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VIOLET AND RED KHg EXCIMER BANDS IN THE SPECTRUM OF THE HIGH PRESSURE K-Hg-Ar DISCHARGE LAMP

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We present time-resolved spectroscopic studies of the high-pressure K-Hg-Ar discharge lamp. In the neighbourhood of the second resonance potassium line (5p-4s transition) at 404.4 and 404.7 nm a group of KHg satellite bands is observed. In the red part of spectrum, we observed a very broad KHg diffuse band with undulations peaking at 611, 616, 623 and 629 nm. Electron density has been estimated by using Inglis-Teller relation, for two electric current regimes — at current maximum and at current reversal.

1. Introduction

Reviwed interest in metal vapour excimer systems is connected with the promise of tunable laser action in the visible or near IR spectral region. Recent experiments indicated that KHg excimer molecule might be a possible candidate[1], and pointed out the need for better understanding of the origin of certain continua in KHg spectrum. We have investigated the emission spectrum of 400 W high pressure lamp filled with potassium-mercury amalgam using time-resolved technique. In this experiment we were interested in determination of basic plasma parameters of K-Hg-Ar discharge, and in spectroscopic studies of certain satellite bands in the violet and red region of discharge spectrum. On this experimental basis we discuss the shape of the continua observed in the spectrum, and propose the shape of potential energy curves for the ground and lowest three excited states of KHg excimer. These estimates are compared to the results of exact calculations of NaHg pseudopotentials curves[2], and to the results of beam experiments[3,4].

In this paper we present measurements of satellite bands in the vicinity of second potassium doublet at 404.4/404.7 nm and diffuse band at 620 nm. Both spectral features we attribute to the emission of KHg excimer molecule.

In addition, we roughly estimated average electron density by using Inglis-Teller relation[5]. This estimate was carried out by determination of last discernible spectral line at time instants when electric current through the lamp was at its maximum or minimum value (current reversal point).

At current maximum forbidden lines from np-4p, nf-4p were easily observable, and they were also used for rough estimation of electron concentration.

2. *Experiment*

The experimental apparatus is shown in Fig. 1. A high-pressure K-Hg-Ar discharge lamp driven with the AC electric current with frequency of 50 Hz has been used in this experiment (Fig. 2a). The burner of this lamp was made of a standard alumina tube used as the burner also in the 400 W high-pressure sodium discharge lamps. Its inner diameter is 7.6 mm, the length is 100 mm and electrode spacing 75 mm. The light from the lamp was spectrally resolved by high-resolu-

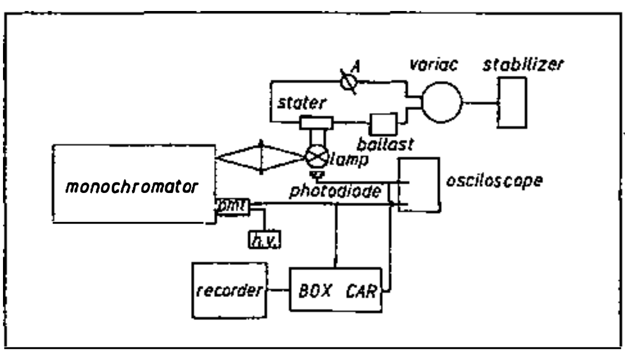

Fig. 1. The experimental apparatus.

tion Jobin-Yvon monochromator (focal length 1.5 m, 1200 grooves/mm grating) and detected by photomultiplier. Detected signal was fed into the box-car averager with a gate aperture of 500 μs and a variable aperture delay (Fig. 2c). Signal from a photodiode, which monitored total lamp intensity (Fig. 2b), was used as the trigger signal for the box-car averager. The processed data were recorded on the strip-chart recorder. Unfortunately, we were unable to perform the usual plasma diagnostics (e. g. Abel inversion, etc.), because the translucent alumina burner transmits the diffused (scattered) light from the discharge.

Special attention was paid to the emission spectra measured at the current reversal and at current maximum. Such measurements are interesting for the spectroscopic purposes, because the relative intensity of lines and continuum emission of KHg plasmas change drastically from current maximum to current minimum

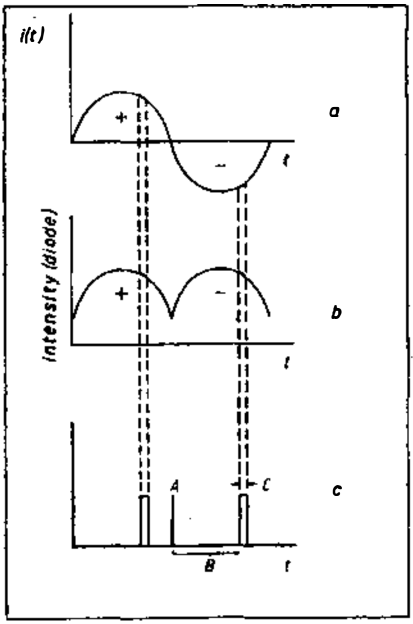

Fig. 2. a) The current through the lamp (frequency: 50 Hz); b) signal from the photodiode (frequency: 100 Hz); c) basic timing relationships for time resolved measurements in this experiment (not in scale). A, B and C denote the trigger signal, the apperture delay and the gate apperture, respectively.

point. At current maximum the plasma temperature and electron density attain its largest values. In that time many allowed and forbidden atomic spectal lines are visible in the emission spectrum and they can be easily identified and analyzed. On the other hand, emission spectra measured at the current reversal point reflect the conditions of plasma with lower electron temperature and lower electron density. In that case the intensities of the atomic lines are much smaller, thus enabling easier observation of all continuous spectral features, i. e. satellites and diffuse bands of molecular origin.

3. *Results*

a) Current maximum mode

In Fig. 3 we present first set of measurements — the spectrum from 450 nm to 670 nm measured at current maximum. From this spectrum we can analyze spectral behaviour of all allowed and forbidden lines. Forbidden lines become plas-

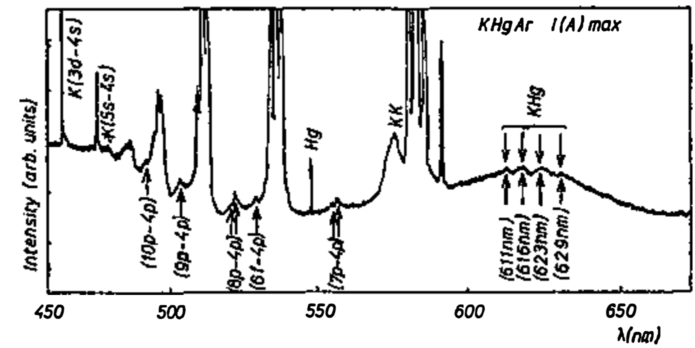

Fig. 3. Emission spectrum of the K-Hg-Ar discharge between 450 and 670 nm at current maximum. The arrows indicate the positions of the forbidden lines and positions of four undulations of KHg diffuse band.

TABLE 1.

transitions *n*p-4p	*j*-*j*	λ_{exp} (nm)	λ_{vac} (nm)	λ_{air} (nm)
7p-4p	3/2—3/2	554.4	554.6	554.4
	1/2—1/2	552.6	552.9	552.7
8p-4p	3/2—3/2	520.9	521.2	521.0
	1/2—1/2	519.6	519.7	519.5
9p-4p	1/2—3/2	502.5	502.6	502.4
	1/2—1/2	500.9	501.1	501.0
10p-4p	1/2—3/2	490.7	491.0	490.8
	1/2—1/2	489.6	489.9	489.7

We present the list of the forbidden transitions belonging to the (np-4p) series, observed in the spectrum of KHg discharge. λ_{exp} are values obtained in the experiment, λ_{vac} are theoretical values for vacuum obtained from known potassium energy levels and then we made correction for air (λ_{air}).

ma allowed because of the strong electric microfields in the plasma. We have identified and listed in Tables 1 and 2 an array of forbidden lines from *n*p-4p series, *n*f-4p series, 5s-4s (magnetic dipole transition at 475 nm) and 3d-4s (electric quadrupole transitions at 464 nm). The exact values of the wavelengths of the above mentioned transitions were obtained from the known potassium energy levels. According to Edlen's formula for the refractive index we correct observations made in the atmosphere of air[9]. Unfortunately, these lines were not suitable for the line shape analysis and relevant plasma diagnostic purposes, because of the strong overlap with other molecular and atomic features in the spectrum.

The broad structure peaking at about 572 nm in Fig. 2 is well known potassium dimer diffuse band. The emission of this yellow diffuse band has been identified to stem from $2^3\Sigma_g^+ - 1^3\Sigma_u^+$ electronic transition in K_2 molecule[6,7].

TABLE 2.

transitions nf-4p	j-j	λ_{vac} (nm)	λ_{air} (nm)	comment
4f-4p	3/2—3/2	660.4	not observed	overlap with KHg diffuse band
5f-4p	3/2—3/2	567.5	not observed	overlap with KK diffuse band
6f-4p	1/2—1/2	527.2	527.0	
7f-4p	1/2—1/2	505.6	not observed	overlap with K (4p-9s)
8f-4p	1/2—1/2	492.4	492.2	

This table shows positions of the forbidden transitions belonging to the (nf-4p) series. λ_{vac} are values for vacuum (theoretical), but we have not observed them all due to other structures in the spectrum (λ_{air}).

The broad diffuse band extended in 550—650 nm range most probably stems from KHg excimer[1]. It has four weak undulations with peaks at 611 nm, 616 nm, 623 nm and 629 nm. These undulations were first observed by Barrat[8], who found two peaks at 616 nm and 623 nm. This band should be analogous to the blue diffuse bands in NaHg[11] and NaCd[12].

The potassium atomic lines from diffuse series (nd-4p, $n = 4$—8), sharp series (4p-ns, $n = 6$—10) and a few lines of mercury are present in the spectrum. The lines of sodium first resonance doublet (3p-3s) and rubidium (6p-5s) are observed, too. These elements are present as impurities in KHg amalgam.

b) Current minimum mode

In the second set of measurements box-car averager was used to sample out the spectrum at the current reversal moments. In Fig. 4a we present spectrum

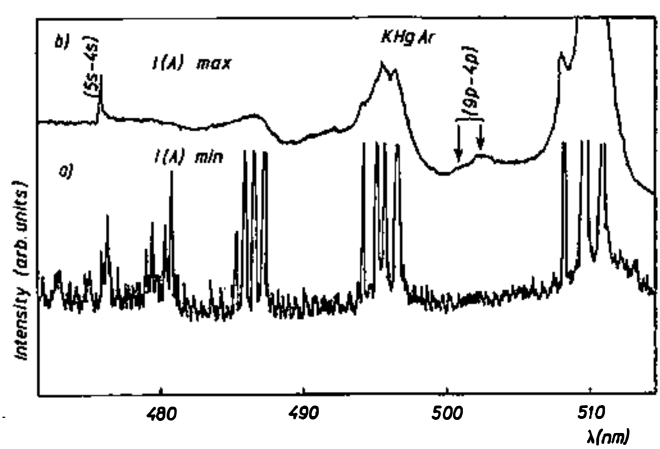

Fig. 4. Emission spectrum between 470 and 515 nm for current reversal (a) and current maximum mode (b). The arrows indicate the positions of forbidden transition np-4p, 6f-4p and 5s-4s. This transitions disappear in the spectrum of current reversal mode. Intensities in Fig. 4a and 4b are not in scale.

between 470 nm and 515 nm. For comparison Fig. 4b shows the same part of the spectrum, but for the maximum electric current through the lamp.

In the current reversal mode potassium atomic lines appear with much lower intensity than in the current maximum mode. There are no forbidden lines from *n*p-4p and *n*f-4p series, but electric quadrupole transition 3d-4s still appears in the spectrum. That suggests that its dipole moment is collisionaly induced by the presence of potassium atoms and, possibly, mercury and argon[10] atoms. Another interesting part of the spectrum at current reversal was the blue and the red wings of the second resonance line doublets of potassium (5p-4s) at 404.4 nm and 404.7 nm broadened by the influence of potassium, argon and mercury atoms in the

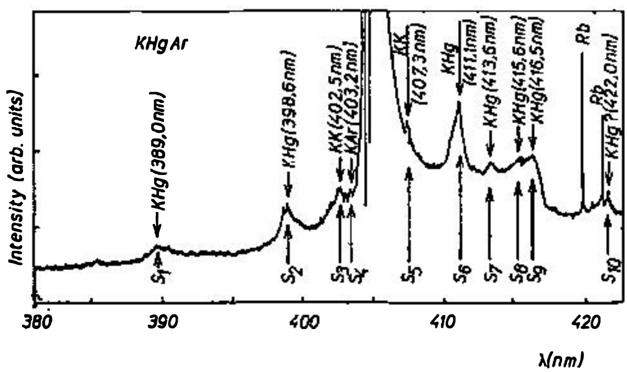

Fig. 5. Quasi-static red and blue wings of the second resonance line of potassium doublet (5p-4s) broadened by the influence of potassium, argon and mercury atoms. Note the Rb impurity lines at 420.2 nm (6p-5s, 3/2-1/2) and at 421.5 nm (6p-5s, 1/2-1/2).

ground state (Fig. 5). Line merging at the series limit shifts towards smaller wavelengths (see Fig. 3 and 4), and we can observe some transitions which are not visible at the current maximum (Table 4). The total intensities of these lines decrease along the series, and lines become increasingly broader. Since the distance betwen lines decreases towards the series limit, this leads to a rapid merging of these lines and to an advance of the apparent series limit toward the red. In Table 4 the advance of the series limit is given for both cases (I_{max} and I_{min}).

4. Discussion

4.1. *The origin of satellite band system*

In Fig. 5 we present the spectral region in the vicinity of the second resonance potassium line. We identify a number of satellite bands denoted as S_1-S_{10}. Additionally, in Table 3 we present the peak positions of the four blue satellite bands ($S_1 - S_4$) and six red satellite bands (denoted as $S_5 - S_{10}$). The energy separations between the satellite band peaks and the resonance line at 404.7 nm are given in Table 3.

TABLE 3.

S_i	λ_{exp} (nm)	E (cm^{-1})	interaction	ΔE (cm^{-1})
		blue wing		
S_1	389.0	25707	K-Hg	998
S_2	398.6	25088	K-Hg	379
S_3	402.5	24845	K-K	136
S_4	403.2	24802	K-Ar	93
		red wing		
S_i	λ_{exp} (nm)	E (cm^{-1})	interaction	ΔE (cm^{-1})
S_5	407.3	24552	K-K	157
S_6	411.1	24325	K-Hg	357
S_7	413.6	24178	K-Hg	531
S_8	415.6	24062	K-Hg	647
S_9	416.5	24009	K-Hg	699
S_{10}	422.0	23697	K-Hg?	1010

Positions of the peaks of four red satellite bands and six blue satellite bands observed in the emission spectrum of K-Hg-Ar discharge lamp are denoted as λ_{exp} and ΔE (cm^{-1}) are their corresponding energy separations from the 404.7 nm potassium line.

TABLE 4.

	I_{max}		I_{min}	
transition	4p-10s	4p-8d	4p-13s	4p-11d
λ (nm)	495.60	496.50	475.40	475.70
$\Delta\lambda$ (nm)	40.40	41.30	20.20	20.50
n_{max}	10	8	13	11
N_e (10^{15} cm^{-3})	5.75	30.70	0.80	2.81
n^*	7.82	7.74	10.80	10.73
N_e^* (10^{15} cm^{-3})	36.38	39.30	3.23	3.39

Wavelengths (λ) of the last visible line of the sharp and diffuse series for I_{max} and I_{min} and their separations ($\Delta\lambda$) from the theoretical series limit. From maximum principle quantum number n_{max} and with effective quantum number n^* we estimated electron density N_e and N_e^*, respectively.

From the existing literature data[10,13,14] the satellites denoted S_3, S_4 and S_5, may be recognized as classical satellite bands stemming from K-K (S_3, S_5) or K-Ar (S_4) interaction.

As it is already discussed for the satellites belonging to the first potassium resonance line[1], the origin of observed two groups of satellite bands at 404.7 nm could be explained qualitatively by the shape of the corresponding difference potential curves, $\Delta V_t(R)$. They should possess extrema correspondign to the satellite band peaks observed in the red and blue wing of second potassium doublet (see Fig. 5). Using measured positions and shape of blue and red satellite bands we may tentatively deduce positions of above mentioned extrema in corresponding $\Delta V_t(R)$. The ground state of KHg molecule should be basically flat[2-4]. So, $\Delta V_t(R)$ should reflect (quantitatively) shape of the relevant upper potential curve, responsible for the formation of these satellite bands. According to the large number of satellite bands at 404.7 nm line we assume that a strong interaction between several potential energy curves with the same quantum-mechanical symmetry must be present. This interaction causes avoided crossings that could lead to the formation of local extrema in the relevant difference potential curve. Any such extremum, provided that the corresponding molecular transition is allowed, may appear in the spectrum in the form of the satellite band, or a diffuse band. Further discussion of these satellite and diffuse bands should be supported by the future ab initio caculations of the relevant interaction potential curves for the KHg excimer system.

From the shape of these satellite bands we may tentatively attribute S_2 satellite as stemming from the local maximum, and S_1, S_6 and S_9 as stemming from local minima in the relevant difference potentials.

4.2. *Advance of series limit and the estimate of the electron density*

In the current reversal mode the last discernible line is 4p-11d at 475.7 nm what is about 20 nm from theoretical series limit. On the other hand, in the current maximum mode last discernible line is 4p-8d at 496.5 nm what is about 40 nm from the theoretical series limit. The shift of experimentally observed series limit (20 nm in current reversal mode versus 40 nm in current maximum mode) is caused by very different electron densities in these two situations (Table 4). In current reversal mode Stark broadening and electron temperature is lower and merging is not so intense. For the same reason we observed some lines (4p-13s, 4p-11d) in the current reversal spectrum that were invisible in the current maximum spectrum. The maximum principal quantum number is larger, and electron density is smaller. This density is calculated from Inglis-Teller relation:

$$\log n_e = 23.26 - 7.5 \log n_{max},$$

where n_e is electron density (cm^{-3}) and n_{max} is maximum principal quantum number. Assuming singly charged perturbers we estimated electron density for both cases, I_{min} and I_{max} (Fig. 4a and 4b).

The electron density has been estimated from the observations of the forbidden lines (Tables 1, 2) in the current maximum mode. The results obtained with the allowed and forbidden lines are the same, because the principle quantum numbers are the same. Inglis-Teller formula is an approximate one, but it should be applicable to the lines from almost all atoms or ions, because the broadening of lines from higher energy levels always becomes almost hydrogen-like[15]. The most notable exception are the lines from »s« levels (lines from sharp series) and because of that in Table 4 we can see large disagreement between estimated electron densities for sharp and diffuse series.

To correct this disagreement we took into consideration quantum defect and we calculated electron density with the effective principal quantum number n^* for the last visible transitions from »s« and »d« levels. In Table 4 we see that the differences between sharp and diffuse series become much smaller.

5. *Conclusion*

We have observed seven KHg satellite bands in the neighbourhood of the second potasisum resonance doublet in the time resolved emission spectra of the high pressure KHg discharge lamp. Beside this, we found four weak undulations at the position of KHg diffuse band with peaks at 611 nm, 616 nm, 623 nm and 629 nm. We performed preliminary plasma diagnostics of this discharge by using line merging at the series limit. Using this technique rough estimate of the electron density at current maximum and at current reversal is obtained.

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LJUBIČASTE I CRVENE KHg EKSIMERSKE VRPCE U SPEKTRU VISOKOTLAČNE K-Hg-Ar ŽARULJE

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U emisionom spektru K-Hg-Ar visokotlačne lampe promatrana je grupa KHg satelita u okolini drugog rezonantnog kalijevog dubleta (5s-4p prijelaz) na 404,4 i 404,7 nm. Uočena je veoma široka KHg difuzna vrpca sa četiri vrha na 611, 616, 623 i 629 nm. Ponašanje linija na granici difuzne i oštre serije kalija iskorišteno je za procjenu gustoće elektrona preko Inglis-Tellerove relacije. Ta procjena izvršena je na spektrima snimanim u trenutku kada je struja kroz lampu mijenjala smjer, odnosno kada je poprimala svoju maksimalnu vrijednost. U maksimumu struje identificirane su zabranjene linije kalija (serija *n*p-4p i *n*f-4p) preko kojih je također izvršena procjena gustoće elektrona u KHg plazmi.