Absolute line strengths for carbon and sulfur*

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Absolute transition probabilities for 124 C I, S I, and S II lines in the range 3600–7400 Å are measured with a spectroscopic shock tube. Relative strengths of two C II lines are also determined. Mixtures of neon and ten different compounds of carbon and sulfur are heated to temperatures 8200–13000°K at pressures $(4.8–27.0)\times10^6$ dyn cm^{-2}. Thermodynamic and photometric variables are measured redundantly. Absolute A values are determined in emission by two or more independent methods which in combination have much less than the traditional sensitivity to systematic errors in source temperature. Estimated accuracies for the more prominent visible lines are 13–30%. Results are compared with theoretical predictions, other experiments, and with quantum-mechanical sum rules.

I. INTRODUCTION

Strengths of visible carbon and sulfur lines have been measured using a variety of spectroscopic light sources, but results to date have tended to disagree by approximately a factor of 2.[1–8] The present work substantially reduces uncertainties in the line strengths of these theoretically and astrophysically important elements.[9–12] Our spectroscopic techniques are less error prone than those traditionally employed for transitions between highly excited states. All essential experimental variables are measured redundantly. Proper selection of operating conditions brings the more prominent C I, S I, and S II lines to comparable brightness at electron densities small enough that Stark broadening does not blend the three spectra. The shock-heating of CH_3SH fixes the carbon-to-sulfur abundance ratio, allowing carbon and sulfur A values to be related in a direct and simple way.

II. EXPERIMENTAL

To minimize the likelihood of the systematic errors often associated with A values measured in emission,[12,13] we observed the following precautions:

(i) Absolute line strengths were obtained by techniques selected for their small sensitivity to possible bias in temperature data and photometric calibrations.

(ii) Two or more independent methods were used to measure thermodynamic variables and to calibrate detectors for absolute sensitivity and spectral response.

(iii) Conditions in the light source (temperature, density, composition) and instrumental parameters (spectroscopic recording materials, slit widths, sampling times) were deliberately varied in a search for possible error trends in the atomic data.

Plasmas behind reflected shock waves were homogeneous and quiescent for periods of 30–150 μsec. Electron densities were generally (2–16) $\times 10^{16}$ cm^{-3}, a range which maintains local thermodynamic equilibrium (LTE) for temperatures of (8200–13000)°K.[14] Plasma durations were too short to permit significant demixing of heavier and lighter constituents. Therefore, the initial chemical composition and two plasma-state variables uniquely specify the populations of all atomic and ionic levels in the light source.

Computed emitter densities can be combined with photometric data in two ways to determine an absolute transition probability A_{mn}. By recording the absolute integrated intensity I_{mn} of an isolated optically thin line of wavelength λ_{mn}, we have

$$A_{mn}^{\mathrm{em}} = \frac{I_{mn}\, 4\pi\lambda_{mn}}{hcl\, N_m(p,T)}, \tag{1}$$

where l is the thickness of the light source and $N_m(p, T)$ is the excited-state density. If the plasma emits some other line λ_{pq}, whose transition probability A_{pq} is well known, then a measurement of the intensity ratio I_{mn}/I_{pq} will also yield a value for A_{mn}:

$$A_{mn}^{\mathrm{em},pq} = A_{pq}\,\frac{\lambda_{mn}\, I_{mn}\, N_p(p,T)}{\lambda_{pq}\, I_{pq}\, N_m(p,T)}. \tag{2}$$

For example, shock heating a gas containing

TABLE I. Techniques used to measure absolute A values.

	Spectrum method	A value or intensity standard
C I	$A_C^{em} = \frac{4\pi I_C \lambda_C}{hclN_C}$	Carbon arc anode (Ref. 15) and blackbody shock-tube plasmas (Ref. 16).
	$A_C^{r,H} = A\frac{I_C \lambda_C N_H}{I_H \lambda_H N_C}$	Usually H_β, but occasionally H_γ.
S I	$A_S^{em} = \frac{4\pi I_S \lambda_S}{hclN_S}$	Carbon arc anode (Ref. 15) and blackbody shock-tube plasmas (Ref. 16).
	$A_S^{r,H} = \frac{I_S \lambda_S N_H}{I_H \lambda_H N_S}$	H_β or H_γ, depending upon plasma brightness.
S I/C I	$A_S^{r,C} = \frac{I_S \lambda_S N_C}{I_C \lambda_C N_S}$	C I ($\lambda = 5052$)[a]
S II	$A_{S\,II}^{r,H} = \frac{I_{S\,II} \lambda_{S\,II} N_H}{I_H \lambda_H N_{S\,II}}$	H_β
	$A_{S\,II}^{r,Ne} = \frac{I_{S\,II} \lambda_{S\,II} N_{Ne}}{I_{Ne} \lambda_{Ne} N_{S\,II}}$	Normally Ne I ($\lambda = 5852$ Å); alternatively, Ne I ($\lambda = 5881$ Å)

[a]This line is employed as a "standard" only for purposes of directly relating absolute A values of neutral carbon and sulfur.

methyl mercaptan (CH_3SH) produces a plasma whose constituents are stoichiometrically related. Lines such as C I ($\lambda = 5052$ Å), S I ($\lambda\lambda = 4695$ Å), and S II ($\lambda = 5453$ Å) can be measured relative to H_β, whose A value serves as an internal standard (A_{pq}), given that the corresponding relative abundances are fixed. Hydrogen Balmer lines can be utilized as internal references in six of the ten test gases listed in Table I.

Table I shows the methods used, as a rule simultaneously, to determine absolute C I, S I, and S II line strengths. Intensity standards for the absolute intensity measurements required by Eq. (1) are the anode crater of a regulated carbon arc[15] and the Planck intensity of shock-tube plasmas measured by the line-reversal technique.[16] For the transspecies relative intensity determinations of Eq. (2), the Balmer lines (H_β, H_γ), and the neon red lines [Ne I ($\lambda = 5852$ Å), Ne I ($\lambda = 5881$ Å)] provide reference A values reliable to better than 1% and approximately 10%, respectively.[12]

Densities of excited states for some prominent visible lines are given in Fig. 1 as functions of temperature at a representative operating pressure and composition.[17] Slopes of the curves indicate sensitivity to temperature error for A values measured via Eq. (1): the corresponding sensitivity for data obtained via Eq. (2) is obtained from *differences* in the slopes.

Figure 2 shows the relative error $A(T)/A(T_0)$ in transition probabilities that would be measured with faulty temperature data. For each of the measurement techniques listed in Table I, the assumed temperature T is allowed to vary continuously from a true temperature T_0 of 11 000 °K. The mean of the simultaneous A_C^{em} and $A_C^{r,H}$ determinations shown in Fig. 2(a) cannot underestimate the true A value for C I ($\lambda = 5052$ Å), regardless of the size or direction of temperature error: errors of ±5% in temperature cause an approximate +5% biasing of results.[18] For the blended multiplet S I ($\lambda\lambda = 4695$ Å), the shot-by-shot

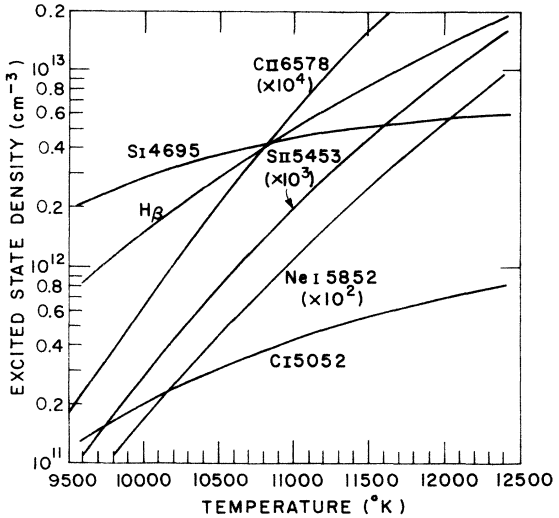

FIG. 1. Temperature dependence of excited-state number densities for lines prominent in shock-tube plasmas. Pressure is 9.0×10^6 dyn cm^{-2} and test gas (molal) composition is 1.0% CH_3SH + 99.0% neon.

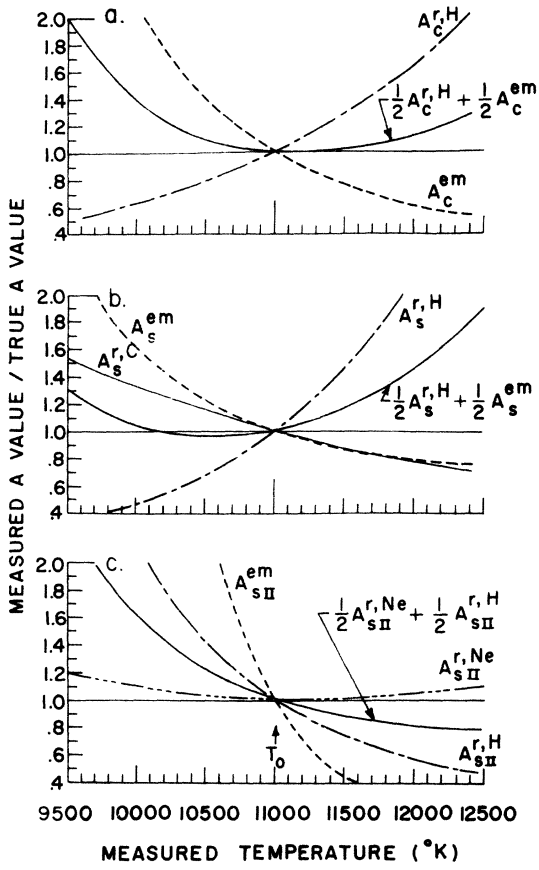

FIG. 2. Relative error in experimental A values determined by various methods, as functions of temperature error $T - T_0$. The true plasma temperature T_0 is 11 000°. Pressure and composition are as in Fig. 1.

mean of A_S^{em} and $A_S^{r,H}$ determinations has a lesser thermal sensitivity than either of these measurements separately, as shown in Fig. 2(b). In contrast to the critical temperature sensitivity of the absolute emission A_{SII}^{em} data for SII ($\lambda = 5453$ Å) determinations via $A_{SII}^{r,H}$ and $A_{SII}^{r,Ne}$ are seen in Fig. 2(c) to be only mildly affected by temperature error.

Test gases, thermodynamic conditions, and spectrographic recording materials used in the experiment are compiled in Table II. Several volatile compounds of carbon and/or sulfur were utilized in order (i) to selectively enhance either H, CI, SI, or SII spectra, (ii) to vary line-to-continuum ratios over factors of 10, and (iii) to test for reaction or absorption of test gas constituents prior to firing the shock tube.

Plasma temperatures and pressures were systematically varied between 8200 and 13 200°K and $(4.8\text{–}27.0) \times 10^6$ dyn cm^{-2}, respectively. This posed a stringent test for the consistency of redundant state and photometric data, caused line widths due to the Stark effect to vary several fold with respect to instrumental widths, and selectively enhanced the brightness of weaker neutral or ionic lines.

The five emulsions tabulated in the fifth column have distinctly different spectral responses and γ characteristics. Relative line strengths recorded on different materials were routinely checked for any indications of faulty photographic calibration or data-reduction procedures.

Instrumentation for time-resolved spectroscopy[19–22] is shown schematically in Fig. 3. Poly-

TABLE II. Summary of experimental conditions.

Runs	Test gas[a]	Temperatures (10^3 °K)	Pressures (10^6 dyn cm^{-2})	Photographic emulsions (Kodak)
24	$(\frac{1}{6}-2)\%CH_4$	9.4–12.9	5.0–19.5	2475
9	$\frac{1}{2}\%CH_4+\frac{1}{2}\%CS_2$	9.8–12.6	6.1–21.9	2475
6	$\frac{1}{2}\%CH_4+\frac{1}{2}\%CCl_4$	10.3–12.2	7.6–18.0	2475, HSIR
7	$(\frac{1}{2}-2\frac{1}{2})\%CH_3Br$	9.1–12.0	5.9–18.5	2475, HSIR
12	$(\frac{1}{2}-1\frac{1}{2})\%CH_3SH$	9.6–12.7	6.3–23.0	2475, I-N
6	$\frac{1}{2}\%H_2S+\frac{1}{2}\%PH_3$	9.9–12.4	6.0–22.0	2475
6[b]	$1\%SO_2$	10.8–13.0	3.6–17.2	2475, I-N
3	$\frac{1}{2}\%CH_3OH$	11.2–11.8	9.0–12.5	I-F
11	$(\frac{1}{2}-2)\%H_2S$	9.6–12.6	4.8–21.8	103-0, I-N, I-F
5	$(\frac{1}{3}-\frac{2}{3})\%Si[CH_3]_4$	8.2–11.9	8.6–27.0	2475, I-N

[a] The carrier gas is in all cases Research Grade neon.

[b] Unlike other listed experimental runs, these data were used to determine relative rather than absolute A values, particularly for SII that would be masked by Balmer lines in plasmas containing hydrogen.

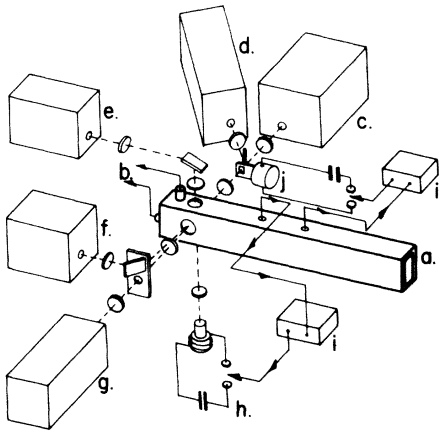

FIG. 3. Diagram of the shock-tube instrumentation: (a) shock-tube test section; windows and associated optics are fused quartz; (b) piezoelectric pressure transducers mounted in the shock tube upper- and end-walls; (c) $\frac{3}{4}$-m spectrograph; (d) 1-m stigmatic spectrograph; (e) $\frac{1}{2}$-m monochromator, with photoelectric recording; (h) fast TRW gray-body flashlamp; (f) six-channel $1\frac{1}{2}$-m photoelectric polychromator, utilizing shaped fibre optics (Ref. 19); (g) twelve-channel, $\frac{1}{2}$-m polychromator, photoelectrically recording 1.0-Å wide portions of the H_β profile; (i) delay pulsers, triggered by ionization gauges in the shock tube, for firing the flashlamp and the fast shutter, (j) (Ref. 19).

chromators (*e*), (*f*), and (*g*) contain 19 photoelectric channels which are calibrated against the anode of a regulated carbon arc[14] and also by the line-reversal technique.[16,23,24] Seventeen of these are employed to measure plasma temperature by a number of simultaneous and independent techniques. The excitation temperature[25] of $H_\beta(11 < E/kT < 14)$, was derived from pressure data and the line's integrated energy. Time-resolved relative-intensity profiles of Balmer lines obtained photographically by spectrometers (*c*) and (*d*) were converted to an absolute scale on a shot-by-shot basis by fitting to the signals from 12 absolutely calibrated photoelectric channels in polychromator (*f*). These photographically recorded H_β and/or H_γ profiles were also fitted to theoretical Stark shapes[26] to give the plasma electron density. Together with measured pressure, this was inverted to find a plasma ionization temperature. Monochromator (*e*) was centered on H_α, which had typical peak optical depths of 0.5–4.0. Viewing the plasma along a path backlighted by the pulsed flashlamp (*h*), these data gave Planck intensity and radiation temperature by the reversal method.[16,24]

The four measured temperatures usually agreed to within 300 °K. No trends were detected over the experimental range ($\Delta T = 5000$ °K). This sustained agreement between the four types of temperature determinations supports our assumptions regarding plasma homogeneity, extent of laminar boundary layers, and LTE.

Pressures recorded by the two transducers (*b*) generally agreed to within the 15% precision set by crystal ringing and reading error. The two sensors differed systematically by 6%, which is commensurate with the accuracy of static and dynamic calibrations.

Spectrographs (*c*) and (*d*) have first-order resolutions of 2.0 and 0.28 Å, respectively. Corresponding wavelength coverages are 6000 and 1700 Å. In early phases of the work, a rotating drum camera[20,21] provided time-resolved recording. Wavelength resolution and signal levels were subsequently improved by employing a fast mechanical shutter[19] (*j*) at an intermediate focal position common to spectrographs (*c*) and (*d*). As a precaution against bias, the two spectrographs were customarily loaded with plates having different spectral response and γ characteristics. We calibrated all emulsions listed in Table II using a regulated carbon arc and pulsed light sources. Controlled attenuation was provided by (i) a seven-step neutral density filter, (ii) a continuously variable filter, and (iii) photomultipliers situated in the photographic focal plane to monitor light levels as entrance slit-widths were systematically varied. No adjacency or reciprocity effects were found for spectral densities or exposure times of interest.

Computer codes[27] for converting digitized photographic densities into intensities utilized absolute photoelectric data and measured temperatures to compensate for radiative trapping. With the exception of C I ($\lambda = 5052$ Å) the carbon and sulfur line-strength data were obtained from photographically recorded profiles.

Precision in the delineating and integrating of a typical line profile was 15%, with the limiting factors being grain noise, reading error, and uncertainty in discriminating far-wing intensities from the background continuum. The histogram in Fig. 4 illustrates the usual scatter in relative *A* values due to random errors in the areas of two-line profiles. The distribution appears to be Gaussian, with a 23% standard deviation. Typically, precision was poorer than this for the weak and broadened S I lines, but slightly better for prominent S II lines.

The energy radiated in C I ($\lambda = 5052$ Å) was simultaneously recorded in two ways—photographically and by a pair of photoelectric channels. Measured Stark widths were used to adjust[21] for far-wing contributions cut off by the 2.0-Å photoelectric channel widths. The two sets of

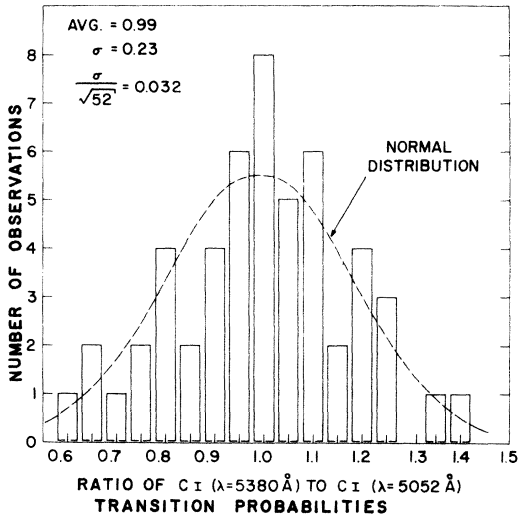

FIG. 4. Histogram of the measured ratio of C I ($\lambda = 5380$ Å) to C I ($\lambda = 5052$ Å) A values, illustrating typical scatter due to relative photographic photometry with fast, grainy emulsions.

integrated C I ($\lambda = 5052$ Å) line intensities agreed on the average to 6%, with approximately 20% scatter.

III. RESULTS AND DISCUSSION

Results of the C I ($\lambda = 5052$ Å) transition-probability measurements by the A_C^{em}, $A_C^{r,H}$ and $\frac{1}{2}(A_C^{em} + A^{r,H})$ techniques are compared in Fig. 5. The

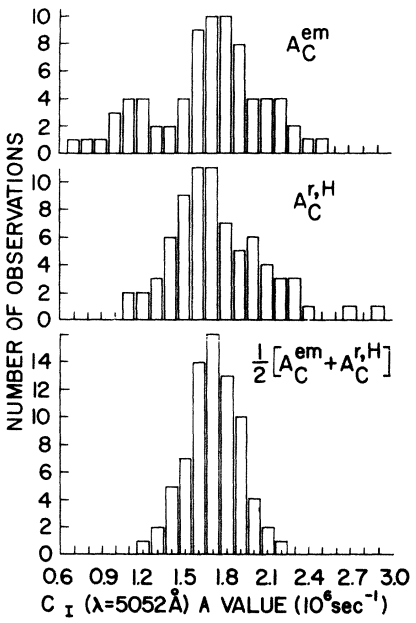

FIG. 5. Histogram of results from various simultaneous measurements of the absolute C I ($\lambda = 5052$ Å) A value.

A_C^{em} and $A_C^{r,H}$ distributions are approximately twice as wide as the distribution of their shot-by-shot average $\frac{1}{2}(A_C^{em} + A_C^{r,H})$. Analysis based on Fig. 2(a) attributes this difference to (2–4)% random error in temperature data, and indicates that the centroid of the $\frac{1}{2}(A_C^{em} + A_C^{r,H})$ results has been shifted upwards by approximately 3%. The adopted C I ($\lambda = 5052$ Å) transition probability (1.60×10^6 sec^{-1}) has been compensated for this systematic effect of random error.[27a]

No correlation was found between measured carbon A values and experimental temperatures, plasma pressures, and electron density. If laminar boundary layers, whose thickness scale inversely with pressure,[23] were spectroscopically important, or if LTE conditions were not attained, such independence would not be expected. Results obtained using the different test gases and recording materials listed in Table II were indistinguishable from one another.

Neutral carbon A values are presented in Table III. Our uncertainties are expressed as 67% confidence limits, and are based on estimates of possible experimental bias and on statistical analysis of scatter. In the majority of runs where the electron density was greater than 4×10^{16} cm^{-3}, the strength of multiplet 6 was measured because Stark broadening merged the individual lines. Faint lines such as C I ($\lambda = 5817$ Å) did not attain useful brightness under most conditions. The relatively prominent C I ($\lambda = 4932$ Å) line and the blended C I ($\lambda\lambda = 5041$ Å) multiplet were particularly diffuse.

Carbon data from the shock tube tend to be factors of 1.2–2.8 smaller than strengths predicted by the central field approximations. It should be noted that the majority of transitions have core-penetrating (s) lower states and thus do no satisfy the reliability criteria[30,31] for use of the Coulomb approximation.

Foster[4,5] used a vortex-stabilized arc to make absolute emission (A_C^{em}) determinations. Ratios of vortex-arc A values to the present findings average 0.97 and 0.82 for the earlier[4] and later[5] of his investigations.

Wall-stabilized multicomponent arcs were the light sources employed by Beth,[1] Richter,[1] Kuck,[1] and Maecker.[1] It has been suggested[10,12] that the absolute scales of these (A_C^{em}) results were biased by unrecognized demixing. Considering their generic similiarity, it is surprising that the absolute and relative A values obtained in these four investigations are not closer to mutual agreement than are the results from pairs of investigations having less similiarity in experimental approach.

To circumvent the difficulties stemming from

TABLE III. Transition probabilities for neutral carbon (10^6 sec^{-1}).

Multiplet[28,29]		g_i-g_k	λ (Å)	This work	NBS[12] (1966)	Henning[2] (1965)	Foster[5] (1962)	Foster[4] (1962)	Doherty[3] (1961)	Beth[1] (1963)	Richter[2] (1958)	Kuck[1] (1955)	Maecker[1] (1953)	*ca*-*LS*[30,31]
(4)	$3s\,^3P^0$-$4p\,^3D$[a]	9-15	λλ=5041	0.19[a]	0.39		0.13	0.21			0.30		0.15	1.55
(5)	$3s\,^3P^0$-$4p\,^3S$	5-3	4826.7	0.10±40%	0.47		0.34							0.24
		3-3	4817.3	0.06±40%	0.28									0.14
		1-3	4812.8	<0.03	0.10									0.05
(6)	$3s\,^3P^0$-$4p\,^3P$	9-9	λλ=4770	1.53±15%	1.6	0.80	0.95	1.26	1.8	1.0	1.2	0.44	0.52	1.34
		5-5	4771.7	1.00±30%	1.2									1.01
		3-1	4770.0		1.5									1.26
		3-3	4766.6	0.48±30%	0.39									0.33
		5-3	4775.9	0.67±30%	0.62									0.52
		3-5	4762.4	0.50±30%	0.38									0.32
		1-3	4762.4		0.52									0.44
(7)	$3s\,^3P^0$-$5p\,^3D$	9-15	λλ=4064	<0.04										0.12
(11)	$3s\,^1P^0$-$4p\,^1P$	3-3	5380.2	1.55±15%	1.6	0.76	1.15	1.20	2.75	1.10	1.25	0.55	0.71	2.24
(12)	$3s\,^1P^0$-$4p\,^1D$	3-5	5052.1	1.60±12%	1.7		1.27	1.61	4.20		1.30		0.86	1.94
(13)	$3s\,^1P^0$-$4p\,^1P$	3-1	4932.0	3.58±15%	4.6	2.20	3.4	4.63	8.6	3.5	3.5	1.3	1.5	5.22
(14)	$3s\,^1P^0$-$5p\,^1P$	3-3	4371.3	0.54±25%	0.97		0.4							1.21
(16)	$3s\,^1P^0$-$5p\,^1D$	3-5	4269.0	0.21±25%	0.32		0.23							0.41
(17)	$3s\,^1P^0$-$5p\,^1S$	3-1	4228.3	0.60±40%										1.70
(18)	$2p^3\,^3D^0$-$4p\,^3P$	15-9	λλ=5798	0.30±20%	0.39	0.21				0.24	0.30	0.21	0.17	
		7-5	5793.5		0.33									
		5-5	5794.5	0.33±30%	0.06									
		3-5	5794.8		0.004									
		5-3	5801.1	0.32±30%	0.29									
		3-3	5800.2		0.01									
		3-1	5805.8	0.13±40%	0.39									
(22)	$3p\,^1P$-$4d\,^1P^0$	3-3	6587.8	1.3±30%	2.4									2.21

[a] Johansson (Ref. 28) classifies this multiplet as $2p'\,^3D_3$-$4f\,(3^{1/2})_{3,4}$, in which case the A value obtained in this work would be 0.17×10^6 sec^{-1}.

demixing, Henning[2] ran pure carbon plasmas in a Kiel-type arc, relying on ratios of C II to C I line intensities to deduce source temperatures.

Doherty[3] measured the relative strengths of carbon and hydrogen lines in the emission from a luminous shock tube. Results of these ($A_C^{r,H}$) determinations are larger than present A values by factors of 1.2–2.8. Doherty also measured absolute strengths for several neutral neon lines, obtaining results generally a factor of 2 smaller than those[11] reported later. A plausible explanation for this pattern of disagreements, as suggested by Fig. 1, is a systematic overestimate (~10%) of experimental temperature in Doherty's work.

Singly ionized carbon

Conditions were suitable in only eight experiments (temperatures > 12 500 °K and exposure times >30 μsec) for recording the two most readily excited visible C II lines, $\lambda = 6578.0$ and $\lambda = 6582.9$. Under these conditions, however, lines normally used as internal A value standards [H_β, NeI ($\lambda = 5852$ Å)] were too bright and exceeded the dynamic range of our emulsions. With reliable transpecies relative A-value determinations precluded by emulsion saturation, and with determinations via the emission (i.e., $A_{C\,II}^{em}$) method ruled out by the critical dependence of emitter densities on source temperature, we measured the ratio $A(\lambda = 6578)/A(\lambda = 6583)$. Our result (0.93 ± 15%) agrees satisfactorily with the value (1.00) predicted by LS coupling.

Neutral sulfur

Stark broadening completely blended the fine structure of visible S I multiplets under all shock-tube conditions. The red multiplets ($\lambda\lambda = 6049$ Å) and ($\lambda\lambda = 5701$ Å) were detected with regularity, but these features were too diffuse (half-widths of more than 50 Å) to be handled in a quantitative way. The quality of S I profiles was generally poorer than C I and S II data recorded at the same time because of pronounced broadening and inherent weakness. Multiplets (1), (2), (3) could not be investigated for want of sufficiently fast infrared emulsions.

Neutral sulfur A values measured with the shock-tube and comparison data appear in Table IV. The A values reported by Bridges and Wiese[6] were obtained by photoelectrically scanning a wall-stabilized arc. Foster[4,5] used a vortex-stabilized arc as the source of S I (and C I) spectra. Tabulated integrals of radial transition moments[30] and LS coupling coefficients were used to calculate the A values listed in the last columns of the table.

The three sets of experimental relative S I strengths agree more closely with one another than with theoretical calculations. The shock-tube findings confirm one observed feature in the solar curve of growth[32,33]: namely, that the calculated strength of the $4s\ ^5S\text{-}5p\ ^5P$ multiplet is too large by at least a factor of 2 relative to the strength of the $4p\ ^5P\text{-}5d\ ^5D$ multiplet.

Present results differ in absolute value from earlier data, being factors of 1.2–1.6 smaller, and factors of 1.1–1.2 larger, respectively, than the findings of Bridges and Wiese[6] and of Foster.[4,5] Our results are in agreement with the value measured by Schulz-Gulde.[8]

Compared to our data, Coulomb approximations for S I are too large by factors of 1.3–3.0, whereas our C I data agreed satisfactorily. Because of this disparity, and to check the internal consistency of the experiments, we measured the strength of S I ($\lambda\lambda = 4695$ Å) directly against the C I ($\lambda = 5052$ Å) A value. Gases such as CS_2 and CH_3SH assured fixed abundance ratios in the shock tube. These measurements ($A_S^{r,C}$ in the notation of Sec. II) involved only a mild susceptibility to errors in experimental temperature; and these optically thin lines do not differ markedly in brightness, shape, or wavelength. The A value

TABLE IV. Neutral sulfur transition probabilities.

Multiplet number	Multiplet	g_i-g_k	λ (Å)	Transition probability (10^6 sec^{-1}) This work	Bridges and Weise[6]	Foster[7]	Schulz-Gulde[8]	NBS[12]	Coulomb approximation[30]
2	$4s\ ^5S^0\text{-}5p\ ^5P$	5-15	4695	0.66 ± 20%	1.03	0.58	0.667	0.74	2.0
4	$4s\ ^3S^0\text{-}5p\ ^3P$	3-9	5279	0.46 ± 22%	0.54	0.35		0.38	0.88
5	$4s\ ^3S^0\text{-}6p\ ^3P$	3-9	4411	<0.05					Cancellation
7	$4p\ ^5P\text{-}6s\ ^5S^0$	15-5	7690	7.8 ± 25%				6.1	6.1
8	$4p\ ^5P\text{-}5d\ ^5D^0$	15-25	6751	9.5 ± 25%	11.0			7.9	7.5
10	$4p\ ^5P\text{-}6d\ ^5D^0$	15-25	6049	<0.20					Cancellation
11	$4p\ ^5P\text{-}7d\ ^5D^0$	15-25	5701	<0.08					Cancellation

of S I ($\lambda\lambda = 4695$ Å) found in this way, 0.64×10^6 sec^{-1}, agrees closely with the value (0.66×10^6 sec^{-1}) obtained from $\frac{1}{2}(A^{em} + A_S^{r,H})$ data.

Ionized sulfur

The $A_{SII}^{r,H}$ and the $A_{SII}^{r,Ne}$ data, shown in Fig. 6 for S II ($\lambda = 5453$ Å) were generally obtained simultaneously. The $A_{SII}^{r,Ne}$ determinations utilize a reference line [Ne I ($\lambda = 5852$)] which resembles S II ($\lambda = 5453$ Å) in excitation potential, wavelength, shape, and brightness better than does H_β. This is offset by the greater uncertainty in the Ne I ($\lambda = 5852$ Å) A value.[12] Treating the two determinations as being equally reliable yielded the S II ($\lambda = 5453$ Å) A-value data shown in Fig. 6. The value adopted is 1.0×10^8 sec^{-1}.

Absolute S II transition probabilities from this investigation are compared with published values in Table V. In most instances, data reduction was not complicated by blending or optical depth problems.

Agreement between this work and the absolute and relative A values of Bridges and Wiese[6] is excellent, the average absolute-value ratio $A_{\text{Bridges}}/A_{\text{This work}}$ being 0.97. This agreement is perplexing in contrast to the factor of (1.2-1.6) discrepancies between the absolute S I results from the same two experiments. Bias in either sulfur abundance or temperature cannot alone account for this pattern or for agreement and disagreement. The likelihood of coupled errors appears remote for the shock tube which is not subject to serious demixing and where the ratio $(A_S^{em} + A_S^{r,H})/(A_{SII}^{r,Ne} + A_{SII}^{r,H})$ is comparatively insensitive to uncertainties in temperature data.

Schulz-Gulde[8] measured the transition probability of S II ($\lambda = 5453$ Å) to be 0.71×10^8 sec^{-1} using a wall-stabilized arc. This is in agreement within error estimates with present results.

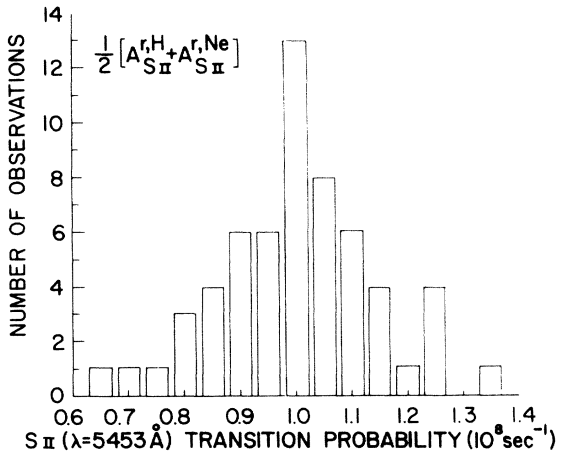

FIG. 6. Histogram of results from simultaneous measurement of the S II ($\lambda = 5453$ Å) absolute transition probability by two techniques.

Working with a vortex-stabilized arc,[4,5] Foster has found[33] a value of 0.78×10^8 sec^{-1} for absolute transition probability of S II ($\lambda = 5453$ Å). Allowing for joint experimental uncertainties, this result satisfactorily overlaps the findings of Bridges and Wiese[6] and the present work.

Calculations in the Coulomb approximation tend to underestimate the shock-tube and wall-regulated-arc data by factors of 1.1–1.6.

We computed the sums from measured, array-averaged f values for transitions involving the $4s$ and $4p$ configurations with the one-electron Thomas-Reiche-Kuhn[34] sum rule ($\sum_{n'} f_n^{n'} = 1$) and the Wigner-Kirkwood[34] partial sum rules

$$\sum_{n'} f_{nl}^{n'\,l-1} = -\frac{1}{3}\,\frac{l(2l-1)}{2l+1};$$

$$\sum_{n'} f_{nl}^{n'\,l+1} = \frac{1}{3}\,\frac{(l+1)(2l+3)}{2l+1}.$$

In forming the sums, shock-tube data were augmented by hydrogenic approximations for high-quantum-number lines and bound-free transitions. For the $4s$ level the f values summed to 1.3, rather than the 1.0 expected from the one-electron model. This disagreement appears due primarily to the large measured strength of the $4s$-$4p$ transition array. The f values listed in Ref. 12 (Coulomb approximations) agree somewhat better, approaching 1.1. It is not clear what modifications should be made in the one-electron sum rules to account for transitions involving equivalent electrons, or that all pertinent levels have been properly classified.[6] For these reasons it is not felt that the 30% discrepancy between our $4s$ data should necessarily be attributed to experimental error.

By adopting hydrogenic approximations for several unobserved arrays, we can compare measured f sums with the partial sum rules for the $4p$ level. Agreement with the sum rule is found within experimental and computational uncertainty.

Table VI compares relative S II line strengths. Data are normalized by assigning value 1.00 to the ($\lambda = 5453$ Å) transition probability. Agreement between the arc[6] and shock-tube data is impressive: 92% of the relative strengths overlap within our experimental uncertainties [(4–14)%]. By the same criteria, 66% of the intermediate-coupling predictions[36] agree with our data. Only 17% of LS coupling calculations agree. Considering how the two sets of experimental data reinforce each other, this comparison is felt to provide a compelling argument for the desirability of

TABLE V. Transition probabilities for ionized Sulfur (10^6 sec^{-1}).

Multiplet[29]	Transition	$J_i - J_k$	λ (Å)	This work[a]	Bridges and Wiese[6]	NBS[12]	Coulomb approximation LS Coupling	Coulomb approximation Intermediate coupling (Ref.35)	Coulomb approximation Intermediate coupling (Ref.36)
(1)	$3s3p^4\,^2P - 4p\,^2S^0$	$1\frac{1}{2}-\frac{1}{2}$	5027.1	$0.46C$	$0.36 \pm 40\%$				
		$\frac{1}{2}-\frac{1}{2}$	5142.3	$0.27A$					
(2)	$3s3p^4\,^2P-4p\,^4P^0$	$1\frac{1}{2}-1\frac{1}{2}$	4121.0	$0.05E$					
(6)	$4s\,^4P - 4p\,^4D^0$	$2\frac{1}{2}-3\frac{1}{2}$	5453.6[b]	$1.01A$	$1.00 \pm 35\%$	0.78	0.77	0.78	0.85
		$1\frac{1}{2}-2\frac{1}{2}$	5432.7	$0.77A$	$0.78 \pm 35\%$	0.61	0.55	0.62	0.68
		$\frac{1}{2}-1\frac{1}{2}$	5428.6	$0.55A$	$0.50 \pm 35\%$	0.38	0.33	0.38	0.42
		$2\frac{1}{2}-\frac{1}{2}$	5564.9	$0.20A$	$0.20 \pm 35\%$	0.16	0.22	0.16	0.17
		$1\frac{1}{2}-1\frac{1}{2}$	5509.6	$0.42A$	$0.45 \pm 45\%$	0.39	0.40	0.37	0.40
		$\frac{1}{2}-\frac{1}{2}$	5473.6	$0.84A$	$0.86 \pm 35\%$	0.74	0.64	0.66	0.73
		$2\frac{1}{2}-1\frac{1}{2}$	5645.6[c]	$0.19E$[c]		0.018	0.04	0.02	0.02
		$1\frac{1}{2}-\frac{1}{2}$	5556.0	$0.29B$		0.15	0.12	0.10	0.11
(7)	$4s\,^4P - 4p\,^4P^0$	$2\frac{1}{2}-2\frac{1}{2}$	5032.4	$0.84B$	$0.87 \pm 35\%$	0.66	0.68	0.76	0.81
		$1\frac{1}{2}-1\frac{1}{2}$	4991.9	$0.38C$		0.15	0.13	0.08	0.33
		$\frac{1}{2}-\frac{1}{2}$	4942.4	$0.35C$		0.15	0.17	0.14	0.15
		$2\frac{1}{2}-1\frac{1}{2}$	5103.3	$0.34D$		0.50	0.43	0.64	0.27
		$1\frac{1}{2}-\frac{1}{2}$	5009.5	$1.07B$		0.70	0.82	0.86	0.94
		$1\frac{1}{2}-2\frac{1}{2}$	4924.1	$0.40A$		0.22	0.30	0.22	0.24
		$\frac{1}{2}-1\frac{1}{2}$	4925.3			0.24	0.43	0.24	0.51
(8)	$4s\,^4P - 4p\,^2D^0$	$2\frac{1}{2}-2\frac{1}{2}$	4779.1	$0.06E$		0.011			
(9)	$4s\,^4P - 4p\,^4S^0$	$2\frac{1}{2}-1\frac{1}{2}$	4815.5	$1.08D$	$0.94 \pm 35\%$	0.64	0.55	0.34	0.88
		$1\frac{1}{2}-1\frac{1}{2}$	4716.2	$0.36C$	$0.34 \pm 35\%$	0.23	0.39	0.50	0.29
		$\frac{1}{2}-\frac{1}{2}$	4656.7	$0.19C$		0.12	0.19	0.33	0.09
(11)	$3d\,^4F - 4p\,^4D^0$	$4\frac{1}{2}-3\frac{1}{2}$	5606.1	$0.38A$	$0.40 \pm 35\%$	0.30	0.22		
		$3\frac{1}{2}-2\frac{1}{2}$	5640.3[c]	$0.49E$[c]			0.20		
		$2\frac{1}{2}-1\frac{1}{2}$	5659.9	$0.44A$	$0.43 \pm 45\%$	0.34	0.19		
		$1\frac{1}{2}-\frac{1}{2}$	5664.7	$0.52A$	$0.48 \pm 35\%$	0.38	0.24		
		$3\frac{1}{2}-3\frac{1}{2}$	5526.2	$0.09C$		0.081	0.026		
		$2\frac{1}{2}-2\frac{1}{2}$	5578.8	$0.11C$		0.074	0.04		
		$1\frac{1}{2}-1\frac{1}{2}$	5616.6	$0.18E$		0.083	0.05		
		$1\frac{1}{2}-2\frac{1}{2}$	5536.7	$0.10D$		0.066	0.002		
(14)	$4s\,^2P - 4p\,^2D^0$	$1\frac{1}{2}-1\frac{1}{2}$	5819.2	$0.11D$	$0.12 \pm 40\%$	0.085	0.114	0.12	0.09
		$\frac{1}{2}-1\frac{1}{2}$	5646.9[c]	$0.49E$[c]		0.68	0.57	0.67	0.57
		$1\frac{1}{2}-2\frac{1}{2}$	5639.9[c]	$0.63E$[c]		0.75	0.68	0.76	0.66
(15)	$4s\,^2P - 4p\,^2P^0$	$1\frac{1}{2}-1\frac{1}{2}$	5014.0	$0.98C$		0.72	0.87	0.92	0.84
		$\frac{1}{2}-\frac{1}{2}$	4917.1	$0.84D$		0.55	0.70	0.73	0.66
		$\frac{1}{2}-1\frac{1}{2}$	4885.6	$0.14E$		0.13	0.17	0.15	0.17
(29)	$3d\,^2F - 4p'\,^2F^0$	$3\frac{1}{2}-3\frac{1}{2}$	3993.5	$0.08D$					
		$3\frac{1}{2}-2\frac{1}{2}$	4007.8	$0.03D$					
(32)	$3d\,^2P-4p'\,^2D^0$	$1\frac{1}{2}-2\frac{1}{2}$	4431.0	$0.09E$					
(36)	$3d\,^2D-4p'\,^2D^0$	$2\frac{1}{2}-2\frac{1}{2}$	4668.6	$0.31E$					
		$1\frac{1}{2}-1\frac{1}{2}$	4648.2	$0.29E$					
(38)	$4s'\,^2D - 4d\,^2F^0$	$2\frac{1}{2}-3\frac{1}{2}$	5320.7	$1.01A$	$1.16 \pm 35\%$	0.84			0.91
		$1\frac{1}{2}-2\frac{1}{2}$	5345.7	$1.24C$	$1.15 \pm 35\%$	0.75			0.84
		$2\frac{1}{2}-2\frac{1}{2}$	5345.7			0.11			0.06
(39)	$4s'\,^2D-4d\,^2D^0$	$2\frac{1}{2}-2\frac{1}{2}$	5212.6	$1.86C$		0.72			0.85
		$1\frac{1}{2}-2\frac{1}{2}$	5212.6			0.098			0.02
		$1\frac{1}{2}-1\frac{1}{2}$	5201.0	$1.66C$		0.68			0.75
		$2\frac{1}{2}-1\frac{1}{2}$	5201.3			0.065			0.13
(40)	$4s'\,^2D - 4d\,^2P^0$	$2\frac{1}{2}-1\frac{1}{2}$	4524.9	$0.97C$		0.98			1.15
		$1\frac{1}{2}-1\frac{1}{2}$	4524.7			0.093			0.27
(43)	$4p\,^4D^0 - 5s\,^4P$	$3\frac{1}{2}-2\frac{1}{2}$	4463.6	$0.76D$		0.53	0.71		
		$2\frac{1}{2}-1\frac{1}{2}$	4483.4	$0.40E$		0.31	0.44		
		$1\frac{1}{2}-\frac{1}{2}$	4486.7	$0.86E$		0.66	0.55		
		$1\frac{1}{2}-1\frac{1}{2}$	4432.4	$0.09E$		0.29	0.24		
(44)	$4p\,^4D^0 - 4d\,^4F$	$3\frac{1}{2}-4\frac{1}{2}$	4162.7	$2.6D$		2.3	2.18		
		$2\frac{1}{2}-3\frac{1}{2}$	4153.1	$1.2E$		2.0	1.88		
		$1\frac{1}{2}-2\frac{1}{2}$	4145.1	$1.1D$		1.8	1.65		
(45)	$4p\,^4D^0 - 4d\,^4D$	$3\frac{1}{2}-3\frac{1}{2}$	4028.8	$0.39D$		0.51	0.47		

TABLE V. *(Continued)*

Multiplet[29]	Transition	$J_i - J_k$	λ (Å)	This work[a]	Bridges and Wiese[6]	NBS[12]	Coulomb approximation LS Coupling	Intermediate coupling (Ref. 35)	Intermediate coupling (Ref. 36)
		$2\frac{1}{2}-2\frac{1}{2}$	3990.9	$0.22D$		0.35	0.32		
		$3\frac{1}{2}-2\frac{1}{2}$	4050.1	$0.12D$		0.11	0.10		
		$2\frac{1}{2}-1\frac{1}{2}$	4003.9	$0.25D$		0.21	0.19		
(46)	$4p\ ^4P^0-5s\ ^4P$	$2\frac{1}{2}-2\frac{1}{2}$	4792.0	$0.98D$		0.37	0.38		
(49)	$4p\ ^4P^0-4d\ ^4D$	$2\frac{1}{2}-3\frac{1}{2}$	4294.4[c]	$1.6D$		1.7	1.6		
		$1\frac{1}{2}-2\frac{1}{2}$	4267.8	$1.1D$		1.2	1.1		
		$\frac{1}{2}-1\frac{1}{2}$	4269.8			0.70	0.65		
		$2\frac{1}{2}-2\frac{1}{2}$	4318.7	$0.65D$		0.49	0.45		
		$1\frac{1}{2}-1\frac{1}{2}$	4282.6	$0.93C$		0.89	0.82		
		$\frac{1}{2}-\frac{1}{2}$	4278.5	$1.4D$		1.4	1.3		
(50)	$4p\ ^4P^0-4d\ ^4P$	$2\frac{1}{2}-2\frac{1}{2}$	3892.3	$1.2D$		0.63	0.56		
(55)	$4p\ ^2D^0-4d\ ^2F$	$1\frac{1}{2}-2\frac{1}{2}$	3923.5	$1.3D$		2.0	1.78		
(59)	$4p\ ^4S^0-4d\ ^4P$	$1\frac{1}{2}-2\frac{1}{2}$	4032.8	$0.4E$		1.2	1.10		
		$1\frac{1}{2}-1\frac{1}{2}$	3998.1	$0.7E$		1.2	1.09		
		$1\frac{1}{2}-\frac{1}{2}$	3979.9	$0.8E$		1.2	1.11		
(66)	$4p'\ ^2D^0-4d\ ^2F$	$2\frac{1}{2}-3\frac{1}{2}$	4259.2	$0.6E$		1.5			
		$1\frac{1}{2}-2\frac{1}{2}$	4257.4			1.4			
		$2\frac{1}{2}-2\frac{1}{2}$	4249.9	$0.6E$		0.10			
(67)	$4p'\ ^2D^0-4D\ ^2G$	$2\frac{1}{2}-3\frac{1}{2}$	4231.0	$1.7E$					

[a] Estimated uncertainty: Absolute A values: $18\% \le A < 22\%$, $22 \le B < 28\%$, $28\% \le C < 38\%$, $38\% \le D < 50\%$, $E > 50\%$.

[b] Foster (Ref. 33), using vortex-stabilized arc, determined the A value of $\lambda = 5453.6$ to be 0.78×10^8 sec^{-1}. Schulz-Gulde (Ref. 8), using a wall-stabilized arc, found the A value of $\lambda = 5453.6$ to be 0.71×10^8 sec^{-1}.

[c] Line completely blended with a line of some other multiplet. Relative intensity lamp data have been used to unfold blends, so that results should be regarded as being uncertain by at least 50%.

using a coupling description sensitive to details of atomic level structure.

To see if configuration interactions have strong influence on line strengths in the $4s$-$4p$ transition array, we test for departures from J-file and J-group sum invariance.[37] In Table VII the ratios of measured file sums to file degeneracies are seen to vary by approximately 20%, with particularly large excursions occurring in the $4p\ ^4D^0_{1/2}$ and $4p\ ^2D^0_{3/2}$ columns. The uncertainty in our $3p4s$-$3p4p$ results is estimated to be slightly less than this discrepancy: misclassifications or configuration mixing be partially responsible. The J-group sums also scatter by ±20% from the J-group sum invariance associated with non-interacting arrays of the αs-αp type.

TABLE VI. Comparison of relative SII A values.

Multiplet	λ (Å)	This work	Bridges[6] *et al*	LS[37] coupling	IC[35] coupling	IC[36] coupling
(6)	5453.6	1.00 Ref	1.00	1.00	1.00	1.00
	5432.7	0.77 ± 0.03	0.78	0.71	0.79	0.79
	5428.6	0.55 ± 0.03	0.50	0.43	0.49	0.49
	5564.9	0.20 ± 0.02	0.20	0.28	0.21	0.20
	5509.6	0.42 ± 0.03	0.45	0.52	0.47	0.47
	5473.6	0.84 ± 0.03	0.86	0.83	0.85	0.86
(7)	5032.4	0.84 ± 0.04	0.87	0.88	0.97	0.95
(9)	4815.5	1.08 ± 0.15	0.94	0.71	0.44	1.03
	4716.2	0.36 ± 0.03	0.34	0.51	0.64	0.34
(11)	5606.1	0.38 ± 0.03	0.40	0.28	···	···
	5659.9	0.44 ± 0.03	0.43	0.25	···	···
	5664.7	0.52 ± 0.04	0.48	0.31	···	···
(14)	5819.2	0.11 ± 0.03	0.12	0.15	0.15	0.11
Fraction of transitions in agreement with present results			92%	17%	33%	67%

TABLE VII. J-file sum rule for ionized sulfur $4s$-$4p$ transition array.

Configuration: $3p^2(^3P)4p$ / $3p^2(^3P)4s$	$^2S^0_{1/2}$	$^2P^0_{1/2}$	$^4P^0_{1/2}$	$^4D^0_{1/2}$	$^4S^0_{3/2}$	$^2P^0_{3/2}$	$^4P^0_{3/2}$	$^2D^0_{3/2}$	$^4D^0_{3/2}$	$^4P^0_{5/2}$	$^2D^0_{5/2}$	$^4D^0_{5/2}$	$^4D^0_{7/2}$	File sum / File weight
$^2P_{1/2}$	4.0[b]	9.9	0[a]	0[a]	0[a]	3.3	0[a]	17.4	0[a]					17.3
$^4P_{1/2}$	0[a]	0[a]	3.7	13.6	1.7	0[a]	9.3	0.03[b]	17.4					22.8
$^2P_{3/2}$	9.3[b]	4.0[b]	0[a]	0[a]	0[a]	24.4	0[a]	4.3	0[a]	0[a]	33.4	0[a]		18.9
$^4P_{3/2}$	0[a]	0[a]	11.8	8.7	6.6	0[a]	8.3	0.01[b]	13.9	14.0	0.09[b]	36.6		25.0
$^4P_{5/2}$					21.2	0[a]	7.9	0.07[b]	6.0	28.2	1.7	10.2	64.6	23.3
File sum / File weight	6.7	7.0	7.8	11.1	7.4	6.9	6.4	5.5	9.3	7.0	8.8	7.8	8.1	

[a] Line too faint for detection.
[b] Calculated using intermediate coupling (Ref. 36).

IV. SUMMARY OF RESULTS

Absolute transition probabilities of 124 visible and infrared lines of C I, S I, and S II were measured in a consistent way. These data which are more complete and more stringently tested than any carbon or sulfur set previously available, are compared with other experiments, with refined intermediate coupling calculations and with various sum rules.

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[27a]*Note added in proof.* Stuck and Wende [Phys. Rev. A 9, 1 (1974)] measure the transition probability of C I (λ = 5052 Å) to be $(1.4 \pm 0.3) \times 10^6$ sec^{-1} in agreement with present results.
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