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Dependence of the discharge mechanism of cryoplasmas generated in He/N_2 on the plasma gas temperature

ヘリウム窒素混合ガスを用いたクライオプラズマ放電機構のガス温度依存性

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We developed a new 0D reaction model that includes the dependency of the reaction rate constants on the gas temperature (T_g). The results of the calculation indicated that the reaction dynamics in cryoplasmas in a mixture of helium and nitrogen vary drastically with T_g and this is mainly due to the changes of the quench reactions of helium metastable atoms depending on T_g. Moreover, we investigated the cryoplasmas by laser absorption spectroscopy and confirmed good agreement between the experimental results and our model.

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_2^m), He ions (He^+, He_2^+, He_3^+), N_2, and nitrogen ions (N_2^+, N_4^+), 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

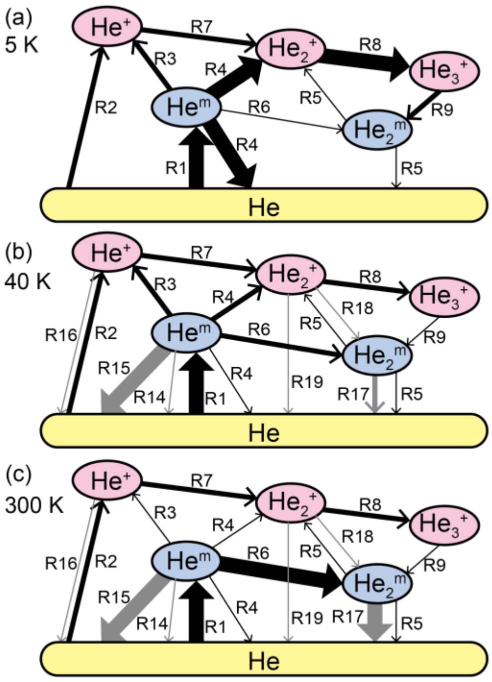

Figure 1 The reactions included in our 0D model and the calculation results of its reaction rate at (a) 5 K, (b) 40 K, and (c) 300 K. The reaction numbers are the same as in Ref. [4]. The thickness of the arrows indicates the magnitude of the reaction rate (thick: $> 10^9$ cm^{-3} μs^{-1}, thin: $< 10^{-6}$ cm^{-3} μs^{-1}, medium: between 10^6 and 10^9 cm^{-3} μs^{-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 (2nd-order reaction, R4), the Penning ionization reaction with N_2 (~1st-order reaction, R15), and the three-body reaction with two He atoms (~1st-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 $He^m(2^3S)$ and $He^*(2^3P)$.

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

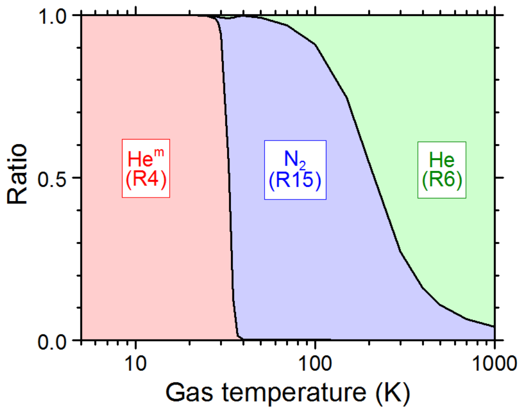

Figure 2 Ratio of the three quench reactions of He^m as a function of the gas temperature. The species indicated in each region such as He^m, N_2, and He are the quencher for He^m at each reaction.

implied that the dominant quench process of He^m at 40 K and 300 K was nearly a 1st-order reaction, while it was nearly a 2nd-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.

Acknowledgments

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