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SPECTROSCOPY OF ATOMS AND MOLECULES

Optical Characteristics of an Electric-Discharge Source of Ultraviolet Radiation Based on a Mixture of Argon with Heavy Water (D_2O) Vapor

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Abstract—The optical characteristics of a barrier discharge in a mixture of heavy water vapor with argon in the wavelength region 200–315 nm are presented. The dependence of the radiation intensity of the OD ($A \rightarrow X$) band at $\lambda = 309$ nm on the partial pressure of the D_2O vapor is studied, the mechanism of hydroxyl formation in the plasma is considered, and optimal compositions of pollution-free and inexpensive mixtures based on Ar–D_2O are determined for application in UV lamps, which are promising for use in photomedicine.

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INTRODUCTION

The optical characteristics of gas-discharge plasma, as well as the physical processes of formation and dissociation of hydroxyl (OH), hydrogen peroxide (H_2O_2), and other products of the water molecule destruction have been extensively studied since the 1930s [1].

The possibility of creating an efficient and selective lamp based on the 306.4-nm OH($A \rightarrow X$) band, the working mixture (Ar–H_2O) of which was excited in a glow discharge, was demonstrated for the first time in [2]. In [3], it was shown that the glow discharge plasma also efficiently emits in the vacuum ultraviolet (VUV) region with $\Delta\lambda \approx 190–140$ nm OH*. However, to create sealed-off hydroxyl lamps, it is better to excite these working mixtures in discharges between electrodes that have no direct contact with the active plasma of products of water molecule destruction.

In particular, the authors of [4] reported the creation of a barrier lamp based on the 309-nm OH($A \rightarrow X$) band with an average radiation power of 1.1 W, the working mixture of which was excited by microsecond high-voltage pulses. Optimal conditions for the UV–VUV emission of hydroxyl of the water vapor plasma formed in a nanosecond capacitor discharge were determined in [5, 6].

Since the use of heavy water vapor is more efficient (by a factor of 1.5–2) in low-pressure hydroxyl-based UV emitters, in this work, we study the emission characteristics of nanosecond barrier discharge in an Ar–D_2O mixture. The results of investigations of the barrier discharge based on a He–D_2O mixture were presented in [8].

In this paper, we present the time-averaged emission spectra of a barrier discharge in Ar–D_2O mixtures of different pressures and compositions, as well as the results of investigations of the effect of the partial pressure of D_2O vapor on the emission intensity of the 309-nm OD($A \rightarrow X$) band.

EXPERIMENTAL CONDITIONS

The discharge tube with two dielectric barriers was made as a coaxial system of two cylindrical KU-1 quartz tubes and was 200 mm long. The outer tube diameter was 24 mm, and the inner tube diameter was 12 mm. A solid aluminum electrode was placed inside the inner quartz tube. An electrode in the form of a nickel wire spiral with a transparency of about 80% was mounted on the outer surface of the discharge tube. The area of the working surface of the discharge tube was about 360 cm^2.

A filamentless barrier discharge was ignited by 20–30-ns pulses from a high-voltage generator. The voltage pulse amplitude was ±20–40 kV, and the pulse repetition rate was 35–1000 Hz.

The plasma radiation was recorded by a 1-m vacuum monochromator and an FEU-142 photomultiplier. The current and voltage pulses were recorded using a Rogovsky belt, a low-inductive voltage divider, and a 6-LOR fast pulse oscilloscope.

CHARACTERISTICS OF THE UV EMITTER

The time-average emission spectra of the discharge in mixtures of argon with D_2O vapor normalized to the relative spectral sensitivity of the vacuum monochromator–FEU-142 system are shown in

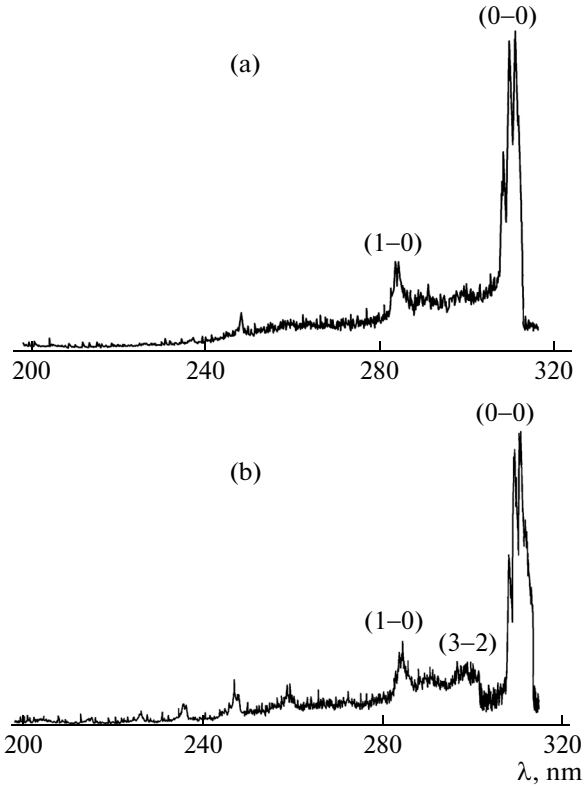

Fig. 1. Emission spectra of a barrier discharge in the Ar–D_2O mixture (band OD($A^2\Sigma^+ \rightarrow X^2\Pi$)) at partial pressures of heavy water vapor $p(D_2O)$ = (a) 0.05 and (b) 0.40 kPa. p(Ar) = 20 kPa.

Fig. 1. The spectra were recorded at different partial pressures of the D_2O vapor with other conditions being the same.

In the spectral range 200–320 nm, the most intense 283-nm OD($A \rightarrow X$, 1–0) and 309-nm OD($A \rightarrow X$, 0–0) bands were observed against the weak background of the deuterium continuum. This continuum was more pronounced at a minimal partial pressure of D_2O vapor. An increase in the partial pressure of D_2O vapor to 400 Pa leads to the appearance of bands with maxima at 289.0 (1–0), 296.4 (3–2), 297.2 (2–0), and 263.8 nm (3–1), which belong to the OD $A^2\Sigma^+ \rightarrow X^2\Pi$ emission [9]. Similarly to the nanosecond discharge in a water jet (or in an air–water suspension) [10], we observed 260- and 275-nm emission bands of nitric oxide (NO), which is mainly formed involving the participation of water molecules rather than of molecular oxygen, which is contained in residual gases in insignificant amounts. The weak emission bands in the spectral range 220–240 nm can also be attributed to NO* molecules. The intensity of NO* bands increases with increasing partial pressure of the D_2O vapor.

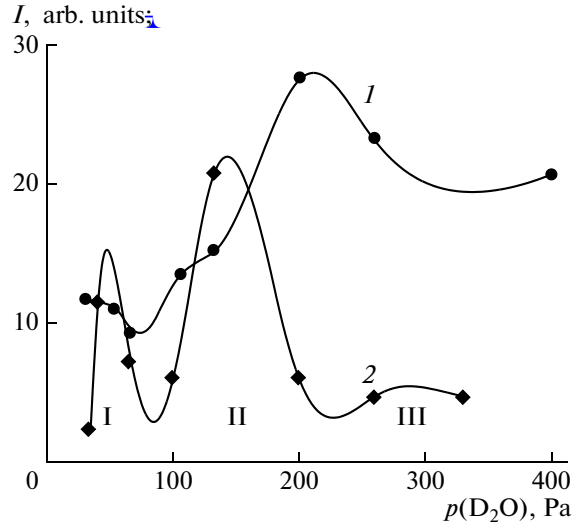

Fig. 2. Dependences of the emission intensity of the OD($A \rightarrow X$) band with the maximum at $\lambda \approx 309$ nm on the partial pressure of D_2O vapor at (*1*) p(Ar) = 20 kPa and (*2*) p(He) = 20 kPa.

Figure 2 shows the dependences of the intensity of the 309-nm OD ($A \rightarrow X$, 0–0) band in He- and Ar-based mixtures in identical relative units (the intensities are obtained by integrating all electronic vibrational bands of the $A \rightarrow X$ system in the spectral range 306–315 nm) on the partial pressure of D_2O vapor at identical pressures of argon and helium. The shapes of these curves are very different for mixtures based on argon and helium. In the literature, there are no similar results for the barrier discharge plasma based on mixtures of He and Ar with ordinary water vapor. In [4], this dependence is not given in an explicit form, while its qualitative description allows one to conclude that the optimal pressure of water vapor falls within the region 100–200 Pa (at optimal argon pressure p(Ar) = 250–350 Pa).

Upon excitation of the argon–water vapor mixture by a 15-keV electron beam, the partial pressure of H_2O water needed to obtain a maximal intensity of the 309-nm band was within the region of 30–90 Pa (at p(Ar) = 25 kPa and in the absence of a structure in the dependence of the intensity on the partial water vapor pressure) [11].

As is seen from Fig. 2b, the dependence of the 309-nm band intensity can be divided into three regions (I–III) of the partial pressures of D_2O vapor. A specific feature of emitters based on water vapor with barrier-discharge pumping compared to glow and high-frequency discharge lamps is that the pressure of inert gases (He, Ar) is approximately an order of magnitude higher. The partial pressure of water vapor in all these emitters lies within the region 30–400 Pa. At this composition of Ar–D_2O mixtures in the high-pressure

plasma, there exists the possibility of formation of complex compounds based on inert gases and water molecule or products of its destruction.

For example, the authors of [12] observed the formation of $Ar_n(H_2O)$ complexes at a water-vapor concentration up to 2% and an argon pressure in the prenozzle chamber of 3 bar, ionization of which by an electron beam lead to the formation of $Ar_n(H_2)^+$, $Ar_n(H)^+$, and $Ar_n(OH)^+$ (n = 1–4) ions [12]. In the cited work, it was assumed that the most efficient channel of energy dissipation upon the interaction of electrons with $Ar_n(H_2O)$ clusters is the dissociation of adsorbed water molecules.

Bearing in mind the discharge pulse shape, which is characterized by a short high-voltage pulse and the formation of two bipolar current pulses (Fig. 3), the kinetics of formation of OD(A) radicals should be considered taking into account the formation of hydroxyl radicals in the ground state and the possibility of their electron-impact excitation to OD(A).

At the lowest pressure of D_2O vapor (Fig. 2, region I, curve *2*), OD(A, X) radicals can be formed as a result of dissociative excitation of D_2O molecules,

$$e + D_2O \rightarrow OD(A, X) + D(1s) + e. \quad (1)$$

The efficiency of this reaction in the plasma weakly depends on the type of the inert gas (helium or argon), because of which, under our experimental conditions, the 309-nm band intensity and the optimal pressure of the D_2O vapor are only slightly different in these mixtures.

An increase in the pressure of the D_2O vapor (Fig. 2, region II, curve *1*) leads to the possibility of the electron-impact excitation of hydroxyl radicals OD(X) with the formation of OD(A),

$$e + OD(X) \rightarrow OD(A) + e \rightarrow OD(X) + h\nu \quad (\lambda \approx 309\ \text{nm}). \quad (2)$$

At $p(D_2O) \geq 150$ Pa, the intensity of the OD($A \rightarrow X$) band sharply decreases due to probably the quenching of OD(A) radicals by D_2O molecules. The 309-nm band emission intensity in this region of partial pressures of the D_2O vapor in the argon-based mixture is higher than in the helium-based mixture approximately by a factor of 1.5, which may be related to the involvement of an additional mechanism of formation of OD(A) radicals due to the energy transfer from metastable argon atoms to D_2O molecules,

$$Ar(m) + D_2O \rightarrow (D_2O)^* + Ar \rightarrow OD(A) + D(1s) + Ar. \quad (3)$$

In the region of higher pressures of D_2O vapor (200–400 Pa) (Fig. 2, region III, curve *2*), the formation of OD(A) radicals can occur via the energy transfer from metastable argon atoms to clusters. Since the 309-nm band in helium media in this region of water vapor pressures is almost absent, the cluster mechanism of OD(A) formation can be considered only for the argon-based mixtures,

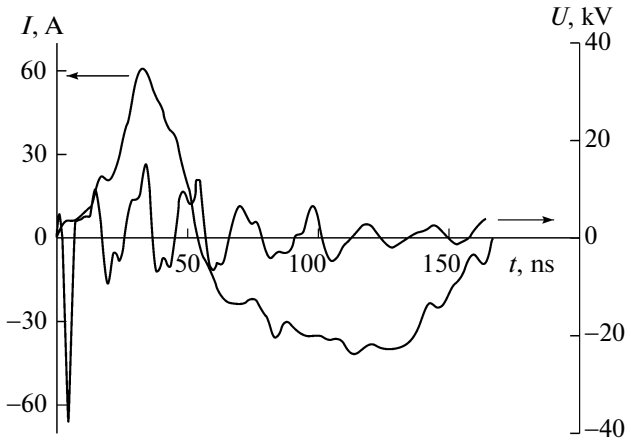

Fig. 3. Oscillograms of the voltage and current pulses of a barrier discharge in the mixture $p(He)$–$p(D_2O)$ = 20–0.04 Pa at capacitor voltage U = 13 kV (f = 100 Hz).

$$Ar(m) + Ar_nD_2O \rightarrow Ar_nD + OD(A) + Ar, \quad (4)$$

$$Ar(m) + Ar_nDO \rightarrow Ar_n + OD(A). \quad (5)$$

Similarly to process (3), the energy transfer from Ar(m) can occur through an intermediate excitation of clusters in the process of their stabilization by collisions with argon atoms.

Thus, we determined the optimal working media for obtaining the most intense OD($A^2\Sigma^+ \rightarrow X^2\Pi$) emission band at $\lambda \approx 309$ nm in a nanosecond barrier discharge in the helium and argon mixtures with heavy water vapor. The specific features of the formation of OD(A) radicals at different partial pressures of the D_2O vapor are considered qualitatively. The Ar–D_2O mixture can be used for developing a pulse-periodic lamp emitting noncarcinogenic UV radiation for application in photomedicine.

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