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Transition probabilities in Kr II and Kr III spectra

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Abstract. On the basis of the relative line intensity ratio (RLIR) method, transition probability values of the spontaneous emission (Einstein's A values) of 14 transitions in the singly (Kr II) and 7 transitions in doubly (Kr III) ionized krypton spectra have been obtained relatively to the reference A values related to the 435.548 nm Kr II and 324.569 nm Kr III, the most intensive transitions in the Kr II and Kr III spectra. Our Kr III transition probability values are the first data obtained experimentally using the RLIR method. A linear, low–pressure, pulsed arc operated in krypton discharge was used as an optically thin plasma source at a 17 000 K electron temperature and 1.65×10^{23} m^{-3} electron density. Our experimental relative A values are compared with previous experimental and theoretical data.

PACS. 52.70.Kz Optical (ultraviolet, visible, infrared) measurements – 32.70.Cs Oscillator strengths, lifetimes, transition moments – 32.70.Fw Absolute and relative intensities

1 Introduction

Due to the development of space born astronomical techniques and devices such as Goddard high resolution spectrograph on the Hubble space telescope, the spectral lines of trace elements, such as krypton, are observed and the corresponding atomic data are of the increasing interest. On the basis of the recent investigation of Planetary Nebulae spectra [1] it was found that krypton is one of the most abundant elements in the cosmos with $Z > 32$. Krypton has been detected also in the spectra of the interstellar medium [2]. Moreover, krypton is present in many light sources and lasers as the working gas. Thus, the singly (Kr II) and doubly ionized (Kr III) krypton spectral lines are very useful for plasma diagnostical purposes. For the modeling or diagnostics of cosmic and laboratory plasmas it is necessary to know the transition probability values (Einstein's A values) [3]. A significant number of papers are dedicated to this topic [4] (and references therein), especially in the case of the Kr II A values. However, the existing experimental and theoretical Kr II A values show evident mutual scatter. In the case of the Kr III A values the situation is similar, but with a considerably smaller number of experimental and theoretical studies dedicated to the investigation of Kr III A values.

This work presents 14 Kr II and 7 Kr III A values obtained on the basis of accurately measured spectral line intensities using the step-by-step technique by the line profile recording [5] and our deconvolution procedure [6] which allows accurate measurements of the line intensities. The well-known [7–9] relative line intensity ratio (RLIR) method was used for the A values determination applied by us already in case of the Ar III, Ar IV, O II, Ne II, N III, N IV, N V and Si III spectra [10–15].

The experimental A^{exp} values are obtained relatively to reference A values for the 435.548 nm Kr II and 324.569 nm Kr III lines, the most intense among the investigated lines in the Kr II and Kr III spectra. Our Kr III transition probability values are the first data obtained experimentally using the RLIR method. Our experimental A values have been compared with the transition probabilities from the references which contain A data corresponding to our chosen reference Kr II and Kr III transitions only.

2 Experiment

A modified version of the linear low pressure pulsed arc [5,10,12–17] has been used as an optically thin plasma source. A pulsed discharge was driven in a Pyrex discharge tube of 5 mm inner diameter and plasma length of 7.2 cm. A capacitor of 14 μF was charged up to 1.5 kV. The working gas was krypton (99.99% purity) at 130 Pa filling pressure mountained by a constant flux. The spectral line profiles recording procedure together with the used experimental set–up system are described in references [13,14,18]. Two recorded Kr III line profiles, as an example, are shown in Figure 1.

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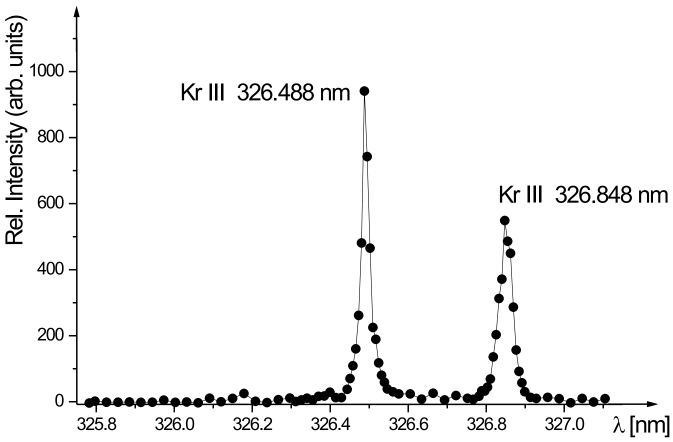

Fig. 1. Recorded Kr III spectral lines at a plasma temperature of 17 000 K and an electron density of 1.65×10^{23} m^{-3}.

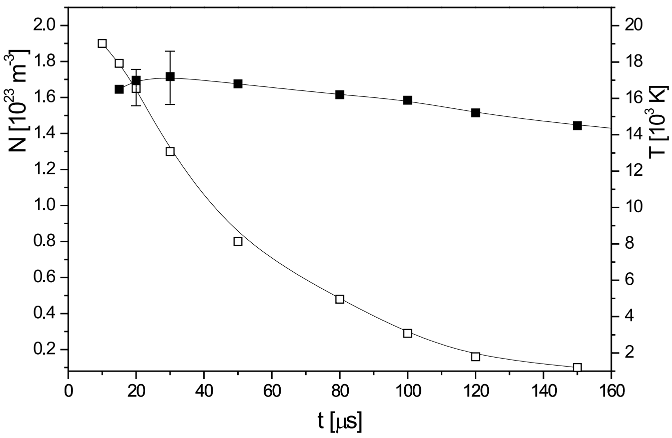

Fig. 2. Temporal evolution of the electron temperature (close symbols) and electron density (open symbols) in the decaying plasma.

One can notice that the investigated spectral lines are well isolated while the continuum is very close to zero within the wavelength range of interest. These facts are important for an accurate determination of line intensities and, correspondingly, for a reliable determination of A values.

The plasma was monitored by the Kr II line radiation and by the discharge current. Variations of the latter were found to be within 4%. All investigated Kr II and Kr III lines are recorded by the same experimental arrangement.

The measured profiles were of the Voigt type due to the convolution of Lorentzian profile from Stark broadening with Gaussian profile from Doppler and instrumental broadening. Line intensities were extracted from the experimental data by fitting convoluted line profiles [6] to the measured spectra. The line intensity (I) corresponds to the area under the line profile and was obtained within 3–5% accuracy from the fit. Great care was taken to minimize the influence of self–absorption on the line intensity determinations. Using a technique described in reference [10] the absence of self-absorption was obtained in the case of the investigated Kr II and Kr III spectral lines.

The plasma parameters were determined using standard diagnostic methods [7–9]. Thus, the electron temperature was determined from the ratios of the relative intensities (Saha equation) of nine Kr II spectral lines (435.548, 457.721, 461.529, 461.917, 463.388, 465.888, 473.900, 476.574 and 483.208 nm) to the five Kr I spectral lines (435.136, 436.264, 446.369, 557.028 and 587.091 nm) with an estimated error of ±9%, assuming the existence of LTE, according to the criterion from references [7,9]. All the necessary atomic data were taken from references [4,19]. The electron temperature decay is presented in Figure 2. The electron density decay was measured using a well-known single laser interferometry technique for the 632.8 nm He–Ne laser wavelength with an estimated error of ±7%. The electron density decay is also presented in Figure 2.

Table 1. Our relative (dimensionless) experimental ($A^{\rm rel}_{\rm exp}$) transition probability values in the Kr II spectrum. Wavelengths, transitions and upper-level energies ($E_{\rm u}$ in eV), are taken from references [4,19]. Transitions are ranged following increasing $E_{\rm u}$ values.

Transition	λ (nm)	$E_{\rm u}$	$A^{\rm rel}_{\rm exp}$
$5s\ ^4P_{5/2}$–$5p\ ^4P^o_{5/2}$	473.900	16.60	0.83 ± 9%
$5s\ ^4P_{5/2}$–$5p\ ^4P^o_{3/2}$	465.888	16.65	0.69 ± 9%
$5s\ ^4P_{3/2}$–$5p\ ^4P^o_{1/2}$	483.208	16.83	0.89 ± 8%
$5s\ ^4P_{5/2}$–$5p\ ^4D^o_{7/2}$	435.548	16.83	1.00 ± 3%
$5s\ ^4P_{3/2}$–$5p\ ^4D^o_{5/2}$	476.574	16.87	0.78 ± 8%
$4d\ ^4D_{5/2}$–$5p\ ^4D^o_{3/2}$	556.865	17.16	0.04 ± 12%
$5s\ ^2P_{3/2}$–$5p\ ^2P^o_{1/2}$	484.661	17.24	0.73 ± 10%
$5s\ ^2P_{3/2}$–$5p\ ^2P^o_{3/2}$	461.529	17.37	0.58 ± 11%
$5s\ ^2P_{3/2}$–$5p\ ^2D^o_{5/2}$	461.917	17.37	0.72 ± 11%
$5s'\ ^2D_{3/2}$–$5p'\ ^2F^o_{5/2}$	463.388	18.48	0.85 ± 18%
$5s'\ ^2D_{5/2}$–$5p'\ ^2F^o_{7/2}$	457.721	18.56	1.15 ± 18%
$5s'\ ^2D_{5/2}$–$5p'\ ^2P^o_{3/2}$	447.501	18.62	0.92 ± 19%
$5s'\ ^2D_{5/2}$–$5p'\ ^2D^o_{5/2}$	408.833	18.88	0.97 ± 21%
$5p\ ^4D^o_{7/2}$–$5d\ ^4F_{9/2}$	378.310	20.11	2.97 ± 30%
$5p\ ^4D^o_{5/2}$–$5d\ ^4F_{7/2}$	377.809	20.15	2.70 ± 30%

3 Transition probability measurements

When the plasma remains at LTE the well–known formula [7–9]

$$(I_1/I_2)_{EXPT} = (A_1 g_1 \lambda_2 / A_2 g_2 \lambda_1)\exp(\Delta E_{21}/kT) \quad (1)$$

can be used for a comparison between measured relative line intensity ratios and corresponding calculated values, taking into account the validity of the Boltzmann distribution for the population of the excited levels in the emitters. In this expression I denotes the measured (EXPT) relative intensity, λ the wavelength of the transition, A the transition probability of the spontaneous emission, ΔE the difference in the excitation energy, and g the corresponding statistical weight. T is the electron temperature of the plasma in LTE and k is the Boltzmann constant.

Table 2. Relative (dimensionless) Kr II transition probability values. $A^{\rm rel}_{\rm exp}$ represent our experimental values. A_N denote tabulated values in NIST atomic spectra data base [4] where absolute and relative values (normalized to a 435.548 nm transition) are mutually equal. Other relative (dimensionless) experimental transition probability values: $A^{\rm rel}_{K}$, [21]; $A^{\rm rel}_{L}$, [20]; $A^{\rm rel}_{D}$, [22]; $A^{\rm rel}_{M}$, [25]; $A^{\rm rel}_{B}$, [24]; $A^{\rm rel}_{FC}$, [23]; $A^{\rm rel}_{BR}$, [26]; $A^{\rm rel}_{SCH}$, [31]; $A^{\rm rel}_{MH}$, [33]; $A^{\rm rel}_{F}$, [34] and $A^{\rm rel}_{MK}$, [32]. Data in brackets denote absolute A values of the reference 435.548 nm transition (in 10^8 s^{-1}).

λ (nm)	$A^{\rm rel}_{\rm exp}$	A_N	$A^{\rm rel}_{K}$	$A^{\rm rel}_{L}$	$A^{\rm rel}_{D}$	$A^{\rm rel}_{M}$	$A^{\rm rel}_{B}$	$A^{\rm rel}_{FC}$	$A^{\rm rel}_{BR}$	$A^{\rm rel}_{SCH}$	$A^{\rm rel}_{MH}$	$A^{\rm rel}_{F}$	$A^{\rm rel}_{MK}$
473.900	0.83	0.76	0.72		0.94	1.50	0.64	0.83	1.35	0.88	1.04	1.02	0.92
465.888	0.69	0.65	0.63	0.84	0.87	1.12	0.63	0.80	1.06			0.80	0.89
483.208	0.89	0.73		0.55	0.86	1.46		0.87	1.39				0.89
		(1.00)	(1.02)	(9.1)	(1.30)		(1.15)	(1.43)	(1.20)	(1.39)	(1.25)	(1.15)	(1.38)
435.548	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
476.574	0.78	0.67	0.66			1.21	0.65			0.72	0.84	1.14	
556.865	0.04												
484.661	0.73					1.75	0.78		2.00				
461.529	0.58	0.54				0.87			1.29				
461.917	0.72	0.81	0.79		0.94	1.47	0.71	0.87	1.35	0.90		0.98	
463.388	0.85	0.71	0.70	0.73	0.86	1.24	0.70	0.78	2.17		0.89	0.77	0.84
457.721	1.15	0.96	0.94	0.76	0.92	1.54	0.69	0.86	2.30		0.96	1.05	
447.501	0.92				1.22	1.12		1.06				1.14	
408.833	0.97				1.10	0.84		1.03	0.91			1.16	
378.310	2.97											1.64	
377.809	2.70											1.34	

On the basis of the measured relative line intensity ratio and electron temperature equation (1) yields ratio of the corresponding transition probabilities or conversely, the transition probability of a particular transition relative to a selected reference A value. As reference A values the transition probabilities of the 435.548 nm Kr II and 324.569 nm Kr III transitions have been chosen. These lines are the most intense and have the highest reproducibility among the investigated Kr II and Kr III spectral lines. Our experimental relative A values ($A^{\rm rel}_{\rm exp}$) are presented in Tables 1 and 4 with estimated accuracies which contain the uncertainties of the line intensity and electron temperature determinations and the uncertainties of the calibration procedure. $A^{\rm rel}_{\rm exp}$ represent averaged values obtained during plasma decay in a time interval for which the criterion of the existence of the LTE is fulfilled. Our $A^{\rm rel}_{\rm exp}$ values provide the possibility for a future comparison with absolute data as well as with data presented in relative form.

4 Results and discussion

Our experimentally obtained $A^{\rm rel}_{\rm exp}$ values are given in Tables 1, 2, 3 and 4.

On the basis of Tables 1–4 one can conclude: first of all, it must be remarked that absolute A values, taken from various references, corresponding to our reference 435.548 nm Kr II and 324.569 nm Kr III transitions lie in a wide range (1.00−1.64; for Kr II and 1.59−3.33; for Kr III) excluding unrealistically high Kr II A (9.1×10^8 s^{-1}) value from reference [20].

Fortunately, the absolute A value of the reference 435.548 nm Kr II transition tabulated by NIST [4] is 1.00×10^8 s^{-1} making the absolute and relative NIST A_N values mutually equal (in the case of our experiment). Our $A^{\rm rel}_{\rm exp}$ values agree well (within ±12%, on average) with 8 Kr II A_N values, especially in the case of the 465.888, 473.900 and 461.917 nm transitions.

Our Kr II $A^{\rm rel}_{\rm exp}$ values show tolerable agreement with previously experimental results by: reference [21] (6 transitions within ±14% on average), reference [22] (8 transitions within ±17% on average), reference [23] (8 transitions within ±14% on average), reference [24] (7 transitions within ±17% on average). In the case of the Kr III transitions the best agreement was found with $A^{\rm rel}_{F}$ values (6 transitions within ±26% on average).

The experimental Kr II $A^{\rm rel}_{M}$ [25] and $A^{\rm rel}_{BR}$ [26] values are significantly larger than our and other experimental values. Although the $A^{\rm rel}_{L}$ [20] values are reasonable, it should be pointed out that their reference value is extremely large (9.1×10^8 s^{-1}).

Our $A^{\rm rel}_{\rm exp}$ values are in a good agreement with theoretical values ($A^{\rm rel}_{FC}$ and $A^{\rm rel}_{MRT}$) predicted on the basis of the LS coupling approximation performed in reference [23] (8 transitions within ±12% on average) and in reference [27] (8 transitions within ±14% on average), and with $A^{\rm rel}_{SG}$ values predicted on the basis of the effective operator formalism presented in reference [28] (11 transitions within ±15% on average).

Theoretical Kr II $A^{\rm rel}_{SC}$ values [29] calculated on the basis of the LS coupling approximation lie far below all cited experimental and theoretical data. The $A^{\rm rel}_{KT}$ values calculated in reference [30] lie below other $A^{\rm rel}$ data except

Table 3. Same as in the Table 2. Relative theoretical Kr II transition probability values: $A^{\rm rel}_{MRT}$, [27]; $A^{\rm rel}_{KT}$, [30]; $A^{\rm rel}_{SG}$, [28]; $A^{\rm rel}_{SC}$, [29]; $A^{\rm rel}_{B}$, [24] and $A^{\rm rel}_{FC}$, [23].

λ (nm)	$A^{\rm rel}_{\rm exp}$	A_N	$A^{\rm rel}_{MRT}$	$A^{\rm rel}_{KT}$	$A^{\rm rel}_{SG}$	$A^{\rm rel}_{SC}$	$A^{\rm rel}_{B}$	$A^{\rm rel}_{FC}$
473.900	0.83	0.76	0.81	0.75	0.76	0.62	0.55	0.76
465.888	0.69	0.65	0.79	0.65	0.62	0.09	0.37	0.68
483.208	0.89	0.73	0.74	0.56	0.69	0.45		0.79
		(1.00)	(1.47)	(1.64)	(1.64)	(1.30)	(1.32)	(1.45)
435.548	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
476.574	0.78	0.67		0.42	0.69	0.31	0.56	
556.865	0.04							
484.661	0.73				0.64	0.007	0.28	
461.529	0.58	0.54		0.48	0.45	0.10		
461.917	0.72	0.81	0.71	0.47	0.75	0.25	0.94	0.84
463.388	0.85	0.71	0.99		0.71		0.78	0.78
457.721	1.15	0.96	0.80		0.86		0.87	0.82
447.501	0.92		0.91		1.12			0.87
408.833	0.97		1.21		1.04			1.11
378.310	2.97							
377.809	2.70							

Table 4. Our relative (dimensionless) experimental ($A^{\rm rel}_{\rm exp}$) transition probability values in the Kr III spectrum and those of the other authors: $A^{\rm rel}_{F}$, [34]; $A^{\rm rel}_{KPA}$, [37] and $A^{\rm rel}_{R}$, [38]. Wavelengths, transitions and upper-level energies ($E_{\rm u}$ in eV), are taken from references [4,19]. Data in brackets denote absolute transition probability values of the 324.569 nm Kr III reference transition (in 10^8 s^{-1}). Transitions are ranged following increasing $E_{\rm u}$ values.

Transition	λ (nm)	$E_{\rm u}$	$A^{\rm rel}_{\rm exp}$	$A^{\rm rel}_{F}$	$A^{\rm rel}_{KPA}$	$A^{\rm rel}_{R}$
$5s\ ^5{\rm S}^o_2$–$5p\ ^5{\rm P}_1$	335.193	21.76	$0.94 \pm 6\%$	0.86	1.11	0.89
$5s\ ^5{\rm S}^o_2$–$5p\ ^5{\rm P}_2$	332.575	21.79	$0.98 \pm 6\%$	0.90	1.02	0.89
				(1.59)	(3.33)	(2.80)
$5s\ ^5{\rm S}^o_2$–$5p\ ^5{\rm P}_3$	324.569	21.88	$1.00 \pm 3\%$	1.00	1.00	1.00
$5s\ ^3{\rm S}^o_1$–$5p\ ^3{\rm P}_2$	350.742	22.32	$1.22 \pm 9\%$	1.16	0.85	0.75
$5s'\ ^3{\rm D}^o_2$–$5p'\ ^3{\rm D}_2$	343.946	23.89	$1.68 \pm 18\%$	1.34	0.86	1.13
$5s'\ ^3{\rm D}^o_1$–$5p'\ ^3{\rm F}_2$	326.848	24.03	$1.59 \pm 20\%$	1.10	0.97	0.08
$5s'\ ^3{\rm D}^o_3$–$5p'\ ^3{\rm F}_4$	326.481	24.26	$1.60 \pm 21\%$	0.92	0.92	0.88
$5s'\ ^3{\rm D}^o_3$–$5p'\ ^3{\rm P}_2$	302.445	24.56	$1.02 \pm 23\%$		1.32	0.80

transitions 473.900 and 465.888 nm in the $5s\ ^4{\rm P}$–$5p\ ^4{\rm P}^o$ Kr II multiplet.

Experimental Kr II $A^{\rm rel}_{SCH}$ [31], $A^{\rm rel}_{MK}$ [32] and $A^{\rm rel}_{MH}$ [33] values agree with our $A^{\rm rel}_{\rm exp}$ values within the noticed experimental accuracies in the cited experiments and our work.

The experimental Kr II $A^{\rm rel}_{F}$ values lie above our $A^{\rm rel}_{\rm exp}$ data by about 20%, on average. Exceptions are the transitions of 378.310 and 377.809 nm in the high lying $5p\ ^4{\rm D}^o$–$5d\ ^4{\rm F}$ multiplet.

The transition 556.865 nm designated in reference [19] as $4d\ ^4{\rm D}_{5/2}$–$5p\ ^4{\rm D}^o_{3/2}$, belongs to the poorly investigated Kr II transitions and we have no other $A^{\rm rel}$ values for comparison. Absolute A values of this transition, observed experimentally, are presented in references [35,36].

It should be pointed out that in the recent study [35] the authors have found satisfactory agreement among their experimental A values and calculated Kr II transition probabilities in reference [28]. Their A data show good agreement with those from reference [24].

Finally, it turns out that in the studies [35,36,39–48] a number of the Kr II and Kr III A values have been obtained, but without ones corresponding to our chosen transitions so that the comparison with our $A^{\rm rel}_{\rm exp}$ data is impossible.

5 Conclusion

On the basis of the accurately obtained spectral line intensities we have obtained 14 Kr II and 7 Kr III transition probability values relatively to the reference transitions at 435.548 nm and 324.569 nm, respectively. The comparison among all available A^{rel} values (except extremely high or small values) and here presented data show agreement (within ±15%) between A^{rel} values corresponding to the 463.388 and 408.833 nm Kr II and 335.193 and 332.575 nm Kr III transitions. Thus, they can be recommended as useful atomic data with accurate A^{rel} values, related to the chosen Kr II and Kr III reference transitions needed in plasma diagnostic or modeling.

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