# Experimental Determination of Transition Probabilities and Stark Widths of S I and S II Lines*†

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(Received 28 February 1967)

Absolute transition probabilities and Stark widths for some prominent multiplets of S I and S II have been determined experimentally. A wall-stabilized arc was operated in $SO_2$ with a small hydrogen admixture. The spectroscopic measurements were performed photoelectrically. Side-on observations were transformed via the Abel inversion to give the radial dependence of the measured quantities. Measurements of the absolute intensity of O I lines and the width of $H_\beta$ served for the plasma analysis; the results of these measurements together with the application of equilibrium and conservation relations for arc plasmas enabled the determination of the temperature and various particle densities. Mass-separation effects are taken into account. The measured Stark widths generally agree well with values calculated from Stark-broadening theory; in the case of the S II lines the agreement with recently calculated values is substantially better than that with earlier theoretical data.

## I. INTRODUCTION

THE high-current, wall-stabilized arc has proven to be a suitable and reliable source for measurements of transition probabilities and line profiles of neutral and singly ionized atoms. This is in great part because this source is generally in a state of local thermal equilibrium. For obtaining transition probabilities on an absolute scale, the density of the emitting species as well as the temperature must be known. While this is relatively easy to accomplish for a one-element arc plasma, it becomes increasingly complex with the number of chemical elements present. Unfortunately, the generation of one-element arc plasmas is readily feasible only for a small number of elements, namely those available in gaseous form under normal temperature and pressure. In other cases one best employs gaseous compounds of the element to be studied, i.e., one has to analyze a multi-element plasma. Sulfur has, with $SO_2$ and $H_2S$, two relatively attractive compounds available.

Despite astrophysical interest in sulfur, very few data for sulfur transition probabilities have been reported as yet in the literature.[1–3] An experimental determination of transition probabilities of some lines of sulfur thus appeared desirable and is one of the two principal subjects of this paper. Parallel to the intensity measurements, the Stark widths of these S I and S II lines were also determined and compared with theoretically predicted widths. Numerical calculations of Stark widths for lines of many elements have become available since 1964[4]; however, relatively few experimental checks have been performed, especially for ionic lines.[5] It will be seen that the present measurements on the S II lines have furnished quite interesting and surprising results, which—together with some other recent measurements on ionic lines—have triggered a revision of the existing Stark-broadening theory.[6]

## II. METHOD

The experimental method employed here follows the standard emission-measurement technique for the determination of atomic transition probabilities which has been often explained before.[7] We shall therefore treat in some detail only the specific problems connected with the determination of the number density of the emitting species.

The transition probability $A_{ki}$ of a transition from a higher atomic level $k$ to a lower level $i$ may be determined from emission intensity measurements via the relation

$$A_{ki}=4\pi I_{ki}(\lambda/hc)[Z(T)/Ng_k]\exp(E_k/kT)\times l^{-1}, \quad (1)$$

where $I_{ki}$ is the total intensity of the spectral line and $\lambda$ its wavelength; $E_k$ and $g_k$ are, respectively, the energy and statistical weight of the upper atomic level $k$; $N$ is the number density of the emitting species; $T$ is the temperature; $Z(T)$ is the partition function; and $l$ is the length of the (homogeneous) plasma layer.

The partition function is readily calculated if the temperature is known,[7] and $E_k$ and $g_k$ are usually available from spectroscopic tables. The transition probability may thus be obtained from an absolute intensity measurement provided one can determine simultaneously $N$ and $T$. However, Eq. (1) holds only under the conditions that local thermal equilibrium exists in the plasma and that the line suffers no self absorption. These assumptions need to be verified.

* Supported in part by Project DEFENDER sponsored by the Advanced Projects Agency, Department of Defense, through the Office of Naval Research.

† Based on a thesis submitted by J. M. Bridges in partial fulfillment of the requirement for the degree of Doctor of Philosophy, University of Maryland.

[1] B. M. Glennon and W. L. Wiese, NBS Misc. Publ. 278 (1966).
[2] M. Miller *et al.*, Bull. Am. Phys. Soc. **11**, No. 6, 818 (1966).
[3] B. D. Savage and G. M. Lawrence, Astrophys. J. **146**, 940 (1966).
[4] H. R. Griem, *Plasma Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1964).
[5] W. L. Wiese, *Plasma Diagnostic Techniques* (Academic Press Inc., New York, 1965), Chap. 6.
[6] H. R. Griem, Phys. Rev. Letters **17**, 509 (1966).
[7] See, e.g., W. L. Wiese and J. B. Shumaker, J. Opt. Soc. Am. **51**, 937 (1961).

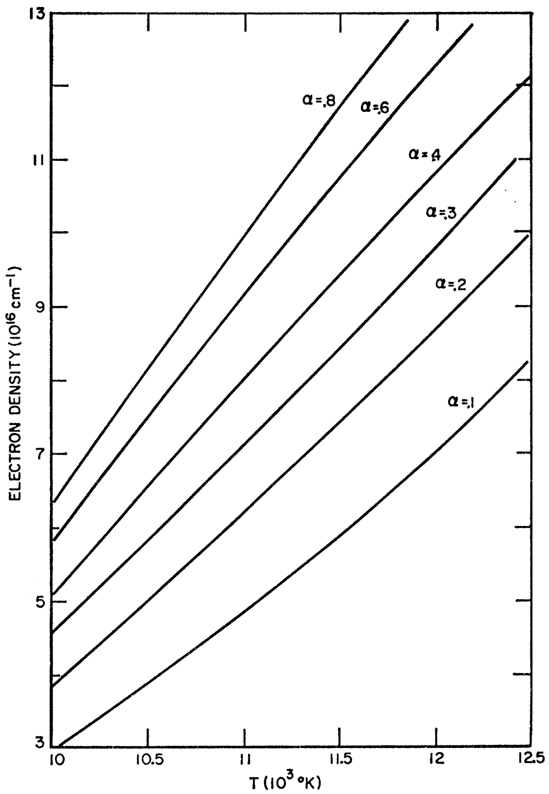


FIG. 1. Calculated electron density versus temperature with sulfur/oxygen density ratio $\alpha$ as parameter.

While it is often possible to measure the temperature directly, one has normally to apply a rather indirect approach for the determination of $N$. Namely, one has to employ a number of equilibrium and conservation equations by which the various densities and the temperature are related.[7] Generally, for a plasma consisting of $X$ elements and $Y$ different species one encounters $Y+1$ unknowns, namely $Y$ densities and the temperature. For these one has available $Y-X-1$ Saha equations, Dalton's law (with a known total pressure of one atmosphere) and the condition of local electrical neutrality; that is, altogether $Y+1-X$ equations. Formerly, stoichiometric ratios have been employed as additional relations. This, however, has turned out to be an incorrect procedure, because recently discovered mass-separation effects may cause the local mixing ratios to be quite different from the initial stoichiometric ratios.[8] It is seen, then, that for a plasma containing $X$ elements one has to determine experimentally at least $X$ unknowns (or equivalent combinations of these) to obtain a complete solution for the densities and temperature.

For the two-element case of $SO_2$, it was decided to measure the width of a strongly Stark-broadened line and the intensity of an oxygen line of known transition probability. The linewidth measurement furnishes, in conjunction with Stark-broadening theory, the electron density; and the line intensity furnishes a relation containing the temperature and the density of neutral oxygen, as may be seen from Eq. (1). Alternatively, the temperature could be also determined directly from measurements of the relative intensities of several O I multiplets.

The practical determination of the sulfur transition probabilities proceeded then as follows: At arc temperatures of about 1 eV, the atomic species present in significant quantities are neutral and singly ionized sulfur atoms, neutral and singly ionized oxygen atoms, and electrons. The relevant equilibrium and conservation relations[9] for the five corresponding densities and the temperature were first combined to express the densities as a function of the following variables: the temperature $T$, and the sulfur-oxygen density ratio $[(N_{S}+N_{S+})/(N_{O}+N_{O+})]$, denoted by $\alpha$. Numerical calculations were performed for a large number of $T$ and $\alpha$ values. As an example, Fig. 1 illustrates the functional dependence of the electron density $N_e$ with respect to these quantities. Next, the intensities of several O I multiplets of well-known transition probabilities were also calculated applying Eq. (1) and plotted as functions of the same variables. For the case of the O I 7156-Å line this is presented in Fig. 2. Measurements of $N_e$ and of the absolute intensity of

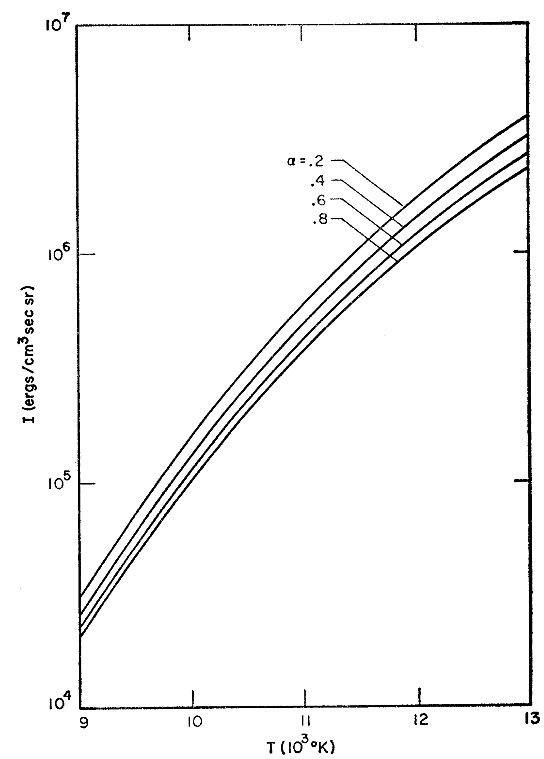


FIG. 2. Calculated intensity of the O I 7156-Å line versus temperature with sulfur/oxygen density ratio $\alpha$ as parameter.

[8] W. Frie and H. Maecker, Z. Physik **162**, 69 (1961).

[9] High-density corrections according to Ref. 4 were applied.

at least one O I multiplet then yielded two relationships between the variables $\alpha$ and $T$. The simultaneous solution for the two quantities was obtained graphically as illustrated in Fig. 3. With the thus determined sulfur densities and temperature the absolute values of the transition probabilities could be immediately computed for those lines of S I and S II whose intensities were measured.

The method outlined above of determining the particle densities in a plasma containing more than one element may be considered as a simplified variation of a procedure applied by Boldt[10] for determining the particle densities in a mixture of argon and carbon dioxide. By measuring, in addition to $T$ and $N_e$, various relative line intensities in plasmas containing the same elements in different proportions, Boldt was able to determine all particle densities without using any predetermined values for transition probabilities. In our analysis of the $SO_2$ plasma, however, we decided to make use of available O I transition probabilities since these are quite reliable.[11] Furthermore, for the case of a sulfur-oxygen mixture we encounter the favorable circumstance that the electron density depends sensitively on the mixing ratio, since the first ionization potentials of these two elements are quite different.

The measurements of the Stark widths and shifts proceeded in a relatively straightforward manner, since under the experimental conditions the line profiles are relatively broad and could be easily resolved with a monochromator of moderate dispersion (10 Å/mm). Other line broadening mechanisms as well as apparatus broadening always gave smaller contributions than Stark broadening, and could readily be accounted for.

## III. EXPERIMENTAL

### Apparatus and Basic Procedure

The light source used for this experiment was a wall-stabilized arc, the details of which have been described previously.[12] A $\frac{1}{8}$-in.-diameter arc channel was used, and for operation with $SO_2$ the copper discs which form the channel for the arc were gold plated to prevent corrosion. Another important change from the previously used configuration was to set the observation window back to 4 cm from the arc axis, and direct a small flow of $SO_2$ into the center chamber just inside the window. This was necessary to prevent the formation there of a cloud of suspended sulfur generated by sulfur atoms upon leaving the arc column. A significant amount of sulfur did deposit out in the arc sections adjacent to the center where the main $SO_2$ flows were directed into and out of the arc, but not enough to cause irregular arc behavior during a run. (Previous to the experiment with $SO_2$, attempts to operate the arc in $H_2S$ proved unsuccessful due to excessive depositing of sulfur which caused arc instabilities after a few minutes operating time). The total flow rate of $SO_2$ gas was about 1400 ml/min. Argon was admitted near the electrodes with a total flow rate of 800 ml/min. Spectroscopic checks were made to verify that no significant quantity of argon ($<0.1\%$) was present in the center arc section. The arc column was observed end-on or side-on with two Ebert-type monochromators: A 0.5 m instrument with reciprocal linear dispersion of 32 Å/mm in first order, and a 0.75 m instrument with reciprocal linear dispersion of 10 Å/mm in first order. An S20-type photomultiplier (EMI 9588B) was used for observations in the wavelength range below about 7500 Å; for longer wavelengths an S1-type phototube (RCA 7102) was employed. The latter tube was cooled with dry ice to improve the signal-to-noise ratio.

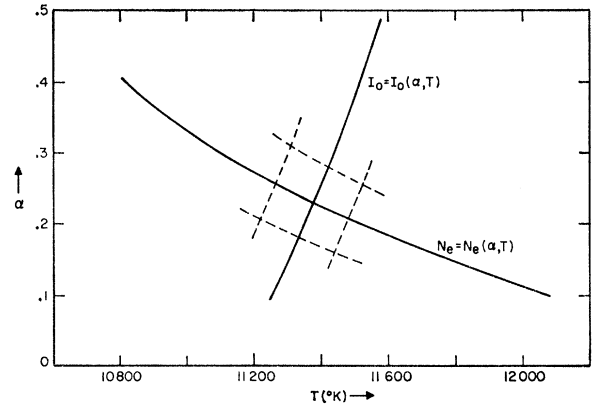


FIG. 3. Graphical solution for temperature $T$ and sulfur-oxygen density ratio $\alpha$ for radial position of 0.4 mm. Dotted lines represent estimated uncertainties in the positions of the curves.

A tungsten strip lamp, calibrated by the Radiation Thermometry Section of the Bureau of Standards, served as the intensity standard. Intensity calibrations were carried out after each run by placing the strip lamp in the arc position.

Most measurements were performed side-on. For measuring the absolute intensity emitted from a given volume element, the arc was positioned with its axis parallel to the entrance slit of the monochromator. By slowly driving the arc image across the entrance slit the projected arc intensity was obtained. For recording the data, a special automatic data recorder[13] was available. This device integrates the signal from the photomultiplier over successive preselected time intervals, and records the integrated values on paper tape. The use of shift registers allows data to be recorded while other data are being read in, so that the recorder can be operated continuously. The data, recorded on paper tape, were then fed to a computer for an Abel inversion

[10] G. Boldt, Z. Naturforsch. **18a**, 1107 (1963).
[11] W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities* (U.S. Government Printing Office, Washington, D.C., 1966), NSRDS-NBS 4, Vol. I.
[12] W. L. Wiese, D. R. Paquette, and J. E. Solarski, Phys. Rev. **129**, 1225 (1963).
[13] D. R. Paquette and W. L. Wiese, Appl. Opt. **3**, 291 (1964).

process, which yielded the radial intensity profile of the arc.

For determining line profiles and intensities, measurements are made at wavelength intervals suitably spaced across the line profile and extending sufficiently far from the line center to get accurately the underlying continuum level. Plotting the (Abel-inverted) intensities from a given arc radius versus wavelength, the linewidths may be obtained directly from the plotted curve and the line intensities obtained by graphical integration. In most cases, however, the line intensities could be measured in a simplified procedure by opening the monochromator exit slit wide enough to let pass most of the line intensity together with the underlying continuum. Then with the same slit settings the continuum intensity on both sides of the line was measured. The continuum intensity at the position of the line could be obtained by interpolation, and was subtracted from the original measurement to yield the uncorrected intensity of the line. A correction must then be made to account for the intensity in the far wings of the line which is not included within the wavelength band passed by the monochromator. This correction is easily computed[14] assuming a dispersion shape for the lines, which is to a very good approximation borne out by the profile measurements.

All the measured lines were examined with regard to self absorption. This was done by comparing the intensity at the line peak to that which would be emitted by a black body at the temperature of the arc. An additional check was also performed by reflecting the arc image back through the arc itself and measuring the increase in intensity. Reflection losses were accounted for by repeating the measurements at wavelengths (in the continuum) where negligible self absorption occurred. Self absorption was found to be appreciable only for the strongest lines measured and required special measurements in a diluted $SO_2$ plasma in these cases.[14]

Some measurements were made with the arc in the end-on position. In this configuration relative intensities could be compared directly since the observed radiation was restricted by a small aperture (1:100) to that of a narrow cone centered at the arc axis, over which volume the plasma properties are approximately uniform.

### Transition-Probability Measurements

As the first step, the plasma conditions had to be determined. In order to obtain the electron density, the strongly broadened hydrogen line $H_\beta$ was employed, for which very reliable Stark-broadening data exist.[5] A 2% admixture of hydrogen was admitted with the $SO_2$, which gave sufficient intensity for observing the $H_\beta$ profile precisely, but was still too small to significantly affect the plasma conditions. A strong S II line, blended with $H_\beta$ at about the half-maximum intensity position on one wing, complicated the measurement. The over-all profile of the blended line was first obtained; next the profile of the sulfur line alone was scanned by making a run without the admixture. Subtracting the two profiles resulted in an intensity profile due to hydrogen alone, from which the half-width of $H_\beta$ was measured. In performing the measurement, the profile was fitted to the theoretical profile of Griem *et al.*[15] The fit of the experimental points to the theoretical profile was sufficiently good that the width of $H_\beta$ was estimated to be determined to within 4%, which represents a contribution of 6% to the error in the electron density.[4,5] With a further uncertainty in $N_e$ estimated not to exceed 7% from Stark-broadening theory,[5] the total error in $N_e$ amounts to about 9%.

The time-consuming $H_\beta$ measurement was not included in each run in which sulfur intensities were measured; this was not considered necessary, since all runs were made under identical conditions, and complete reproducibility of the particle densities and temperature was obtained within the experimental errors for the runs in which $H_\beta$ was measured.

The measurement of the absolute intensity of one O I line of known transition probably was now sufficient to determine the plasma conditions. As a check against possible systematic errors and also to obtain increased accuracy, the intensities of several multiplets were measured in each run. The prominent O I multiplets at 7773, 8227, 7949, 7157, and 7477 Å were used. Their transition probabilities were taken from a recent critical compilation.[11] For a given density, the intensity measurements of the various multiplets gave values for the temperature which agreed to within $\pm 150°$. The results from these measurements were averaged in the final analysis. Analyzing the data from several arc radii, the radial temperature and particle-density distributions were computed and are shown in Fig. 4.

Using the relative intensities of the above-listed O I multiplets, the temperature was also determined directly from the slope of the plot of $\ln(I_{ki}\lambda/A_{ki}g_k)$ versus the various $E_k$. [This may easily be seen by regrouping Eq. (1).] This temperature determination has the advantage that only relative transition probabilities are required and only relative intensities need to be measured; nevertheless, due to the small differences in the values of $E_k$ for the measured multiplets, this determination resulted in a less accurate value for $T$ than that obtained by the above method. The temperature determined from the relative intensity measurement is estimated to be accurate within 3%, which is about twice the uncertainty estimated from the earlier determination using the absolute intensity measurement. The two results did agree within the combined experimental errors.

[14] J. M. Bridges, dissertation, University of Maryland, 1966 (unpublished).

[15] H. R. Griem, A. C. Kolb, and K. Y. Shen, Astrophys. J. **135**, 272 (1962).

The intensity of each S I multiplet was measured in at least four runs. Among the S I multiplets, only for the $4\,^5S^o$–$4\,^5P$ multiplet ($\lambda=9212$–$9237$ Å) were the lines sufficiently resolved that the individual line intensities could be determined. For all others, only the total multiplet intensities were measured. Of the S II lines, only the 3 strongest were observed with the arc side-on; the remaining lines were measured relative to these strongest lines with the arc end-on; three such runs were made. In the latter configuration the line-to-continuum ratio was more favorable and the relative line intensities could be more accurately measured. Since all observed S II lines have upper levels of approximately the same energy, these relative intensity measurements are practically independent of $T$ and not subject to large error even if the observed central portion of the arc were not quite homogeneous.

Data from two runs were analyzed at several radii and no systematic variation of sulfur transition probabilities was found. Data from all of the remaining runs were analyzed at one radial position only.

### Stark Widths and Shifts of Sulfur Lines

The Stark widths and shifts of several S I and S II lines were measured both end-on and side-on. For the end-on measurements, a wider arc channel of 4.8 mm diameter was used to eliminate completely any bulging

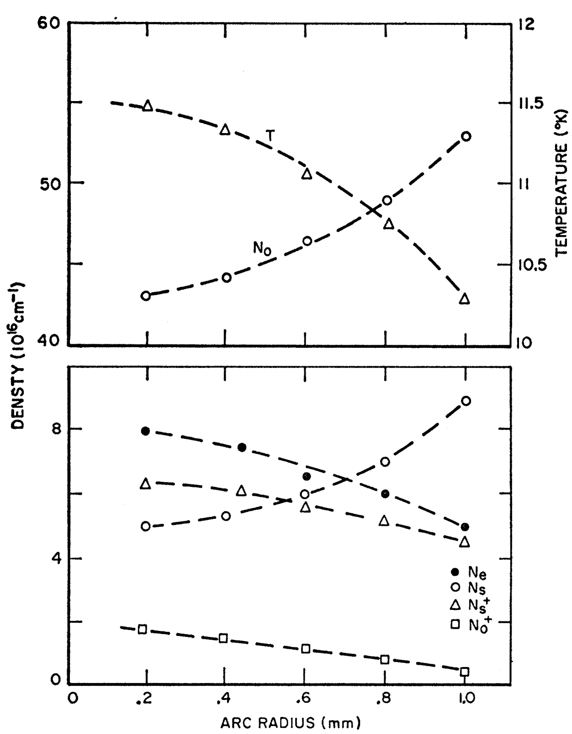


FIG. 4. Radial distribution of the various densities and the temperature in the arc. (The subscripts at the densities $N$ denote: S = neutral sulfur, $S^+$ = singly ionized sulfur, O = neutral oxygen, $O^+$ = singly ionized oxygen, $e$ = electrons).

of the arc column in the insulating sections. In addition to Stark broadening, both instrumental broadening and Doppler broadening are significant under the experimental conditions and were taken into account. The instrumental function was found by scanning the profiles of lines of very small intrinsic widths generated in a low-pressure discharge. For the slit opening mostly used, namely 10 $\mu$, the apparatus function resembled a Gaussian of 0.15 Å half-width. The Doppler half-width was calculated from the known arc temperature to be about 0.07 Å. Assuming the observed line profile to be a Voigt profile, and knowing the width of the Gaussian contribution (instrumental and Doppler widths folded), the width of the dispersion contribution, i.e., the Stark width, was easily found.[5,16] The Doppler broadening and slit function contributed only a very small amount to be observed widths of the S I lines, but were an appreciable percentage of the observed S II widths, as may be inferred from the numerical results.

The theoretical Stark-broadening data[4] refer to individual spectral lines; the broadening parameters are the same for all lines within a multiplet. But, in this experiment as was already mentioned, almost all measured S I multiplets could not be resolved into lines since the latter overlap completely. For the comparison with theory, the individual line profiles thus had to be retrieved from the observed multiplet profiles. First, it was observed that the intensities of three resolved lines of the $4s\,^5S^o$–$4p\,^5P$ multiplet of S I were within 5% of those obtained under the assumption of $LS$ coupling. For the other S I multiplets with completely overlapping lines the intensity ratios from $LS$ coupling were therefore assumed to be valid, too. By assuming then, as in the theory, that the lines of a multiplet were all shifted and broadened by the same amounts, the individual line widths could be easily deduced from the observed over-all multiplet shapes.

For the line-shift measurements, lines from a thorium electrodeless lamp were used for the wavelength calibration.

## IV. RESULTS AND DISCUSSION

### Transition Probabilities

In Tables I and II are listed the transition probabilities determined for the S I and S II lines and multiplets, along with the total estimated uncertainties. Also given for comparison are values calculated with the Coulomb approximation by Bates and Damgaard.[17]

The main contribution to the over-all uncertainty originated in the simultaneous determination of sulfur density and temperature. This error in turn arises from an estimated error in the $N_e$ determination of 9%

[16] J. T. Davies and J. M. Vaughan, Astrophys. J. **137**, 1302 (1963).

[17] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. London **A242**, 101 (1949).

TABLE I. Measured S I transition probabilities in $10^7$ sec$^{-1}$ and comparison with the Coulomb approximation.[a]

| Multiplet[b] | $J_i$–$J_k$ | λ (Å) | This experiment | Coulomb approximation |
|---|---|---|---|---|
| $4s\,^5S^\circ$–$4p\,^5P$ (1) | | 9222 | 4.0±35% | 2.68 |
| | 2–3 | 9212.9 | 4.1±35% | 2.68 |
| | 2–2 | 9228.1 | 3.9±35% | 2.68 |
| | 2–1 | 9237.5 | 3.9±35% | 2.68 |
| $4s\,^5S^\circ$–$5p\,^5P$ (2) | | 4695 | 0.103±30% | Cancellation |
| $4s\,^3S^\circ$–$4p\,^3P$ (3) | | 10 456 | 3.0±35% | 2.18 |
| $4s\,^3S^\circ$–$5p\,^3P$ (4) | | 5279 | 0.054±30% | Cancellation |
| $4p\,^5P$–$4d\,^5D^\circ$ (6) | | 8685 | 1.6±30% | 1.22 |
| $4p\,^5P$–$5d\,^5D^\circ$ (8) | | 6752 | 1.10±35% | 0.76 |

[a] Entries for which $J$ values are omitted refer to complete multiplet.
[b] The numbers in parentheses refer to the multiplet numbers given by C. E. Moore, Natl. Bur. Std. (U.S.) Tech. Note **36** (1959).

(as discussed earlier), errors in the O I intensity measurements of about 10%, and estimated uncertainties in the O I transition probabilities of not more than 10%.[11] These errors give rise to a relative uncertainty of about 30% in the transition probabilities, as may be conveniently inferred from Fig. 3. To this main contribution must be added the experimental errors in the sulfur line-intensity measurements of order 10%, which lead to over-all uncertainties estimated not to exceed errors of 30–40%.

As previously noted, the determination of transition probabilities by the method we have used requires the plasma to be in a state of local thermal equilibrium (LTE). Our assumption that deviations from LTE are negligible over the axial region of the arc is based upon fulfillment of theoretical equilibrium criteria for stationary inhomogeneous sources[4] as well as upon results of numerous previous arc experiments conducted under rather similar conditions (see, e.g., Ref. 12).

Comparing the experimental transition probabilities with those from the Coulomb approximation (assuming *LS* coupling), one finds that the experimental values are generally higher by varying amounts. The Coulomb approximation gives, among the tabulated values, the most reliable data for lines of the transition arrays $4p$–$4d$ and $4p$–$5d$ of S I and $4s$–$4p$ of S II. This follows from the general criteria for the applicability of this method. It is noted that for these lines almost constant factors of 1.40 and 1.30 for S I and S II, respectively, exist between the theoretical and measured data. Part of this difference (which is within the experimental error limits) is probably due to the relatively large uncertainties obtained in determining the sulfur densities and temperature. These affect all S I lines and

TABLE II. Measured S II transition probabilities in $10^7$ sec$^{-1}$ and comparison with Coulomb approximation.

| Multiplet[a] | $J_i$–$J_k$ | λ (Å) | This experiment | Coulomb approximation |
|---|---|---|---|---|
| $3s3p^4\,^2P$–$3s^23p^24p\,^2S^\circ$ (1) | $\frac{3}{2}$–$\frac{1}{2}$ | 5027.2 | 3.6±40% | |
| $4s\,^4P$–$4p\,^4D^\circ$ (6) | $\frac{5}{2}$–$\frac{7}{2}$ | 5453.8 | 10.0±35% | 7.83 |
| | $\frac{3}{2}$–$\frac{5}{2}$ | 5432.8 | 7.8±35% | 5.54 |
| | $\frac{1}{2}$–$\frac{3}{2}$ | 5428.6 | 5.0±35% | 3.30 |
| | $\frac{5}{2}$–$\frac{5}{2}$ | 5564.9 | 2.0±35% | 2.21 |
| | $\frac{3}{2}$–$\frac{3}{2}$ | 5509.7 | 4.6±35% | 4.03 |
| | $\frac{1}{2}$–$\frac{1}{2}$ | 5473.6 | 8.6±35% | 6.43 |
| $4s\,^4P$–$4p\,^4P^\circ$ (7) | $\frac{5}{2}$–$\frac{5}{2}$ | 5032.4 | 8.7±35% | 6.90 |
| $4s\,^4P$–$4p\,^4S^\circ$ (9) | $\frac{5}{2}$–$\frac{3}{2}$ | 4815.5 | 9.4±35% | 5.66 |
| | $\frac{3}{2}$–$\frac{3}{2}$ | 4716.2 | 3.4±35% | 4.00 |
| $3d\,^4F$–$4p\,^4D^\circ$ (11) | $\frac{9}{2}$–$\frac{7}{2}$ | 5606.1 | 4.0±35% | 1.89 |
| | $\frac{5}{2}$–$\frac{3}{2}$ | 5659.9 | 4.3±35% | 1.64 |
| | $\frac{3}{2}$–$\frac{1}{2}$ | 5664.7 | 4.8±35% | 2.04 |
| $4s\,^2P$–$4p\,^2D^\circ$ (14) | $\frac{3}{2}$–$\frac{3}{2}$ | 5819.2 | 1.2±40% | 1.16 |
| $3d\,^4D$–$4p\,^4P^\circ$ (19) | $\frac{7}{2}$–$\frac{5}{2}$ | 6305.5 | 2.3±35% | 1.31 |
| $3d\,^2F$–$4p\,^2D^\circ$ (26) | $\frac{5}{2}$–$\frac{3}{2}$ | 6312.7 | 2.6±40% | 1.97 |
| $4s'\,^2D$–$4p'\,^2F^\circ$ (38) | $\frac{5}{2}$–$\frac{7}{2}$ | 5320.7 | 11.6±35% | 8.45 |
| | $\frac{3}{2}$–$\frac{5}{2}$ | 5345.7 | 11.5±35% | 7.78 |

[a] The numbers in parentheses refer to the multiplet numbers given by C. E. Moore, Natl. Bur. Std. (U.S.) Tech. Note **36** (1959).

TABLE III. Comparison of measured relative line strengths to strengths predicted by *LS* coupling and intermediate coupling for lines belonging to the $4s$–$4p$ transition array of S II. (The data are normalized for the 5453.8-Å line to the absolute line strength obtained from the Coulomb approximation.)

| Multiplet[a] | $J_i$–$J_k$ | λ (Å) | This experiment | Intermediate coupling | *LS* coupling |
|---|---|---|---|---|---|
| $4s\,^4P$–$4p\,^4D^\circ$ (6) | $\frac{5}{2}$–$\frac{7}{2}$ | 5453.8 | 50.2 | 50.2 | 50.2 |
| | $\frac{3}{2}$–$\frac{5}{2}$ | 5432.8 | 29 | 29.2 | 26.1 |
| | $\frac{1}{2}$–$\frac{3}{2}$ | 5428.6 | 12.4 | 11.9 | 10.3 |
| | $\frac{5}{2}$–$\frac{5}{2}$ | 5564.9 | 8.0 | 8.10 | 11.3 |
| | $\frac{3}{2}$–$\frac{3}{2}$ | 5509.7 | 11.7 | 12.2 | 13.3 |
| | $\frac{1}{2}$–$\frac{1}{2}$ | 5473.6 | 10.8 | 10.7 | 10.3 |
| $4s\,^4P$–$4p\,^4P^\circ$ (7) | $\frac{5}{2}$–$\frac{5}{2}$ | 5032.4 | 25.6 | 29.0 | 26.3 |
| $4s\,^4P$–$4p\,^4S^\circ$ (9) | $\frac{5}{2}$–$\frac{3}{2}$ | 4815.5 | 16.3 | 7.32 | 12.4 |
| | $\frac{3}{2}$–$\frac{3}{2}$ | 4716.2 | 5.5 | 10.2 | 8.16 |
| $4s\,^2P$–$4p\,^2D^\circ$ (14) | $\frac{3}{2}$–$\frac{3}{2}$ | 5819.2 | 3.6 | 2.82 | 4.53 |
| $4s'\,^2D$–$4p'\,^2F^\circ$ (38) | $\frac{5}{2}$–$\frac{7}{2}$ | 5320.7 | 53.9 | 50.2 | 50.2 |
| | $\frac{3}{2}$–$\frac{5}{2}$ | 5345.7 | 40.9 | 32.9 | 35.1 |

[a] The numbers in parentheses refer to the multiplet numbers given by C. E. Moore, Natl. Bur. Std. (U.S.) Tech. Note **36** (1959).

similarly, all S II lines by the same amounts, which is in agreement with the almost constant factors observed. On the other hand, the above quoted transitions must be regarded as only moderately excited, for which the Coulomb approximation does not produce very precise values. For the same classes of transitions in O I and O II, where the analogous outer electron configurations are encountered, the results of the Coulomb approximation agree with other theoretical and experimental results generally in the range from 10–25%.[11]

The large and irregular differences between the Coulomb approximation and this experiment for the $3p^23d$–$3p^24p$ transitions of S II are not unexpected. In these cases there are shell-equivalent electrons in the lower state. Thus the effects of configuration interaction become very important, which are not included in the theory. As has been demonstrated by Weiss,[18] these effects may alter the theoretical results drastically.

Our value for the S I multiplet at 4695 Å is higher by a factor of two than that reported recently by Miller *et al.*,[2] however, this disagreement is not greater than the combined experimental errors. No other experimental results are available for comparison.

Garstang[19] has computed relative line intensities for the multiplets of the $4s$–$4p$ array of S II based on the intermediate-coupling scheme. Table III lists the relative line strengths, i.e., essentially relative intensity values, for all measured lines of this array according to *LS* coupling, intermediate coupling, and our experimental results. The values are normalized to agree with the Coulomb approximation value for the 5454-Å line. For the lines of the $4s\,^4P$–$4p\,^4D^\circ$ multiplet, the experimental values substantiate intermediate coupling rather convincingly; for the other scattered material no preference is noticeable. For the two lines of the $4s\,^4P$–$4p\,^4S^\circ$ multiplet, a puzzling disagreement exists among the three ratios, and suggests a possible error in the classification.

The experimentally determined value for the sulfur/oxygen ratio near the arc axis turned out to be about one-half of the stoichiometric ratio for $SO_2$. Had we assumed the stoichiometric ratio rather than using the experimentally determined value, the values for the transition probabilities would be lowered by about the same amount, i.e., they would be about 20% below the values from the Coulomb approximation, on the average.

### Stark Widths and Shifts

In Table IV the measured Stark widths of the S I lines are presented along with the estimated uncertainties and compared with the values calculated by

TABLE IV. Comparison of measured Stark widths and shifts of S I lines to calculated values.

| Multiplet[a] | λ (Å) | Full half-width (Å) Experiment | Full half-width (Å) Theory | Shift (Å) Experiment | Shift (Å) Theory | $N_e$ ($10^{16}$ cm$^{-3}$) | $T$ ($10^3$ °K) |
|---|---|---|---|---|---|---|---|
| $4s\,^5S^\circ$–$4p\,^5P$ (1) | 9222 | 1.5±0.2 | 1.48 | ··· | ··· | 6.3 | 12.2 |
| $4s\,^5S^\circ$–$5p\,^5P$ (2) | 4695 | 3.4±0.3 | 3.6 | 1.7±0.2 | 1.6 | 7.0 | 11.2 |
| $4s\,^3S^\circ$–$4p\,^3p$ (3) | 10 455 | 2.3±0.3 | 1.98 | ··· | ··· | 6.3 | 12.2 |
| $4s\,^3S^\circ$–$5p\,^3P$ (4) | 5280 | 3.0±0.3 | 3.5 | ··· | ··· | 7.0 | 11.2 |
| $4p\,^5P$–$5d\,^5D^\circ$ (8) | 6752 | 26.0±2.0 | 24.0 | 1.0±1.5 | 1.4 | 7.5 | 11.4 |

[a] The numbers in parentheses refer to the multiplet numbers given by C. E. Moore, Natl. Bur. Std. (U.S.) Tech. Note **36** (1959).

[18] A. W. Weiss (to be published).

[19] R. H. Garstang, Monthly Notices Roy. Astron. Soc. **114**, 118 (1954).

TABLE V. Comparison of measured Stark widths of S II lines to calculated values ($N_e=7.0\times10^{16}$, $T=11\ 100°$K).

| | | | Full half-width (Å) | | |
|---|---|---|---|---|---|
| | | | This | Theory | |
| Multiplet[a] | $J_i$–$J_k$ | λ (Å) | experiment | Ref. 4 (1964) | Ref. 6 (1966) |
| $3s3p^4\ ^2P$–$3s^23p^2\ ^4p\ ^2S°$ (1) | $\frac{3}{2}$–$\frac{1}{2}$ | 5027 | 0.39±0.05 | 0.12 | 0.25 |
| $4s\ ^4P$–$4p\ ^4D°$ (6) | $\frac{5}{2}$–$\frac{7}{2}$ | 5453.8 | 0.39±0.05 | 0.074 | 0.32 |
| | $\frac{3}{2}$–$\frac{5}{2}$ | 5432.8 | 0.42±0.05 | 0.074 | 0.32 |
| | $\frac{1}{2}$–$\frac{3}{2}$ | 5428.6 | 0.39±0.05 | 0.074 | 0.32 |
| | $\frac{3}{2}$–$\frac{3}{2}$ | 5509.7 | 0.42±0.05 | 0.074 | 0.32 |
| | $\frac{1}{2}$–$\frac{1}{2}$ | 5473.6 | 0.45±0.05 | 0.074 | 0.32 |
| $4s\ ^4P$–$4p\ ^4P°$ (7) | $\frac{5}{2}$–$\frac{5}{2}$ | 5032.4 | 0.53±0.05 | 0.065 | 0.35 |
| $4s\ ^4P$–$4p\ ^4S°$ (9) | $\frac{5}{2}$–$\frac{3}{2}$ | 4815.5 | 0.7 ±0.1 | 0.057 | 0.22 |
| | $\frac{3}{2}$–$\frac{3}{2}$ | 4716.2 | 0.7 ±0.15 | 0.057 | 0.22 |
| $3d\ ^4F$–$4p\ ^4D°$ (11) | $\frac{9}{2}$–$\frac{7}{2}$ | 5606.1 | 0.37±0.05 | 0.078 | 0.42 |
| $4s'\ ^2D$–$4p'\ ^2F°$ (38) | $\frac{5}{2}$–$\frac{7}{2}$ | 5320.7 | 0.53±0.05 | ··· | 0.31 |
| | $\frac{3}{2}$–$\frac{5}{2}$ | 5345.7 | 0.46±0.05 | ··· | 0.31 |

[a] The numbers in parentheses refer to the multiplet numbers given by C. E. Moore, Natl. Bur. Std. (U.S.) Tech. Note **36** (1959).

Griem.[4] The calculated values are for the electron density determined from the measured width of $H_\beta$. Since this experimental determination of $N_e$ contains an uncertainty of 9%, the calculated values are uncertain by this amount in addition to purely theoretical errors.

For the S I multiplets, good agreement is observed between the experimental and theoretical results. In all cases the agreement is within the combined experimental and theoretical error estimates. The ratio of experimental to theoretical widths, averaged over the five multiplets, turns out to be 1.01. Similar excellent agreement for such averaged ratios has been measured for Cs I[20] and O I[21] lines.

Also given in Table IV are the measured and calculated[4] values for the Stark shifts of two multiplets of S I. Here again the measured and calculated values agree within the combined error limits.

In Table V are listed the measured Stark widths of the S II lines and compared with the theoretical data calculated by Griem.[4,6] The linewidths obtained form the earlier theory[4] are all drastically smaller than the measured values. The ratio of experimental to theoretical widths, averaged over the measured lines, turns out to be 6.9. Similar discrepancies have been found for Ar II[22,23] and Ca II[24,25] lines. Griem then extended the theory recently[6] by taking into account the strong Coulomb interaction between perturbing electrons and emitting ions (this was not important for neutral emitters), and by considering collision induced transitions between upper and lower atomic levels. Applying the new data, the ratio of experimental to theoretical widths averaged over the measured multiplets is 1.6. Leaving out multiplet 9, the ratio comes out as 1.3. Even though this represents a vast improvement, the situation is still not nearly as satisfactory as for the neutral S I lines. A very large discrepancy (factor of 3.2) remains for the S II multiplet No. 9. It is significant that for this same multiplet the relative line intensities grossly disagreed with the calculated data from *LS* coupling as well as intermediate coupling (Table III). This again points to a possible error in the classification.

## ACKNOWLEDGMENTS

We would like to thank Dr. T. D. Wilkerson for helpful discussions and John Nagy and Donald Paquette for assistance in taking data.

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