\lambda_{\text{vd Waals}} + \Delta\lambda_{\text{Nature}} + \Delta\lambda_{\text{Resonance}} \quad (10)$$

$$\Delta\lambda_{\text{vd Waals}} = (11.2 - 2.12 \times 10^{-4} T_{\text{gas}} (\text{K})) T_{\text{gas}}^{0.7} P (\text{atm}) \quad (11)$$

The three diagnostics provide complementary but model-dependent estimates of the plasma state. The CN spectral fit yields effective rovibrational population temperatures of emitting CN molecules; the O I Boltzmann plot yields the apparent O I excitation temperature, T_{exc} , from an effective Boltzmann-type representation of the selected O I upper-level populations; and the Stark analysis provides an electron-density estimate after correction for instrumental and non-Stark broadening. Together, these results support the non-equilibrium character of the discharge, but they do not establish global LTE or directly determine the complete electron energy distribution function.

3.3. Evolution of Characteristic Spectral Lines

To further elucidate the influence of different discharge conditions on the generation behavior of reactive species, this section selects several representative characteristic spectral lines and analyzes their response to variations in gas composition and discharge frequency.

Figure 6a,b present the variation trends of the emission intensities of typical species under different CO₂/N₂ composition conditions, including N I (3p-3s, 746 nm), O (3p-3s, 844.6 nm), C I (247.8 nm), CN (B²Σ⁺ → X²Σ⁺, 388 nm), and N₂ (C³Π_u → B³Π_g, 337.1 nm). The results show that, with increasing CO₂ content, the emission intensities of O and C atoms continuously increase, whereas those of N atoms, the CN violet system, and the N₂ second positive system gradually decrease. Although the emission intensity of atomic carbon increases to some extent with the rise in CO₂ proportion, its overall relative intensity remains low. This observation indicates that carbon-containing species in the system predominantly exist in molecular forms such as CO and C₂. This trend indicates that the evolution of different species is not independent but is jointly governed by coupled reaction pathways within the system. However, variations in spectral intensity alone are insufficient to distinguish the respective formation and consumption processes of these species. For example, the decrease in CN emission may result either from limited formation or from enhanced loss. Therefore, it is necessary to carry out a systematic analysis of the dominant reaction pathways from the perspective of reaction mechanisms.

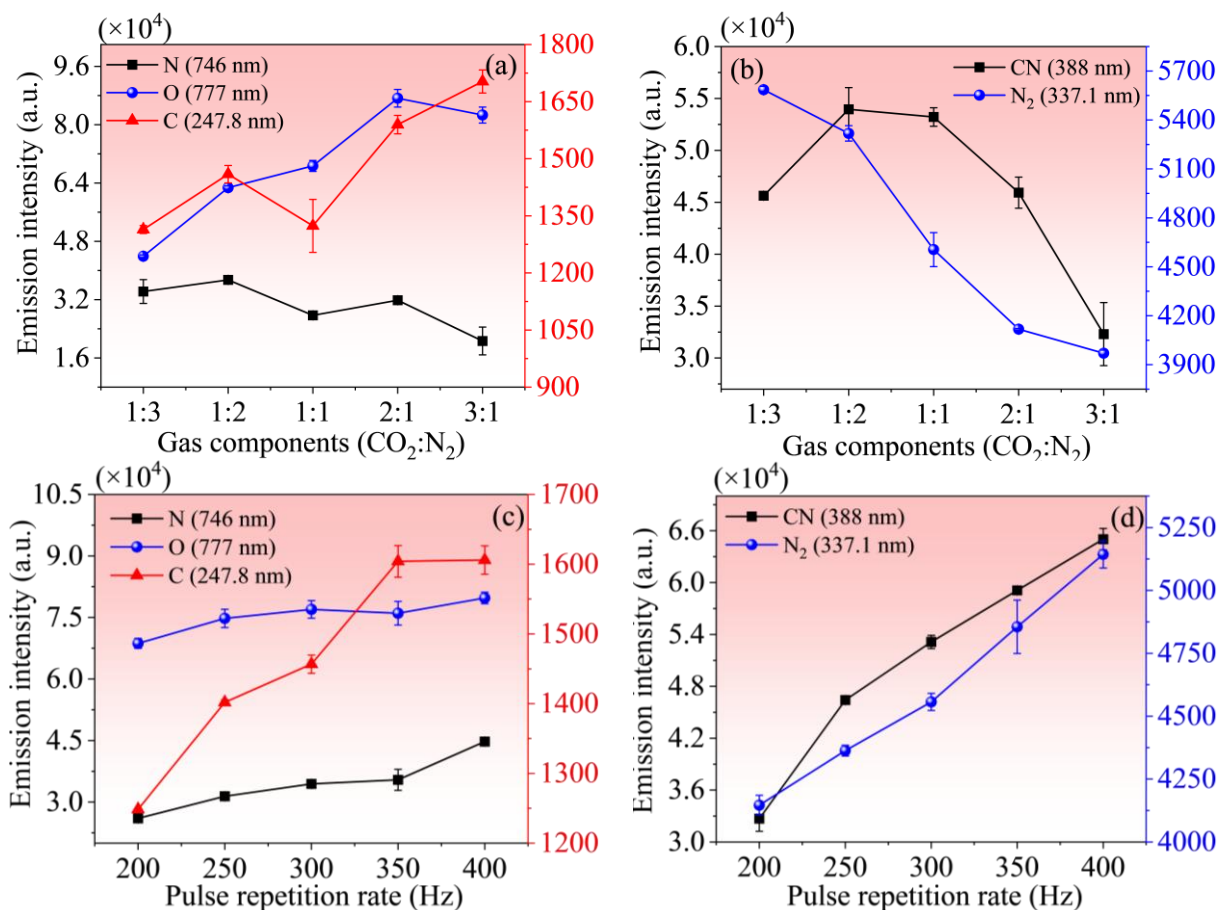


Figure 6. Variation trends of emission intensities of N I ($3p-3s$, 746 nm), O ($3p-3s$, 777.2 nm), C I (247.8 nm), CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, 388 nm), and N₂ ($C^3\Pi_u \rightarrow B^3\Pi_g$, 337.1 nm) with gas composition (a,b) and pulse repetition frequency (c,d).

In microsecond-pulsed spark discharges, energetic electrons can induce molecular excitation and dissociation through inelastic collisions [29,30]. For CO₂ molecules, the primary electron-impact dissociation process can be described by Equation (3).

Subsequent dissociation processes can be described as follows:



Therefore, as the CO₂ fraction increases, the O I and C I emission signals increase. This trend is consistent with enhanced contributions from CO₂-derived excited oxygen- and carbon-containing species. This result is consistent with previously reported observations in CO₂ discharge plasma studies, which show that high-energy electron collisions significantly promote the dissociation of CO₂ molecules and lead to the generation of a large number of reactive oxygen atoms [31,32].

In contrast, the excitation and dissociation of N₂ molecules mainly involve the following processes:



As the CO₂ content increases, the fraction of N₂ decreases, which directly reduces the population of its excited states. Meanwhile, the O atoms generated in the system can consume reactive nitrogen species through the following reactions. The reactions listed in Equations (15)–(20) are introduced as literature-supported representative pathways for qualitatively interpreting the observed C-N-O-related emission trends.



Therefore, the emission intensities of N atoms and excited states of N₂ molecules are further suppressed.

For CN-related chemistry, carbon-, nitrogen-, and oxygen-containing reactive species may participate in both formation and conversion processes. The following reactions are introduced as literature-supported representative pathways for the qualitative interpretation of the observed emission trends:



However, as the CO₂ fraction further increases, the O-related emission becomes more pronounced. The following oxygen-involving reactions are included as representative conversion pathways:



At the same time, these oxygen atoms also directly destroy the already formed CN radicals:



Accordingly, the decrease in CN-related emission at higher CO₂ fractions is qualitatively consistent with a change in the relative balance between CN-associated formation pathways and oxygen-related conversion pathways. The present OES measurements do not resolve the relative rates of the reactions listed above or the concentrations of the participating species.

Based on the above reaction processes, a coupled C-N-O reaction network was constructed, as shown in Figure 7. The network summarizes representative reaction pathways reported for CO₂/N₂ plasma systems and describes the possible interconversion among carbon-, nitrogen-, and oxygen-containing reactive species. Electron-impact activation of CO₂ and N₂ generates C-, N-, and O-containing precursors, while subsequent C-N coupling and O-involving conversion processes jointly affect the CN-related emission behavior. With increasing CO₂ fraction, the enhancement of O-related emission accompanied by the attenuation of N- and CN-related emission is qualitatively consistent with an increasing contribution of oxygen-involving conversion pathways. Therefore, the observed CN-related emission variation can be interpreted as the result of competition between C-N coupling processes and O-related conversion processes.

In addition to variations in reactive species concentrations, the gas composition also affects the energy distribution processes within the discharge system. CO₂ is a linear triatomic molecule that possesses three fundamental vibrational modes: the symmetric stretching mode (ν_1), the bending mode (ν_2), and the asymmetric stretching mode (ν_3). Among them, the bending mode is doubly degenerate. These vibrational modes exhibit relatively large excitation cross sections in low-energy electron collisions, enabling CO₂ to efficiently absorb electron energy during the discharge process and store it in the vibrational degrees of freedom. Previous studies have shown that vibrational energy transfer in CO₂/N₂ mixed systems is mainly governed by vibration–vibration (V-V) and vibration–translation (V-T) processes, in which N₂ molecules effectively promote vibrational energy accumulation because of their relatively slow V-T relaxation rate [33]. As the CO₂/N₂ ratio increases from 1:3 to 1:1, the accumulation of vibrational energy in the system becomes stronger, resulting in an increase in the vibrational temperature from 7050 K to 7850 K.

However, when the CO₂ content continues to increase, the number density of N₂ molecules in the system decreases, which weakens the capability for vibrational energy accumulation. At the same time, CO₂ molecules exhibit relatively faster V-T relaxation processes, causing vibrational energy to transfer more readily into translational degrees of freedom. Consequently, the vibrational temperature decreases further from 7850 K to 7230 K.

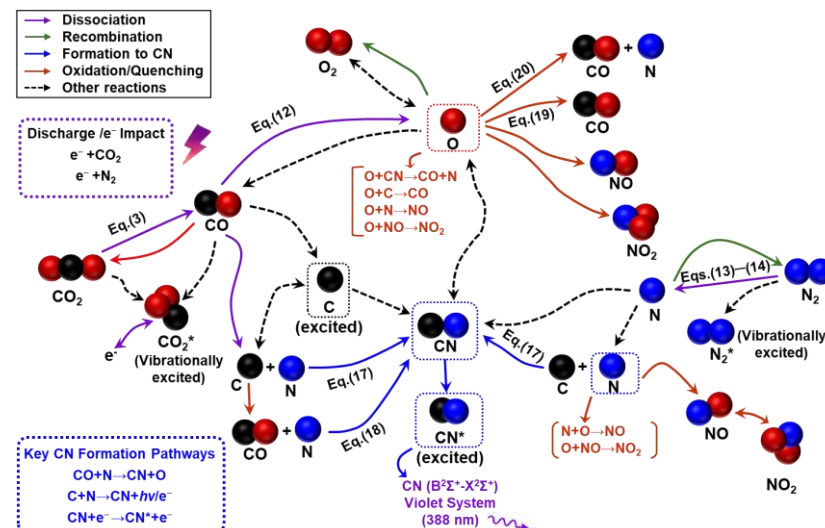


Figure 7. Simplified literature-based C–N–O reaction network used for the qualitative interpretation of the observed emission trends. The labeled arrows correspond to the representative reactions listed in Equations (3) and (12)–(20). The network is not a kinetic model, and reaction rate coefficients or reaction fluxes were not determined in the present work.

The experimental results show that the rotational temperature increases from 1950 K to 2190 K with increasing CO₂ content. Since the rotational temperature is generally close to the gas temperature, this result indicates that the overall thermal effect in the system gradually becomes stronger. Several factors may contribute to this behavior. First, CO₂ molecules possess more vibrational degrees of freedom, which enhances the transfer of vibrational energy into translational motion. Second, the dissociation of CO₂ and related reaction processes release thermal energy into the system. Third, a higher CO₂ concentration increases the collision frequency within the plasma, thereby promoting energy thermalization processes.

Figure 6c,d show that the emission intensities of all observed species increase to different extents as the pulse frequency rises from 200 Hz to 400 Hz. This behavior is mainly attributed to the increase in the number of discharge events per unit time, which provides the system with a higher average input power and consequently increases both the electron density and the proportion of high-energy electrons in the electron energy distribution function. Under these conditions, a larger number of molecules undergo excitation and dissociation processes, resulting in the overall enhancement of the emission intensities of O, C, N, CN, and N₂ species. Similar phenomena have been widely reported in pulsed plasma studies, where increasing the discharge frequency enhances energy deposition per unit time and thereby strengthens particle excitation and dissociation processes [34–38]. Meanwhile, the vibrational temperature increases from 7850 K to 8100 K, whereas the rotational temperature exhibits only slight fluctuations within the range of 2120–2170 K, as shown in Figure 8. These results indicate that vibrational degrees of freedom are more sensitive to variations in discharge frequency. High-frequency discharges continuously inject non-equilibrium energy into the system, allowing vibrational excitation to accumulate progressively. In contrast, rotational degrees of freedom are more closely asso-

ciated with thermalization through heavy-particle collisions, and therefore their variation remains relatively limited. This phenomenon further demonstrates that microsecond-pulsed spark discharges exhibit typical characteristics of non-equilibrium plasmas.

In summary, the spectral behavior and temperature evolution of CO_2/N_2 mixed gases under microsecond-pulsed spark discharge conditions exhibit pronounced characteristics of non-equilibrium plasmas. An increase in CO_2 content promotes the generation of atomic oxygen and carbon-containing reactive species, while simultaneously enhancing the oxidative consumption of N- and CN-related species. The vibrational temperature is jointly regulated by the vibrational energy transfer mechanisms between CO_2 and N_2 molecules and therefore exhibits a trend of first increasing and then decreasing with changes in gas composition. In addition, an increase in pulse frequency generally strengthens particle excitation processes and the accumulation of non-equilibrium energy within the plasma. These results demonstrate that the distribution of reactive species and the energy allocation in the plasma can be effectively controlled through the adjustment of gas composition and pulse repetition frequency modify the relative emission responses of the selected C-, N-, O-, and CN-related spectral features under the present discharge conditions. These observations provide qualitative OES-based insight into C–N–O coupling behavior, whereas direct CO_2 conversion efficiency, product yield, and reaction selectivity were not evaluated in this work. Such regulation provides important experimental evidence for CO_2 conversion and related plasma-assisted chemical reaction processes.

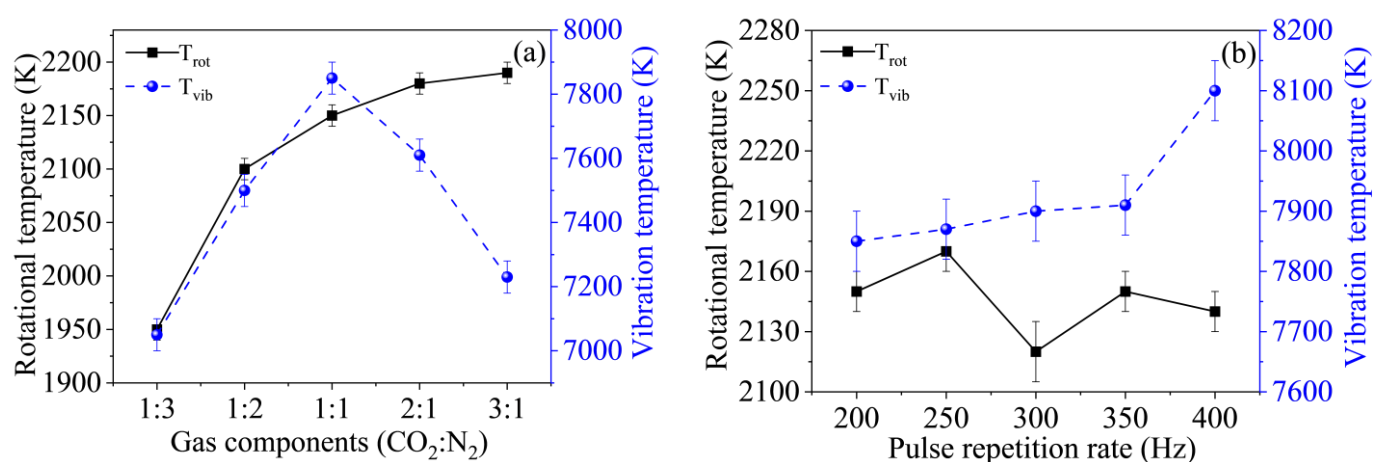


Figure 8. Vibrational temperature (T_{vib}) and rotational temperature (T_{rot}) under different gas compositions (a) and different pulse repetition frequencies (b).

3.4. Intensity Ratio and CN Formation Characterization Factor Analysis

Based on the above full-spectrum and normalized spectral analyses, the intensity ratio (R) and the CN formation index (CFI) were used to compare the relative variations in CN-, C-, N-, and O-related emission signals under different discharge conditions. Compared with a single emission signal, an intensity ratio can partially reduce the influence of overall discharge-intensity fluctuations and is useful for describing relative spectral trends. Each ratio and CFI value was calculated from three independent measurements and is presented as the mean $\pm$ standard deviation. As noted in Section 2.2, the intensity ratios and CFI are emission-based semi-quantitative descriptors. They do not directly represent species concentrations, reaction rates, CN yield, or CN formation efficiency.

The CN-related emission response may be influenced by the relative variation of carbon-, nitrogen-, and oxygen-containing species, including the representative C–N–O reaction pathways discussed in Section 3.3 [33,39,40]. As the CO_2/N_2 ratio increased from 1:3 to 3:1, the apparent O I excitation temperature, T_{exc} , increased from (9900 ± 200) K to

(11,200 ± 200) K, whereas the electron density decreased from $(2.37 \pm 0.02) \times 10^{15} \text{ cm}^{-3}$ to $(1.91 \pm 0.02) \times 10^{15} \text{ cm}^{-3}$. These opposite trends indicate changes in the relative O I excitation-state distribution and electron-density condition of the discharge. Because the present non-equilibrium spectroscopic diagnostics do not directly determine the electron energy distribution function, the variations in T_{exc} and n_e are not interpreted as a unique change in the fraction of high-energy electrons. Instead, they are considered auxiliary plasma parameters that may influence the observed relative emission responses. This tendency is consistent with the experimentally observed continuous decrease in the proportion of atomic nitrogen species. In addition, previous studies have shown that, in oxygen-containing plasma systems, O atoms continuously consume CN radicals and carbon-containing free radicals through oxidation reactions [3,6,41]. Therefore, as the concentration of O atoms increases, competitive reaction pathways such as Equation (20) become progressively stronger. These processes jointly suppress the steady-state accumulation of CN radicals from both the formation and consumption perspectives.

Further analysis based on the variation in intensity ratios provides a more direct understanding of the relative competition among different reaction pathways. As shown in Figure 9, the ratio of $I_{\text{CN}(388)}/I_{\text{N}(746)}$ increases from 1.3 to 1.56 with increasing CO₂ content and reaches a maximum value of 1.92 under the 1:1 condition. To some extent, this ratio reflects the CN emission contribution corresponding to each unit of nitrogen-related active species. The increase in this ratio indicates that, under moderate CO₂/N₂ mixing conditions, the limited nitrogen-containing reactive species participate more efficiently in CN formation processes. This behavior may imply that CO-involved pathways play a relatively more important role in CN generation. However, the enhancement in relative formation efficiency does not lead to an increase in the total CN concentration. The main reason is that the ratio of $I_{\text{O}(777)}/I_{\text{CN}(388)}$ continuously increases from 0.92 to 2.55, indicating that oxygen-related emissions gradually become dominant in the discharge system. This phenomenon indicates that the oxidative consumption pathways gradually become stronger as the CO₂ fraction increases. Previous studies have likewise reported that the continuous accumulation of O atoms in CO₂-related plasmas significantly enhances the oxidation of CN radicals and carbon-containing free radicals [17]. The observed variations in T_{exc} and n_e indicate changes in the excitation and electron-density conditions of the discharge. However, the present diagnostics do not resolve the electron energy distribution function and cannot establish a unique change in CO₂ or N₂ activation capability. As a result, the competitive inhibitory effect of O atoms on CN formation progressively intensifies. In addition, the ratio of $I_{\text{CN}(388)}/I_{\text{C}(247)}$ reaches its maximum value of 40.2 under the 1:1 condition and subsequently decreases to 18.9. This result indicates that, under moderate CO₂/N₂ mixing conditions, carbon-containing reactive species exhibit a relatively high conversion efficiency toward CN formation. However, under high-CO₂ conditions, a portion of carbon species preferentially participates in the formation of oxygen-containing products such as CO, thereby reducing the relative contribution of CN formation. Similarly, the continuous increase in $I_{\text{O}(777)}/I_{\text{C}(247)}$ further demonstrates that carbon-containing species become progressively dominated by oxidation pathways with increasing CO₂ concentration.

Based on the above emission characteristics, the CN characterization index (CFI) was calculated from the integrated CN, C I, N I, and O I emission signals. Compared with a single intensity ratio, the CFI combines the relative variations in the four selected spectral features. In the following discussion, changes in CFI are interpreted only as variations in the relative CN-related emission response within these selected signals. The experimental results show that the CFI decreases monotonically from 0.36 to 0.23 as the CO₂/N₂ ratio increases. Because the CFI combines the CN molecular-band emission with atomic C, N, and O line emissions, its value can also be affected by species-dependent excitation mech-

anisms, transition probabilities, collisional quenching, and plasma parameters. Although the spectral response of the optical system was corrected, no separate correction for these species-dependent population effects was applied. Therefore, the CFI is used only to compare relative spectral trends under the present experimental conditions. This trend indicates that the reaction pathways favorable for CN formation are progressively suppressed by oxidation-related processes. The observed variation may be associated with several factors. First, the decrease in the N I emission contribution weakens the supply of nitrogen-containing reactive species required for CN formation. Second, the increase in atomic oxygen concentration enhances the oxidative consumption of both CN radicals and carbon-containing species. In addition, although CO₂ provides more carbon-containing precursors, a portion of these carbon species tends to be converted into stable oxygen-containing products such as CO. Consequently, their effective contribution to CN formation does not increase correspondingly. Further consideration of the electron density variation shows that the continuous decrease in electron density may weaken effective electron-impact collision processes in the plasma, which is unfavorable for sustaining CN formation pathways that rely on multistep collision reactions. In contrast, the activation and dissociation of CO₂ can still proceed continuously under these conditions. Therefore, the decrease in CFI can, to some extent, be regarded as consistent with an increasing influence of oxygen-related conversion pathways in the system.

To assess the influence of energy deposition in the frequency series, the pulse energy was calculated from the measured voltage-current waveforms according to $E_p = \int V(t)I(t)dt$. Over the investigated frequency range, the pulse energy varied from 20.17 to 23.26 mJ, whereas the average input power increased from 0.89 to 0.92 W. In contrast, the pulse repetition frequency exhibits a different regulatory effect on CN formation. When the frequency increases from 200 Hz to 400 Hz, the normalized fraction of CN rises from 25% to 34%, the proportion of atomic nitrogen increases from 20% to 23%, while the proportion of atomic oxygen decreases from 53% to 42%. These results indicate that higher pulse frequencies enhance the relative contribution of nitrogen-containing reactive species and simultaneously weaken the dominant role of oxygen atoms in the discharge system. From the perspective of intensity ratios, $I_{CN(388)}/I_{N(746)}$ first increases with frequency and reaches a maximum value of 1.66 at 350 Hz, followed by a slight decrease. This behavior suggests that the CN-to-N emission ratio reaches its maximum value under intermediate frequency conditions. Meanwhile, the ratio of $I_{O(777)}/I_{CN(388)}$ decreases from 2.1 to 1.22, indicating that the competitive inhibition effect of oxygen atoms on CN formation is significantly reduced. In addition, the continuous increase in $I_{CN(388)}/I_{C(247)}$ reflects an increase in the relative CN-to-C emission ratio, whereas the decrease in $I_{O(777)}/I_{C(247)}$ indicates a decrease in the relative O-to-C emission ratio.

On this basis, the CFI increases from 0.25 to 0.34 with rising pulse frequency, indicating that the relative contribution of CN within the overall reaction system is significantly enhanced. Similar behaviors have also been reported in studies of pulsed discharges and non-equilibrium plasmas, where increasing the discharge frequency enhances energy deposition per unit time and promotes vibrational excitation as well as molecular activation processes [19,42]. The frequency-dependent emission trends may reflect both the increased average energy input associated with the higher pulse repetition frequency and possible changes in the discharge conditions between successive pulses. At the same time, the enhancement of non-equilibrium characteristics helps sustain a higher population of vibrationally excited species, thereby facilitating reaction pathways such as CO + N that contribute to CN formation. In addition, the reduced relative abundance of O atoms further weakens the oxidative loss of CN radicals, which is more favorable for the accumulation of CN species in the plasma system.

In summary, the formation of CN radicals is governed by a dynamic balance among the supply of atomic nitrogen, the utilization efficiency of carbon-containing reactive species, and the competitive consumption by atomic oxygen. Variations in the gas composition primarily affect CN formation by regulating the competition between oxidation-related pathways and carbon–nitrogen coupling pathways in the plasma system. In contrast, the pulse repetition frequency mainly controls the reaction processes by modifying the energy input and the degree of non-equilibrium within the discharge. Within the present OES analysis, the CFI provides a semi-quantitative descriptor for comparing relative CN-related emission variations under different discharge conditions. Therefore, it provides a useful framework for understanding carbon–nitrogen coupling mechanisms in CO₂/N₂ plasma systems and offers valuable guidance for optimizing the formation of target products.

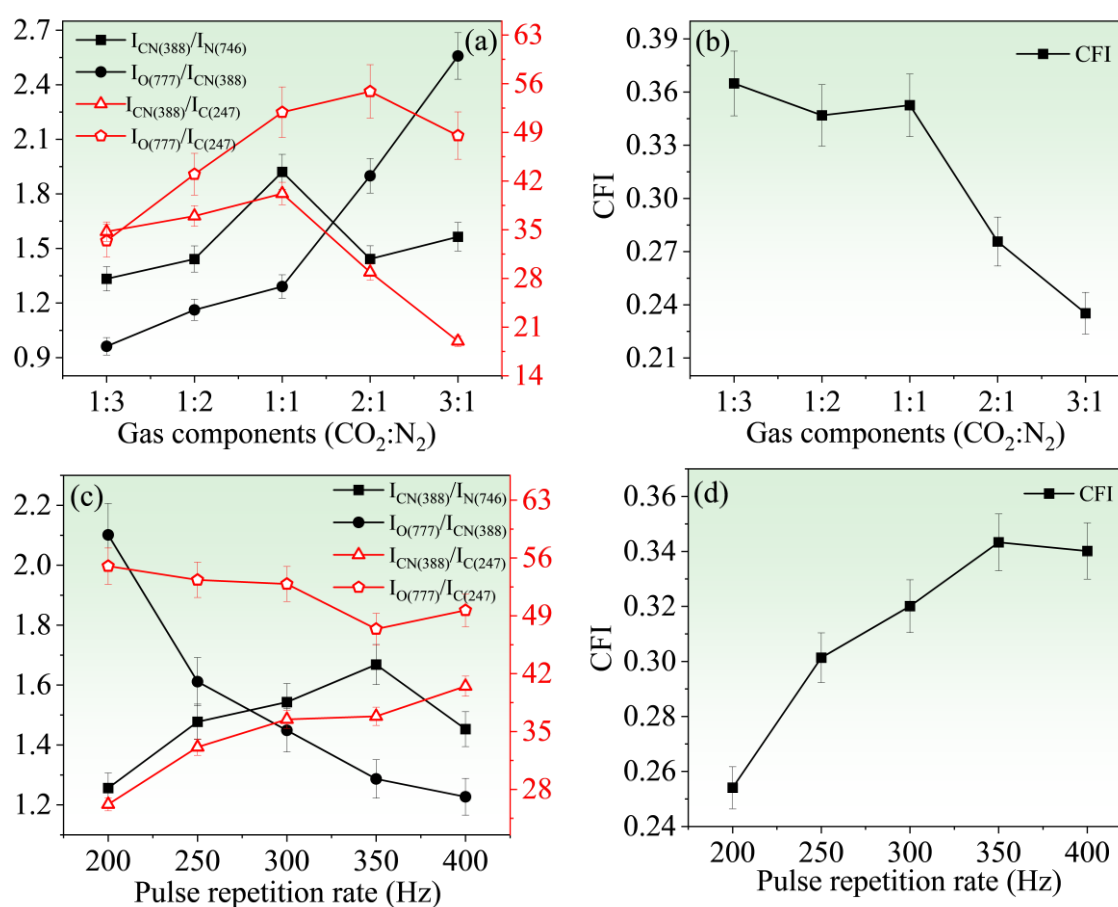


Figure 9. Selected emission intensity ratios (a,c) and the emission-based CN characterization index (CFI) (b,d) under different gas compositions and pulse repetition frequencies.

4. Conclusions

This study presents a comparative optical emission spectroscopic investigation of pure N₂, pure CO₂, and CO₂/N₂ mixtures under atmospheric-pressure microsecond-pulsed spark discharge conditions. The novelty of the work lies in the condition-resolved analysis of the coupled relative emission behavior of C-, N-, O-, and CN-related spectral features under variations in gas composition and pulse repetition frequency. By combining full-spectrum comparison, CN rovibrational fitting, atomic-line-based plasma diagnostics, and emission-ratio analysis, the study provides a spectroscopic basis for examining C–N–O coupling behavior in pulsed CO₂/N₂ discharges.

First, from the perspective of spectral characteristics, this study performs a unified full-spectrum comparative analysis across different discharge systems and establishes a systematic correlation between atomic/molecular emission features and underlying reaction pathways. The results show that the pure N₂ discharge is dominated by the second positive system of N₂ and atomic nitrogen (N I) emission lines, whereas the pure CO₂ discharge is mainly characterized by atomic carbon and atomic oxygen emissions. In contrast, the N₂/CO₂ mixed system exhibits a pronounced CN violet-band emission, indicating the coexistence of carbon-containing and nitrogen-containing reactive species in the mixed discharge. This full-spectrum-based comparative approach provides a more comprehensive diagnostic framework for describing the evolution of reactive species in complex gas discharge systems.

Second, an emission-based CN characterization index (CFI) was introduced from the integrated emission signals of C, N, O, and CN to compare their relative variations under different discharge conditions. By incorporating the coupled changes in the selected spectral features, the CFI provides a semi-quantitative indicator of the CN-related emission response in the present discharge system. Because the index combines atomic-line and molecular-band emissions, its value is also influenced by the excitation and quenching characteristics of the selected species.

Third, plasma parameter diagnostics indicated pronounced non-equilibrium characteristics of the discharge. The distinct difference between the fitted vibrational and rotational temperatures reflected non-equilibrium rovibrational energy partitioning of the emitting CN molecules. The apparent O I excitation temperature, T_{exc} , and electron density, determined from the O I Boltzmann plot and Stark-broadening analysis, respectively, provided complementary information on the excitation and electron-density conditions of the discharge. The corresponding uncertainties are reported in the revised Results Section. In addition, the variation in O-related emission with gas composition was consistent with an increasing contribution of oxygen-involving conversion processes to the observed CN-related emission behavior.

In summary, the observed CN-related emission behavior was associated with the combined influence of gas composition, pulse repetition frequency, and the relative C–N–O emission characteristics of the discharge. Increasing the CO₂ fraction was accompanied by enhanced O-related emission and reduced N- and CN-related emission, whereas increasing the pulse repetition frequency modified the relative emission responses of the selected species. These trends are consistent with changes in the balance between C–N coupling processes and oxygen-related conversion processes. Within the present OES analysis, the CFI provides a semi-quantitative index for comparing these relative spectral variations.

Overall, this study systematically investigated the N₂/CO₂ microsecond-pulsed spark discharge system through full-spectrum analysis, plasma-parameter diagnostics, and emission-ratio analysis. The results provide spectroscopic insight into the relative C–N–O coupling behavior under different discharge conditions and establish an experimental basis for future plasma-chemical kinetic modeling, particle-balance analysis, and independent product or radical diagnostics in CO₂/N₂ plasma systems.

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Abbreviations

The following abbreviations are used in this manuscript:

CFI emission-based CN characterization index

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