1. Introduction

The temperature of neutral species in a plasma ($T_g$) is one of the important parameters in plasma science and technology, but so far, the influence of $T_g$ on plasma physics and chemistry in non-equilibrium plasmas has not been investigated in detail yet. On the other hand, cryoplasmas are a special type of non-equilibrium plasmas whose $T_g$ can be controlled between room temperature and a few Kelvins [1,2]. Cryoplasmas have the potential for various applications in new plasma processes such as the treatment of very-heat-sensitive and frozen materials. For example, plasma damage to nano-porous low-$k$ materials could be suppressed owing to the low kinetic energy of radical species [3]. Since the $T_g$ of cryoplasmas span a wide range of almost two orders of magnitude, the effect of $T_g$ on various phenomena is expected to be emphasized in these cryoplasmas. In this study, to investigate the dependency of the reaction dynamics on $T_g$ in the cryoplasmas, we developed a new 0D reaction model in a mixture of helium (He) and nitrogen (N$_2$). Also we investigated the cryoplasmas by time-resolved laser absorption spectroscopy (LAS) to measure the density of the metastable helium atom (He$^m$) and the reaction dynamics related to He$^m$.

2. 0D reaction model considering $T_g$

For the investigation of the plasma chemistry in the cryoplasmas, we developed a zero-dimensional (0D) time-dependent global model with a new reaction set in a He/N$_2$ system [4]. We considered 10 species, namely electron, He atom, He metastable species (He$^m$, He$^{m*}$), He ions (He$^+$, He$^{+*}$, He$_3^+$), N$_2$, and nitrogen ions (N$_2^+$, N$_2^{+*}$), and 19 reactions. The most distinguishing feature of the model was that the dependencies of the reaction rate constants on $T_g$ in many reactions were taken into account and almost all values were collected from previous studies (see Ref. [4]). In this study, we

Figure 1. The reactions included in our 0D model and the calculation results of its reaction rate at (a) 5 K, (b) 40 K, and (c) 300 K. The reaction numbers are the same as in Ref. [4]. The thickness of the arrows indicates the magnitude of the reaction rate (thick: $> 10^9$ cm$^{-3}$ s$^{-1}$, thin: $< 10^6$ cm$^{-3}$ s$^{-1}$, medium: between $10^6$ and $10^9$ cm$^{-3}$ s$^{-1}$). The gray arrows indicate the reactions included He and N$_2$, while the black arrows indicate the reactions included only He.
introduce the results of the model calculation in He with N$_2$ (0.01%) at a total number density of 2.4 × 10$^{19}$ cm$^{-3}$, which is almost equal to that of ambient air.

Figure 1 shows the reactions related to He in our model (the reaction numbers are the same as in Ref. [4]) with arrows whose thickness depends on its reaction rate, which indicates the reaction frequency per 1 cm$^3$ and per microsecond, at 5, 40, and 300 K. At 5 K, since pure He was obtained due to solidification in spite of the mixture with N$_2$, the reactions related to N$_2$ do not occur. As shown in Fig. 1, the dominant reactions varied with $T_g$.

Concerning the quench reactions of He$^m$, Fig. 2 shows the ratio of three quench reactions of He$^m$ in our model at each temperature: the mutual collision of He$^m$ ($2^{nd}$-order reaction, R4), the Penning ionization reaction with N$_2$ ($1^{st}$-order reaction, R15), and the three-body reaction with two He atoms ($1^{st}$-order reaction, R6). The dominant quench reaction drastically changed between 30 and 40 K due to the change of the ratio of N$_2$ because of the limitation of the sublimation pressure of N$_2$ at cryogenic temperatures. Above 40 K, the dominant quench reaction varied from a Penning reaction (R15) to the three-body reaction with two He atoms (R6) with increasing $T_g$. This temperature dependency was mainly due to the strong dependency of the reaction rate constant of the three-body reaction (R6) on $T_g$. In Fig. 2, the dominant quench reaction of He$^m$ changed with $T_g$ even near and above room temperature. This implies that the importance of $T_g$ on a plasma chemistry in high-density media near and above room temperature. The results of the calculation also showed that the lifetime of He$^m$ at 5 K was much longer than that at 300 K because neither the reactions of R6 nor R15 work well at 5 K.

3. Laser absorption spectroscopy

In order to confirm the validity of the calculation results, LAS measurements were conducted on a dielectric barrier discharge in He with air impurity at the same number density. The plasmas were generated using stainless steel electrodes (5 mm × 10 mm) with polyimide barriers (thickness: 0.125 mm) separated by a gap distance of 0.5 mm. The burst of the AC voltage (amplitude: ~750 V) of 10 kHz was applied (ON/OFF: 50 ms/50 ms). The laser wavelength was 1083 nm which corresponds to the energy gap between He$^m$(2$^1$S) and He$^2$(2$^3$P).

The results showed that the lifetime of He$^m$ at 14 K was more than 100 times longer than that at 300 K. Also, the decay curve at 14, 40, and 300 K implied that the dominant quench process of He$^m$ at 40 K and 300 K was nearly a $1^{st}$-order reaction, while it was nearly a $2^{nd}$-order reaction at 14 K.

4. Conclusion

The 0D reaction model could reproduce the long lifetime of He$^m$ and the dependence of the quench reactions of He$^m$ on $T_g$. The results of the model calculation suggested that the discharge mechanism generated in He/N$_2$ depends strongly on $T_g$ at cryogenic temperature and also near and above room temperature.

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