Stark broadening of singly ionized silicon*

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Linewidths and shifts of the five prominent visible Si II multiplets are measured in a conventional shock tube. The Stark effect from impacting plasma electrons is the dominant broadening mechanism. Electron densities range widely [$(4\text{–}15)\times 10^{16}$ cm^{-3}], but temperatures (9500–12 500°K) do not. Optical depth and source inhomogeneity are rarely troublesome. Depending upon interference, blending, and signal-to-noise ratios, broadening-parameter accuracies are between 15–25% and shift uncertainties are 15–100%. Comparison data are examined.

I. INTRODUCTION

Theoretical modeling of Stark-effect broadening has proven considerably more challenging for ionic than for neutral emitters.[1,2] Refinements of the past decade[3-6] have only partially reduced the reliability gap between ionic and neutral treatments.[7-10] Recently, experimental widths and shifts for ionic emitters ($3\leq Z\leq 20$) were mustered for an evaluation of semiclassical theory.[10] The average ratio of measured-to-predicted widths w_m/w_c for the 33 multiplets tested was 1.06 ± 0.05, but for the four Si II multiplets ($^2S-{}^2P^o$, $^2P^o-{}^2S$, $^2D-{}^2P^o$, $^2P^o-{}^2D$) included, w_m/w_c ranged from 0.33 to 1.50.[10] This large spread is puzzling:

(i) The Si II intermultiplet variation in the parameter kT/E, where E is the energy separating the nearest dipole-allowed perturbing level,[1] is slight. One has $1.2\lesssim kT/E\lesssim 3.7$ in a regime where Gaunt factors $g(kT/E)$ vary slowly.[3,11]

(ii) The Si II multiplets appear similar in their susceptibility to broadening by strong collisions. Authors vary regarding the importance of strong interactions (e.g., 67–87% of the broadening in one estimate versus 39–51% in another[5]) but concur in regarding intermultiplet differences as being slight.

(iii) Completeness of classification[12] and availability of gf values,[13] prerequisites for sound broadening calculations,[1] are as good for this ion as for other $3\leq Z\leq 20$ elements whose w_m/w_c ratios are markedly better. In a separate survey,[14] first-ion experimental broadening w_m was compared with predictions w_c of semiempirical formulas.[3] Systematic variation of w_m/w_c with χ_E/χ_I, where χ_E and χ_I are excitation and ionization potentials, was reported. In the $0.6\lesssim\chi_E/\chi_I\lesssim 0.8$ range encompassing the visible Si II multiplets, the w_m/w_c ratio average approached unity[14] when w_m were obtained with an electromagnetic T tube[14-16] and a plasma jet.[17] In these light sources temperature was 8 500–12 000 °K, and electron density was $(0.3\text{–}6.5)\times 10^{16}$ cm^{-3}, respectively—conditions satisfying the validity criterion for the impact approximation: (collision volume) $\times$ (density) $\ll 1.0$.[1]

Besides testing perturbation theory for plasma environments, Si II broadening parameters are applicable *per se* to the diagnosis of near and remote plasmas. Sophisticated codes[18] use gf values, broadening parameters, and observed equivalent widths to compute stellar conditions and abundances. The role of silicon burning in heavy element synthesis,[19,20] the practice of using silicon as a solar abundance reference for heavier elements, and silicon's contribution to the opacity of late-type stars[21] all heighten interest in silicon's astrophysical abundance. Equivalent widths of bright Si II lines also show promise as luminosity indicators.[22] Reliable Stark broadening and shift data should help further clarify the relationship between stellar luminosity and microturbulence.

II. THEORETICAL

The generally recognized theories[1,4-6,23] for Stark broadening of ion lines share the basic features of the impact approximation.[24] Broadening-related cross sections are estimated by assuming that impinging electrons follow classical hyperbolic trajectories and radiating ions behave quantum mechanically. The scattering S matrix is developed in accordance with second-order perturbation theory, with dipole and quadrupole terms being retained in the multipole expansion of electrostatic interactions.

Five impact broadening theories are tested here. Four of these [Jones, Bennet, and Griem (JBG)[1,4], Yukov[23], Sahal-Brechot (SB),[5,25-27] and Cooper-Oertel (CO)[6] (in revised codes run by Bengtson[28])] differ primarily in the modeling of inelastic collisions, in the choice of wave functions for radiating ions, and in computational techniques. A "semiempirical" (SE) approach by Griem,[1,3] although somewhat older, is also compared because of its ready applicability (involving tabular material instead of complex computer codes).[29]

Coupling effects important in close collisions require selection of cutoffs to conserve flux[30] and to keep the S matrix unitary. For the sake of microreversibility, SB and CO symmetrize cross sections[31] and, thereby, also reduce a tendency to overestimate semiclassical cross sections near threshold.[30] This may account for these two theories predicting (cf. Table II) smaller widths than their JBG counterparts. Feshbach resonances are likely to contribute to the broadening by elastic collisions, prompting extrapolation through thresholds to account for resonances with functions continuous in energy.[32] JBG affects this by use of unsymmetrized cross sections, while SB goes to the semiclassical limit[33] of the quantum Gailitis expression.[34] The SB predictions are larger than the corresponding CO ones, in part, because the latter do not make the same explicit allowance for resonances.

The value of using sophisticated ionic wave functions is appraised differently by the various authors. JBG,[4] CO,[6] and SE[3] rely on the Coulomb-LS coupling approximations[35,36] smoothed-over fine structure components, and routinely test if sum rules for dipole-allowed transitions are satisfied. The SB calculations operate with complex atomic structure, using Racah algebra for the angular part and configuration interaction for the radial part of the wave functions. The formula used by Sahal-Brechot for the quadrupole part of the interaction has been described elsewhere.[27] The 24 Si II configurations used by SB have been calculated by Nussbaumer,[37] following the method of Eissner and Nussbaumer.[38]

Opinion divides over how to treat ion-ion broadening.[1,24] In the present ion density regime (10^{16}–10^{17} cm^{-3}), it is arguable if either impact or quasistatic assumptions are altogether justified. Table I compares Si II ion-ion partial widths from (i) quasistatic quadrupole interaction and (b) impact (hyperbolic) encounters. The two sets of results are typically 12-fold smaller than corresponding electron impact widths. If scalar additivity is assumed (on grounds that ion-ion broadening is felt mainly in line wings[39]), then the electron impact widths given in Table II should be increased approximately 8% before being compared with shock tube data. If electron impact and quasistatic widths are folded together as *per* the GBKO approximation,[7] increases of 3–5% over Table II values would be in order. In either case, (i) our experiments cannot discriminate between these competing ion-ion assumption, and (ii) ion-ion partial widths interfere with our tests of electron impact broadening theories, but pose little ambiguity compared to the (factor-of-two for Si II) discordances in available comparisons of theory and experiment.

TABLE I. Computed ion-induced contributions to Si II half-widths (Å). ($N_e = 10^{17}$ cm^{-3}, $T = 10\,000$ °K).

Multiplet	(1)	(2)	(3)	(4)	(5)
(a) Quasistatic	0.062	0.14	0.105	0.13	0.218
(b) Impact	0.065	0.174	0.109	0.186	0.237

Accuracy of calculated shifts are inherently limited by uncertainty in the phase of the S matrix for close encounters. More highly excited emitting states tend to involve more participating angular momenta, increasing the likelihood that the net phase will approach zero.

III. EXPERIMENTAL

Luminous spectroscopic plasmas were formed behind reflected shock waves in the gas-driven 7×9-cm tube. With 70 bar of ambient-temperature hydrogen driving shocks into 5–40 Torr of test gas, plasmas persisted in essentially steady state for 35–150 μsec. Previous testing has shown that in most experiments the shocks were well-formed and homogeneous[36,40] (except for a laminar, time-dependent boundary layer). Judicious selection of test gas composition [0.1–1.0% of SiH_4 or $SiHCl_3$ or $Si(CH_3)_4$ in a neon carrier] and filling pressure caused electron densities to vary fourfold while: (a) temperatures were held between 9 500–12 500 °K with most in a 11 000 ± 1 000 °K band, (b) maintaining the prerequisites for quantitative photometry, i.e., Si II and hydrogen Balmer lines reaching sufficient brightness to register on time-resolved spectrograms, but remaining optically thin.

The test section, instrumentation for diagnosing plasma, and spectrophotometric recording are shown in Fig. 1. A maximum of 19 photoelectric channels were used: 12 in polychromator *f* to monitor narrow segments of the H_β profile from peak to far wing; 3 sets of line-and-nearby-background channels (polychromator *g*), each pair having matched bandpass to essentially integrate the total emission of prominent neon lines. Viewing on an

TABLE II. Stark-broadening parameters of Si II lines (Å) ($N_e = 10^{17}$ cm^{-3}, $T = 10^4$ °K).

Multiplet[12]	Transition[13]	λ (Å)	n [a]	$\frac{\sigma}{\sqrt{n}}$ (%)	Experimental half-intensity width: This work [b] w_m	Chapelle *et al.*[17] (1972)	Puric [c] *et al.*[16] (1974)	Theoretical electron impact width, w_c: Sahal-Brechot [e] (1976)	Cooper Oertel [d] [6–28] (1976)	Yukov[23] (1972)	JBG[1,4] (1973)	Griem[3] (1968)	Cross-theory multiplet average of w_m/w_c	$\frac{w_c^{max} - w_c^{min}}{w_m}$ (%)	Strong collision contribution via JBG	SB
(1)	$3p^2\,^2D_{5/2} - 3s^2\,^2P^o_{3/2}$	3856.0	10	5	1.07± 20%	···	0.54	0.50	···	···	1.16	0.59	1.61	62%	69%	50%
	$3p^2\,^2D_{3/2} - 3s^2\,^2P^o_{1/2}$	3862.6	20	4	1.05± 20%	···	0.48									
(2)	$4s\,^2S_{1/2} - 4p\,^2P^o_{3/2}$	6347.1	9	7	1.96± 20%	1.1	···	1.71	1.4	···	2.34	1.79	1.11	48%	73%	51%
	$4s\,^2S_{1/2} - 4p\,^2P^o_{1/2}$	6371.4	14	5	1.93± 20%	1.15	1.04									
(3)	$3d\,^2D_{3/2} - 4f\,^2F^o_{5/2}$	4128.1	20	5	1.58± 25%	···	···	0.99	0.9	0.9	1.37	1.20	1.52	30%	67%	50%
	$3d\,^2D_{5/2} - 4f\,^2F^o_{1/2}$	4130.9	22	5	1.60± 25%	···	···									
(4)	$4p\,^2P^0_{1/2} - 5s\,^2S_{1/2}$	5957.6	13	4	2.78± 15%	···	···	2.83	2.5	···	2.58	2.81	1.03	12%	87%	43%
	$4p\,^2P^0_{3/2} - 5s\,^2S_{1/2}$	5979.9	23	4	2.75± 15%	···	···									
(5)	$4p\,^2P^0_{1/2} - 4d\,^2D_{5/2}$	5041.0	50	2	2.53± 15%	···	···	2.62	2.2	2.0	2.90	2.33	1.10	34%	75%	39%
	$4p\,^2P^0_{3/2} - 4d\,^2D_{5/2}$	5056.0	39	3	2.69± 15%	···	···									
					Average per theory of w_c/w_m:			0.80	0.74	···	1.04	0.83				
					Standard deviation/average:			30%	18%	···	14%	21%				

[a] Number of shock tube experiments yielding useful date: $\sigma/\sqrt{n}$ is the random error via analysis of variance.
[b] Mean shock tube temperature is 11 300 °K. Tolerance estimates are 90% confidence levels.
[c] TEE tube temperature ranging about 10 600 °K.
[d] Computer codes developed by Bengtson[2,6] along lines of the Cooper-Oertel treatment.
[e] This work.

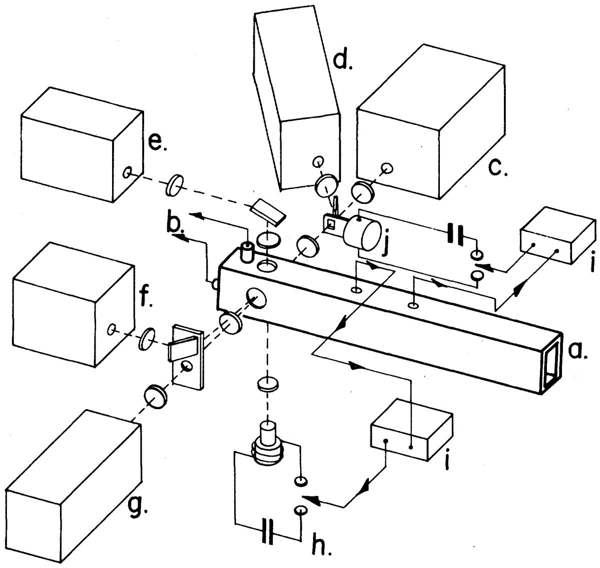

FIG. 1. Shock-tube test section and associated instrumentation: (a) test section of I. D. 6.7×9.2, fitted with quartz windows near the reflecting wall; (b) quartz pressure tranducers; (c) photographic 1 meter spectrograph, covering 1 700 Å with 0.3–0.4 Å resolution; (d) $\frac{3}{4}$-m-wide band spectrograph covering 2500–8500 Å; (e) monochromator for photoelectrically recording line-reversal data; (f) 12-channel polychromator monitoring H_β; (g) three pairs of line and nearby background channels to record integrated line brightness; (h) continuous flash lamp; (i) delay generator; (j) exploding wire-driven shutter.

axis orthogonal to these, a narrow-pass channel (monochromator *e*) is centered on an optically thick plasma feature like H_α for the purpose of recording the intensity reversal cycle when a bright flashlamp (*h*) briefly backlights the spectroscopic plasma. Stigmatic 1.0 m photographic spectrographs (*c*, *d*) were framed by a fast mechanical shutter (*j*) and associated synchronizing gear (*d* and *i*). Framing time of the shutter was preadjusted (20–100 μs) based on anticipated plasma brightness and steady-state test time. Pressure transducers (*b*) were fitted to side and end walls.

Thermodynamic state variables were measured in each experiment. Brightness temperatures[7,41] were deduced from the integrated energies (photoelectrically recorded line-plus-background minus background of Ne I λ5852 Å and H_β, two lines with different excitation energies and shapes. A radiation temperature *via* the line-reversal technique[42] was simultaneously determined. No systematic difference was found between these redundant data. Accuracy of the combined temperature determinations was 3–6%, depending upon plasma brightness and composition. Pressure measured by the two quartz transducers had typical accuracy of 10%. These state determinations can be used for computing electron densities with 20–30% reliability, and on the average, these Saha-Boltzmann derived electron densities agreed satisfactorily with those obtained independently by fitting (red-blue wing average) experimental H_β profiles to theoretical Stark shapes.[1,43] After fitting profiles at 10–12 points, Balmer half-width precisions were typically 10% (15% in electron density). Monitoring the ratio of H_β peak separation-to-half-width helped to flag occasional plasma inhomogeneities.[44] Profiles of Si II lines were recorded in the same exposures as the H_β profiles in order to circumvent any assumptions of repeatability (gas-driven shock tubes have poor repeatability).

The 1.0 meter Czerny-Turner spectrograph used for recording ion line shapes had reciprocal dispersion of 7.5 Å/mm and a best resolution of 0.3 Å. The mechanical shutter[45] was triggered by the incident shock *via* time delay generators and adjusted to sample within the source's steady-state durations (35–150) μs), or for shorter periods if specular densities were high. Stability of the plasma during the photographic exposure was monitored by photomultipliers in the focal plane. (Data were discarded if brightness fluctuated excessively). Photographic emulsions (Kodak No. 2475, and *I-F*) were calibrated against a carbon arc anode using stepped wedges and continuously variable filters.[46] Spectral densities were converted to relative intensity records by a computer code.[47] Absolute intensities of H_α and H_β, monitored by photoelectric polychromators, allowed for compensation of mild radiative trapping (ion line peaks with $0.5 < \tau$). When optical depths or emulsion densities were unfavorable, data were rejected.

Strategies for reducing chances for systematic error capitalized on the source's homogeneity, freedom from demixing, and dynamic range. These included (i) driving electron densities over a factor of 4 at essentially constant temperatures, thereby allowing regression tests for possible bias in deconvolution or photometric calibration; (ii) redundantly measuring both photometric and thermodynamic variables to check for instrumental effects and to test our LTE and laminar source assumptions; (iii) obtaining Si II linewidths relative to simultaneously recorded Balmer widths, in effect nulling out consequences of any mild plasma inhomogeneity; (iv) operating where competing mechanisms cause slight broadening compared to Stark effect (electron impact widths were severalfold greater than combined instrumental, Doppler and Van der Waals widths).

Deconvolution of isolated lines involved fitting to Voigt shapes.[48] This was done both by hand, using a least ten points for a dimensionless ($\ln\alpha$ vs α) fit, and also by a Fourier transformation method.[49] Ion line half-widths obtained independently by these two ways generally agreed within 10%. Grain noise, and weak interferences were the main factors limiting precision. Another source of random error was Van der Waals broadening. Neon density (typically 98% of particles) data for each run was used to approximately[30] compensate for the Van der Waals half-widths (0.01–0.09 Å). However, these corrections are regarded as uncertain[1,7] by at least a factor of 2, and since electron and neon densities in the shock tube are not simply correlated, this competing broadening acted as a random error on the Lorentzian component of observed widths. Following deconvolution of instrumental width (0.3 Å full width at half-maximum, intermediate in shape between Gaussian and triangular) and Doppler (typically 0.08 Å) contributions, the random error in a typical (single) determination of Stark halfwidth was 15–20% for isolated lines and 20–25% for the partially blended multiplet (1) and (3) lines.

Accuracy was unchanged throughout the experimental range (Fig. 2). At low electron densities, deconvolution involved relatively small Stark width-to-instrumental width ratios (i.e., 2 : 1 to 3:1), while at large electron densities plasmas were less steady over exposure times. Editing of photographic exposure, optical depth, blending, interference, and source fluctuations reduced a field of 300-plus experiments to the 9–50 runs enumerated in Table II.

Shifts were measured relative to wavelength fiduciaries from low-pressure lamps, recorded subsequent to shock tube firing (without disturbing the spectrographic plate). Displacements with respect to several bracketing fiduciaries were read from the plates by digitizing photoelectric comparators (Grant and Hilger-Watt). Precision in locating the peaks of reference and Si II lines was ± 0.008 Å, and ±0.008 – 0.04 Å, respectively. Wavelength interpolation from fiduciary lines was done with a "spline" smoothing function.[50] Worst-case graphical analysis showed that multiplet (1), (3), and (5) blending could not significantly complicate line shifting.

A second technique was used to redundantly measure some Si II shifts. Applying approximate corrections for their own slight shifts,[7] plasma neon lines were taken for wavelength fiduciaries. Conservatively, the theory of neutral-line Stark shift is regarded as being uncertain by not more than 50%.[1,3,41] Accordingly, positions of the neon $3s$-$3p$ lines at $Ne = 10^{17}$ cm^{-3} would be no more uncertain than 0.10–0.15 Å. This error is small compared with the larger Si II line shifts (of order 0.3–1.5

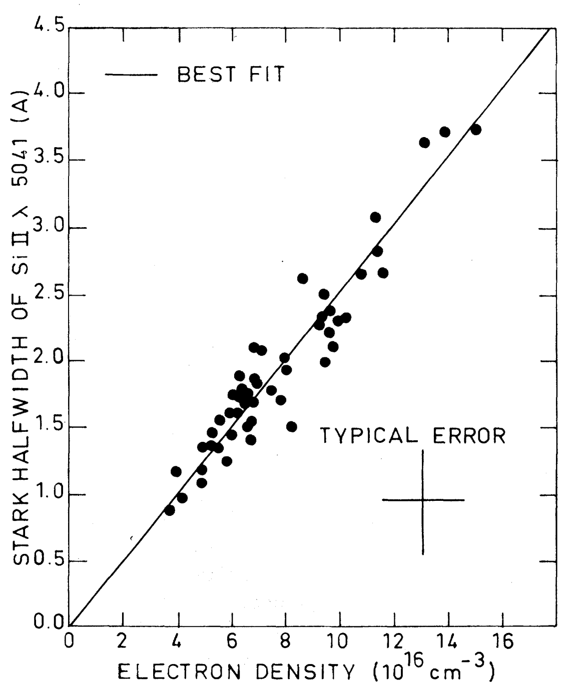

FIG. 2. Stark effect half-intensity widths of Si II λ5041.0 Å observed as functions of measured electron density.

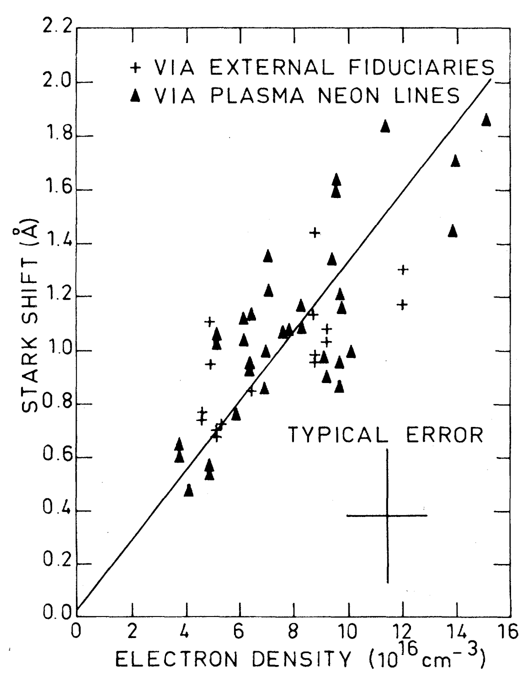

FIG. 3. Red shifts of multiplet (4) lines, measured relative to two kinds of wavelength standards as functions of shock-tube electron densities.

TABLE III. Stark shift of Si II lines (Å). ($N_e = 10^{17}$ cm^{-3}, $T = 10^4$ °K).

		Experimental [a]		Theoretical, d_c				Shift/half-halfwidth					
Multiplet [12]	(Å)	This work, d_m (Å)	Puric [16] *et al.*	Sahal-Brechot (1976)	Yukov [23] (1972)	JBG [14] (1974)	Griem [3] (1968)	This work [b]	Puric (1974)	Sahal-Brechot (1976)	Yukov (1972)	JBG (1974)	Griem (1968)
(1)	3856.0	0.20 ± 0.20	0.06	0.08	···	0.49	−0.19	0.38	0.24	−0.32	···	−0.84	−0.64
	3862.6	0.20 ± 0.20	0.06										
(2)	6347.1	−0.31 ± 0.07	···	−0.43	···	−1.01	−0.61	−0.29	0.15	−0.50	···	−0.86	−0.68
	6371.4	−0.25 ± 0.06	0.08										
(3)	4128.1	−0.32 ± 0.30	···	−0.04	−0.14	−0.49	−0.19	−0.40	···	−0.08	−0.31	−0.72	−0.28
	4130.9	−0.32 ± 0.30	···										
(4)	5957.6	1.32 ± 0.20	···	1.3	···	1.40	1.01	0.97	···	0.92	···	1.09	+0.78
	5979.9	1.35 ± 0.20	···										
(5)	5041.0	1.10 ± 0.15	···	1.38	0.75	1.53	0.98	+0.85	···	1.05	0.75	1.06	−0.84
	5056.0	1.15 ± 0.15	···										
	Average of $(d_m - d_c)/(\frac{1}{2} w_m)$:			0.039	···	0.013	0.252						
	Standard deviation of $(d_m - D_c)/(\frac{1}{2} w_m)$:			0.350	···	0.500	0.329						

[a] Negative shift is towards the blue.
[b] Multiplets — averages used.
[c] A value of $d/w = -1.0$ measured by H. F. Berg is cited in Ref. 3 as private communication.

Å). The strength of this method is that subject and references lines originate at the same time and place, circumventing possibilities for bias due to different geometries or handling. Considering both reading error and uncertainty in fiduciary line wavelength, most Si II shifts measured this way are estimated to err not more than 30%–35%.

Multiplet (4) shifts referenced against both the "internal" and lamp wavelength standards are displayed in Fig. 3. No systematic difference (slope or intercept) is evident in results from the two (redundant) methods.

IV. RESULTS AND DISCUSSION

Widths of Si II lines measured with the shock tube are compared with the literature in Table II. The number of determinations is n, and random error in terms of variance is $\sigma/\sqrt{n}$. Tolerances (90% confidence estimates) are largest for multiplet (3) due to merging of λ4128.1 Å and λ4130.9 Å. Blending with λ3853.7 Å spoiled many λ3856.0 Å profiles. Fairly often, λ6347.1 Å peak optical depths exceeded 0.5, and profiles were discarded. Signal-to-noise ratios hindered quantitative reduction of the relatively weak λ5957.6 Å line.

Temperature-electron density regimes in earlier experiments[14-17] were similar to present ones. For the single instance (λ6371.4 Å) where three-way experimental comparison is possible, Puric and Chappelle agree on a width one half as large as we measured in the shock tube. A similar factor-of-two disparity runs through the comparison of all the lines (λ6371.1, 3862.6, and 3856.0 Å) measured jointly by us and by Puric. If the source of bias was error in experimental source conditions, then measured shift-to-width ratios should agree better than width-to-electron density data: Table III shows that this is not the case.

Electron impact widths predicted theoretically are arrayed chronologically in the table. The CO codes cannot presently treat the two-electron transition ($3s3p^2 - 3s^24p$) of multiplet (1). Except for multiplet (1), differences between the CO, SB and Yukov predictions are characteristically 10-20%. Consideration of configuration mixing leads SB to a multiplet (1) result one half as large as predicted by the others, an observation confounded further by the factor-of-2 disagreement between the various experimental width determinations for this multiplet.

From the widths w_c predicted by the various authors we get an average and standard deviation for ratios w_c/w_m, where w_m refers to the multiplet-mean of shock tube measured widths. Ion contributions, which may add 4–10% to the impact widths, have not been included in w_c—an uncertainty that can mask whether the JBG or SE widths better approximate the shock-tube data. In terms of both mean value and scatter, present w_c/w_m data conform closely to the earlier (several element) set.[10] The comparatively simple SE formula appears as successful as more complex treatments.

Five multiplets hardly constitute bases for strong statistical inference, but the data do suggest that: (a) all theories fare better when applied to a higher lying multiplets, and (b) intertheory differences decline with increasing multiplet numbers. The (Table II) column headed "average of w_m/w_c" refers to multiplet value averaged across the theories. Differences between multiplets, per theory (rows), are comparable to intertheory differences per multiplet (columns). Multiplet (4) and (5) w_m/w_c values are markedly closer to unity than those for multiplet (1)–(3). The spread between high and low predictions, $(w_c^{\max} - w_c^{\min})/w_m$ shrinks progressively going from multiplet (1) to multiplet (5).

Plausible explanations for this systematic behavior include: (i) strong collisions become less important as one decends in Table II (supported by SB, but not the JBG, partitioning of strong-weak interaction partial widths, as mentioned earlier), (ii) more perturbing levels come into play at the higher principal quantum number, tending to statistically smooth uncertainties in individual cross sections and gf values.

Measured and comparison shifts are shown in Table III. Shock-tube measurements of multiplets (2) and (4) were made relative to both narrow plasma lines and low-pressure lamp fiduciaries. Results from the T tube and shock tube agree on the direction of multiplet (1) shift, but differ in magnitude by a factor of 4. Impact approximation predicted shifts include no allowance for Van der Waals or plasma polarization effects.[1] Predictions of the various theories differ both in the direction and magnitude of multiplet (1)–(3) shifts, approaching factor-of-2 concensus only for multiplet (4) and (5). Scatter tallies at the foot of the table do not indicate that any of the theories have a decided edge in predicting ion line shifts, ratios of $(d_m - d_c)/0.5w_m$ being typically comparable to those found earlier for other medium weight ions.[10]

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