$He(2^3S)$ and $He_2(a^3\Sigma_u^+)$ metastable densities, measured by broadband absorption technique, in atmospheric pressure helium rf discharge

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Abstract: Atomic and molecular metastable helium species are an important source of ionization in low electron density atmospheric pressure plasmas due to efficient Penning ionization with impurities. In this contribution, we report for the first-time measurements of absolute densities of $He(2^3S)$ and $He_2(a^3\Sigma_u^+)$ metastable species in a capacitively coupled parallel plate atmospheric pressure helium RF discharge using broadband absorption spectroscopy. The spatial distribution profiles of these species correlate well with the sheath structure. The maximum density of $He(2^3S)$ atoms, measured in the sheath edge is 3-4 times larger than that of $He_2(a^3\Sigma_u^+)$ molecules at the same location.

Keywords: $He(2^3S)$, $He_2(a^3\Sigma_u^+)$, metastable species, broadband absorption spectroscopy, atmospheric pressure plasma.

1. Introduction

In the last few decades, there has been a lot of interest in atmospheric pressure plasmas, particularly in nanosecond pulsed discharges generated at high repetition rates or discharges driven at high frequencies [1,2]. This allows for long-lived species from the previous discharge to play a crucial role in the subsequent discharge ignition, leading to the generation of more stable discharges at lower voltages. Owing to its high energy, helium metastable states play an important role in driving discharge kinetics, understanding energy transport mechanisms as well as in explaining afterglow kinetics in pure helium discharges [3–5]. In this regard, metastable species produced in helium play an important role in plasma ionization. With an excitation energy of 19.82 eV, atoms in the lowest excited metastable state of helium $He(2^3S)$ can act as an important source of ionization through Penning ionization reactions with gas impurities such as N_2, O_2 and H_2O, which have ionization energies in the range of 12-15 eV [6]. In addition, helium metastable species can enable or contribute to stepwise ionization, secondary electron emission, or increase the production of reactive species.

Recently, Czarnetzki *et al* has measured Rydberg molecules in atmospheric pulsed helium discharges and shown that Rydberg molecules might be an important source of energy in helium afterglows [7]. Also, a large amount of work has been reported on atomic metastable species measured by laser diodes [3,5,8–10]. However, very few measurements have been performed on molecular metastable states in atmospheric pressure helium plasmas while they can be an important energy source in the afterglow.

In this contribution, broadband absorption spectroscopy is employed for the first time to measure absolute densities of both atomic $He(2^3S)$ and molecular $He_2(a^3\Sigma_u^+)$ metastable species of helium in a radio-frequency (rf) driven capacitively coupled helium plasma.

2. Methods

The plasma reactor used in this study is a capacitively coupled glow discharge system powered by rf (13.56 MHz) voltage. A schematic of the plasma system is shown in figure 1. The plasma is generated between two parallel copper electrodes separated by a gap of 2 mm. Both electrodes have a surface area of 9.5 × 19.1 mm^2, and are embedded in a homemade polytetrafluoroethylene housing, with provisions for inlet for the feed gas and outlet for the effluent. One of the electrodes is connected to the RF power source (E&I A150), which amplifies the RF signal generated by a function generator, while the other electrode remains grounded. The generator is matched to the plasma reactor with a homemade π matching circuit. Both electrodes are water cooled to minimize thermal drift of the system over time. The

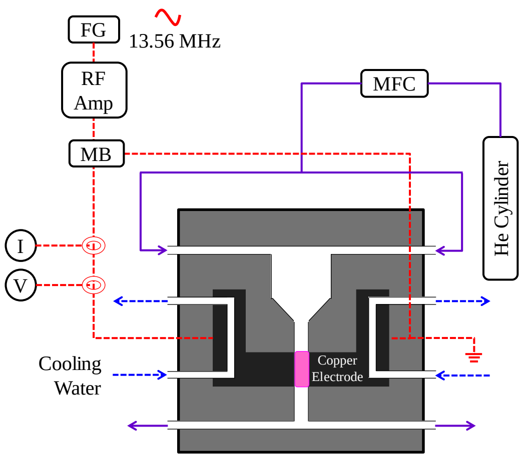

Fig. 1. Experimental schematic of the plasma source.

plasma is operated in "pure" helium (ultra-pure carrier grade 99.9995%) at atmospheric pressure at a high flow rate of 5 standard litres per minute, and the gas residence time in the discharge is 21 ms. The gas velocity in the discharge gap is 0.43 m/s, and the flow remains laminar.

The discharge power is measured using a high voltage probe (Tektronix P5100A) and a Rogowski coil (Pearson Electronics, Model 2878). The power is kept constant at 15 W with < 10% uncertainty.

Broadband absorption spectroscopy is employed for the measurement of the metastable species densities. The light source used is a laser-stabilized lamp (Energetiq EQ-99 LDLS), which is focused into the discharge with a lens of a focal length of 10 cm and a pinhole. A lens with a focal length of 5 cm focuses the beam exiting the plasma reactor onto the entrance slit of a monochromator (ARC AM-510). A charged coupled device (CCD) camera (Andor iDus 420) is used as a detector. The beam size in the plasma is ~0.2 mm. To measure the density of metastable species at different positions between electrodes, the plasma reactor, mounted in a translation stage, was moved by steps of 100 µm along the gap, the whole optical system remaining fixed.

The absolute path-averaged densities, N, of the metastable states can be deduced from the Beer-Lambert law [11]:

$$W \equiv \int \left(1 - \frac{I(\lambda)}{I_0(\lambda)}\right) \mathrm{d}\lambda = \int \left(1 - \exp(-\sigma \times L \times N)\right) \mathrm{d}\lambda \tag{1}$$

where W is the area under the fractional absorption, I and I_0 the transmitted intensities in the presence and absence of absorbing species, respectively, σ the absorption cross-section and L the beam path length through the plasma. The oscillator strengths (f) and broadening parameters are taken from [12].

For not very weak absorption lines (f is only 0.064 for the 388.8 nm line, which is not strong), as in this study, the measured W in equation 1 cannot be related to the absorbing metastable state density with any analytical expression. So, a calculation is performed to deduce W for different values of N by considering the spectral shape of the absorption line (including Doppler and van der Waals broadenings) along with the oscillator strength of the line. Comparing the deduced W values with those obtained experimentally, the absolute density of He(2^3S) metastable atoms is determined at several positions across the discharge gap.

For $He_2(a^3\Sigma_u^+)$, the (0-0) and (1-1) band peaks are identified and an absorption spectrum of the $He_2(a^3\Sigma_u^+)$ state is shown in figure 2. The rotational temperature of the $He_2(a^3\Sigma_u^+)$ state is consistent with the gas temperature. A Voigt function is used to fit the wavelength isolated Q and R rotational lines, providing the respective area under the different rotational line profiles. Using a similar approach as before, the density in different rotational levels are determined. Assuming a Boltzmann distribution in the rotational levels, the density in different rotational level can be related to the total density of $He_2(a^3\Sigma_u^+;\ v=0)$. Absorption lines from $He_2(a^3\Sigma_u^+;\ v=1)$ level indicate v=1 vibrational level density being about 20% of the total density. The rotational temperature of the OH(A–X) emission [13], from small water impurity in the feed gas, provides similar gas temperature than that from $He_2(a^3\Sigma_u^+)$ absorption spectra.

3. Results and discussions

The gas temperature is in the range of 320 to 350 K. The spatial distribution profiles of the densities of both He(2^3S) and $He_2(a^3\Sigma_u^+)$ states between the electrodes are shown in figure 3. The plot shows a steep rise in density close to the electrodes followed by a sharp decline toward the bulk of the discharge. The metastable distribution profile corresponds well with the emission intensity profile of a pure helium discharge operated in the α-mode at atmospheric pressure and has already been studied using models [14]. The highest metastable density of

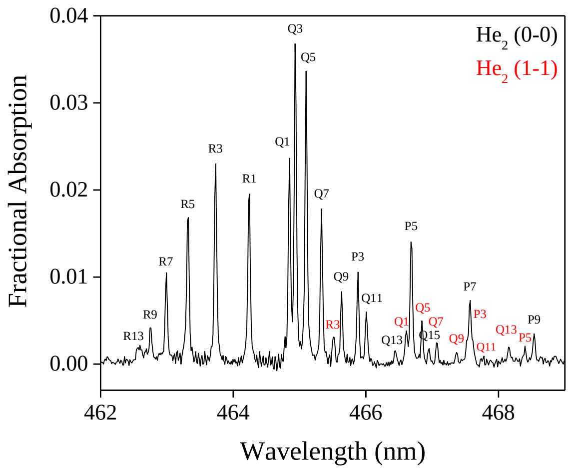

Fig. 2. Absorption spectra of $He_2(a^3\Sigma_u^+ \rightarrow e^3\Pi_g)$ with identified (0-0) band peaks.

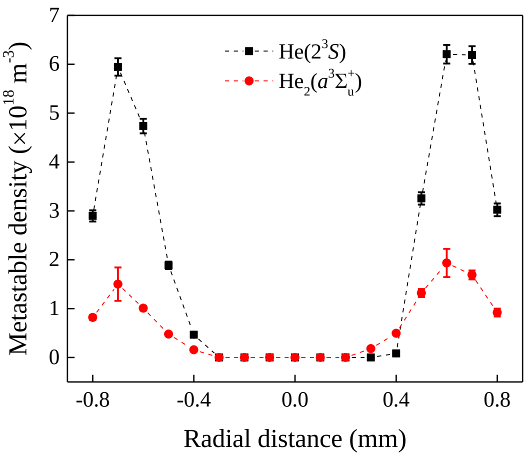

Fig. 3. Spatial distribution of He(2^3S) and $He_2(a^3\Sigma_u^+)$ densities across the plasma gap.

~6×10^{18} m^{-3} for 2^3S state is observed at around 100 μm from the surface of the electrodes, where most excitation and ionization processes take place. The metastable density decreases close to the surface of the electrode as the electron density in the rf-driven sheath is quite low to sustain efficient excitation and ionization of the ground state helium atoms [3]. In the bulk, the density drops below the detection limit of the system, which is most likely caused by the lower electron temperature in the positive column and the short lifetime of metastable atoms, that does not allow for significant transport by diffusion [3]. Similar density distribution profile is observed for molecular metastable, as $He_2(a^3\Sigma_u^+)$ is produced in a 3-body reaction from $He(2^3S)$ atoms. A maximum $He_2(a^3\Sigma_u^+)$ state density of ~2×10^{18} m^{-3} is measured in the sheath edge. The maximum density of $He(2^3S)$ atoms is 3-4 times larger than that of $He_2(a^3\Sigma_u^+)$ molecules.

4. Conclusion

The measurement of densities of atomic as well as molecular metastable species of helium in a radio-frequency discharge has been studied for the first time by broadband absorption. The spatial measurement shows the maximum density of ~6×10^{18} m^{-3} and ~2×10^{18} m^{-3} for $He(2^3S)$ atoms and $He_2(a^3\Sigma_u^+)$ molecules, respectively at ~100 μm from the electrode surface.

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