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Excimer formation in high-pressure microhollow cathode discharge plasmas in helium initiated by low-energy electron collisions

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Abstract

We report the observation of intense continuous vacuum ultraviolet radiation in the range 60–100 nm from microhollow cathode discharge plasmas in high-pressure He (up to 600 Torr). Two prominent emissions, a narrow, sharply peaked feature in the region of 58–65 nm and a broad emission from 65 to 95 nm are attributed to the He_2^* first- and second-excimer continuum emission, respectively. We also observed several narrow atomic emission lines in the 95–125-nm range that correspond to atomic O, N, and H emission lines. We attribute the presence of these atomic line emissions to near-resonant energy transfer processes involving the He_2^* excimers and trace concentrations of the impurities O_2, N_2, and H_2 in the discharge feed gas. The processes leading to the atomic line emissions in the present case are similar to the near-resonant energy transfer process observed previously in high-pressure microhollow cathode discharge plasmas in Ne/H_2 gas mixtures, which resulted in the emission of intense, monochromatic atomic hydrogen Lyman-α radiation (P. Kurunczi et al. J. Phys. B: At. Mol. Opt. Phys. 32 (1999) L651). He_2^* excimer formation in a microhollow cathode discharge plasma is initiated by low-energy electron collisions (excitation of the metastable He levels or ionization of the He atoms) followed by three-body collisions. The emission of He_2^* excimer radiation from a microhollow cathode discharge plasma indicates that these discharges are very efficient sources of energetic electrons, as the formation of He_2^* excimers requires a sufficiently large number of electrons with energies well above 20 eV. (Int J Mass Spectrom 205 (2001) 277–283) © 2001 Elsevier Science B.V.

Keywords: Low-energy electron collisions; Hollow cathode discharges; High-pressure plasmas; Excimers; Energy-transfer processes

1. Introduction

Discharge plasmas at high pressures (up to atmospheric pressure), where single-collision conditions do no longer prevail, provide a fertile environment for the experimental study of collisions and radiative processes dominated by step-wise excitation processes, that is, the excitation of an already excited atomic/molecular state and by three-body collisions leading, for example, to the formation of excimers. The dominance of collisional and radiative processes beyond binary collisions involving ground-state atoms and molecules in such environments allows for many interesting applications of high-pressure plasmas such as high-power lasers [1–5], opening switches [6], novel plasma-processing applications and sputtering [7,8], EM absorbers and reflectors [9],

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Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

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remediation of gaseous pollutants [10–12], and excimer lamps and other noncoherent vacuum-ultraviolet (VUV) light sources [13–15]. One approach toward the generation and maintenance of a high-pressure plasma is based on the hollow-cathode discharge (HCD) concept and exploits the inverse scaling of the hole diameter with the operating pressure [16,17], which makes atmospheric-pressure operation possible [14,17–20], if the hole diameter is of the order of ~0.1 mm (microhollow cathode discharge, MHCD). HCD devices consist of a metallic cathode with a hole, an arbitrarily shaped metallic anode, and an insulator between the two metallic electrodes. The HCD shows several modes of operation as a function of gas pressure p, hole diameter D, cathode-anode separation d, and discharge current I. At values of the product $p \times D$ below 10 Torr/cm and low currents (<1 mA), a normal glow discharge develops along the path of the vacuum electric field. As the current increases, a transition to the hollow cathode mode occurs in which the ionization is concentrated along the axis of the discharge and the discharge is sustained by energetic pendulum electrons [16,17,21]. If the current is increased further, an abnormal glow discharge develops. The hole diameter D is inversely proportional to the pressure up to ~10 Torr/D (where D is measured in centimeters) for noble gases and for N_2 [14,16,17], so that atmospheric-pressure operation requires a hole diameter of the order of 0.1 mm (microhollow cathode discharge, MHCD).

In this article, we report the observation of He_2^* excimer emissions in the 60–100-nm spectral region from MHCD plasmas in high-pressure He. The first observation of He_2^* excimer radiation dates back to the very early part of the twentieth century [22,23]. Extensive spectroscopic studies of H_2^* and other rare gas excimer emissions were carried out in the 1950s and 1960s by Tanaka and coworkers [24–28]. In these studies, the excimers were typically formed in some type of high-pressure discharge such as a dielectric barrier discharge, a microwave discharge, or a pulsed condensor discharge. The light-emitting plasma volume in all these discharges was of the order of a few mm^3 cubed to a few cm^3 cubed. By contrast, the MHCD used in these studies represents essentially a point-like source with a plasma volume of only about 5×10^{-3} mm^3. Very high power densities of up to several hundred Watts per mm^3 can be achieved in such a source, which thus forms a very bright point source of VUV (and other) radiation.

2. Excimer formation and low-energy electron collisions

HCD and MHCD devices have been used extensively for the generation of noncoherent UV and VUV excimer radiation using either pure rare gases or rare gas–halide mixtures [14,17]. Rare gas atoms have a ^1S_o electronic ground state. The lowest excited states result from the promotion of a (np) valance electron to the $(n + 1)s$-level (n = 2, 3, 4, 5 for Ne, Ar, Kr, Xe) leading to four P states, two of which are metastable, while the other two states decay to the ground state via dipole-allowed transitions. The most common routes to rare gas excimer formation are either via electron-impact ionization

$$e^- + X \rightarrow X^+ + 2e^-, \quad (1a)$$

$$X^+ + 2X \rightarrow X_2^+ + X, \quad (1b)$$

$$X_2^+ + e^- \rightarrow X^* + X, \quad (1c)$$

$$X^* + 2X \rightarrow X_2^* + X, \quad (1d)$$

where X = He, Ne, Ar, Kr, or Xe and the asterisk denotes a metastable rare gas atom, or alternatively, directly via excitation of metastable rare gas atoms by electrons

$$e^- + X \rightarrow X^* + e^-,$$

$$X^* + 2X \rightarrow X_2^* + X.$$

In either case, the excimer molecules are formed in three-body collisions involving a metastable rare gas atom and two ground-state atoms. Efficient excimer formation requires both a sufficiently large number of electrons with energies above the threshold for the metastable formation (or ionization), and a pressure that is high enough to have a sufficiently high rate of three-body collisions. In He, the minimum energy to

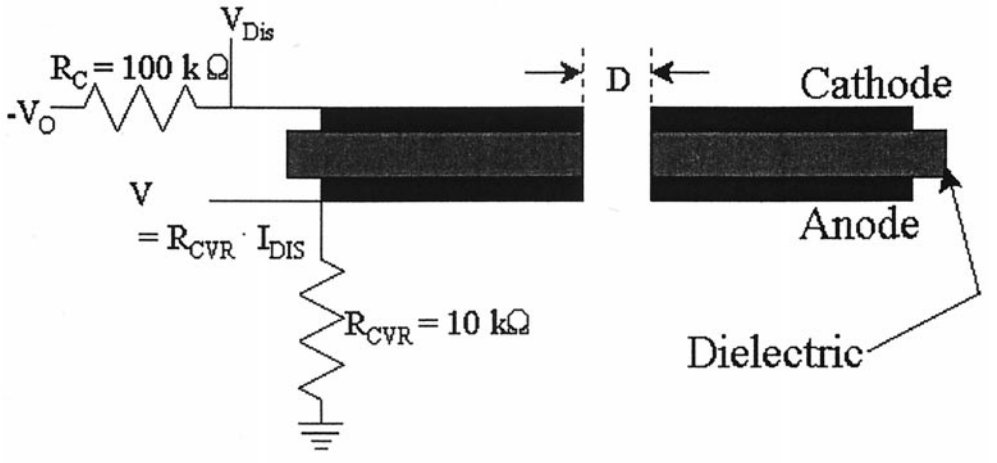

Fig. 1. Schematic diagram of the microhollow cathode discharge device and the electric circuit used in the present experiments. The cathode material is molybdenum, and the dielectric is mica.

form a metastable He atom by electron impact on ground-state He is ~20 eV, and the ionization energy of He is >24 eV [29].

Rare gas excimer emission spectra are dominated by transitions from the lowest-lying bound $^3\Sigma_u$ excimer state to the repulsive ground state (second continuum) [30,31] with peak emissions at 170 (Xe), 145 (Kr), 130 (Ar), 84 (Ne), and 75 nm (He). The so-called first-excimer continua in the rare gases are observed on the short-wavelength side of the second continua and are attributed to the radiative decay of vibrationally excited levels of the $^1\Sigma_u$ excimer state. Most work to date has been carried out in Xe, Kr, and Ar, where the high-pressure MHCD can be sealed off with a window (LiF or MgF_2), for VUV spectroscopic investigations, of the excimer emissions in the 130–170-nm region. Spectroscopic investigations of the Ne_2^* and He_2^* excimers, however, require a specially designed open MHCD source [32] connected directly to a VUV monochromator, as no material is transparent <105 nm.

3. Experimental details

The electrodes of the MHCD used in the present experiments (Fig. 1) are made of 0.1-mm-thick molybdenum foils separated by a 0.25-mm spacer of mica with a hole of typically 0.1–0.2 mm in diameter in the cathode, the dielectric, and the anode. Supply voltages V_o are typically 400–700 V and sustaining (discharge) voltages $V = R_{CVR}\, I_{DIS}$ are in the range of 150–300 V depending on the gas pressure and the actual geometry of the MHCD. Discharge currents I_{DIS} vary between 1 and 10 mA. The circuit includes a resistor R_{CVR}, which allows us to monitor the discharge current directly on an oscilloscope along with the discharge sustaining voltage V_{DIS}. We can also operate the MHCD in a pulsed dc mode with frequencies up to tens of kHz, pulse lengths from 100 ns to 1 ms and variable pulse separation and duty cycle using a versatile pulse generator. The MHCD is mounted directly to the entrance slit of a Minuteman 302-V 0.2-m VUV monochromator (wavelength range 50–250 nm, reciprocal linear dispersion of 4 nm/mm). Helium excimer radiation from the MHCD enters the VUV monochromator through a 0.2-mm pinhole between the discharge region and the monochromator, which is differentially pumped to provide an operating pressure in the 10^{-5}-Torr range in the detector chamber. The VUV photons are detected by a channel electron multiplier or a suitable VUV photomultiplier connected to a standard pulse-counting system. The entire data acquisition and analysis process is controlled by a PC using LabView. A

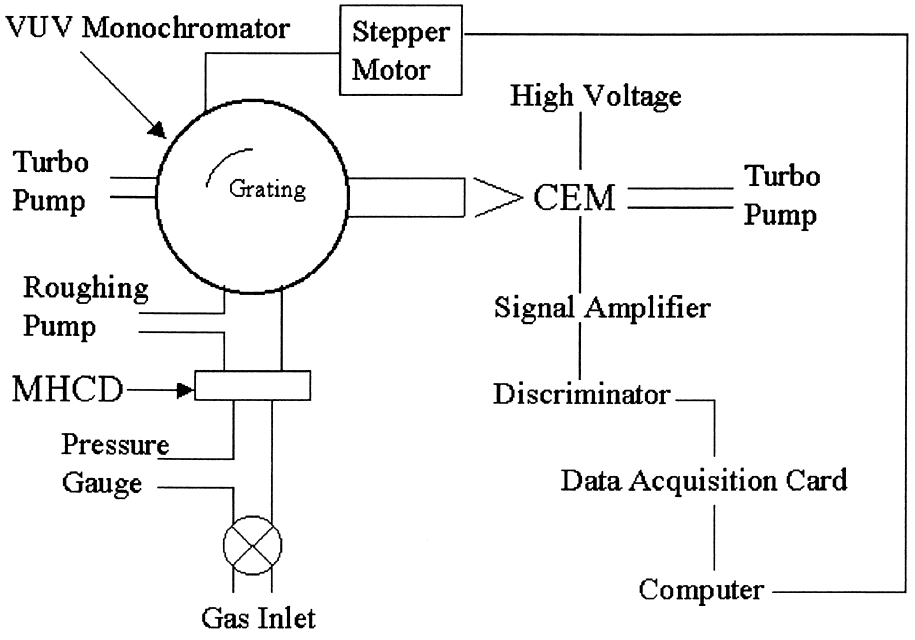

Fig. 2. Schematic diagram of the experimental apparatus used in the present experiments. MHCD denotes the microhollow cathode discharge device, and CEM refers to the channel electron multiplier that is used for the detection of the vacuum ultraviolet photons.

schematic diagram of the experimental set-up is shown in Fig. 2.

4. Results and discussion

Fig. 3a shows the emission spectrum recorded from an MHCD plasma in He at a pressure of 600 Torr. Two emission features are readily observed. The narrow, sharply peaked emission from 58 to 64 nm is attributed to the He_2^* first-excimer continuum, whereas the broad feature extending from 64 nm to almost 100 nm is characteristic of the He_2^* second-excimer continuum. The presence of the helium excimer emissions from MHCD plasmas is indicative of the fact that these discharges are very effective sources of electrons with energies well above 20 eV. It is quite remarkable that discharge-sustaining voltages of 200 V or below for this discharge plasma result in an energy distribution function of the plasma electrons where a significant number of electrons have energies >20 eV.

We also note that the emission spectrum in Fig. 3a shows several atomic line emissions in the wavelength range from 95 to 125 nm. These line emissions are identified as atomic O, N, and H lines, including the prominent hydrogen Lyman-α and Lyman-β lines at, respectively, 102.5 and 121.6 nm and the nitrogen resonance lines at 113.4 and 120.2 mm. The line emissions at 98, 104, and 115 nm correspond to atomic oxygen lines. We attribute the presence of these line emissions to near-resonant energy-transfer processes between the He_2^* excimers and trace concentrations of the impurities H_2, N_2, and O_2 in the discharge feed gas. The emission of these atomic lines is similar to the intense hydrogen Lyman-α and Lyman-β and atomic nitrogen emissions that were observed earlier in emissions from MHCD plasmas in high-pressure Ne/H_2 and Ne/N_2 mixtures [32,33]. Table 1 summarizes the energies required for the emission of the atomic lines in Fig. 3 in comparison with the energies contained in the He_2^* excimers. As can be seen, on the basis of energy considerations, all O, N, and H atomic-emission lines depicted in Fig. 3a can be attributed to near-resonant energy-transfer

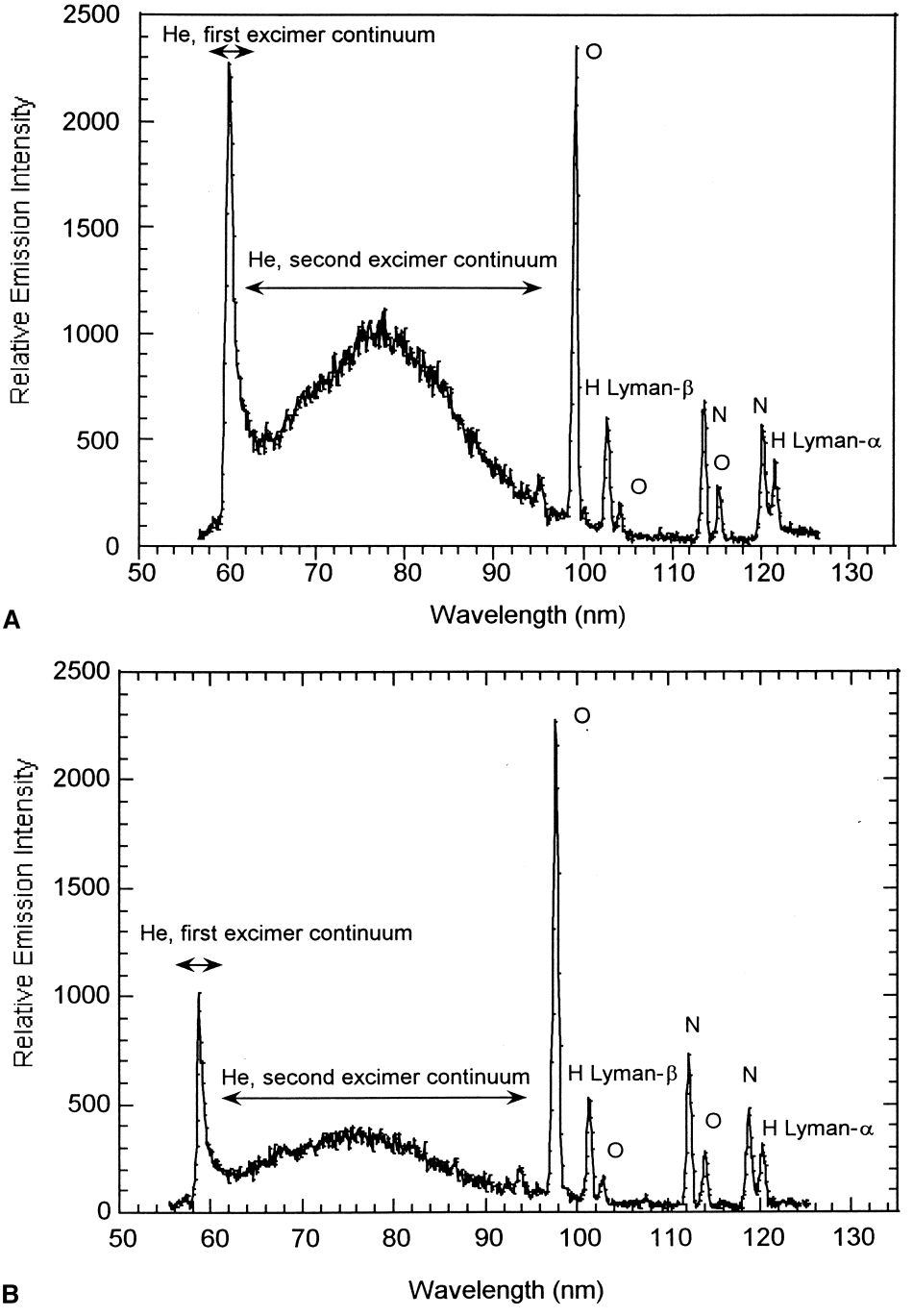

Fig. 3. (*a*) Emission Spectrum from a MHCD plasma in 600 Torr He with trace impurities of H_2, N_2, and O_2. The first and second He_2^* excimer-emission continua have been marked. Also indicated are several O, N, and H atomic line emissions (see text for further details). (*b*) Same as (*a*) for a He pressure of 400 Torr.

Table 1
Summary of energies involved in near-resonant energy transfer processes between He_2^* excimers and O_2, N_2, and H_2 molecules

Molecule	Dissociation Energy	Wavelength and Energy of Atomic Line	Total Energy Needed for Atomic Line Emission	Energy Contained in He_2^* Excimer
H_2	4.48 eV	121.6 nm/10.20 eV	14.68 eV	12.40–21.38 eV
H_2	4.48 eV	102.5 nm/12.10 eV	16.58 eV	12.40–21.38 eV
N_2	9.85 eV	113.4 nm/10.94 eV	20.79 eV	12.40–21.38 eV
N_2	9.85 eV	120.3 nm/10.31 eV	20.16 eV	12.40–21.38 eV
O_2	5.08 eV	98 nm/12.65 eV	17.73 eV	12.40–21.38 eV
O_2	5.08 eV	104 nm/11.92 eV	17.00 eV	12.40–21.38 eV
O_2	5.08 eV	115 nm/10.78 eV	15.86 eV	12.40–21.38 eV

processes from the He_2^* excimers to O_2, N_2, and H_2. Further studies to elucidate the microscopic details of these energy-transfer processes are currently underway.

Fig. 3b shows a similar emission spectrum obtained at a somewhat lower He pressure (400 Torr). The same emission features are apparent. Two main differences are noteworthy: first, the excimer emissions are weaker (compared to the atomic line emissions), as one would expect at the lower pressure, because the rate of three-body collisions, which are necessary to form the excimers, increases with increasing pressure in a nonlinear fashion [34]); second, the intensity of the He_2^* first-excimer continuum is somewhat larger at the lower pressure compared to the intensity of the second continuum. This can be attributed to the fact that the vibrationally excited He_2^* excimer molecules that emit the first continuum are more efficiently quenched at the higher gas pressure. A similar observation has been reported in the case of the Ne_2^* excimer emissions at different gas pressures [34].

5. Conclusions

We report the observation of intense continuous vacuum ultraviolet radiation in the range 60–100 nm from a microhollow cathode discharge plasmas in high-pressure He (up to 600 Torr). A narrow, sharply peaked emission feature in the region 58–65 nm is attributed to the He_2^* first-excimer continuum and a broad emission from 65 to 95 nm is identified as the He_2^* second-excimer continuum emission. We also observed several narrow atomic emission lines in the 95–125-nm range that correspond to atomic O, N, and H emission lines, which we attribute to near-resonant energy-transfer processes involving the He_2^* excimers and trace concentrations of the impurities O_2, N_2, and H_2 in the discharge feed gas. The emission of He_2^* excimer radiation from a microhollow cathode discharge plasma indicates that these discharges are very efficient sources of energetic electrons, as the formation of He_2^* excimers requires a sufficiently large number of electrons with energies well above 20 eV.

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