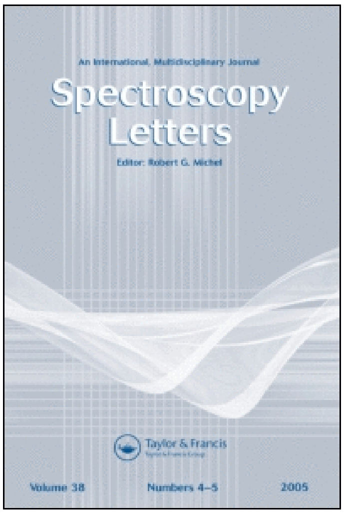

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SPECTROSCOPIC MEASUREMENT OF PLASMA TEMPERATURES IN A HOLLOW CATHODE DISCHARGE

KEY WORDS: plasma temperature, excitation temperature, rotational temperature, hollow cathode

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ABSTRACT

Excitation temperatures of atoms and ions and rotational temperatures of molecules have been investigated in a hollow cathode discharge under different experimental conditions. These temperatures have been found to be 3900-4300 K or 5200-5700 K for Fe I, 6100-7500 K for Ar I, 23000-29000 K for Ar II, 1400-2400 K for N_2 and 1000-2300 K for N_2^+.

INTRODUCTION

The hollow cathode discharge has often been used by spectroscopists. The discharge is very stable. Lines emitted by the hollow cathode discharge are of high reproducibility. The excited lines are narrow and sharp at a negligible background.

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In molecular spectroscopy the hollow cathode discharge is applied to excite spectra of diatomic molecules.[1,2] The hollow cathode lamp with metal electrodes and rare gas filling is a standard source of wavelengths.[3,4] In spectrochemical analyses the hollow cathode lamps are used both in emission and absorption.[5-8] A comparison of the hollow cathode discharge with other sources was carried out by Caroli et al.[9-11]

Plasma temperature is an important parameter responsible for excitation processes. A few studies have concerned with spectroscopic measurements of plasma temperatures in the hollow cathode discharge. The measurements of excitation temperatures of atoms and ions[12-15] have not been combined with the rotational temperature measurements.[16,17] Setz and Maierhoffer[18] determined the rotational temperatures of N_2^+ and CN and the excitation temperature of Ar I, but the lines used for the excitation temperature measurement were not reported, as in some other papers.[14,15] Sometimes the upper state energies of the lines used to calculate the excitation temperature are very close together so that this temperature determination is questionable. Thus there is a difficulty to appreciate and compare some temperature measurements.

In this study the spectroscopic measurements of plasma temperature derived from atomic /Fe I, Ar I/, ionic /Ar II/ and rotational /N_2, N_2^+/ lines have been presented.

EXPERIMENTAL

A demountable hollow cathode discharge lamp was used to produce plasma. The discharge run at 50 and

100 mA d.c. intensity. Two kinds of uncooled cathodes were used, a conventional closed at one end cathode /6 mm inner diameter, 35 mm total length and 20 mm bore depth/ and an open-ended cathode /6 mm inner diameter and 20 mm bore depth and total length/. The cathodes were made of iron and graphite. Argon, argon with air, helium or helium with air flowing continuously through the lamp were the carrier gases. Plasma spectra were recorded in the first and fourth orders of a plane grating spectrograph PGS-2 on Agfa-Gevaert and Kodak plates. The slit width was 0.080 mm. Exposure times varied between 5 and 360 s. The line blackening was measured with the aid of a recording microphotometer MD-100 /Zeiss-Jena/. The density curves were constructed using a three-step filter of the spectrograph. The variation of the photographic emulsion sensitivity with the wavelength was taken into account. Two standard lamps /a deuterium lamp and a tungsten lamp/ of exactly known absolute spectral radiance were used as reference continous light sources.

MEASUREMENTS

As in other studies[10,14,19,20] the dependence of the spectrum intensity on discharge parameters /pressure, current, carrier gas/ was observed here. Lines excited in the conventional hollow cathode were stronger than those emitted by the open-ended hollow cathode discharge. Molecular spectrum was greatly affected by the carrier gas and the discharge current. Argon was more suitable to excite the N_2 spectrum while helium was favorable for the N_2^+ excitation. The N_2 and N_2^+ band intensities increased strongly with the discharge current.

Assuming the multithermal equilibrium model[21] plasma temperatures have been determined. The excitation temperatures of Fe I, Ar I and Ar II were calculated[22] from the slopes of the plot of ln $I\lambda/gA$ against E, where I is the line intensity, λ is the line wavelength, A is the transition probability, g and E are statistical weight and energy of the upper state. The following lines /λ in nm/ were used here for the temperature determination:

Fe I

294.130	297.011	298.357	298.729	299.443	299.951
300.095	300.814	300.957	301.763	301.898	302.584
303.739	372.256	372.438	373.240	373.332	373.437
374.949	375.360	378.788	379.851	381.584	382.043
382.444	382.588	382.782	383.422		

Ar I

696.543	703.025	706.722	706.873	731.172	731.601
737.212	738.398				

Ar II

365.529	371.821	372.931	373.789	376.527	378.638
385.037	386.852	392.572	392.863	393.255	394.427
394.610	396.836	397.936	401.386	403.380	404.290

The transition probabilities given by Corliss and Bozman[23] and Bridges and Kornblith[24] were taken for the Fe I lines. The transition probabilities for the Ar I and Ar II lines were taken according to Wiese et al.[25] The least squares procedure was applied to fit the data. The excitation temperatures of Fe I, Ar I and Ar II along with their standard deviation uncertainties are listed in Tables 1-3.

The rotational temperatures were determined[26] by plotting ln $I\nu^4/S_J$ against F'/J/, where I is the rotational line intensity, ν is the line frequency,

TABLE 1

The Excitation Temperatures Derived from Fe I

Cathode	Carrier gas /pressure in Torr/	Current mA	T K	gA Ref.
Fe[a]	Ar/5/	100	4270 ± 170 5490 ± 360	23 24
Fe[a]	Ar/5/	50	4110 ± 140 5530 ± 330	23 24
Fe[b]	Ar/5/	100	4300 ± 160 5680 ± 390	23 24
Fe[b]	Ar/5/	50	4070 ± 150	23
Fe[a]	Ar/5/+air/1/	100	3980 ± 360	23
Fe[a]	Ar/4/+air/1/	50	3930 ± 380 5200 ± 620	23 24
Fe[a]	Ar/9/+air/1/	100	4220 ± 400	23
Fe[a]	He/19/+air/1/	50	4040 ± 300	23
C[a]+Fe_2O_3[c]	He/19/+air/1/	50	4110 ± 470	23

a - the cathode closed at one end

b - the open-ended cathode

c - the sample placed into the hollow cathode

S_J is the Hönl-London factor, F'/J/ is the rotational energy of the upper state and J is the rotational quantum number. The R_0 /15≤J≤40/, R_1 /12≤J≤35/, R_2 /10≤J≤37/ and P_2 /35≤J≤45/ lines of the $C^3\Pi - B^3\Pi$ 0-0 band of N_2 at 337.1 nm and the R and P lines of the $B^2\Sigma^+ - X^2\Sigma^+$ 0-0, 0-1 and 0-2 bands of N_2^+ at 391.4 nm, 427.8 nm and 470.9 nm, respectively were used. The molecular constants of the N_2 and N_2^+ molecules given by Huber and Herzberg[27] were employed. The

TABLE 2

The Excitation Temperatures Derived from Ar I

Cathode	Carrier gas /pressure in Torr/	Current mA	T K
C[a]	Ar/5/	100	7500 ± 440
C[a]	Ar/10/	100	6990 ± 440
C[a]	Ar/5/	50	7160 ± 540
C[a]	Ar/10/	50	6660 ± 390
Fe[a]	Ar/5/	100	6570 ± 520
Fe[a]	Ar/10/	100	6150 ± 570
Fe[a]	Ar/5/	50	6140 ± 410
Fe[a]	Ar/10/	50	6440 ± 400

TABLE 3

The Excitation Temperatures Derived from Ar II

Cathode	Carrier gas /pressure in Torr/	Current mA	T K
C[a]	Ar/5/	100	24300 ± 1800
C[b]	Ar/5/	100	22900 ± 1700
C[a]	Ar/10/	100	24800 ± 1200
C[b]	Ar/10/	100	26400 ± 1600
C[a]	Ar/5/	50	25600 ± 1800
C[a]	Ar/10/	50	27200 ± 1600
Fe[a]	Ar/5/	100	26500 ± 2900
Fe[a]	Ar/4/+air/1/	100	27900 ± 4000
Fe[a]	Ar/9/+air/1/	100	28400 ± 4500
Fe[a]	Ar/4/+air/1/	50	27900 ± 4200
C[a]+Fe_2O_3[c]	Ar/4/+air/1/	50	28300 ± 4700

a - the cathode closed at one end

b - the open-ended cathode

c - the sample placed in the hollow cathode

TABLE 4

The Rotational Temperatures from N_2 and N_2^+

Cathode	Carrier gas /pressure in Torr/	Current mA	N_2 0–0	N_2^+ 0–0	N_2^+ 0–1	N_2^+ 0–2
Fe^a	Ar/4/+air/1/	100	2190	1980		
Fe^a	Ar/9/+air/1/	100	2360	2290		
Fe^a	Ar/4/+air/1/	50	1540	1140	990	1080
$C^a+Fe_2O_3{}^c$	Ar/4/+air/1/	50	1400	1080		1020
C^a	Ar/4/+air/1/	50	1500	1010	960	1000
Fe^a	He/19/+air/1/	50	–[d]	1120	970	1120

a - the cathode closed at one end

c - the sample placed in the hollow cathode

d - the spectrum was too weak to determine temperature rotational temperatures obtained under the different experimental conditions are listed in Table 4.

DISCUSSION

It was confirmed here that the excitation temperatures measured in the hollow cathode discharge are higher for ions than for atoms. The excitation temperatures are considerably higher than the rotational temperatures.

Under the used experimental conditions there is not evident relationship between the excitation temperatures and the discharge parameters. This was also observed for the temperatures of Fe I, Mn I /from lines with the upper state energies $E \leq 5.5$ eV/ and Ti I by Dobrosavljević and Marković[14] and for the temperatures of Fe, He, Ar, Kr and Xe by Mehs and Niemczyk.[15] The temperatures derived in this study from the Fe I lines are close to those given in other papers.[12-14] There is a discrepancy between the Ar I temperatures: 11000-12000 K[18], 4500-4900 K[12], 2000-3000 K[15], here 6200-7500 K. Our temperatures from Ar II are close to the temperatures from O II /25000-35000 K[12]/ but considerably lower than those obtained previously from Ar II /up to 100 000 K[12]/.

In contradistinction to the excitation temperatures, the rotational temperatures vary with current in the argon discharge /see Table 4/. Such a effect was also observed in argon by Setz and Maierhoffer[18] and in helium /but not in argon/ by Broekaert.[16] The rotational temperatures derived here from the N_2 and N_2^+ bands are well comparable with the results from N_2^+ and CN /500-1000 K[18], 800-1700 K[16]/ and from the $R_2/1/-R_2/7/$ lines of OH /1070-1760 K[17]/

but lower than the temperatures from the $R_2/7/-R_2/14/$ and $R_2/14/-R_2/20/$ lines of OH /4100–4700 and 6200–8000 K[17]/. It was observed here the population of molecules in the rotational levels of the $C^3\Pi$ state of N_2 and of the $B^2\Sigma^+$ state of N_2^+ corresponded to a Boltzmann distribution.

Our measurements and calculations have indicated that only a great number of lines /with a wide range of the upper state energies/ used for the excitation temperature determination can give reliable results. There is a clear relation between the transition probability values employed in the calculations and the calculated temperature /see Table 1/.

Interesting method of the excitation temperature determination was reported recently.[28] However in this method in addition to the transition probability values /the transition probabilities can be easily transformed into the oscilltor strengths/ the life time values must be known.

More advanced study of dependence between temperature and plasma composition is undertaken.

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