PHYSICAL REVIEW A VOLUME 14, NUMBER 3 SEPTEMBER 1976

Stark-broadening study of neutral nitrogen lines

V. Helbig,* D. E. Kelleher, and W. L. Wiese
Institute for Basic Standards, National Bureau of Standards, Washington, D. C. 20234
(Received 17 May 1976)

Extensive photoelectric measurements of the plasma-broadened line shapes of 42 neutral nitrogen lines have been carried out with a wall-stabilized arc. The arc current was varied from 20 to 100 A to achieve a variation in the axial electron density from about 5×10^{16} to 1.5×10^{17} cm^{-3}. Most observations were made end-on, and the arc was operated in pure nitrogen as well as argon with a small admixture of nitrogen to avoid self-absorption problems, which mainly arose with the red and near-infrared lines. The electron density was determined from the well-known Stark half-width of the hydrogen H_β line, for which purpose a trace of hydrogen was added to the plasma. Our principal results are as follows: (a) Good agreement with the recent theoretical work by Griem and co-workers has been obtained; (b) consistent with theoretical predictions, ion-broadening effects are not noticeable; (c) the Stark widths and shifts for different lines in a multiplet are identical within the experimental precision ($\approx 3\%$) as predicted by the theory; and (d) measurements performed over a range of transitions involving different quantum states agree equally well with the theoretical data, indicating that the atomic-structure part of theory is very adequate.

I. INTRODUCTION

The experimental Stark-broadening literature on isolated lines of neutral atoms, which has recently been critically surveyed and compiled by Konjevic and Roberts,[1] contains very little material on nitrogen—an element of considerable interest in gaseous-discharge investigations. The available experimental nitrogen Stark-broadening data[2-5] contain, moreover, some significant inconsistencies with the theoretical Stark-broadening data by Benett and Griem.[6,7] Specifically, the following points deserve further investigation:

(a) The overall line profiles measured by Stampa[2] have yielded asymmetrical profiles, contrary to theoretical prediction, and the profiles by Morris *et al.*[3] also exhibit significant deviations from Lorentzian shapes.

(b) The half-widths of different lines in the same multiplet have been measured with differences as great as 25%,[3,4] but calculations predict identical widths for such component lines.

(c) Almost no shift measurements exist.

(d) The study by Konjevic and Roberts[1] indicates the desirability of performing measurements, under the same conditions, of a number of emission lines which originate in different quantum states in order to test the theory over a range of such states. The states should preferably range from some excited atomic states fairly close to the core to others where the excited electron is relatively far out. Experimental investigations of this type do not exist to our knowledge.

This study is an attempt to respond to the above-indicated problems and needs. It is obvious that rather high accuracy must be achieved to obtain definitive answers. We have therefore taken great efforts to achieve the needed accuracy, and we were considerably aided in our goal by the availability of an advanced spectrometric setup which had been applied before to other plasma line-broadening studies[8,9] and which we shall therefore describe only briefly to the extent needed here.

II. EXPERIMENT

A. Apparatus

The light source used in these studies was a wall-stabilized cascade arc with a channel diameter of 3.2 mm, similar to the one described in Ref. 8, and it was operated at various currents between 20 and 100 A. Initially, the measurements were performed side-on as well as end-on to test the agreement between the two modes of observation. After agreement within the experimental precision was found, the bulk of the measurements were performed observing the arc in the less laborious end-on mode. The central portion of the arc column was operated at atmospheric pressure in pure nitrogen, while the (inhomogeneous) end regions, including the electrode areas, were kept in pure argon. This assured that the observed nitrogen lines were emitted from a well-defined homogeneous layer.

The transition zones between the two gases were located at about one-third and two-thirds of the length of the arc column. No significant changes in the electron density and temperatures should occur in the transition zones, since the two gases nitrogen and argon have similar thermal properties in the applied temperature range. For the measurement of the red nitrogen lines, self-absorption was estimated to become significant, and therefore the entire arc column was run essentially in argon, with only a small admixture of 0.5% nitrogen in the central one-third of the arc column added for the strongest lines.

The arc column was imaged onto the entrance slit of a 2.25-m Ebert monochromator with a 1800-line/mm grating. The apparatus profile was determined with a low pressure mercury-discharge lamp, and the half-width of the apparatus profile was measured to be 0.09 Å in first order, with the slits set at 35 μm. Two photomultipliers with different spectral response were used for the detection of the visible and near-infrared lines. Cutoff filters were used to separate different orders of the spectra. The signals were amplified, recorded with a digital recording system which had been developed earlier in our laboratories,[9,10] and stored on magnetic tape. In addition, the data were recorded on a two-channel strip-chart recorder. For radiometric calibrations and determinations of the spectral efficiency of the spectrometric setup, we used a calibrated tungsten strip lamp.

B. Plasma diagnostics

For the determination and interpretation of Stark-broadening parameters, the knowledge of the temperature and electron density is essential. The accurate knowledge of the electron density is especially critical, since Stark widths and shifts are proportional to this quantity to first order, according to theory.[7] We have determined the electron density by utilizing well-known Stark-broadening data for the hydrogen line H_β. We added small amounts of hydrogen to the nitrogen plasma, measured the Stark half-width of H_β, and applied an experimentally obtained relationship[8] between the Stark width and the electron density to determine the latter. The H_β line is particularly suitable as a reference line, since numerous experimental as well as theoretical investigations indicate that electron densities obtained from its Stark width should be accurate to within 10% for the range of this experiment. (For two recent reviews and comparisons, see Refs. 7 and 8.)

The temperature has generally been determined from the plasma equilibrium and conservation relations, applying the known electron density from H_β and assuming local thermodynamic equilibrium (LTE).[11] According to the detailed investigations by Shumaker and Popenoe,[5,12] LTE exists for this type of arc plasma at electron densities above 10^{17} cm^{-3} for N_2 and 5×10^{16} cm^{-3} for Ar. Some of our measured electron densities, at low arc currents, are somewhat below these values. Investigations by Garz[13] on similar arcs show that small deviations from the LTE values appear for argon which amount to a few percent for the temperatures studied. Since the line-broadening parameters depend only weakly on the temperature, we did not attempt to refine the temperature determinations beyond the LTE assumption. We estimate that even in the most unfavorable case the errors introduced into the temperature are not larger than 5%.

The temperature has also been determined—in the side-on observations—from absolute intensity measurements of some N I lines.[11] Again, the plasma equilibrium and conservation equations were applied, LTE was assumed, and the atomic transition probabilities compiled by Wiese *et al.*[14] were utilized. The obtained temperatures agree within a few percent with the above-determined values in the range where LTE exists.

C. Measurement of the Stark widths and shifts

The profiles of lines which were well separated from others were recorded with a strip-chart recorder, and the half-widths were determined graphically. For all such lines—the signal-to-noise ratios in the intensity measurements were usually very high, permitting observations far into the line wings—the profiles were found to adhere very closely to Lorentzian shapes. For some of these lines, as well as for all cases of overlapping lines in multiplets, the data were also recorded on magnetic tape and were analyzed with a computer program which yielded the widths and relative shifts of the individual lines. The program was designed to fit the sum of up to eight Lorentzian profiles to the experimental points, and the fitting parameters were the maximum line intensity, half-width and relative shift for each of the lines, and a (sloping) linear background.

Since observed line shapes are usually the result of a combination of factors, their contributions have to be analyzed and determined in order to isolate the contribution originating from Stark broadening. While the experimental conditions and the instrumentation were chosen so as to make Stark broadening the dominant part, other line-broadening mechanisms must be considered. These are instrumental broadening, as well as Doppler, Van der Waals, foreign-gas resonance, and natural broadening. To illustrate the magnitude of the various broadening mechanisms under our experimental conditions, we have listed in Table I the numerical values for two multiplets. These multiplets are unfavorable cases with respect to the dominance of Stark broadening. Listed are the measured instrumental width, typical Doppler widths derived from the plasma temperature, and estimates for the other broadening mechanisms,[15] and these data are compared to the observed total linewidths. It is seen that Stark broadening is indeed always the

TABLE I. Various contributions to observed half-widths for two multiplets representing unfavorable cases (at low and high electron densities).

	Plasma conditions			
	$N_e = 5.9\times10^{16}$ cm^{-3}	T=11 700 K	$N_e = 1.49\times10^{17}$ cm^{-3}	T=14 160 K
Multiplet	$3s\,^2P$-$3p\,^2P^o$	$3s\,^4P$-$4p\,^4S^o$	$3s\,^2P$-$3p\,^2P^o$	$3s\,^4P$-$4p\,^4S^o$
Full half-widths (Å):				
Observed overall width	0.82	0.915	1.92	2.31
Doppler (Gaussian)	0.179	0.086	0.196	0.095
Apparatus (Gaussian)	0.10	0.090	0.10	0.090
Van der Waals [a]	0.026	0.014	0.015	0.007
Resonance [a]	0.0	0.012	0.0	0.006
Natural [b]	2.4×10^{-3}	3.7×10^{-4}	2.4×10^{-3}	3.7×10^{-4}
Derived Stark half-width	0.74	0.87	1.88	2.29

[a] Estimates according to Ref. 15.

[b] With transition probability data from Ref. 14.

dominant broadening factor, and the other contributions to the total observed width are so small that they may be readily taken into account from standard Voigt-profile analysis.[16,17] The changes, i.e., the reduction from the observed width to the Stark width, amount at most to 4% for the high electron densities, but are normally of the order of 1% or less. For the lowest electron densities ($\sim 5\times10^{16}$ cm^{-3}), the contributions of Doppler and apparatus broadening become appreciable for the infrared multiplets 1, 2, and 3 and yield Stark widths which are about 20% smaller than the observed widths.

An additional distortion of line profiles may arise from self-absorption effects. The optical depth $\tau(\lambda)$ of the plasma column was checked by collecting the radiation emitted from the plasma in the extension of the optical path and focusing it back into the plasma by a spherical mirror, thus adding it to the light beam. The optical depth $\tau(\lambda)$ may then be determined as

$$\tau(\lambda) = \ln\{[A(\lambda') - 1]/[B(\lambda) - 1]\}, \quad (1)$$

where A is the ratio of the signals with and without the reflected light included, measured at an optically thin ($\tau \ll 1$) nearby location of the spectrum (i.e., in the continuum at λ'), and B is the same ratio at the wavelength λ where τ is to be measured. This measuring technique was found to be most effective if one scans slowly over the range of a line and uses a mechanical chopper to obtain ratios B for various locations over the line profile. A variation in B over the line profile indicates appreciable optical depth which may readily be corrected to the optically thin case if τ stays below about 1.0. For all lines below 5500 Å, the optical depth remained below 0.05, requiring minor corrections at most. But for some of the long-wavelength lines in the 7400–9000-Å range, we encountered optical depths as high as 0.3 near the line centers, even though we had the nitrogen plasma strongly diluted, i.e., we operated with an argon-nitrogen mixture of about 100 : 1.

With respect to the shift measurements, we defined the shift as the point which bisects the half-width. This point coincides with the point of maximum intensity (and lies on the symmetry axis), since the lines are symmetrical within the measurement precision. The shifts were measured in the following manner: We monitored the rotation of the grating lead screw on a specially added channel of the strip-chart recorder. Discrete steps were produced in a monitor signal which corresponded to certain positions of the monochromator lead screw. Tests with a microwave lamp showed that these signals could be reproduced very accurately, provided the direction of the scan motion was not altered. In principle, with such a setup it is possible to measure the shifts directed by first scanning over very precisely known spectral line positions and afterwards over the spectrum which contains the shifted lines.

As reported previously,[8] the spectrometer showed a slight periodic compression and dilation of the wavelength scale which, for the 1800-lines/mm grating we used, amounted to about ± 0.2 Å for every rotation of the screw, i.e., over a wavelength range of 30 Å. Since the shifts were expected to range between 0.2 and 2 Å, this technique could be successful only for reference lines close to the shifted lines. The potentially "best" reference lines fulfilling this condition are the unshifted lines themselves. We thus attempted to produce the nitrogen lines in a low-pressure microwave discharge and succeeded in observing the strong multiplets at 7450, 8200, and 8600 Å. Attempts to produce the other nitrogen lines failed, however. Therefore the shifts of these other lines were measured with a different technique, for which the above listed multiplets could be used as test cases.

Counter numbers from the monochromator were obtained for the line centers via the monitor signal on the strip chart and were plotted versus electron density (obtained by variation of the arc current); extrapolation to zero electron density yields the counter number of the unshifted line. This variation may immediately be converted into a shift (in angstrom units), since the number of angstrom units per counter number is known. A small amount of nonlinearity enters into the functional dependence of shift on density due to the variation in arc temperature. We estimated the error of the shifts caused by the temperature dependence using the theoretical data of Benett and Griem[6,7] and found changes of the order of 1–2% for all but the $3s\,^2P$-$4p\,^2S^o$ multiplet. The somewhat stronger predicted temperature dependence in the latter case causes an additional uncertainty, which has been taken into account in the error estimates.

III. RESULTS AND DISCUSSION

Stark profile and half-width and shift measurements were carried out for practically all lines of 11 N I multiplets. The profiles of all overlapping lines (as well as some others) were analyzed with the earlier-described curve-fitting technique, using the digital data recorded on magnetic tape. An illustration of the end-on line-profile measurements is shown in Fig. 1, where the Stark profiles for the three lines of the $3s\,^4P$-$3p\,^4S^o$ multiplet are superposed. The intensities for the three (isolated) lines have been scaled by the inverse LS-coupling intensity ratios (1 : 2 : 3 for 7468 : 7442 : 7423 Å). Thus in this presentation the measured points overlap completely and may be fitted to the same Lorentzian profile. The three lines approximate the Lorentzian shape very well and yield the same half-widths, within the experimental precision.

For the multiplet discussed above as well as for $3s\,^2P$-$4p\,^2S^o$, side-on and end-on runs were carried out. As an example of a comprehensive side-on measurement, Fig. 2 shows Stark profiles for the 7468-Å line for four different radial positions, corresponding to the four indicated electron densities. The comparison of end-on and side-on measurements revealed no significant differences in the Stark widths and shifts for the two different modes of observation, and we have therefore carried out the bulk of the measurements in the simpler end-on mode. An indication of the good agreement between side-on and end-on measurements may be obtained from Fig. 3, where, for the two above-mentioned multiplets, the (full) half-widths are plotted versus the shifts, and the end-on data are identified by circles, while side-on results are listed as triangles.

As another example of line-profile measurements, Fig. 4 illustrates the case of three partly overlapping lines of the $3s\,^4P$-$3p\,^4D^o$ multiplet. This multiplet was studied in an argon plasma with a small N_2 admixture to minimize the optical depth. Still, the optical depth was found to be non-negligible and thus was determined at every wavelength point with the earlier-described mirror technique. After correcting the intensity values to the optically thin case (the largest correction being 15%) and subtracting the continuous background (which was obtained from a pure argon plasma at the same electron density), the measured points were fitted to a sum of three Lorentzian profiles, and excellent agreement has been obtained as far out in the

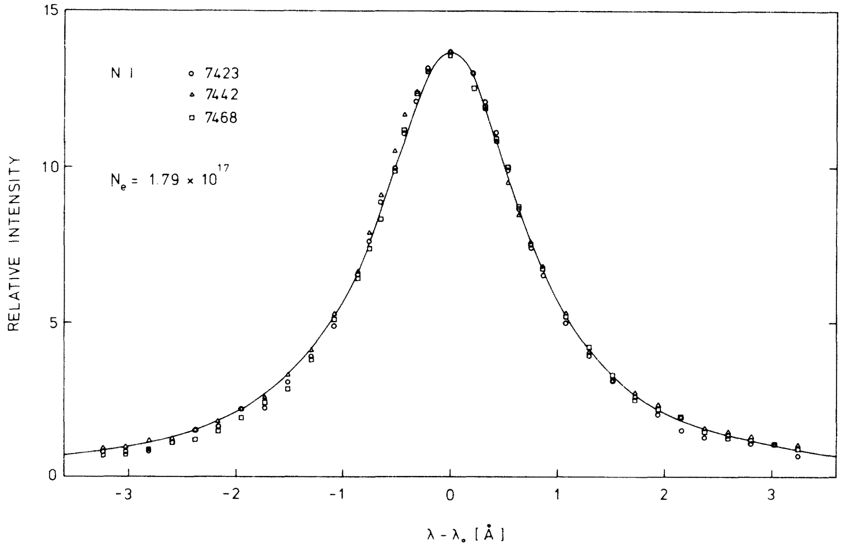

FIG. 1. Profiles for the three lines of the $3s\,^4P$-$3p\,^4S^o$ multiplet from end-on measurements. The intensity scales for the three lines differ by the inverse LS-coupling intensity ratios, i.e., 1:2:3 for 7423:7442:7468 Å. The three line shapes thus become identical within the experimental precision. They have been fitted to a Lorentzian profile, which they approximate very closely.

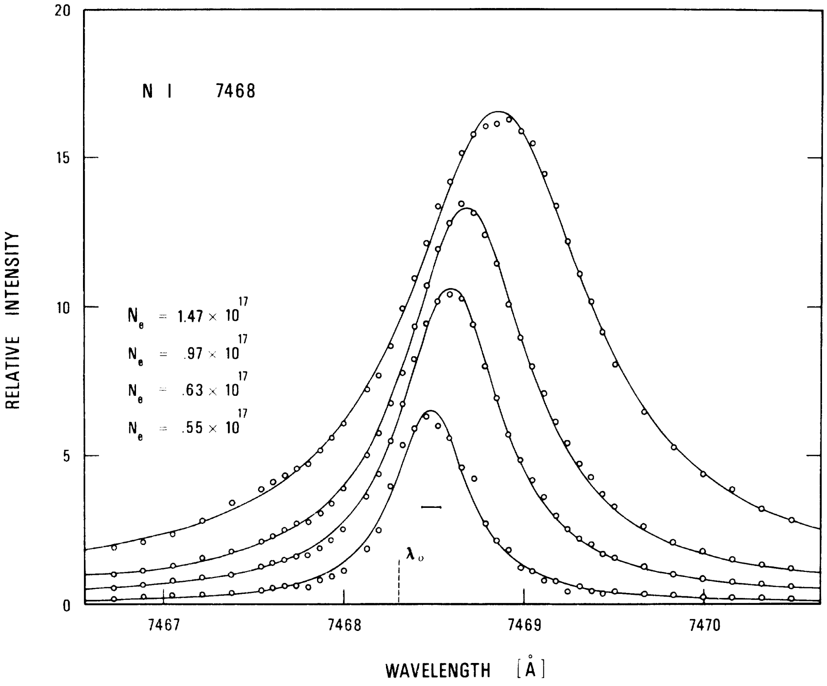

FIG. 2. Stark profiles for the 7468-Å line (one of the lines given in Fig. 1) from side-on measurements for four different radial positions, corresponding to the indicated electron densities (N_e). The measured points are again fitted to Lorentzian profiles, with very close fits resulting. The vertical broken line shows the position λ_0 of the unshifted line for $N_e \rightarrow 0$. The horizontal bar indicates the half-width of the apparatus profile.

wings as measurements have been made.

According to the theoretical work by Griem and co-workers,[7,18,19] the line profiles are primarily determined by electron impact broadening, which yields symmetrical Lorentzian line shapes. Ion broadening, treated by Griem and co-workers with a static approximation, leads to some additional broadening and causes an asymmetry in the profile, lifting the line wing in the direction of the shift.

Generally, we have found that the nitrogen lines adhere to symmetrical Lorentzian shapes in the investigated electron density range, which indicates negligible influence of ion broadening for our experimental conditions. This observation is supported by our results on the widths and shifts (see Fig. 3 and below), where the better agreement with theory is obtained when the ion contribution is neglected there. The result is also consistent with the theoretical predictions for our conditions, as will be discussed in more detail later. Our results are, however, in disagreement with the findings of Morris *et al.*,[3] who obtain pronounced differences between their measurements and Lorentzian profiles for the $3s\,{}^4P$-$3p\,{}^4D^o$ multiplet (i.e., the lines of Fig. 4) and the multiplet $3s\,{}^4P$-$3p\,{}^4S^o$. Their observed deviations from Lorentzian shapes may be explained by insufficient corrections for the optical depth for the case of the first multiplet. Stampa[2] has also observed small asymmetries, but indicates that these may be due to inhomogeneous end

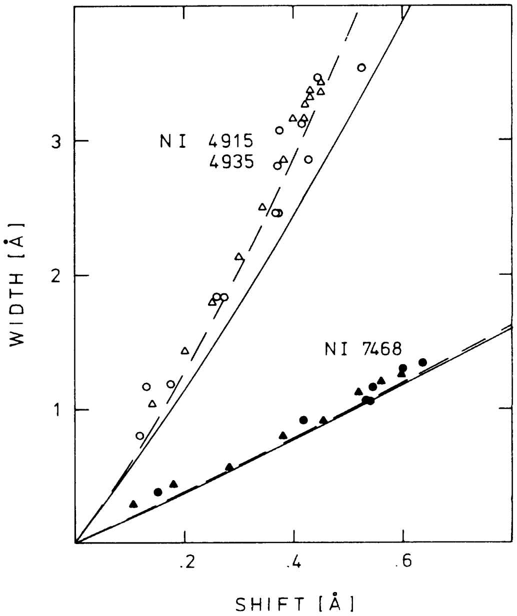

FIG. 3. Line shifts vs full half-widths for some lines of $3s\,{}^2P$-$4p\,{}^2S^o$ and $3s\,{}^4P$-$3p\,{}^4S$ multiplets. Side-on measurements (triangles) are seen to agree very closely with end-on measurements (circles). The theoretical shift-to-width ratios are presented in two ways, with the ion-broadening contribution included (solid lines) and the electron impact broadening only (broken line). The shifts are given on an absolute scale; they are red shifts for N I 7468 Å, but blue shifts for N I 4915/4935 Å.

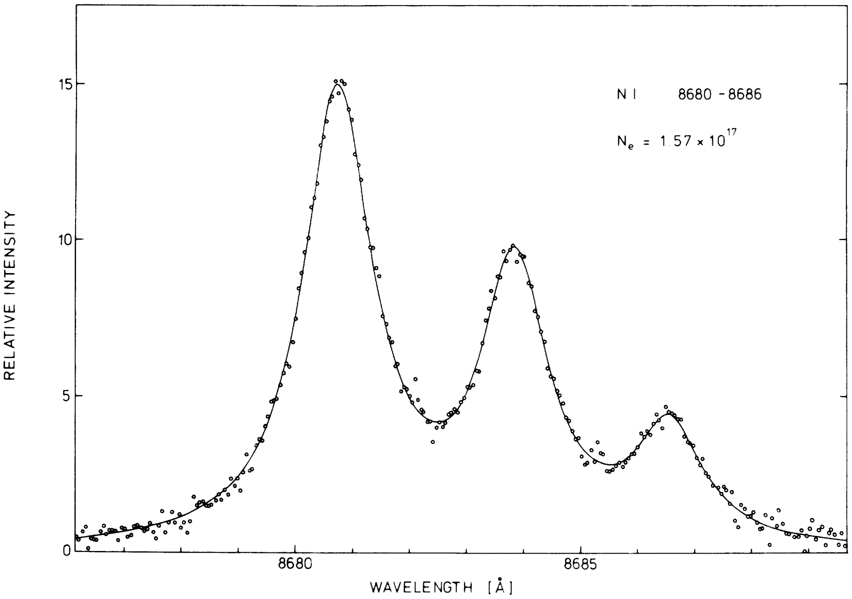

FIG. 4. Fit of the three partly overlapping lines of the $3s\,{}^4P$-$3p\,{}^4D^0$ multiplet with Lorentzian profiles (fitted according to the LS-coupling line strengths and assuming identical half-widths).

layers of his plasma.

Figure 3 illustrates a first comparison with the theoretical Stark-broadening data of Benett and Griem.[6,7] These authors performed large-scale numerical calculations on the basis of the generalized impact approximation developed by Griem *et al.*[18] The calculations by Benett and Griem supersede earlier similar calculations by Griem[15] and include numerous small improvements which have the effect of increasing the calculated widths for the investigated N I lines by a few percent compared to the earlier results. An exception is the $3p\,{}^2S^o$-$3d\,{}^2P$ multiplet, where the calculated width is decreased by about 20%, which definitely yields better agreement with the experiment. For the shifts, however, the changes between the earlier theoretical data[15] and the recent tabulated material[6,7] are much greater, with differences of 50% or more in both directions. The new theoretical shift data represent a substantial improvement.

The general theoretical results for the Stark (half) half-width w_{th} and shift d_{th} are[7]

$$w_{\text{th}} \approx w_e + 1.75A(1-0.75R)w_e, \tag{2}$$

$$d_{\text{th}} \approx d_e \pm 2.00A(1-0.75R)w_e. \tag{3}$$

The sign in the shift equation is equal to that of the low-temperature limit for d. The parameter R is a measure of the importance of Debye shielding and ion-ion correlations,[7] and R was, for the conditions of this experiment, always calculated to be below the required limit of $R \lesssim 0.8$. The electron impact width w_e, the shift d_e, and the ion-broadening parameter A (i.e., a measure of the relative importance of ion broadening) are tabulated in Refs. 6 and 7. (The two tabulations contain essentially identical data. Where small differences exist, we have used the data from Ref. 7.) As Griem has discussed in detail,[7] A should be in a range $0.05 \lesssim A \lesssim 0.5$. For the investigated N I multiplets, the A's are in the range from 0.02 to 0.09 for our experimental conditions. Thus according to the theory the application of the ion-broadening term is

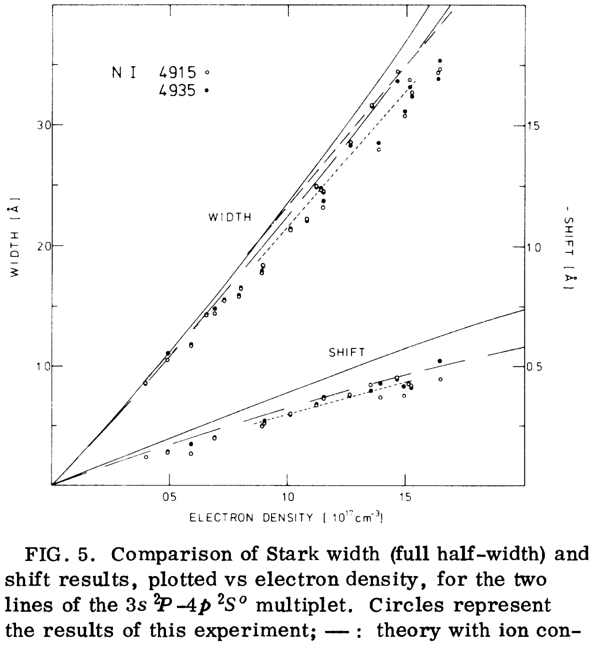

FIG. 5. Comparison of Stark width (full half-width) and shift results, plotted vs electron density, for the two lines of the $3s\,{}^2P$-$4p\,{}^2S^0$ multiplet. Circles represent the results of this experiment; —— : theory with ion contribution included ($0.02 < A < 0.06$); — — : theory without ion contribution; ... : Nubbemeyer and Wende's measurement (Ref. 4); ---: Stampa's measurements (Ref. 2); -·-: Shumaker's measurements (Ref. 5).

TABLE II. Experimental results.

		Plasma parameters		Measured Stark parameters[b]	
Multiplet (No.)[a]	Wavelength[a] (Å)	Temperature range (K)	Electron density range (10^{17} cm^{-3})	Full half-width w (Å)	Shift[c] d (Å)
$3s\,^2P$-$3p'\,^2D^o$ (10)	4099.94 4109.95 4113.98[d]	11 700–13 220	0.59–1.15	4.23–8.32	(−0.82)–(−1.59)
$3s\,^4P$-$4p\,^4S^o$ (6)	4137.64 4143.43 4151.48	11 700–14 160	0.59–1.49	0.87–2.30	0.39–0.98
$3s\,^4P$-$4p\,^4P^o$ (5)	4214.80 4216.10 4218.86 4222.10 4223.13 4224.88 4230.47[e]	11 650–13 780	0.57–1.36	0.77–1.72	0.15–0.36
$3p\,^2P^o$-$3d'\,^2S$ (135)	4385.53 4392.42	11 700–14 640	0.59–1.64	0.48–1.52	0.20–0.57
$3s\,^2P$-$4p\,^2S^o$ (9)	4914.94 4935.12	11 040–14 640	0.40–1.64	0.80–3.44	(−0.12)–(−0.48)
$3p\,^2P^o$-$3s''\,^2S$ (131)	5401.46 5411.89	11 700–14 640	0.59–1.64	0.34–0.95	(−0.17)–(0.47)
$3s\,^4P$-$3p\,^4S^o$ (3)	7423.64[f] 7442.29 7468.31	11 270–14 780	0.45–1.79	0.39–1.52	0.19–0.77
$3s\,^4P$-$3p\,^4P^o$ (2)	8184.87[e] 8188.02 8200.36 8210.72 8216.35 8223.14 8242.39	11 370–14 280	0.45–1.64	0.38–1.32	0.16–0.58
$3s\,^2P$-$3p\,^2P^o$ (8)	8567.74[f] 8594.01 8629.24 8655.89	11 650–13 550	0.54–1.35	0.67–1.70	0.29–0.73
$3s\,^4P$-$3p\,^4D^o$ (1)	8680.28[f] 8683.40 8686.15 8703.25 8711.70 8718.83 8728.89 8747.36	11 370–14 600	0.45–1.74	0.40–1.57	0.12–0.47
$3p\,^2S^o$-$3d\,^2P$ (15)	9028.92[f] 9060.47	11 750–14 250	0.61–1.52	2.37–5.44	1.19–2.96

[a] Wavelength data and multiplet numbers are given by C. E. Moore, NSRDS-NBS 3 (U.S. GPO, Washington, D.C., 1975), Sec. 5.

[b] Total error, mainly from plasma diagnostics, is estimated to be in the range 10–12% for the widths (except for multiplet No. 15, where it is 15%) and 12–14% for the shifts (except for multiplets 8 and 9, where it is 16% and 19%, respectively).

[c] Negative numbers indicate "blue" shifts; all other shifts are red shifts.

[d] This line could not be investigated.

[e] Only the 4230.35-Å line was measured in the listed electron density range; all other lines were measured relative to this line at lower electron densities.

[f] All lines of this multiplet were measured in an argon plasma with a small nitrogen admixture to avoid self-absorption.

questionable. We therefore present the theoretical data both with the A value included and by omitting it ($A=0$), i.e., we set $w_{\text{th}}=w_e$ and $d_{\text{th}}=d_e$ (electron impact parameters only).

Returning now to Fig. 3, it is observed that the agreement between experiment and theory is best if the ion contribution is neglected ($A=0$, broken line). It should be noted that the plasma analysis does not enter sensitively (not at all for the 7468-Å line) into the presentation of results in this figure.

Figure 5 shows a comparison of measured and calculated widths and shifts for the $3s\,^2P$-$4p\,^2S$ multiplet as a function of the (experimentally determined) electron density. The graph includes the earlier measurements by Stampa,[2] Nubbemeyer and Wende,[4] and Shumaker.[5] The agreement between all experiments is quite close, certainly within the mutual error limits. The theoretical shift data are more affected by the inclusion or exclusion of the ion-broadening parameter A than the width data and are thus seen to be primarily responsible for the differences in Fig. 3.

All other results of our Stark-width and -shift measurements are presented in Table II. Numerous individual measurements have been made within the temperature and density ranges given by the upper and lower limits in the table. The experimental points have been fitted to a straight-line dependence on electron density, as predicted by the theory, and the end points of this straight line correspond to the listed temperature and electron density values. Shifts to shorter wavelengths, i.e., "blue" shifts, are identified by a minus sign. The measured broadening parameters, presented only once for each multiplet, are averaged values for the lines in a multiplet. Unless noted in the table, we have measured *all* lines in each multiplet and obtained *identical* results within our measurement precision.

In Table III we compare our data (subscript m) with theory (th) and other measurements. The ratios $w_{\text{expt}}/w_{\text{th}}$ and $d_{\text{expt}}/d_{\text{th}}$ represent data for the end points of the same electron density interval as for our measured values above. Two sets of experiment/theory ratios are listed for those multiplets for which theoretical comparison data are available; the top numbers represent the ratios based on theoretical data which include the ion contribution, and in the numbers immediately below the ion contributions are omitted from the theoretical values. The omission of the calculated ion contribution gives slightly improved ratios, in almost all cases, over the whole electron density range. [At the upper end, A is largest ($0.03<A<0.09$).] It is also seen that the agreement between this experiment and theory is better at smaller electron densities (first number) than at the higher electron densities, but the experimental Stark-width values always stay below the theoretical ones.

The remaining columns of Table III contain comparisons with other experimentally determined Stark widths and shifts. The agreement, except for Stampa's shift data[2] for the 4392-Å line, is within the mutually estimated error limits. The Stark-width data by Morris *et al.*[3] are their averages over over several lines in a multiplet. The differences for the individual lines in a multiplet are appreciable, up to 20%, and seem to indicate the presence of some self-absorption in their experiment, since the strongest lines in the multiplets usually possess the largest Stark widths. If one would take the width data of Morris *et al.*[3] for the weakest lines only, the agreement would improve by about 10%. We have no explanation for the discrepancy between our shift data and Stampa's for the 4392-Å line.

In Table IV we present our recommended experimental Stark-width and -shift parameters for temperatures around 10 000 K and electron densities in the range 10^{16}–10^{17} cm^{-3}. (The parameters are reduced to an electron density of 10^{16} cm^{-3}.) These values are about 10–20% smaller than the theoretical parameters.

In addition to the profile and shift and width measurements, other subjects of our study have been (a) possible differences in the Stark broadening for lines within a multiplet, (b) the temperature dependence of the line-broadening parameters, and (c) possible systematic trends in the theoretical parameters with the quantum numbers of the involved transitions, especially the upper atomic states.

(a) In two earlier experimental Stark-broadening studies on nitrogen,[3,4] appreciable differences for the widths of different lines in the same multiplet were found. The largest measured difference was 24%, while theory predicts identical Stark widths for all lines in a multiplet. We have therefore carried out numerous measurements on individual lines in multiplets, with the general result that we do not confirm the earlier experiments. Instead, we have found that the linewidths in multiplets agree within ± 2% (standard deviation of a measurement). Figure 1 may serve as an example of our results. For the shifts we have found the same result, although within somewhat larger error limits.

(b) Since theory predicts a dependence of the shift/width ratio (d/w) with temperature (d/w depends on the temperature only, and this fact has been proposed as a technique for plasma temperature determinations[20]), we investigated this ratio for the $3s\,^2S$-$4p\,^2P$ multiplet, where the most precise measurements could be made. Within the rel-

TABLE III. Comparisons with theory and other experiments. The comparisons with theory have been made for the end points of the electron density and temperature ranges listed in Table II and the comparisons with other experiments have been made at the following electron densities: Morris *et al.* (Ref. 3): 1.6×10^{17} cm^{-3}; Nubbemeyer and Wende (Ref. 4): 0.8×10^{17} cm^{-3}; Stampa (Ref. 2): average over the electron density range $(0.86\text{–}1.52)\times10^{17}$ cm^{-3}; Shumaker (Ref. 5.): average over the electron density range $(0.40\text{–}1.64)\times10^{17}$ cm^{-3}.

Multiplet (No.)	Wavelength (Å)	Ratios: experiment/theory		Comparison with other experiments			
		$w_{\text{expt}}/w_{\text{th}}$	$d_{\text{expt}}/d_{\text{th}}$	$w_{\text{expt}}/w_{\text{Morris}}$	$w_{\text{expt}}/w_{\text{Stampa}}$	$w_{\text{expt}}/w_{\text{Nubbemeyer}}$	$d_{\text{expt}}/d_{\text{Stampa}}$
$3s\,{}^2P\text{-}3p'\,{}^2D^o$	4099.94					0.97	
(10)	4109.95						
$3s\,{}^4P\text{-}4p\,{}^4S^o$	4137.64	0.81–0.78 [a]	0.96–0.92 [a]				
(6)	4143.43					0.91	
	4151.48	0.86–0.84 [b]	1.06–1.05 [b]				
$3s\,{}^4P\text{-}4p\,{}^4P^o$	4214.80						
(5)	4216.10						
	4218.86	0.81–0.70 [a]	1.09–1.05 [a]				
	4222.10					0.83 [c]	
	4223.13	0.83–0.72 [b]	1.21–1.18 [b]				
	4224.88						
	4230.47						
$3p\,{}^2P^o\text{-}3d'\,{}^2S$	4385.53						
(135)	4392.42				0.94		1.62
$3s\,{}^2P\text{-}4p\,{}^2S^o$	4914.94	0.91–0.84 [a]	0.73–0.77 [a]				
(9)	4935.12	0.96–0.89 [b]	0.84–0.97 [b]	... [d]	0.96	0.96	0.99
$3p\,{}^2P^o\text{-}3s''\,{}^2S$	5401.46						
(131)	5411.89				0.89		1.00
$3s\,{}^4P\text{-}3p\,{}^4S^o$	7423.64	0.82–0.74 [a]	0.77–0.77 [a]				
(3)	7442.29			0.91			
	7468.31	0.86–0.78 [b]	0.82–0.82 [b]				
$3s\,{}^4P\text{-}3p\,{}^4P^o$	8184.87						
(2)	8188.02						
	8200.36	0.84–0.75 [a]	0.88–0.85 [a]				
	8210.72			0.80			
	8216.35	0.88–0.79 [b]	0.92–0.89 [b]				
	8223.14						
	8242.39						
$3s\,{}^2P\text{-}3p\,{}^2P^o$	8567.74						
(8)	8594.01	0.81–0.78 [a]	0.72–0.71 [a]				
	8629.24	0.85–0.82 [b]	0.76–0.75 [b]	0.75			
	8655.89						
$3s\,{}^4P\text{-}3p\,{}^4D^o$	8680.28						
(1)	8683.40						
	8686.15						
	8703.25	0.90–0.83 [a]	0.84–0.81 [a]				
	8711.70	0.92–0.86 [b]	0.89–0.86 [b]	0.80			
	8718.83						
	8728.89						
	8747.36						
$3p\,{}^2S^o\text{-}3d\,{}^2P$	9028.92	0.89–0.78 [a]	0.89–0. 87 [a]				
(15)	9060.47	0.96–0.85 [b]	0.96–0.96 [b]	0.75			

[a] Ion-broadening contribution is included in theoretical data.

[b] Ion-broadening contribution is excluded from theoretical data, i.e., $w_{\text{th}}=w_e$, $d_{\text{th}}=d_e$.

[c] Comparison is made with the mean value of five lines of this multiplet measured by Nubbemeyer and Wende (Ref. 4).

[d] For multiplet No. 9 a comparison with Shumaker's data (Ref. 5) is available and a ratio $w_{\text{expt}}/w_{\text{Shumaker}}=0.89$ is obtained.

TABLE IV. Recommended experimental Stark-broadening parameters for the electron density range (3×10^{16})–(3×10^{17}) cm^{-3} and temperatures of 10 000–16 000 K. w and d are given for a nominal electron density of 10^{16} cm^{-3}.

Multiplet (No.)	Wavelength (Å)	$2w_{\rm expt}$	$d_{\rm expt}$	Multiplet (No.)	Wavelength (Å)	$2w_{\rm expt}$	$d_{\rm expt}$
$3s\,^2P$-$3p'\,^2D^o$	4099.94	0.719	−0.138	$3s\,^4P$-$3p\,^4S^o$	7423.64	0.085	0.043
(10)	4109.95			(3)	7442.29		
	4113.98				7468.31		
$3s\,^4P$-$4p\,^4S^o$	4137.64	0.152	0.066	$3s\,^4P$-$3p\,^4P^o$	8184.87	0.081	0.036
(6)	4143.43			(2)	8188.02		
	4151.48				8200.36		
$3s\,^4P$-$4p\,^4P^o$	4214.80	0.130	0.027		8210.72		
(5)	4216.10				8216.35		
	4218.86				8223.14		
	4222.10				8242.39		
	4223.13			$3s\,^2P$-$3p\,^2P^o$	8567.74	0.125	0.054
	4224.88			(8)	8594.01		
	4230.47				8629.24		
$3p\,^2P^o$-$3d'\,^2S$	4385.53	0.089	0.034		8655.89		
	4392.42			$3s\,^4P$-$3p\,^4D^o$	8680.28	0.090	0.027
$3s\,^2P$-$4p\,^2S^o$	4914.94	0.207	−0.029	(1)	8683.40		
(9)	4935.12				8686.15		
					8703.25		
$3p\,^2P^o$-$3s''\,^2S$	5401.46	0.058	−0.029		8711.70		
	5411.89				8718.83		
					8728.89		
					8747.36		
				$3p\,^2S^o$-$3d\,^2P$	9028.92	0.371	0.195
				(15)	9060.47		

atively small temperature range of this experiment, better agreement with theory is obtained when only the electron impact broadening is considered, as illustrated in Fig. 6.

(c) For the numerical calculations of nitrogen Stark-broadening parameters, Benett and Griem have applied approximation methods of atomic theory, specifically, the Coulomb approximation by Bates-Damgaard,[21] to calculate the necessary matrix elements. Since the main contributions are given by the transitions between the upper state and nearby perturbing levels, one would expect that this this central-field approximation works very well. Still, there might be noticeable differences for different quantum states. To check this experimentally, we have included as many quantum states as possible in our measurements. In Figs. 7 and 8 we plot experimental versus theoretical width and shift parameters and have identified the upper states of the investigated multiplets by the respective quantum bumbers. Within our range of $3p$, $3d$, and $4p$ states, no trend is noticeable, i.e., the use of the Coulomb approximation appears to be very adequate.

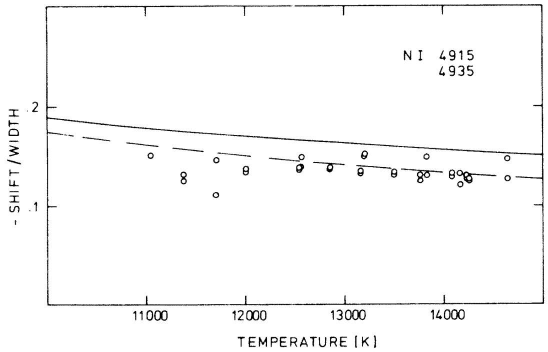

FIG. 6. Dependence of the shift/width ratio on temperature for the $3s\,^2P$-$4p\,^2S^o$ multiplet. ○: experimental points; —: theory with ion contribution included; ---: electron impact theory only.

IV. ERROR DISCUSSION

Uncertainties in our data originate from a number of factors which may be grouped into three categories: (a) statistical measurement errors, (b) uncertainties in the plasma diagnostic tech-

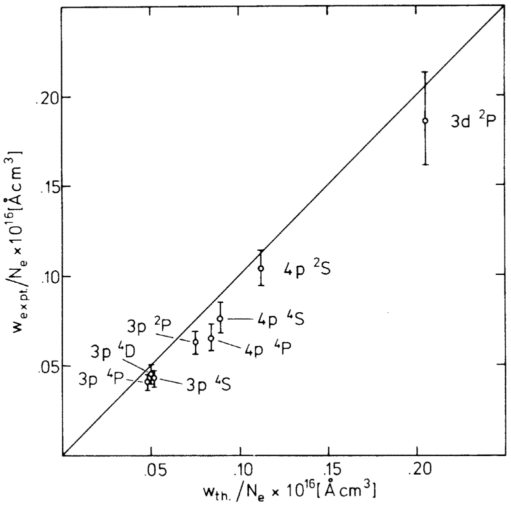

FIG. 7. Experimental vs theoretical width parameters (electron impact theory only). The upper atomic states of the investigated multiplets are identified.

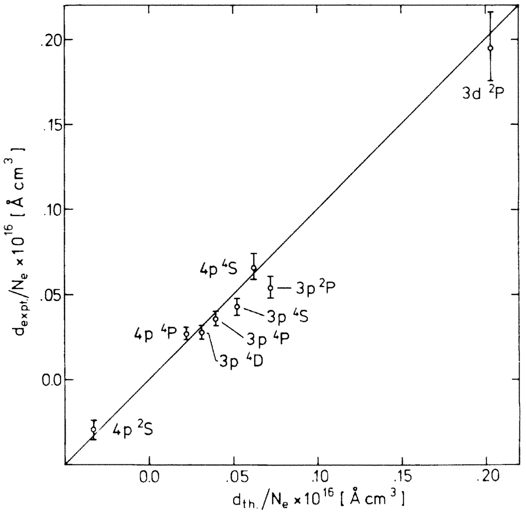

FIG. 8. Experimental vs theoretical shift parameters (electron impact theory only). The upper atomic states of the investigated multiplets are identified.

nique, and (c) uncertainties in the Stark-width and -shift analysis.

The measurement errors were obtained via standard statistical techniques, utilizing the fairly large number of measurements. The uncertainties (standard deviations of the mean values) range from 1% to 4% for the widths and 1% to 5% for the shifts. (However, for the weak multiplet $3s\,^4P$-$3p\,^4D^o$, the standard deviation for the shift amounts to 10%.)

The accuracy of our experimental data is principally limited by uncertainties in the plasma diagnostic technique and, specifically, by the uncertainty in the applied experimental relation[8] between the hydrogen H_β Stark width and the electron density. According to a recent general comparison by Wiese *et al.*[8] of all theoretical and experimental data on this width-density relationship, we have estimated this uncertainty to be about 10% over the range of this experiment. Two other non-negligible uncertainties arising from the plasma diagnostics are an uncertainty in our temperature determination of about 5% and the imprecision in the actual H_β width measurement of about 2%.

Main uncertainties in the nitrogen-line Stark-width and -shift determinations, aside from the above-discussed statistical measurement errors, stem from the corrections for other broadening mechanisms and self-absorption and from the assumption of a homogeneous plasma volume. As the comparison of broadening mechanisms in Table I shows, Stark broadening is by far the dominant mechanism, and corrections for other broadening contributions—Doppler and instrumental broadening—are usually of the order of 3% or less, with uncertainties in these corrections an order of magnitude smaller and therefore negligible. For the lowest electron densities these corrections grow, however, to about 20%, so that uncertainties reach about 2%. Self-absorption has always been checked with the earlier-discussed mirror technique and has been minimized by diluting the nitrogen plasma with argon for some measurements. For the case of the $3s\,^4P$-$3p\,^4D^o$ multiplet, where it becomes appreciable, the uncertainty resulting from the correction in the width is estimated to be at most 3%. The assumption of a homogeneous plasma layer for the end-on measurements has been checked by the side-on/end-on comparison of the data. It is cautiously estimated that deviations from homogeneity cause uncertainties in the widths and shifts that do not exceed 5%.

By treating all of these uncertainties as independent errors, we arrive at total errors in the ranges 10–12% for the widths and 12–14% for the shifts. (Three exceptions are listed in Table II.) These can can be further reduced in the future if more accurate data for the main source of the uncertainties, the H_β Stark-broadening parameter, become available.

V. SUMMARY

The principal results of this Stark-broadening study of nitrogen lines may be summarized as follows:

(1) The Stark widths and shifts for different lines in a multiplet agree within the precision of the experiment (precision for the relative widths ≈ 3%), as predicted by the theory.

(2) The line shapes are symmetrical profiles of the Lorentzian type. Consistent with the theoretical predictions, no asymmetries—which would be an indication of ion-broadening contributions—could be detected.

(3) Our experiment confirms, for the most part, the earlier, less comprehensive Stark-width and -shift measurements by Stampa,[2] Morris *et al.*,[3] Nubbemeyer and Wende,[4] and Shumaker.[5] Exceptions are Stampa's shift measurement of the 4392-Å line, the asymmetrical profiles measured by Stampa[2] and Morris *et al.*,[3] and the differing widths for lines in the same multiplet measured by Morris *et al.*[3]

(4) The experimental width and shift data agree well with theory,[6,7] and better agreement is obtained without including the small (and doubtful) calculated ion-broadening contributions. This is consistent with the line profile observations [point (3) above], where no indication of ion-broadening contributions was found. It is also consistent with theoretical criteria, according to which the ion-broadening parameters of the investigated multiplets are so small that their inclusion is a borderline case.

(5) Our measurements on a number of transitions involving different quantum numbers show no trends compared to the calculated data, indicating that the atomic theory applied in the line-broadening calculations—at its current level of approximation—covers the range of the involved quantum states very adequately.

ACKNOWLEDGMENT

One of us (V.H.) would like to thank the Deutsche Forschungsgemeinschaft for support during his stay at the U. S. National Bureau of Standards.

---

*Permanent address: Institut für Experimentalphysik, Universität Kiel, Kiel, Germany,

[1] N. Konjevic and J. R. Roberts, J. Phys. Chem. Ref. Data (to be published).

[2] A. Stampa, Z. Astrophys. 58, 82 (1963).

[3] J. C. Morris, R. U. Krey, R. L. Garrison, AVCO Corporation, Space Systems Division, Report No. AVSSD-0049-68-RR, 1968 (unpublished).

[4] H. Nubbemeyer and B. Wende, Z. Angew. Phys. 27, 214 (1969).

[5] J. B. Shumaker, J. Quant. Spectrosc. Radiat. Transfer 14, 19 (1974).

[6] S. M. Benett and H. R. Griem, University of Maryland Technical Report No. 71-097, 1971 (unpublished).

[7] H. R. Griem, *Spectral Line Broadening by Plasmas* (Academic, New York, 1974).

[8] W. L. Wiese, D. E. Kelleher, and D. R. Paquette, Phys. Rev. A 6, 1132 (1972).

[9] W. L. Wiese, D. E. Kelleher, and V. Helbig, Phys. Rev. A 11, 1854 (1975).

[10] D. R. Paquette and W. L. Wiese, Appl. Opt. 3, 291 (1964).

[11] For a review of this method see, e.g., W. L. Wiese, in *Methods of Experimental Physics*, edited by B. Bederson and W. L. Fite (Academic, New York, 1968), Vol. 7B, Chap. 10.

[12] J. B. Shumaker and C. H. Popenoe, J. Res. Natl. Bur. Stand. (U.S.) A 76, 71 (1972).

[13] D. Garz, Z. Naturforsch. A 28, 1459 (1973).

[14] W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities*, NSRDS-NBS 4 (U.S. GPO, Washington, D.C., 1966), Vol. I.

[15] H. R. Griem, *Plasma Spectroscopy* (McGraw-Hill, New York, 1964).

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

[17] W. L. Wiese, in *Plasma Diagnostic Techniques*, edited by R. H. Huddlestone and S. L. Leonard (Academic, New York, 1965), Chap. 6.

[18] H. R. Griem, M. Baranger, A. C. Kolb, and G. Oertel, Phys. Rev. 125, 199 (1962).

[19] H. R. Griem, Phys. Rev. 128, 515 (1962).

[20] D. D. Burgess, Phys. Lett. 10, 286 (1964).

[21] D. R. Bates and A. Damgaard, Philos. Trans. R. Soc. Lond. A 242, 101 (1949).