Influence of Ionization Degrees on Conversion of CO and CO$_2$ in Atmospheric Plasma near the Ground$^*$

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Abstract A zero-dimensional model is used to study the processes of physical and chemical reactions in atmospheric plasma with different ionization degrees near the ground (0 km). The temporal evolutions of CO, CO$_2$ and other main reactants (namely OH and O$_2$), which affect the conversion of CO and CO$_2$, are obtained for afterglow plasma with different initial values. The results show that the consumption rate of CO is largest when the initial electron number density $n_{e0}=10^{12}$ cm$^{-3}$, i.e. the ionization degree is 0.000004%. The number density of CO$_2$ is relatively small when $n_{e0}=10^{16}$ cm$^{-3}$, i.e. the ionization degree is 0.04%, whereas they are very close under the condition of other ionization degrees. Considering the total number densities of CO and CO$_2$ and the consumption rate of CO comprehensively, the best condition is $n_{e0}=10^{13}$ cm$^{-3}$, i.e. the ionization degree is 0.00004% for reducing the densities of CO and CO$_2$ in the atmospheric plasma. The temporal evolutions of N$^+$, Ar$^+$, CO$^+$ and CO$_2^+$ are also shown, and the influences on the temporal evolutions of CO and CO$_2$ are analyzed with increasing ionization degree.

Keywords: ionization degree, carbon dioxide, carbon monoxide, atmospheric plasma

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(Some figures may appear in colour only in the online journal)

1 Introduction

With vehicle possession and the development of industry rapidly increasing, the influence of vehicle and industrial emissions on air pollution is also growing. 61% of CO, 87% of C$_6$H$_m$ and 55% of NO$_2$ in the atmosphere in cities comes from vehicle and industrial emissions [1], in which CO is not only destroying the ecological balance of nature, but also doing serious harm to human health. A concentration of CO as low as 0.0667% may cause up to 50% of the body’s hemoglobin to convert to carboxyhemoglobin [2]. A level of 50% carboxyhemoglobin may result in seizure, coma, and fatality. In addition, industrial waste gases also contain large amounts of CO and CO$_2$. The data given by NOAA (ftp://ftp.cmdl.noaa.gov/ccg/CO2) display that the concentration of CO$_2$ in the atmosphere has increased by about 27% from 1958 to May 2013, caused by human activities, such as the combustion of fossil fuels and deforestation. CO$_2$ is one of the main greenhouse gases [3], which causes about 9%-26% of the greenhouse effect (this data come from http://en.wikipedia.org/wiki/global_warming). Too much CO and CO$_2$ released in air is bound to threaten the survival of life on earth. Thus, controlling our anthropogenic emission of CO and CO$_2$ is urgent.

In general, the cycles of CO and CO$_2$ are relatively independent in natural air [4]. It needs strong chemical reaction conditions for oxidizing CO to CO$_2$ by combustion with O$_2$ [5]. CO near the ground in the atmosphere is mainly absorbed by the microorganisms in the soil, while CO spreading to the higher space is converted to CO$_2$ only through a series of chemical [6-8] or photochemical reactions. Thus, CO and CO$_2$ become the main carbon oxide materials in the atmosphere, in which CO$_2$ is the most abundant. The toxicities of CO for biology in the atmosphere cannot be ignored for increasing the number densities and long lifetime [9], especially for the potential of increasing the pollution of CO$_2$. Therefore, the interest in researching CO and CO$_2$ has been very high. Most researchers pay close attention to the changes of CO and CO$_2$ densities in the atmosphere [10-14]. Someone has also been keen to study how to reduce the emission of waste gases and control air pollution. Among the numerous high and new techniques for controlling air pollution, electrostatic adsorption combined with plasma technology [15] has become the first choice because of its high efficiency and low consumption of energy. These studies are important to understand and control the emission of CO.
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and CO2. It is also important to understand the conversion processes and the dependent conditions of CO and CO2, which had been emitted to the atmosphere. But studying the conversion of CO by experiment is difficult because of its low densities in natural air (about 0.1 ppm). To track the direction of reactions for pollutants, and prevent the formation of secondary pollution, it is necessary to figure out the physical and chemical reaction processes of the atmospheric components by using numerical simulations [16–19]. Thus a zero-dimensional model is built in this work to study the conversions of CO and CO2 with different ionization degrees. In order to reduce the density of CO in the atmosphere, we should make more CO convert to CO2, then make CO2 participate in a more complex carbon circulatory system, not shown in this paper [15], thus to maintain normal background levels for natural air.

In the present work, the temporal evolutions of carbon species in atmospheric plasma are studied after a narrow single discharge pulse with different intensities, which can produce different ionization degrees for air. The physicochemical reactions are simulated for atmosphere species from the onset of the reaction to $10^{-1}$ s. The results show that the influence of ionization degrees on the conversion of CO and CO2 is not linear, but this has never been reported in the literature.

2 The model and numerical simulation

The atmosphere is a very complex system, it contains many components. Atmosphere can be ionized after a narrow pulse produced by laser, lightning or other kinds of high voltage discharges, which generate atmospheric plasma. In general, atmospheric plasma is in local thermal equilibrium with a low temperature, inside which not only a variety of physical changes (e.g. excitation, ionization, recombination and so on), but also complex chemical reaction processes (e.g. oxidation and reduction) would occur. We will not go into any details about the mechanism of the gas discharge and parameter of the pulse here; we only focus on the processes of the physicochemical reactions after the pulse.

Considering a small volume of plasma produced in open air, we build a zero-dimensional model in space, which includes the main physical and chemical reactions, but ignores spatial processes such as diffusion and flow. As the initial conditions of simulation, the same number of electrons and positive ions with the same ratio as that in natural air are produced by the pulse. Then various physical and chemical reactions immediately take place so that species are produced or consumed, and finally reach a certain equilibrium. Each reaction takes place in the same time and priority level. The temperature of atmospheric plasma $T_{air}$ is set to be 291 K, the electron temperature $T_e$ is $2.32\times10^5$ K, and the atmospheric pressure is $1.01\times10^5$ Pa near the surface of the ground [4] (i.e. 0 km height). In the model, 56 species [20] and 427 reactions are considered, which includes most of the atmospheric chemical reactions closer to the natural atmosphere in the open. The evolution of each species in the atmosphere with different ionization degrees was simulated after the narrow discharge pulse. Different ionization degrees of air can produce different initial electron number densities by any form of discharge. In order to simulate expediently, the initial electron number density $n_{e0}$ is equal to $10^7$ cm$^{-3}$, $10^8$ cm$^{-3}$, $\ldots$, $10^{16}$ cm$^{-3}$ respectively in this work, corresponding to ionization degrees of 0.00000000004%, 0.0000000004%, $\ldots$, 0.04%. It takes into account that oxidizing CO into CO2 needs strong chemical conditions, which cannot be satisfied in the atmosphere. While the OH can also oxidize CO into CO2, which inherently exist in the atmosphere, and chemical reactions occur as follows [6–8]:

$$\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \quad (1)$$

$$\text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \quad (2)$$

Above-mentioned reactions can take place at room temperature and atmospheric pressure with rate coefficients of $1.5\times10^{-13}$ cm$^3$-mol$^{-1}$-s$^{-1}$ and $2.4\times10^{-13}$ cm$^3$-mol$^{-1}$-s$^{-1}$ respectively. Although the rate coefficients of reaction (1) and reaction (2) are in the same order, the number density of O$_2$ in reaction (2) is bigger in the general atmosphere, so the effect of reaction (2) is bigger than that of reaction (1) in consumption processes of CO. The rate coefficients in the code come from the atomic and molecular database in low-temperature plasma, which was established by the Hebei University (in website: http://cpst.hbu.edu.cn/wuli/atmospheric/index.asp).

The quasi-steady-state approximation (QSSA) method [21] is used to solve the constant coefficient nonlinear equations. In our model the reaction rate equations are shown as follows [18,19]:

$$\frac{dy_i}{dt} = f_i(y_1, y_2, \cdots, y_i) \quad (i = 1, 2, \cdots, 56), \quad (3)$$

$$f_i = \sum_{l \geq j}^{56} n_{jl} k_{jl} y_j y_l + \sum_{m \geq 2}^{56} n_{jlm} k_{jlm} y_j y_m, \quad (4)$$

where $y_i$ denotes the number density of the $i$th species and $f_i$ is a function involving the rate coefficient for reactions among the $j$th, $l$th, and $m$th species. The terms $k_{jl}$ and $k_{jlm}$ refer to two-body and three-body reaction rates, respectively. The term $n_{jl}$ or $n_{jlm}$ is an integer.
3 Results of numerical simulation and discussions

The temporal evolutions of each species in the atmospheric plasma are obtained in the numerical simulation. The conversion behavior of CO and CO₂, which this work involves is shown in Fig. 1.

Fig. 1 shows the reaction diagram on the conversion of CO and CO₂ in the model, in which the arrows indicate the directions of the reactions and the species on the arrows’ handles are the corresponding reactants participating in the carbon circulation. As shown in Fig. 1, CO can be converted to CO⁺, and CO₂ can be converted to CO₂⁺ mutually, in which CO⁺ and CO₂⁺ mainly come from the ionization of CO and CO₂ in the onset of discharge, and their initial number densities increase with increasing ionization degrees. While CO₂ converted to CO⁺, and CO converted to CO₂ are one-way occurrences, which conversion efficiency is relevant to the densities of N⁺ and OH (O₂), respectively. As shown in the evolution diagram, CO and CO₂ are the main species of the circulatory system, whose evolutions are the focus in this paper. In fact, CO₂ in atmospheric plasma is also involved in other carbon cycles [15], which include the CO₃⁻, CO₄⁻, CO₃⋅H₂O and CO₄⋅H₂O. Considering the length of the article, this text does not make a detailed analysis of these parts.

CO⁺ and CO₂⁺ are generated after the ionization of CO and CO₂ respectively, and they will also participate in the entire carbon cycle. Firstly, the influence of CO⁺ and CO₂⁺ on the evolutions of CO and CO₂ was analyzed as follows.

CO⁺ and CO₂⁺ colliding with a great deal of O₂ will generate CO and CO₂ by exchanging charges, these kinds of reactions are the main formatting for CO in the model. At the same time, CO and CO₂ colliding with N⁺ and Ar⁺ in air, will generate CO⁺ and CO₂⁺ by exchanging charges too. These are the mutual conversions of CO with CO⁺ and CO₂ with CO₂⁺, shown in Fig. 1. N⁺ and Ar⁺ are the main species that influence these two important converting reactions, in which the N⁺ is the key reactant in the conversions of CO₂ to CO⁺. Therefore, it is very important to be concerned about the evolutions of N⁺ and Ar⁺. Fig. 2 and Fig. 3 respectively show the temporal evolutions of N⁺ and Ar⁺ densities for different ionization degrees, in which \(n_{e0}\) is set to 10⁷ cm⁻³, 10⁸ cm⁻³, . . . , 10¹⁶ cm⁻³, respectively.

![Fig.1 The reaction diagram about the conversion of CO and CO₂ in the model](image)

![Fig.2 Temporal evolutions of N⁺ densities with different ionization degrees as \(n_{e0}\) is equal to 10⁷ cm⁻³, 10⁸ cm⁻³, . . . , 10¹⁶ cm⁻³, respectively](image)

![Fig.3 Temporal evolutions of Ar⁺ densities with different ionization degrees as \(n_{e0}\) is equal to 10⁷ cm⁻³, 10⁸ cm⁻³, . . . , 10¹⁶ cm⁻³, respectively](image)
density of $N^+$ appear as a rebound during $4 \times 10^{-10}$- $3 \times 10^{-9}$ s and a peak value near $10^{-7}$ s, which then sharply declines too. The temporal evolutions of $Ar^+$ densities are simple, as shown in Fig. 3. The evolution rule in each ionization degree is very similar, all of which show that they decay more slowly before $10^{-9}$ s, after sharply declining, and that the lifetime of $Ar^+$ is shorter.

The temporal evolutions of $CO^+$ and $CO_2^+$ densities are also relatively simple under the influences of $N^+$ and $Ar^+$. Fig. 4 and Fig. 5 respectively show the temporal evolutions of $CO^+$ and $CO_2^+$ densities for different ionization degrees, in which $n_{e0}$ is set to $10^7$ cm$^{-3}$, $10^8$ cm$^{-3}$, ..., $10^{16}$ cm$^{-3}$, respectively. Most of $CO^+$ are converted to CO because there are a lot of $O_2$ in the atmosphere. This will result in the decay of number densities, as shown in Fig. 4. When the reactions carried out about $10^{-11}$ s, the number density of $CO^+$ decreases rapidly for the other initial electron densities except for $10^7$ cm$^{-3}$, $10^8$ cm$^{-3}$. It indicates that $CO^+$ is mainly converted to CO. Of course, the trend of strong growth will be fed back to the changes of the number density for $CO^+$. When the reactions carried out during $10^{-9}$-$10^{-7}$ s, the number densities of $CO^+$ also increase slightly, but rapidly decay in the end because of frequent collisions with $O_2$. It is easy to see with the combination of Fig. 2 and Fig. 3 that the temporal evolutions of $CO^+$ densities are mainly affected by the evolutions of $Ar^+$ densities before $10^{-11}$ s, and later by that of $N^+$. For the same reason, the temporal evolutions of $CO_2^+$ and $CO^+$ densities have a high similarity, as shown in Fig. 4 and Fig. 5. The temporal evolutions of $CO_2^+$ densities are mainly affected by the evolutions of $Ar^+$ densities before $10^{-8}$ s, and later by that of $N^+$, especially at $10^{-7}$ s, the peak value of $N^+$ makes $CO^+$ and $CO_2^+$ appear as peak values or the slowing down of decay. Overall, the number densities of $CO^+$ and $CO_2^+$ decay quickly, and have little influence on that of CO and $CO_2$.

### Fig. 4 Temporal evolutions of $CO^+$ densities with different ionization degrees as $n_{e0}$ is equal to $10^7$ cm$^{-3}$, $10^8$ cm$^{-3}$, ..., $10^{16}$ cm$^{-3}$, respectively.

The consumption of CO in the atmospheric plasma mainly depends on the reaction (1) and reaction (2). But the number density of OH in natural atmosphere is very small, so the conversion rate of CO into $CO_2$ is not very big, certainly it also depends on the conditions of temporal evolutions for OH and $O_2$. Fig. 6 and Fig. 7 respectively show the temporal evolutions of $O_2$ and OH densities for different ionization degrees, in which $n_{e0}$ is set to $10^7$ cm$^{-3}$, $10^8$ cm$^{-3}$, ..., $10^{16}$ cm$^{-3}$, respectively.

### Fig. 6 Temporal evolutions of $O_2$ densities with different ionization degree as $n_{e0}$ is equal to $10^7$ cm$^{-3}$, $10^8$ cm$^{-3}$, ..., $10^{16}$ cm$^{-3}$, respectively.

As shown in Fig. 6, the densities of $O_2$ in the atmosphere near the ground change in the same order, which is consistent with the fact that the proportion of $O_2$ in the natural atmosphere is relatively stable. When the ionization degrees are extremely small, i.e. $n_{e0}$ is equal to $10^7$ cm$^{-3}$, $10^8$ cm$^{-3}$ and $10^9$ cm$^{-3}$ respectively, the number densities of $O_2$ do not change with time, i.e. they remain constant. Only $n_{e0}=10^{10}$ cm$^{-3}$, the number densities of $O_2$ just change slightly after $t=4 \times 10^{-5}$ s. And after $n_{e0}>10^{10}$ cm$^{-3}$, there appear many obvious changes in the evolution of $O_2$ number.
densities with increasing ionization degree. Overall the rules of their evolutions are very similar, which show that slowly decrease at first and rapidly then. After \(10^{-4}\) s, the number densities of \(O_2\) reached a stable value, respectively.

The initial number densities of \(OH\) are all same values in the beginning of the reactions with different ionization degrees. This value is negligible compared to the atmospheric background of \(2.5 \times 10^{19}\) cm\(^{-3}\). But in view of the oxidation of \(OH\) for \(CO\), the analysis on the rules of temporal evolutions for \(OH\) densities was done.

As shown in Fig. 7, the number densities of \(OH\) decrease to \(2.7 \times 10^{-16}\) \(n_{e0}\) with different ionization degrees at \(t=10^{-13}\) s, in which \(n_{e0}\) is the initial electron density. At this time, the number density of \(OH\) increases only when \(n_{e0}=10^{16}\) cm\(^{-3}\). In addition to this, the rules of temporal evolutions for \(OH\) densities are quite similar and almost not affected by the changes of ionization degrees when \(n_{e0}=10^7\) cm\(^{-3}\), \(10^8\) cm\(^{-3}\), \(10^9\) cm\(^{-3}\), \(10^{10}\) cm\(^{-3}\), \(10^{11}\) cm\(^{-3}\), \(10^{12}\) cm\(^{-3}\), \(10^{13}\) cm\(^{-3}\), \(10^{14}\) cm\(^{-3}\). Before \(t=10^{-8}\) s, the number densities of \(OH\) decrease very slowly, and then the rates of decreasing are accelerated gradually. Near \(2 \times 10^{-7}\) s, the number density of \(OH\) decreases to a minimum, then begins to increase to the peak near \(2 \times 10^{-5}\) s and then rapidly decay. When \(n_{e0}=10^{15}\) cm\(^{-3}\) and \(10^{16}\) cm\(^{-3}\), the temporal evolutions of \(OH\) densities decrease straightly, and the decay rates gradually increase from \(t=10^{-13}\) s. In fact, the cycle of \(CO\) and \(CO_2\) in the troposphere is weak because of low densities and short lifetime for \(OH\) near the ground. The most of \(CO\) enter into the upper part of troposphere by diffusion, reacting with the higher density of \(OH\) (\(10^4\) to \(10^6\) cm\(^{-3}\)) and consumed \([4]\).

The consumptions of \(CO\) are greatly influenced by the evolutions of \(O_2\) densities because of high level, no matter how the densities of \(OH\) changes, as shown in Fig. 8.

\[\frac{n_{\text{initial}} - n_{\text{in-spots}}}{n_{\text{initial}}} \times 100\%\]  

Negative consumption rate is the growth rate.

As shown in Fig. 8, the consumption rates of \(CO\) are very small especially in the lower ionization degrees, i.e. \(n_{e0}=10^7\) cm\(^{-3}\), \(10^8\) cm\(^{-3}\). It is almost zero before \(10^{-1}\) s, certainly because the ionization degrees of the atmospheric plasma are too low.

When \(n_{e0}=10^9\) cm\(^{-3}\), the consumption rates of \(CO\) just increase after \(10^{-7}\) s, but the amplitude increasing is very small. When \(10^9\) cm\(^{-3}\) \(\leq n_{e0} \leq 10^{14}\) cm\(^{-3}\), the consumption rates of \(CO\) change to below 10% and the rules of changing are simple. Fast increasing of consumption rates during \(10^{-9}\) to \(10^{-7}\) s contribute to the extreme values of \(OH\) density at \(t=2\times10^{-7}\) s. Thereafter, the consumption rates of \(CO\) gradually increase. When \(t \approx 2\times10^{-5}\) s, the consumption rates of \(CO\) increased dramatically, corresponding to the peak densities of \(OH\) and the decreasing of \(O_2\) density in the same period. After \(10^{-3}\) s, the consumption rate of \(CO\) tends to be stable under each ionization degree, which is maximum value during reactions. The maximum value varies with ionization degrees, i.e. when \(10^9\) cm\(^{-3}\) \(\leq n_{e0} \leq 10^{12}\) cm\(^{-3}\), they increase with increasing ionization degrees, but when \(10^{12}\) cm\(^{-3}\) \(\leq n_{e0} \leq 10^{14}\) cm\(^{-3}\), they decrease with increasing ionization degrees. When \(n_{e0}=10^{12}\) cm\(^{-3}\), the consumption rate of \(CO\) is about 9.2%, which is the largest value. The initial electron densities are \(10^{12}\) cm\(^{-3}\), \(10^{13}\) cm\(^{-3}\), \(10^{14}\) cm\(^{-3}\), \(10^{10}\) cm\(^{-3}\), \(10^9\) cm\(^{-3}\), \(10^8\) cm\(^{-3}\), \(10^7\) cm\(^{-3}\), corresponding to the consumption rates of \(CO\) from the largest to the smallest. When \(n_{e0}=10^{15}\) cm\(^{-3}\),
10^{16} \text{ cm}^{-3}$, the consumption rates of CO first increase and then decrease, i.e. the densities of CO increase when the reactions carried out to $4 \times 10^{-7}$ s and $2 \times 10^{-8}$ s, respectively, decrease slightly at about $10^{-5}$ s, and then has remained more stable values, which increase with increasing ionization degrees. Especially when $n_{e0}=10^{16} \text{ cm}^{-3}$, the biggest growth rates of CO density are close to 60%, as shown in Fig. 8. It should be noted that the actual rates of CO are five times for Fig. 8 when $n_{e0}=10^{16} \text{ cm}^{-3}$.

So far a conclusion could be drawn that the ionization degree should not be too high to make more of CO oxidation converted to CO$_2$. The best ionization degree should be 0.000004%, i.e. $n_{e0}=10^{12} \text{ cm}^{-3}$.

By reaction (1) and reaction (2), part of the CO is converted to CO$_2$. However, CO$_2$ is an important greenhouse gas and the anthropogenic emissions should be reduced. Fig. 9 shows the temporal evolutions of CO$_2$ densities for different ionization degrees, in which $n_{e0}$ is set to $10^7 \text{ cm}^{-3}$, $10^8 \text{ cm}^{-3}$, $10^9 \text{ cm}^{-3}$, $10^{10} \text{ cm}^{-3}$, $10^{11} \text{ cm}^{-3}$, respectively.

As shown in Fig. 9, the temporal evolutions of CO$_2$ densities are in same order of magnitude. The densities of CO$_2$ under each ionization degree are very close near $6 \times 10^{-9}$ s, and also near $2 \times 10^{-5}$ s except $n_{e0}=10^{16} \text{ cm}^{-3}$.

When $n_{e0}=10^7 \text{ cm}^{-3}$, $10^8 \text{ cm}^{-3}$, $10^9 \text{ cm}^{-3}$, the densities of CO$_2$ remain essentially unchanged from beginning to end. When $n_{e0}=10^{10} \text{ cm}^{-3}$, $10^{11} \text{ cm}^{-3}$, $10^{12} \text{ cm}^{-3}$, $10^{13} \text{ cm}^{-3}$, $10^{14} \text{ cm}^{-3}$, the densities of CO$_2$ first increase, then decrease near $10^{-9}$ s, and successively drop to the minimum values during $10^{-7}$-$10^{-5}$ s, which change with ionization degrees. The initial electron densities are $10^{10}$ cm$^{-3}$, $10^{11}$ cm$^{-3}$, $10^{12}$ cm$^{-3}$, $10^{14}$ cm$^{-3}$, $10^{13}$ cm$^{-3}$ corresponding magnitude of changing from the smallest to the biggest. Later the densities of CO$_2$ increase rapidly and remain stable near about $10^{-4}$ s, which slightly larger than the initial value. The initial electron densities are $10^{10}$ cm$^{-3}$, $10^{14}$ cm$^{-3}$, $10^{11}$ cm$^{-3}$, $10^{13}$ cm$^{-3}$, $10^{12}$ cm$^{-3}$, corresponding the stable values from small to large. When $n_{e0}=10^{15}$ cm$^{-3}$, $10^{16}$ cm$^{-3}$, the densities of CO$_2$ change same as each other but are smaller in vast majority of reaction time than that when $n_{e0}=10^{10}$ cm$^{-3}$, $10^{11}$ cm$^{-3}$, $10^{12}$ cm$^{-3}$, $10^{13}$ cm$^{-3}$, $10^{14}$ cm$^{-3}$. Especially when $n_{e0}=10^{16}$ cm$^{-3}$, the density of CO$_2$ in period of stability (after $10^{-4}$ s) is the smallest in all ionization degrees. Combining the Fig. 8, it’s informed that the ionization degrees affect the evolutions of CO and CO$_2$ densities inversely. Only when ionization degree is appropriate, reducing the density of CO can be done with less increasing density of CO$_2$. Thus the densities of CO and CO$_2$ must be added, considering the influence of the ionization degree on the evolutions of main carbon oxide species, as shown in Fig. 10.

**Fig. 9** Temporal evolutions of CO$_2$ densities with different ionization degrees as $n_{e0}$ is equal to $10^7 \text{ cm}^{-3}$, $10^8 \text{ cm}^{-3}$, $10^9 \text{ cm}^{-3}$, $10^{10} \text{ cm}^{-3}$, respectively.

**Fig. 10** Temporal evolutions of total number densities for CO and CO$_2$ with different ionization degrees as $n_{e0}$ is equal to $10^7 \text{ cm}^{-3}$, $10^8 \text{ cm}^{-3}$, $10^9 \text{ cm}^{-3}$, $10^{10} \text{ cm}^{-3}$, respectively.

Because the densities of CO$_2$ are relatively large, the temporal evolutions of total densities for CO and CO$_2$ (as shown in Fig. 10) differs little from the ones of CO$_2$ as shown in Fig. 9, while just be influenced slightly by ionization degrees after $10^{-4}$ s. Fig. 10 shows that the total densities of CO and CO$_2$ are the smallest when $n_{e0}=10^{16} \text{ cm}^{-3}$. But under this condition, the density of CO in the atmosphere is the largest (as shown in Fig. 8) and air toxicity increases, so it’s not suitable to eliminate CO. For the same reason, it’s also not suitable to eliminate CO and CO$_2$ when $n_{e0}=10^{15} \text{ cm}^{-3}$. No matter how little the densities of CO or these of CO$_2$ are changing in whole reactions when $n_{e0}=10^7 \text{ cm}^{-3}$, $10^8 \text{ cm}^{-3}$, $10^9 \text{ cm}^{-3}$, $10^{10} \text{ cm}^{-3}$, which make no sense to reduce the densities of CO and CO$_2$. The total densities of CO and CO$_2$ are very close when $n_{e0}=10^{11} \text{ cm}^{-3}$, $10^{12} \text{ cm}^{-3}$, $10^{13} \text{ cm}^{-3}$, $10^{14} \text{ cm}^{-3}$, corresponding total densities from small to large. Therefore, the best condition for reducing the densities of CO and CO$_2$ in the atmo-
spheric plasma is $n_{e0}=10^{13}$ cm$^{-3}$, i.e. the ionization degree is 0.00004%.

4 Conclusion

Excessive anthropogenic emissions of CO and CO$_2$ are harmful to the environment. It is necessary to understand the processes of chemical reactions for CO and CO$_2$ in the atmosphere. In this paper, a zero-dimensional model is used to simulate the temporal evolutions of CO, CO$_2$ and other main reactants in atmospheric plasma with different ionization degrees near the ground (0 km). The results show that the temporal evolutions of CO$^+_2$ densities and CO$^+$ densities are very similar, which are influenced greatly by Ar$^+$ early and after by N$^+$. Overall the number densities of CO$^+_2$ and CO$^+$ decay fast, so it has little effect on the evolutions of CO$_2$ and CO densities. In the atmospheric plasma, the consumption of CO mainly depends on OH, but only can be oxidized small part because the density of OH is extremely small in the natural atmosphere and decays quickly. The maximum consumption rate of CO is more affected by the ionization degrees, in which when $n_{e0}=10^{12}$ cm$^{-3}$, i.e. the ionization degree is 0.000004%, the consumption rate of CO is largest. The consumption rates of CO decrease with $n_{e0}=10^{12}$ cm$^{-3}$, $10^{13}$ cm$^{-3}$, $10^{14}$ cm$^{-3}$, $10^{15}$ cm$^{-3}$, $10^{16}$ cm$^{-3}$, $10^{17}$ cm$^{-3}$, and $10^{18}$ cm$^{-3}$, $10^{19}$ cm$^{-3}$, $10^{20}$ cm$^{-3}$, and $10^{21}$ cm$^{-3}$. When $n_{e0}=10^{15}$ cm$^{-3}$ and $10^{16}$ cm$^{-3}$, the densities of CO actually increase. There are large differences in the evolution rules of CO$_2$ densities in the same order of magnitude. When $n_{e0}=10^{16}$ cm$^{-3}$, the densities of CO$_2$ are relatively small and close under the other conditions. Considering the total number densities of CO and CO$_2$ and the consumption rate of CO comprehensively, the best condition for reducing the densities of CO and CO$_2$ in the atmospheric plasma is $n_{e0}=10^{13}$ cm$^{-3}$. These conclusions have important implications for the control of air pollution.

References