Asymmetry patterns of plasma-broadened isolated lines (C I)

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We have measured detailed profiles of plasma-broadened neutral-carbon lines, utilizing a wall-stabilized arc source and a specially designed data acquisition and processing system. We analyzed the lines in terms of symmetric Lorentzian profiles in order to isolate the deviations due to asymmetries and found regular patterns of an antisymmetric nature around the line centers. The asymmetry patterns have a common shape with a minimum, maximum, and zero crossing at the same points on a reduced wavelength scale, but they vary widely in their amplitudes. These findings are in excellent qualitative agreement with the quasistatic theory of ion broadening due to the quadratic Stark effect. A comparison and match of experimental and theoretical amplitudes has thus been used to determine the ion broadening parameters of these lines, which are in satisfactory agreement with directly calculated values.

I. INTRODUCTION

According to Stark broadening theory,[1] the shapes and shifts of plasma-broadened isolated lines of neutral atoms are mainly determined by electron impacts with the radiating atoms, and a smaller contribution arises from the electric microfields generated by the—essentially static—plasma ions. While electron-impact broadening produces a symmetrical, shifted profile of the Lorentzian type, the ion contribution—primarily due to the quadratic Stark effect—introduces asymmetries as well as additional contributions to the width and shift of the profile.

Excited atoms in a plasma are subject to the quadratic Stark effect due to the electric microfields generated by the slow moving ions and thus experience small changes in their excitation energies. Since the interaction with other energy levels is repulsive, and since there are usually more nearby interacting levels above a given excited level than below, the levels are normally shifted to smaller values. This effect is normally much more pronounced for the upper level of a transition since its sensitivity to the perturbing electric microfields is much greater than that of the more tightly bound lower level. Therefore, the transitions are most often shifted to lower frequencies, i.e., they exhibit red shifts. The distribution of electrical microfields in a plasma due to the various ion perturber configurations not only leads to an effective shift and width but also introduces asymmetries into the line profile, which are superimposed on the symmetrical electron-impact-broadened line shape. Actually, magnetic sublevels should suffer slightly different shifts but these differences have been estimated to be very small.[1] Therefore, they are averaged over in current Stark broadening theory and no differences are expected in the general form of the asymmetries due to the different spectroscopic structures of various upper levels.

In fact, the only *atomic* variable entering into the calculations is the ion broadening parameter which contains a sum of matrix elements for electric dipole transitions between the upper and lower levels of the transition and nearby perturbing levels. Stark broadening theory, as introduced by Griem *et al.*,[2,3] calculates this ion broadening parameter A (at first called α) which, at the level of refinement for this theory, is a constant for all lines within a multiplet. This theory has also provided normalized line profiles, numerical values for the electron width and shift, and asymptotic wing formulas for both the line wings.

Asymmetries in Stark-broadened lines have been observed in a number of experiments and have been the subject of special studies by Roder and Stampa[4] on helium, Kelleher[5] on helium, Goly and Grabowski[6] on carbon, Nubbemeyer[7] on nitrogen, and Brandt, Helbig, and Nick[8] on krypton. The goals of these experiments have been to compare all or parts of the experimental and theoretical profiles and to determine values for the ion broadening parameter A.

In several experiments,[4,5,8] approximate values for A have been obtained by comparing the intensity of the two line wings at the wavelength positions $\lambda_0+\Delta\lambda$ and $\lambda_0-\Delta\lambda$, where λ_0 is the position of the line center. According to the theoretical asymptotic wing formulas, this ratio may be used to determine values of A.[4] This approach does not yield precise values for A, however, due to the circumstance that the data are taken at positions far from the line center in the extended wings where the line intensities are generally smaller than the intensity of the underlying continuum radiation. Thus the accurate determination of this background intensity becomes a critical issue. Very often, contributions from the wings of neighboring lines complicate the situation.

Nubbemeyer[7] has made a direct comparison of measured and calculated asymmetries. For four N I lines with very large asymmetries, he compared experimental and theoretical profiles for the wavelength region near the line centers. By defining and applying an asymmetry function, he isolated the asymmetrical parts of the profiles and has found good agreement for three lines, but a significant deviation for the fourth one. Goly and Grabowski[6] compared their complete experimental profiles for the lines of the $2p\,3s\ ^3P^o$–$2p4p\ ^3P$ multiplet at 4770 Å with calculated synthetic spectra for this multiplet and found good agreement for $A=0.070$ at an electron density of 7×10^{16} cm^{-3} and a temperature of 10 500 K.

For our experimental work on several C I lines with a steady-state stabilized arc source, we have developed a powerful data acquisition and processing system so that we could perform very detailed measurements of the plasma-broadened line shapes, isolate the asymmetries, and perform comparisons with theory. We have found significant asymmetries near the line centers and have determined the ion broadening parameter A by a comparison and match of the asymmetries in theoretical and experimental profiles. We observed that the only variable for the various lines is the amplitude of the asymmetries, while the other features remain remarkably constant, as predicted by theory.

II. INSTRUMENTATION AND METHOD

We have recently described[9] our experimental setup and the measurement techniques in detail so that we may confine the following discussion to items of particular relevance to the present measurements. We employed a wall-stabilized arc of 88-mm length and 4.2-mm channel diameter which we operated at atmospheric pressure and for currents between 45–60 A. For the observation of the carbon lines we used in the midsection of the arc carbon dioxide admixed with argon in various concentrations, covering the range from 100 vol % CO_2 to 10 vol % CO_2, and operated the arc with pure argon in the electrode areas. Furthermore, we admixed traces of hydrogen (0.1–1 vol %) with the working gas in order to determine the electron density from measurements of the Stark width of the hydrogen Balmer line H_β.

The plasma was always observed end-on and its enlarged image was focused by a concave mirror onto the entrance slit of a 2.25-m Czerny-Turner monochromator. A rectangular diaphragm limited the effective aperture to about $f/80$, and the entrance slit of the monochromator was masked to a height of 0.6 mm so that only a narrow region along the central axis of the arc was observed. For the alignment of the system a laser was placed behind the exit slit of the monochromator in order to retrace the entire optical path. The monochromator, equipped with an 1800-line/mm holographic grating, had a linear dispersion of 2.4 Å/mm. Both the entrance and exit slits were set at 22.5 μm which produced an instrumental linewidth [full width at half maximum intensity (FWHM)] of about 0.05 Å.

The spectral radiance was measured by a photomultiplier with a broadband GaAs photocathode, which was cooled to 243 K for improved dark current and higher stability. After amplification and conversion to voltage signals, the data were recorded on-line with a minicomputer which also controlled the monochromator scanning operation. Complete line profiles were obtained by stepwise scanning with a 5-s digital integration time for each step to measure precisely up to 200 points across the spectral range of a line. Corrections for minor dark-current variations were made, and changes in the spectral sensitivity of the system were routinely corrected for by utilizing a calibrated tungsten strip lamp as a transfer standard. Each line was scanned at least seven times to minimize statistical errors. Self-absorption effects were found to be negligibly small for all investigated lines.[9]

III. PLASMA ANALYSIS

A large part of the analysis of the asymmetries does not require knowledge of the plasma conditions, but for the comparison with theory the plasma electron density (N_e) and the temperature (T) must be known. We have determined the electron density by measuring the Stark width of the hydrogen line H_β and by applying the theoretical relationship between the two quantities derived from the Stark broadening theory.[10] This relationship is now accurately established, as several recent experiments have shown.[11–13] Under the assumptions that the plasma is in local thermodynamic equilibrium (LTE) and that the initial gas mixture ratios are conserved, the usual plasma equilibrium and conservation equations can be applied and yield the temperature for known pressure and electron density.[14]

The assumption of LTE appears to be fully justified since our measured electron density is above the critical limit, established by recent experimental and theoretical work.[15,16] The assumption of conservation of the gas-mixture ratios,[14,17] while not correct, nevertheless serves as a sufficiently good approximation for the temperature determination. This follows because the elements involved (Ar, H, C, and O) have rather similar ionization potentials, so that even large "demixing" effects would cause only small changes in the temperature. Furthermore, due to the relatively weak temperature dependence of both the electron-impact half-width and the ion broadening parameter, the temperature enters much less sensitively into the experiment-theory comparisons than the electron density.

IV. ASYMMETRY PATTERNS

We carried out very detailed, highly precise recordings of the plasma-broadened profiles of numerous lines of neutral argon and carbon, employing as many as 200 individual data points per line profile. We have clearly seen asymmetries, which are best observed by fitting the experimental profiles with a least-squares procedure to a (symmetrical) Lorentzian profile and by analyzing the residual deviations of the data points from the "best-fit" Lorentzian. Figure 1 shows this situation graphically for two separate scans of the C I line at 5052.2 Å. It contains not only the experimental data points, their best-fit Lorentzians, and the nearly flat continuum background, but also the residual deviations of the data points from the composite fitted curves. Starting from the line center, the longer wavelength side exhibits for this line first negative and then positive deviations from a symmetrical curve, and finally a gradual return to zero with almost the exact opposite deviations occurring for shorter wavelengths. While these deviations are quite small, at most of the order of 2% of the peak value of the line, they are very reproducible from scan to scan. Figure 2, a compos-

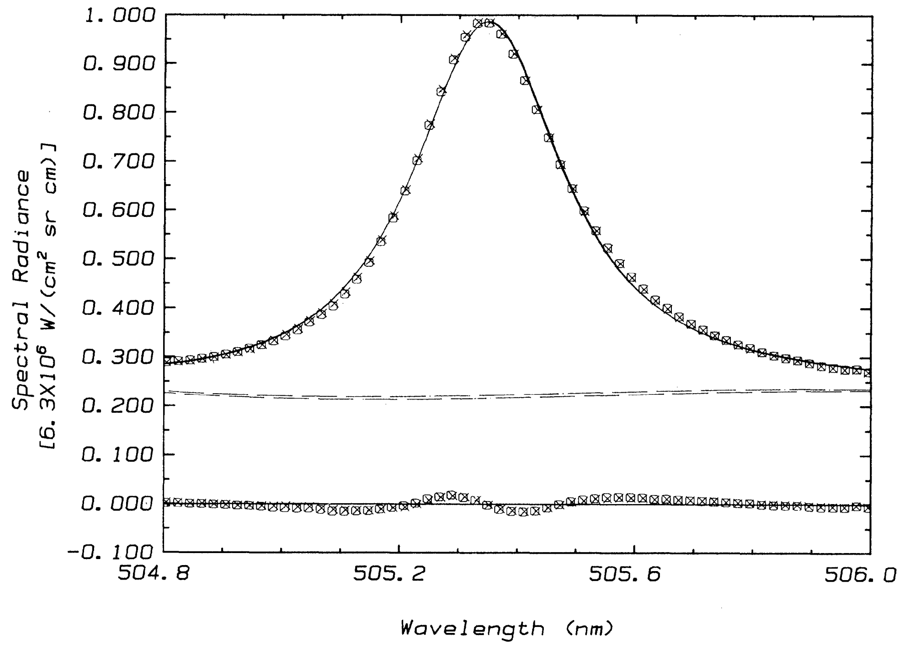

FIG. 1. Two scans of the C I 5052.2-Å line taken under the same plasma conditions (crosses and open squares) and an illustration of the least-squares procedure which yields the residual deviations used in the asymmetry analysis. The solid line (actually two completely overlapping lines) represents the least-squares fit synthetic spectra which are composed of a Lorentzian profile and continuum background radiation (approximated by a cubic polynomial) indicated by the two dot-dashed (—·—) lines. At the bottom of the figure the residual deviations are plotted which are obtained by subtracting the fitted symmetric spectrum from the data points. These small deviations clearly show the characteristic "damped oscillations" about the baseline which are the result of asymmetries in the measured line profiles.

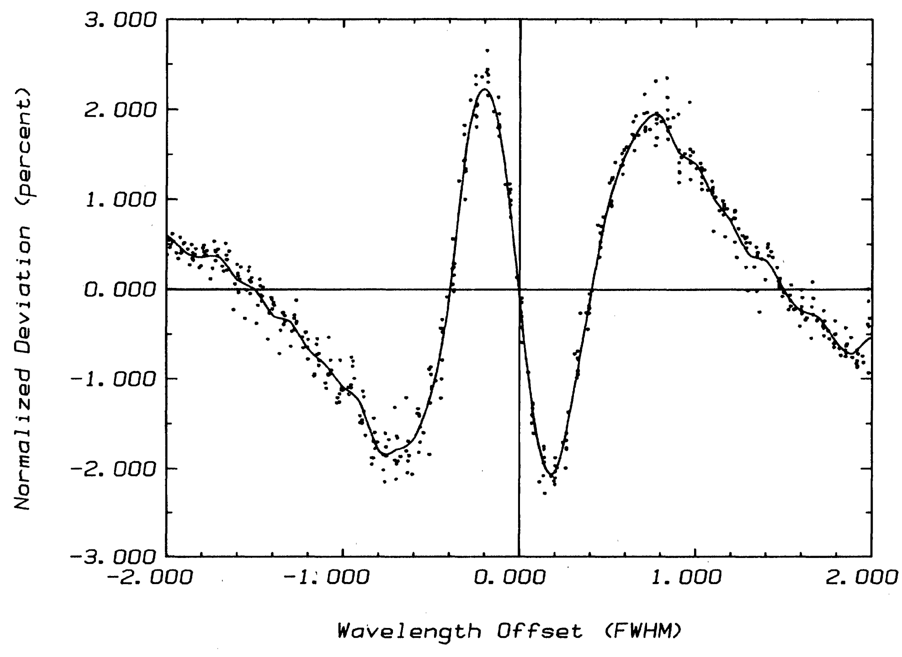

FIG. 2. Normalized deviations, given as percentage of the peak spectral radiance of the least-squares-fit Lorentzian, for eight separate scans of the C I 5052.2-Å line under slightly varying plasma conditions. The deviations are plotted as a function of the wavelength distance from the peak of the corresponding least-squares-fit Lorentzian in units of its half-width (FWHM). Also given is the smoothed average (solid line). The deviations are obtained by subtracting the least-squares-fit synthetic spectra from the spectral radiance measurements.

ite graph for eight individual scans of the 5052.2 Å line used in Fig. 1, illustrates the quality of such data for the residual deviations.

Electron densities and temperatures were determined repeatedly throughout the course of this experiment. Electron densities ranged from 7.4×10^{16} cm^{-3} to 8.3×10^{16} cm^{-3} and temperatures from 11 350 K to 12 730 K. The individual scans of Fig. 2 were carried out at various conditions within this limited range, but are reduced to the same scale by normalizing them in terms of the half-width and peak radiance.

In order to exclude any possibility that this oscillating behavior of the deviations might be somehow caused by the monochromator and its scanning system, we have run the scanning sequence in reverse order but obtained the same effect. Also, we have investigated a number of different lines occurring at different wavelengths and possessing quite different half-widths. For all of them, the same pattern of deviations from a symmetrical profile is observed, which demonstrates the existence of a true physical effect and precludes any possible accidental correlation with the experimental apparatus.

For quantitative studies the normalized deviations $\Delta(\delta\lambda)$ of the data points from the fitted Lorentzian may be expressed as

$$\Delta(\delta\lambda)=\frac{I(\lambda_0+\delta\lambda)-L(\lambda_0+\delta\lambda)}{L(\lambda_0)}, \tag{1}$$

where $I(\lambda)$ is the observed spectral radiance profile, and $L(\lambda)$ is the corresponding least-squares-fit Lorentzian. The observed antisymmetric nature of the deviations suggests that they should be decomposed into symmetric,

$$\Delta_s(\delta\lambda)=\tfrac{1}{2}[\Delta(\delta\lambda)+\Delta(-\delta\lambda)], \tag{2}$$

and antisymmetric,

$$\Delta_a(\delta\lambda)=\tfrac{1}{2}[\Delta(\delta\lambda)-\Delta(-\delta\lambda)], \tag{3}$$

functions of the wavelength distance $\delta\lambda=\lambda-\lambda_0$ from the line center wavelength λ_0 obtained for the fitted Lorentzian.

These antisymmetric and symmetric deviation functions are given in Fig. 3 for the same line we utilized earlier. The wavelength scale is a reduced scale, given in units of the full width at half maximum intensity obtained for the fitted Lorentzian. It is seen that the deviations are almost entirely of antisymmetric character, and this has been found to be true for every investigated line.

We have found very similar patterns for the deviations for all investigated C I lines, which are illustrated in the composite picture (Fig. 4), which shows the antisymmetric deviation functions for eight lines of the C I 3*s*-4*p* transition array observed in this study (the symmetric deviation functions for all these lines are always zero to within the precision of these measurements). The amplitudes of the deviations change, but the characteristic shape of these functions remains essentially constant, with a well-defined minimum at about 0.15–0.2 FWHM, a zero-crossing at about 0.4 FWHM, and a broad maximum around 0.7 FWHM. While the three singlet transitions are fairly well isolated, the lines of the triplet multiplets are all blended to some degree. Thus the deviation data become less reliable beyond about 0.5 FWHM. In the case of the 4771.7-

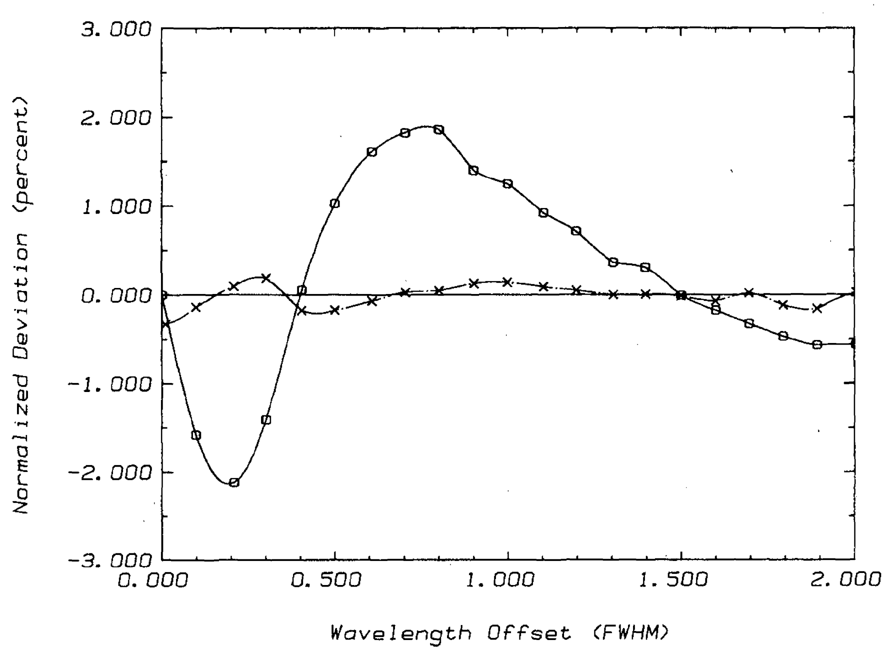

FIG. 3. Symmetric and antisymmetric deviation functions, Eqs. (2) and (3), for the average deviations of the C I 5052.2-Å line. The solid line represents the smoothed average of the antisymmetric part of the normalized deviations from the least-squares-fit Lorentzian. The open squares along this curve indicate the values of the discrete averages taken over intervals of about 0.1 FWHM. The symmetric part of the normalized deviations, indicated in the same fashion by the dot-dashed line and the crosses, is seen to be essentially zero within the experimental precision.

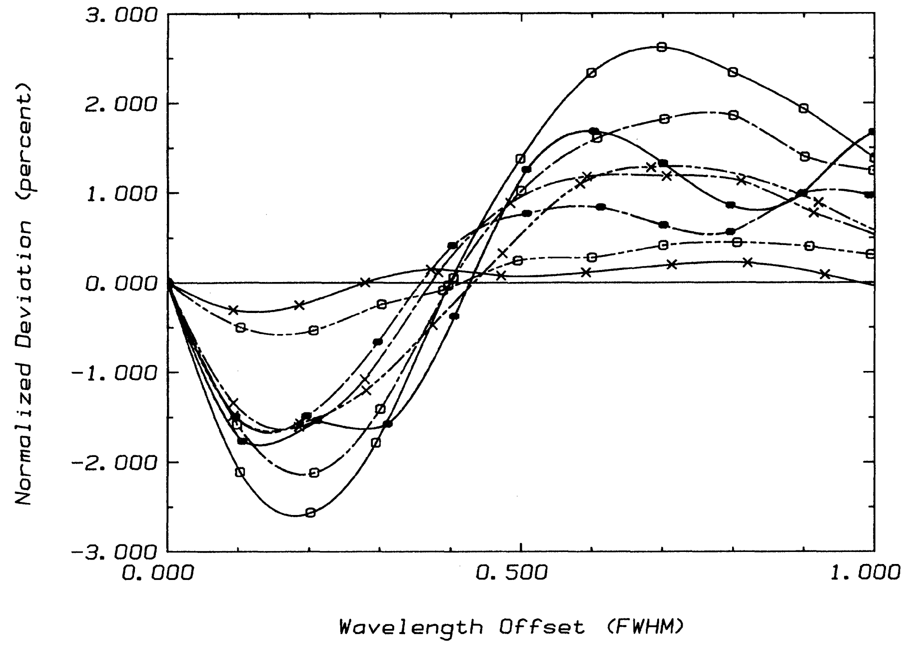

FIG. 4. Antisymmetric parts of the normalized deviations for eight lines of the 3*s*-4*p* transition array of C I. The three curves marked by open squares correspond to the singlet transitions of this array: the solid line is for the 4932.0-Å line; the short-long dashed line is for the 5052.2-Å line; and the short-short-long dashed line is for the 5380.3-Å line. The two curves marked by closed ovals correspond to transitions of the triplet *P*-*S* multiplet: the solid line is for the 4826.8-Å line and the short-long dashed line is for the 4817.4-Å line. The three curves marked by crosses correspond to transitions of the triplet *P*-*P* multiplet: the solid line is for the 4771.7-Å line; the short-long dashed line is for the 4775.9-Å line; and the short-short-long dashed line is for the pair of blended lines at 4762.3 and 4762.5 Å.

Å line the blending with the weak line at 4770.0 Å is so severe that the entire deviation pattern is probably not reliable. Furthermore, the rather large degree of random variation for the two lines of the $3s\,^3P^o$-$4p\,^3S$ triplet is mostly due to the fact that these lines are rather weak.

In spite of these limitations, it is apparent from the experimental data that the different atomic properties of the various transitions are reflected only in the various amplitudes of the asymmetries. Thus the neglect, by the theory, of effects of the splitting of levels with different magnetic quantum numbers by the ion fields seems to be fully justified within the precision of the experimental data.

V. COMPARISON WITH THEORY

Griem developed in 1962 a Stark broadening theory for isolated lines of heavy elements in plasmas[3] and calculated general line profiles [1] $j_{A,R}(x)$ where x is the wavelength distance $\Delta\lambda$ from the line center, shifted by the electron-impact shift d, and divided by the electron-impact half half-width (HWHM), i.e., $x=(\Delta\lambda-d)/(\Delta\lambda_{\rm HWHM})$. ($R$ is the Debye shielding parameter,[3] which is about 0.55 for this experiment.) Griem showed that electron-impact broadening is the main cause of this line broadening, and ion broadening due to quadratic Stark effect increases the line width and shift slightly, and introduces asymmetries into the otherwise symmetrical, Lorentzian-shaped profile. His calculated profiles are very general functions which apply to all isolated lines with ion broadening parameters A in the range $0.05<A<0.5$, and the atomic structure enters only through A. We analyzed his tabulated theoretical profiles[1] in the same manner as described for the measured ones and found the same type of deviations, again with maxima and minima and nodes at practically the same positions, as in the experimental data (Fig. 5). The ion broadening parameter enters only into the amplitudes of the deviations, as is seen by varying its magnitude. The overall agreement between experimental and theoretical patterns is excellent, but due to the limited scope of Griem's tabulations[1] (they cover only the range -1 to $+2.5$ FWHM) a detailed quantitative comparison is difficult.

It should be noted that while our measurements and theory are in agreement that the maxima and minima and nodes of the asymmetries occur *always* at the same locations, Nubbenmeyer[7] found that of four vacuum ultraviolet (vuv) N I lines he analyzed, one line had a node at a location significantly different from theory.

VI. DETERMINATION OF THE ION BROADENING PARAMETER

Since experimental and theoretical profiles are in such close overall agreement, one obtains a new approach to determine ion broadening parameters A by measuring the magnitudes of the minima of the antisymmetric deviations and utilizing the theoretical correlation between A and these minima. In order to apply this approach, we

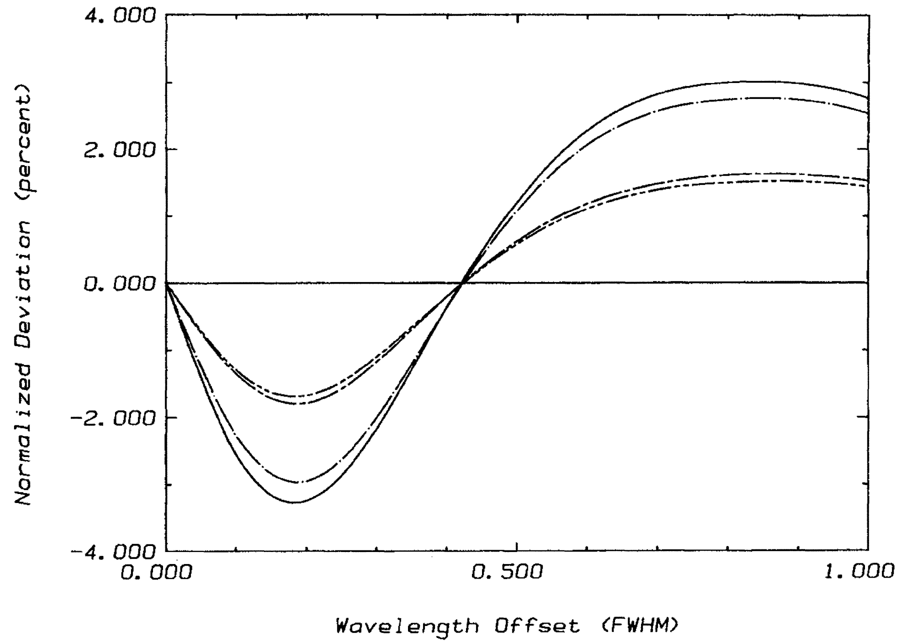

FIG. 5. Antisymmetric parts of the deviations obtained by analyzing the theoretical profiles tabulated by Griem (Ref. 1) in the same fashion as the measured data. The solid line corresponds to the theoretical profile for ion broadening parameter $A=0.2$ and plasma parameter $R=0.4$; the dot-dashed line to $A=0.2$ and $R=0.6$; the short-long dashed line to $A=0.1$ and $R=0.4$; and the short-short-long dashed line to $A=0.1$ and $R=0.6$.

determined the amplitudes of the minima of the theoretical curves for various values of A and R (see Fig. 5) and obtained, by interpolation, general correlations between these minima and A for various R. The A values corresponding to the measured minima are compared in Table I with those directly calculated by Griem[1] with dipole matrix elements obtained from the Coulomb approximation.[18]

While the agreement is very good for the well-isolated singlet transitions, large deviations occur for the triplet lines. This is not surprising, however, since—as noted earlier in the discussion of Fig. 4—random uncertainties in the data for the relatively weak $^3P^o$-^3S transitions are substantial, and appreciable systematic uncertainties also arise as a result of blending within these multiplets. In particular for the C I line at 4771.7 Å, the blending with

TABLE I. Comparison of experimental and theoretical line-shape data. Typical range of experimental conditions: $N_e=(7.4-8.3)\times10^{16}$ cm^{-3}, $T=11\,350-12\,230$ K (mean values $N_e=7.93\times10^{16}$ cm^{-3}; $T=11\,600$ K). Debye shielding and ion-ion correlation parameter $R\approx0.55$.

Transition array	Multiplet	Wavelength (Å)	Stark half-width (FWHM)[a] $\Delta\lambda_{meas}$	$\Delta\lambda_{calc}$	Ion broadening parameter A A_{meas}	A_{calc}
$2p\,3s$-$2p\,4p$	$^1P^o$-^1D	5052.2	3.08±6%	3.08	0.129±15%	0.102
	$^1P^o$-^1P	5380.3	2.29±5%	2.17	0.030±20%	0.032
	$^1P^o$-^1S	4932.0	3.90±6%	4.90	0.164±15%	0.136
	$^3P^o$-^3S	4812.9	1.68±15%	2.08		0.034
		4817.4	1.92±10%	2.08	0.097±30%	0.034
		4826.8	1.88±10%	2.08	0.096±30%	0.034
	$^3P^o$-^3P	4771.7	2.08±10%	2.28	(0.016)	0.083
		4766.7	2.04±15%	2.28		0.083
		4775.9	2.09±10%	2.28	0.094±30%	0.083
		4770.0	1.75±25%	2.28		0.083
		4762.5		2.28	0.096±30% (4762.5 and 4762.3)	0.083
		4762.3		2.28		0.083

[a]Corrections of the total measured width for Doppler and instrumental broadening have been made, but are very small (< 1% of total). Contributions due to van der Waals and resonance broadening were estimated to be negligibly small.

the weaker line at 4770.0 Å is so severe that the measured A value may be completely unreliable and, thus, is only given in parentheses in the table. For the other lines of these multiplets (at 4812.9, 4766.7, and 4770.0 Å), the combination of weak signals and strong blending precludes the evaluation of any reasonable values for A.

The results for the well-isolated, strong singlet lines include a case with an A value below 0.05 where the theory may not be applicable because quadrupole interactions might become significant. Nevertheless, the agreement in this case is very good, both for A and the Stark halfwidth.

Generally, the results of Table I indicate that the utilization of the amplitude of the measured asymmetry pattern is a potentially accurate and versatile technique for measuring values of the ion broadening parameter A for a broad range of atomic transitions. Since the crucial range of measurement lies close to the core of the lines (within 1 FWHM of the line center), and since the technique does not require accurate measurements of the weak far wing radiances, it may be applied to fairly weak lines with substantial continuum background, and to lines with nearby neighboring lines, provided the degree of blending is not too severe.

VII. CONCLUSIONS AND SUMMARY

In summary, our detailed measurements of plasma broadened C I line profiles yield the following general results and conclusions.

(i) A regular pattern of deviations from a symmetrical Lorentzian profile exists for all investigated lines.

(ii) The only variation in the patterns is their amplitude, while the maxima, minima and nodes in the deviations remain at the same positions on a reduced wavelength scale.

(iii) The amplitude of the patterns is directly related to the theoretical ion broadening parameter A.

(iv) The agreement with the theoretical asymmetry pattern is very close.

(v) The agreement between calculated ion broadening parameters and those derived from measured amplitudes utilizing the theoretical profiles is very satisfactory over the whole range of measured A's ($0.03 < A < 0.16$), considering difficulties due to overlapping lines, etc.

(vi) Also, there is no difference in the asymmetry pattern for a well-isolated line with $A < 0.05$, nor is there any discernible tendency for this line to have an overall measured Stark width that is appreciably larger than calculated. Thus it appears that the theory can be extended to include A values smaller than 0.05.

(vii) The variation of the gas mixtures from 100 vol % CO_2 to a 10 vol % CO_2 in Ar produces an appreciable change in the mass of the perturber ions and the reduced mass of the "radiator-perturber" system thus changes by a factor of about 1.5. Within this limited range no changes in either the asymmetry patterns or the widths of the profiles have been noticed which could possibly indicate ion dynamic effects. This is consistent with recent theories,[1,19] which indicate that ion dynamic effects should be negligible at the densities and temperatures of this experiment.

ACKNOWLEDGMENTS

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