ISSN 1330–0008
CODEN FIZAE4

BRANCHING RATIOS AND TRANSITION PROBABILITIES OF MERCURY VISIBLE TRIPLET SPECTRAL LINES

ŽELJKA MIOKOVIĆ[a], HRVOJE SKENDEROVIĆ[b] and VLADIS VUJNOVIĆ[b]

[a] *Electrotechnical Faculty, Osijek, Croatia*
[b] *Institute of Physics of the University, Bijenička c.46, Zagreb, Croatia*

Dedicated to Professor Mladen Paić on the occasion of his 90$^{\text{th}}$ birthday

Received 7 July 1995

Revised manuscript received 6 October 1995

UDC 533.95

PACS 35.80.+s

We have measured branching ratios of mercury visible triplet lines 404.7, 435.8 and 546.1 nm (7^3S_1-$6^3P_{0,1,2}$) by controlling the absorption. The absolute transition probabilities have been determined by using critically selected lifetime of the upper level and measured branching ratios.

1. *Introduction*

One of the most reliable methods for determination of the transition probabilities consists in measuring the lifetimes and branching ratios of multiplet components. The lifetime of level k is related to the transition probabilities of components ki:

$$\tau = \frac{1}{\sum_i A_{ki}} \tag{1}$$

$$A_{km}\tau_k = \frac{A_{km}}{\sum_i A_{ki}} = R_{km} \tag{2}$$

where R_{km} is the so called branching ratio, i.e. the relative number (fraction) of transitions from the upper level to the component km. The branching ratio is determined by the relative measurements of intensities of all components.

The lifetime of mercury level 7^3S_1 and branching ratio of the visible triplet lines were measured many times (see Ref. 1). We took over the lifetime (8.0±0.4) ns from Ref.1 since it is actually very close to the average of several selected measurements.

The measured branching ratio shows much larger spread than one would expect for the kind of experiments, namely for the purely relative intensity measurements. They were mainly performed in emission. In all but one experiment, the branching ratio of the spectral line 546.1 nm was found to be larger than the branching ratio of the line 435.8 nm. Only the measurement of Benck et al. [1] showed opposite trend, although the experiment was conducted very thoroughly and under conditions in which the radiation trapping can be reduced. We decided to measure in emission by controlling the line absorption.

2. *Observations and results*

The experimental source was a low pressure mercury discharge (Russian made PRK-2, with interelectrode distance of 15 cm, inner radius of 15.2 mm) which was placed in the optical system allowing for the double path and absorption measurements [2]. Two monochromators were used, one for the visible and ultraviolet (1.5 m normal incidence grating spectrometer Jobin Yvon THR), and a monochromator with glass prism (Zeiss Jena SPM2) having the photoresistive PbS diode (Hamamatsu) for detecting the near infrared. Monochromators were intensity calibrated by a tungsten-strip etalon lamp.

The source burned vertically and was observed in the axial plane. Abel transformation was not applied. The lamp was operated with DC current from 9 mA (voltage drop across the electrodes of 66 V) to 86 mA (voltage drop 70 V). The wall temperature of 40 °C corresponds to the partial mercury pressure of 2.6 Pa.

The monochromators allowed monitoring of all 4 spectral lines originating at the 7^3S_1 level. The infrared intercombination line 1207.0 nm (7^3S_1-6^1P_1) showed a branching ratio less than 0.2% even at highest used current when the visible lines suffered from strong absorption. We excluded the line from further consideration since its contribution is negligible and its transition probability cannot be determined without an excessive error.

The branching ratio was measured in emission which was corrected for absorption in the source. The absorption was determined by using the method of two identical tubes. The optical system images the sources with a mirror on itself, thus optically doubling the source. The direct path intensity is I_λ, the intensity obtained with the mirror is $I_{\lambda \mathrm{M}}$. In the last case, the source absorbs a part of its own intensity and also adds a direct intensity:

$$I_{\lambda\mathrm{M}} = \omega R I_\lambda + I_\lambda \qquad (3)$$

where ω is the plasma transmission and R is the effective mirror reflectivity, accounting for the reflectivity of mirror and transmission of the intervening optical components.

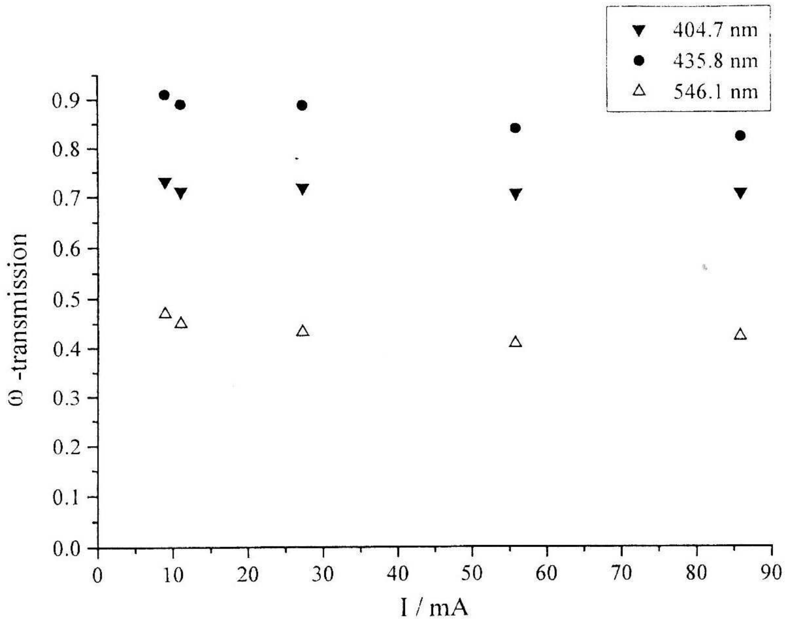

Fig. 1. Measured plasma transmission as a function of the discharge current.

The resulting transmission and ω for the visible triplet is shown in Fig. 1 as a function of the current. In the observed source there is a perceptible absorption especially for the transitions ending on the metastable levels $6^3\mathrm{P}_0$ and $6^3\mathrm{P}_2$. It is to be assumed that at lower pressure and with a decrease of the line width, such spectral lines are absorbed by the shell of long living metastable atoms diffusing from the central part of the discharge. (These spectral lines are broadened only by the Van der Waals impact and quasi-static mechanisms.)

The effect is the most pronounced for the spectral line 546.1 nm and at smaller extent for the line 404.7 nm. An estimate of the absorption coefficient which should be proportional to the transition probability, to the fourth power of the wavelength and inversely proportional to the halfwidth, gives satisfactory explanation for the difference in absorptions of these spectral lines. They suffer of different absorption due to different transition probabilities and wavelengths. We also explored a possibility that the lower metastable level $6^3\mathrm{P}_0$ is "less metastable" than higher metastable level $6^3\mathrm{P}_2$. Namely, there is a possibility that $6^3\mathrm{P}_0$ is pumped to the level 7^3D_1 by the spectral line 253.476 nm which has a wavelength very close to the strong intercombination resonant line 253.652 nm. The latter should be widened at least 0.176 nm in order to have frequencies coincident with the transition to 7^3D_1. However, measurements of the resonant line profile in the observed low pressure discharge showed a halfwidth of 0.005 nm, being insufficient for the relaxation effect.

In order to recover branching ratios without absorption, measured intensities were divided by the square root of the transmission. Such operation in the first approximation extrapolates intensities observed from the axially symmetric source having absorption, onto average emissivities [3]. Corrected branching ratios together with uncorrected are presented in Fig.2. The correction for the absorption is not excessive owing to the fact that branching means the ratio. We select values of the corrected branching ratios from measurements at the lowest current. These, together with the resulting transition probabilities are in Table 1 compared with other measurements.

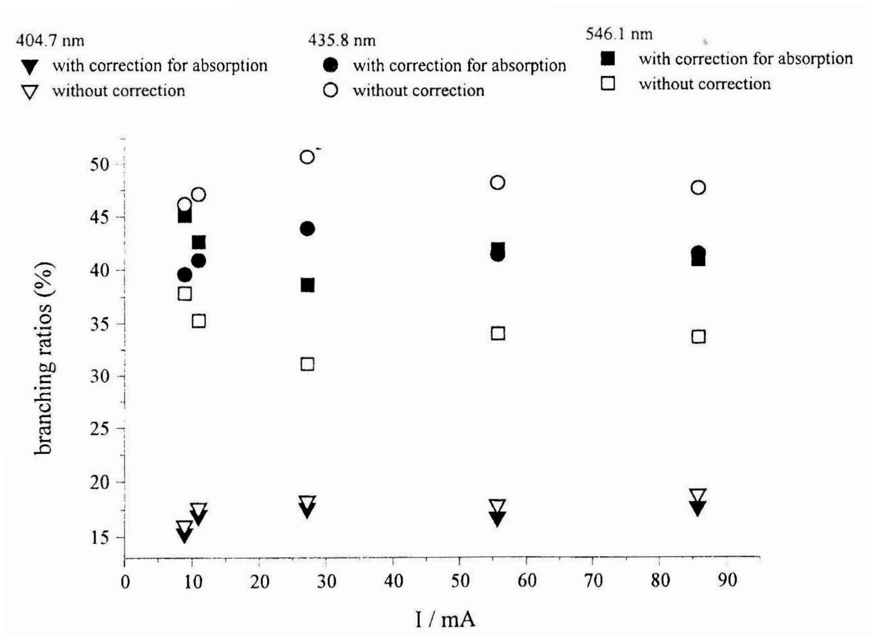

Fig. 2. Branching ratios as function of the discharge current, uncorrected and corrected for absorption.

Our branching ratio is given by 1 : 2.6 : 2.95. The evidence by many measurements definitely establishes a deviation of the branching ratios of the triplet 7^3S_1-$6^3P_{0,1,2}$ from the LS-coupling in which the branching ratio should read 1 : 3 : 5. To mention, instead of satisfying the interval rule 1 : 3, the energy differences within fine structure levels $6^3P_{0,1,2}$ follow the ratio 1 : 2.6.

TABLE 1.
Branching ratios have errors quoted equal to the standard deviation (in the form of last digits). The error of the transition probabilities is expressed in percents. This error was obtained as a convolution of two Gaussian functions.

	This work		Other works	
Spectral lines	Branching ratios (%)	Transition probability (10^8 s^{-1})	Branching ratios (%)	Transition probability (10^8 s^{-1})
404.7 nm	15.3(20)	0.191(12%)	16.69(13)[1] 16.9(13)[a] 13.9[b] 19.2[c] 15.5(8)[d] 13.2(14)[e]	0.207(10%)[1] 0.206(5%)[a] 0.176[b] 0.190[c] 0.187(5%)[d] 0.52[e]
435.8 nm	39.6(20)	0.495(6%)	44.6(26)[1] 36.6(15)[a] 35.2[b] 39.2[c] 35.3(14)[d] 39.4(40)[e]	0.557(8%)[1] 0.446(5%)[a] 0.421[b] 0.491[c] 0.425(5%)[d] 1.2[e]
546.1 nm	45.1(20)	0.564(7%)	38.8(23)[1] 46.5(16)[a] 50.8[b] 41.6[c] 49.2[d] 47.4[e]	0.487(8%)[1] 0.566(5%)[a] 0.633[b] 0.671[c] 0.592(5%)[d] 1.1[e]
1207.2 nm	< 0.2		< 0.3[1] 0.8[b] 0.25[d]	

[a]P.van der Weijer and R. M. M. Cremers, J. Appl. Phys. **54** (1983) 2835;
[b]W. Pilz and J. Seehawer, Proc.12th ICPIG, Pt.1, p.146: Contrib.Papers, Eindhoven, Aug.18-22 (1975);
[c]P. Jean, M. Martin, J. Barrat and J. Cojan, C. R. Acad. Sc. Paris **264** (1967) 1709;
[d]E. R. Mosburg and M. D. Wilke, J. Quant. Spectrosc. Radiat. Transf. **19** (1978) 69;
[e]R. J. Anderson, E. T. P. Lee and C. C. Lin, Phys. Rev. **157** (1967) 31.

References

1) E. C. Benck, J. E. Lawler and J. T. Dakin, J. Opt. Soc. Am. B **6** (1989) 11;
2) H. Skenderović, V. Vujnović, N. Demoli and J. Rukavina, Fizika A **3** (1994) 127;

3) H. Skenderović, M. Sc. Thesis, The University of Zagreb (1994).

OMJERI GRANANJA I VJEROJATNOSTI PRIJELAZA ŽIVINA TRIPLETA U VIDLJIVOM DIJELU SPEKTRA

Mjereni su omjeri grananja spektralnih linija iz živina tripleta u vidljivom dijelu spektra: 404.7, 435.8 i 546.1 nm (7^3S_1-$6^3P_{0,1,2}$) i pritom je određivana apsorpcija u izvoru. Apsolutne vjerojatnosti prijelaza određene su upotrebom odabranog vremena života gornjeg nivoa i izmjerenih omjera grananja.