Atomic transition probabilities for the Ar I 4s-5p transition array

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We have determined the transition probabilities for 23 lines of the Ar I 4s-5p array by emission spectroscopy utilizing a wall-stabilized arc. The seven remaining lines of this transition array were either very weak or overlapped strongly with other lines so that they could not be reliably measured. We placed our relative data on an absolute scale by applying the result of a recent critical analysis for the prominent 4s-5p line at 430.01 nm.

I. INTRODUCTION

The atomic transition probabilities of some 4s-5p transitions of Ar I, located in the blue region of the spectrum, have been the subject of considerable debate in the literature, and its most prominent line, the transition at 430.01 nm, has been measured many times in emission experiments.[1–18] The resulting transition-probability data cluster around either one of two numbers, which differ by about 30%, and there are practically no results in between. But a recent critical analysis[19] of these numerical data has resolved this issue satisfactorily and has shown that the properly revised and adjusted data are actually in close agreement. As discussed there in detail, four central aspects need to be carefully addressed in emission experiments: (1) the plasma diagnostic approach; (2) the definition of the plasma source, especially homogeneity along the line of sight; (3) the measurement of total line intensities; and (4) the validity of the local thermodynamic equilibrium (LTE) model (this is always assumed). A few of the Ar I emission experiments[5–8] did not fulfill conditions (2) and (4) and were therefore not considered for the final analysis. Several other results[1–3,9–12,16] were corrected for missing line-wing intensity contributions, and two results were modified with newly available improved diagnostic data.[1,4] Also, as noted in the critical analysis, theoretical data are unreliable for the 4s-5p transitions because of strong cancellation effects in the transition integral. [Lifetime measurements of 5p levels cannot be utilized for determinations of the absolute scale of 4s-5p lines, since numerous transitions (branches) originate from the 5p levels, not only to the 4s levels, but to the 3d and 5s levels for which almost no transition probabilities are available.] For further details on the emission work, Ref. 19 should be consulted; here we present in Table I the results of the 14 available emission experiments, as critically analyzed and revised there, for the 430.01-nm line (revised data carry an asterisk). The table demonstrates the close consistency between all these data and yields an accurately established mean value of $A_{430}=0.374\times10^{6}$ s^{-1}, with the largest deviation from the mean being only 8%.

In contrast to the 430.01-nm line, very few data exist for other lines of this transition array. Only two comprehensive studies for the whole transition array have been carried out, by Wende[10] and Bues *et al.*[11] In these two experiments, the line-intensity measurements were done by graphical integration (planimetry) of the areas under the photoelectrically obtained line profiles, after subtracting out the underlying continuum. (No corrections for line-wing intensity contributions were added; however, for relative measurements within the transition array, i.e., measurements of ratios against a reference line, the line-wing contributions should cancel to first order, if wing cutoffs are consistently applied in a manner that compensates for varying linewidths. The overall measurement uncertainties were estimated by the authors[10,11] to be normally of the order of 10–20% for the transition probabilities of the stronger lines and 40% and more for the weaker lines. With the utilization of laboratory computers, the measurement of total line intensities may be significantly improved. Thus, a comprehensive new measurement of the relative transition probabilities of the 4s-5p lines utilizing advanced line-integration techniques, coupled with the now accurately established absolute scale based on the 430.01-nm line, appears to be timely and is the subject of this paper.

II. EXPERIMENTAL APPROACH

We have measured the relative transition probabilities of the Ar I 4s-5p lines by employing the emission of a wall-stabilized arc source.[20,21] The arc was operated at atmospheric pressure at currents of 40 and 45 A, and had a channel diameter of 4.2 mm. We observed the argon line radiation end-on with a 2.25-m Czerny-Turner monochromator. A cooled photomultiplier with a broadband GaAs photocathode served as the detector. In order to avoid contributions from the inhomogeneous areas near the two electrodes, we operated these regions in helium. The Ar I line profiles were scanned in a stepwise manner, and at each wavelength setting the specific line intensity was recorded for a period of 5 s. Periodic dark current readings were taken and the spectrometric system was calibrated against a tungsten strip lamp standard calibrated by the Radiometric Physics Division of the National Bureau of Standards. The wavelength advance, the intensity recordings, and the calibration procedures were controlled by a minicomputer.[21] Approximately 200 data points were recorded across a line profile, and the photomultiplier signals were digitized and stored in the computer. Digital least-squares fitting techniques were then applied to approximate the measured line

TABLE I. Atomic transition probability data (A values) for the 430.01-nm Ar I 4s-5p transition. An asterisk indicates a result revised according to a recent critical analysis (Ref. 19).

Author	A value (in 10^6 s^{-1})
Drawin[a]	0.358*
Gericke[b]	0.390*
Richter[c]	0.372*
Popenoe and Shumaker[d]	0.343*
Chapelle *et al.*[e]	0.377*
Wende[f]	0.372*
Bues, Haag, and Richter[g]	0.372*
Wujec[h]	0.366*
Van Houwelingen and Kruithof[i]	0.370*
Nubbemeyer[j]	0.391
Preston[k]	0.372
	0.369
Baessler and Kock[l]	0.384*
Nick[m]	0.374
Hirabayashi *et al.*[n]	0.394
Mean value	0.374

[a]Reference 1.
[b]Reference 2.
[c]Reference 3.
[d]Reference 4.
[e]Reference 9.
[f]Reference 10.
[g]Reference 11.
[h]Reference 12.
[i]Reference 13.
[j]Reference 14.
[k]Reference 15, line intensity and line-shape diagnostics.
[l]Reference 16.
[m]Reference 17.
[n]Reference 18.

shapes by analytical curves.

This is an attractive approach for the experimental conditions, since the line profiles are expected to be closely approximated by a Lorentzian shape. Such shape is due to the circumstance that the dominant line-broadening mechanism for a moderately dense, low-temperature plasma is Stark broadening of the argon atoms by electron impacts, which results in the Lorentzian shape. This theoretical result has indeed been closely confirmed by numerous experimental studies, although small asymmetries, in the 1–3% range, have been observed,[20] as was theoretically predicted on the basis of minor ion-broadening contributions. The nonlinear least-squares fitting was carried out in an iterative manner as described in more detail elsewhere.[21] For the background radiation, which is in most cases essentially constant over the range of a line, a cubic polynomial was assumed so that instances where noticeable line wing contributions from nearby spectral lines occur could be adequately taken into account.

The integrated spectral radiance for each line was thus obtained from the area under the fitted Lorentzian, with the background function subtracted. To test the accuracy of the fitting procedure, the standard deviation of each fitted curve from its corresponding data points was calculated for each scan analyzed in this work and was found to be typically in the range 0.5–1%. The fitting procedure also proved to be rather insensitive to minor deviations of the actual line shapes from Lorentzians, caused by the above-mentioned ion-broadening effects, because the contributions of these slight asymmetries in the observed line shapes were found to cancel each other almost completely. This was shown by us in detailed studies of these ion-broadening effects for many lines of differing atomic elements and transition arrays.[22] An important exception to these observations arises in the case of closely spaced, overlapping lines of significantly different intensities. In these cases the asymmetries of the stronger lines can significantly alter the apparent intensity of weaker adjacent lines, and increase the uncertainties of intensity measurements dramatically, whether Lorentzian fitting or planimetry is employed.

The line emission was checked for possible self-absorption by placing a concave mirror behind the arc which imaged the arc back into itself[21] and thus effectively doubled the optical path length, aside from reflection and transmission losses. A mechanical shutter, placed between mirror and arc, was alternately opened and closed for recordings at different wavelength settings. No measurable variations in the thus obtained intensity ratios were found for positions either near the line centers or at the line wings. Thus, self-absorption for the measured Ar I lines (which are all relatively weak) was found to be less than 1%.

The relative transition probabilities were referenced against the 430.01-nm line, since, as discussed earlier, its absolute value is very well established. According to Table I, we have set this transition probability at the mean value of 15 emission results, i.e., $A_{\rm ref}=0.374\times10^6$ s^{-1}. We cautiously estimate that its uncertainty does not exceed $\pm5\%$, since 14 of the 15 listed emission data fall within a $\pm5\%$ band about the mean value. We then determined the A values for other 4s-4p lines utilizing the relation

$$A_x = A_R \frac{g_R}{g_x}\frac{\lambda_x}{\lambda_R}\frac{I_x}{I_R}\exp\left[\frac{E_x-E_R}{kT}\right], \qquad (1)$$

where the subscripts x and R denote values associated with the 4s-5p line under consideration and the 430.01-nm reference line, respectively, and where I is the total line radiance, λ the wavelength, E the excitation energy of the upper atomic level and g its statistical weight, k the Boltzmann constant, and T the absolute temperature. This relation is valid for a state of LTE in a plasma, which has been shown—both experimentally and theoretically—to exist in argon arc plasmas[19] for electron densities N_e greater than about 5×10^{16} cm^{-3}, and thus applies to our plasma conditions (see below). (Actually, for the measurement of relative transition probabilities for lines within a transition array only *partial* LTE is required for lines which originate from closely spaced excited atomic states. This condition is much less stringent and much lower electron densities suffice, since the range of typically encountered excitation energies is quite small compared with the thermal energy, kT.)

The determination of relative transition probabilities requires a measurement of the plasma temperature or, for partial LTE, the excitation temperature. In this experiment, we determined the electron density by the technique[20,23] of measuring the plasma Stark broadening of the hydrogen Balmer line H_β. This line was observed by adding a trace of hydrogen gas to the plasma. This accurately established method yielded densities of $N_e = 6.21\times10^{16}$ cm^{-3} and 6.98×10^{16} cm^{-3} for the 40- and 45-A arcs, respectively, which ensured that the arc source was operated within the regime of LTE.[19] Subsequently, the plasma equilibrium and conservation equations for atmospheric pressure arcs were applied to derive the plasma temperature T from N_e. Numerical values of 11 880 K$\pm$2% for the 40-A arc and 12 090 K$\pm$2% for the 45-A arc were obtained.

III. RESULTS AND DISCUSSION

We have determined the transition probabilities of 23 lines of the Ar I $4s$-$5p$ transition array with an advanced emission technique and a computerized data acquisition system, which has resulted in a significantly more accurate data set than the other two data sets in existence. Table II shows our results and comparisons with the earlier measurements by Wende,[10] and by Bues, Haag, and Richter.[11] All three data sets are normalized to the same

TABLE II. Results and comparison with other experiments. The $1s_4$-$3p_8$ transition at 430.01 nm is taken as the reference line and its transition probability is set at 0.374×10^6 s^{-1} for the three experiments. For footnotes c–h, also see Sec. III.

Transition (Paschen notation)	Wavelength λ (nm)	Transition probability (10^6 s^{-1}) This experiment	Wende[a]	Bues *et al.*[b]
$1s_2$-$3p_1$	425.94	3.96$\pm$8%	3.9	4.02
$1s_2$-p_2	433.53	0.433$\pm$12%	0.35	0.373
$1s_2$-p_3	433.36	0.558$\pm$10%	0.58	0.548
$1s_2$-p_4	434.52	0.306$\pm$8%	0.27	0.311
$1s_2$-p_5	451.07	1.19$\pm$8%	1.2	1.14
$1s_2$-p_6[c]	458.93	0.008$\pm$21%	0.0036	0.007
$1s_2$-p_7	459.61	0.100$\pm$8%	0.089	0.093
$1s_2$-p_8	462.84	0.0388$\pm$8%	0.039	0.037
$1s_2$-p_{10}	470.23	0.166$\pm$8%	0.11	0.102
$1s_3$-$3p_2$	418.19	0.588$\pm$8%	0.55	0.524
$1s_3$-p_4[d]	419.10			0.534
$1s_3$-p_7[e]	442.40		0.0065	0.008
$1s_3$-p_{10}	452.23	0.0866$\pm$8%	0.090	0.090
$1s_4$-$3p_1$[f]	398.0			
$1s_4$-p_2	404.60		0.037	0.044
$1s_4$-p_3	404.44	0.346$\pm$10%	0.34	0.308
$1s_4$-p_4	405.45	0.0300$\pm$10%	0.023	0.028
$1s_4$-p_5	419.83	2.46$\pm$12%	2.7	2.50
$1s_4$-p_6	426.63	0.303$\pm$8%	0.28	0.348
$1s_4$-p_7	427.22	0.770$\pm$8%	0.76	0.837
$1s_4$-p_8	430.01	0.374($\pm$5%)	0.374	0.374
$1s_4$-p_{10}[g]	436.38		0.012	0.012
$1s_5$-$3p_2$	394.90	0.488$\pm$12%	0.42	0.450
$1s_5$-p_3	394.75	0.048$\pm$16%	0.053	0.065
$1s_5$-p_4	395.7			
$1s_5$-p_6	415.86	1.49$\pm$8%	1.3	1.40
$1s_5$-p_7	416.42	0.279$\pm$8%	0.27	0.310
$1s_5$-p_8[h]	419.07			0.244
$1s_5$-p_9	420.07	0.953$\pm$10%	0.99	0.932
$1s_5$-p_{10}	425.12	0.116$\pm$8%	0.092	0.123

[a]Reference 10.
[b]Reference 11.
[c]Blended with very narrow Ar II line at 458.99 nm, but could be resolved.
[d]Blended with $1s_5$-$3p_8$ transition at 419.07 nm—not resolvable.
[e]Very weak line, blended with strong Ar II transition at 442.60 nm—not measured.
[f]Too weak for reliable measurement.
[g]Very weak and blended with Ar II line at 436.21 nm—not measured.
[h]Blended with $1s^3$-$2p^2$ transition at 419.10 nm—not resolvable.

absolute value for the 430.01-nm reference line. The agreement, especially with Bues, Haag, and Richter,[11] is quite close. But in one case, for the weak transition at 458.93 nm, our difference with Wende's result lies outside the mutually estimated error limits.

Several lines of the Ar I 4*s*-5*p* array warrant specific comments with regard to measurements of their transition probabilities. The lines of shortest wavelengths, 394.90 nm ($1s_5$-$3p_2$) and 394.75 nm ($1s_5$-$3p_3$), lie in a region of the spectrum where the emission of tungsten strip standard lamps, as employed in this work, is quite low and thus the uncertainty in the absolute intensities of these lines is increased. Additionally, both lines are relatively weak and strongly overlap each other, which especially causes uncertainties for the weaker line at 394.75 nm. A similar situation prevails for the 404.44 nm ($1s_4$-$3p_3$), 404.60 nm ($1s_4$-$3p_2$), and 405.45 nm ($1s_4$-$3p_4$) lines which are also short-wavelength weak lines. An accurate determination of the intensity for the 404.60-nm line is virtually impossible under our plasma conditions due to its almost complete blending with the much stronger 404.44-nm line.

Coincidences of Ar II lines with Ar I lines severely affected three lines studied in this work.[24] The Ar II lines at 436.21 nm and 442.60 nm made measurements of the very weak Ar I lines at 436.38 nm ($1s_2$-$3p_{10}$) and 442.40 nm ($1s_3$-$3p_2$) impossible for our plasma conditions. In the case of the weak line at 458.99 nm ($1s_2$-$3p_1$), an Ar II line (wavelength 458.99 nm) showed up very close to the peak of the Ar I line. Since the Ar II line was extremely narrow and non-Lorentzian, its contribution could be approximately separated out by excluding the few affected points from the line profile prior to the least-squares fitting procedure. Although this procedure appears to have worked adequately, it increased the uncertainty of the data determined for the Ar I 458.9-nm line.

Complete line blending also made the determination of individual transition probabilities for the Ar I 419.07-nm ($1s_5$-$3p_8$) and 419.10-nm ($1s_3$-$3p_4$) lines impossible, and the two lines at 398.0 nm ($1s_4$-$3p_1$) and 395.7 nm ($1s_5$-$3p_4$) proved to be too weak to be observed at all. (The 395.7-nm line is the predicted wavelength of an as yet unobserved transition of the Ar I 4*s*-5*p* array.)

For the remaining 23 lines we have listed our normalized results in Table II, and have also provided an overall uncertainty estimate for each line. This takes into account both random errors and estimates for systematic errors. Specifically, we have included the standard deviations of the mean measured intensity ratios from several runs, as well as random and systematic errors due to the temperature determination, the intensity calibration procedure, the continuum background level, possible slow drifts in the arc emission, and the photoelectric detection system, and the uncertainty in the *A* value of the reference line (the latter is estimated not to exceed $\pm 5\%$). We assume that all errors are independent errors, and thus obtain the overall error as the square root of the sum of the squares of the individual contributions. In many instances the tabulated accuracy has been attained in spite of considerable overlap of adjacent lines, as in the case of the 419.83-nm ($1s_4$-$3p_5$) line with the 420.07-nm ($1s_5$-$3p_9$) line and the 433.53-nm ($1s_2$-$3p_2$) line with the 433.36-nm ($1s_2$-$3p_3$) line. In these instances of comparable line intensities, the least-squares fitting procedure appears to have performed very well in extracting individual line intensities from blended spectra. But as usual, the greatest accuracy (and best agreement with other measurements) occurs for strong, well-isolated lines. The accuracy, and degree of agreement with other results, for weak isolated lines is limited by statistical uncertainties intrinsic to the measurement process itself. For overlapping lines a major cause of uncertainties (and of disagreements between otherwise accurate sets of measurements) is line asymmetry. This is particularly evident when a weak line is partially blended with a much stronger line: A slight asymmetry of the stronger line can substantially alter the apparent intensity of the weaker line. This introduces a critical dependence on Stark broadening, and especially ion-broadening effects, into the measurements of intensities of overlapping lines and may account for many discrepancies seen in the literature between otherwise accurate sets of transition probabilities. While least-squares fitting to symmetric Lorentzian profiles is an effective and accurate procedure for well-isolated, slightly asymmetric lines where the effects of asymmetries tend to cancel due to their nearly antisymmetric nature,[20] this procedure becomes less effective for overlapping lines of greatly differing intensities. Accurate measurements of individual line intensities from blended spectra observed in emission from LTE and partial LTE plasmas will only result from curve-fitting techniques which properly take into account the antisymmetric ion-broadening contributions to the otherwise symmetric Lorentzian profiles predicted by electron-impact Stark broadening alone.

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[24]In addition, an Ar II line at 430.065 nm is blended with the Ar I 430.010-nm reference line. However, no trace of this Ar II line has been observed, and we estimate that for our experimental conditions the intensity of this line is only 0.0007 of the Ar I line.