

⁹S. Feneuille, *J. Phys. (Paris)* **28**, 61 (1967).¹¹S. Feneuille, *J. Phys. (Paris)* **28**, 315 (1967).¹⁰B. Wybourne, private communication (Paris). 1968.¹²B. R. Judd, *Physica* **33**, 174 (1967).

Self-Broadening of Cesium Resonance Lines at 8521 and 8944 Å*

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Absorption profiles of cesium resonance lines at 8521 and 8944 Å have been measured for the wavelength range from 0.5 to 30 Å from the line centers using a tungsten ribbon light source, cell lengths L from 0.31 to 6.1 cm, and Cs densities N from 2×10^{14} to 2×10^{16} cm⁻³. The wavelength dependence of the absorption coefficients are consistent with a Lorentzian form and values of $\gamma f/N = 1.08 \times 10^{-7}$ and 0.30×10^{-7} cm³ sec⁻¹ are obtained for 8521 and 8944 Å lines. Here γ is the collisional (or Lorentzian) half-width and f is the oscillator strength. The values of $\gamma f/N$ deduced from total fractional absorption data agree with those determined from the line profiles. Our results agree well (to within 15%) with those of Gregory and with theory, but disagree with more recent data. A source of error in some previous determinations of half-widths is the fact that even when the calculated absorption is very large, the measured transmission at the line center is significant; about 3.5×10^{-2} compared to $\sim 10^{-100,000}$ predicted from our measurements in the wings of the lines for $N = 1.14 \times 10^{15}$ cm⁻³ and $L = 5.9$ cm. This effect is shown to result from transmission through the monochromator at wavelengths in the far wings of the instrument function.

I. INTRODUCTION

The broadening of cesium resonance lines, Cs 8521 Å ($6^2P_{3/2} - 6^2S_{1/2}$) and Cs 8944 Å ($6^2P_{1/2} - 6^2S_{1/2}$), due to collisions with Cs atoms has been studied by several investigators. However, there is a two-order-of-magnitude discrepancy between the collisional half-widths¹ given by the early work of Gregory² and the recent data of Pollock and Jensen³ for the Cs 8521 Å resonance line. As pointed out by Reck, Takebe, and Mead,⁴ a significant difference between the two studies is in the method of interpretation of the data. Gregory² deduced the collisional half-width for the cesium resonance lines from the wings of the absorption line profile, while Pollock and Jensen³ obtained their value from the width at half maximum of the apparent absorption coefficient curve. This difference has led to the proposal⁴ that theories of collision broadening applicable in wings of the line are not valid near the resonance line center. Our objectives are to measure carefully the absorption coefficients in the same spectral range as in the earlier experiments and to determine accurate values for the self-broadening collision frequencies for the lowest resonance states of cesium. In the course of this work we have found one possible cause of the disparity among the frequencies for self-broadening collisions obtained in previous experiments. The experimental apparatus and procedures are reported in Sec. II. A theoretical treatment of the experiment is presented in Sec. III, and the results are given in

Sec. IV. Section V contains a discussion of the present work and its relation to earlier work.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

A schematic diagram of the experimental arrangement is shown in Fig. 1. It consists of a light source, an absorption cell, and a photoelectric detection system. The light source is a 100-100-W tungsten-strip projection lamp (Westinghouse EDW), which is housed in a blackened aluminum box and is powered by a current-regulated (0.01%), dc power supply. The lamp has brightness temperature of 2490°K as measured by a calibrated Leeds and Northrup optical pyrometer. Light emitted from this lamp is collimated by an

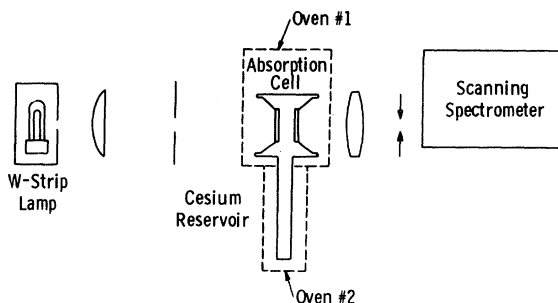


FIG. 1. Schematic diagram of the experimental setup.

achromatic lens (2-in. diam and 2.5-in. focal length) and is further intercepted by an iris, so that a beam of ~1-in. diam and ~40-min divergence is formed. After passing through the absorption cell, this beam is collected by another achromatic lens (178-mm focal length) and focused on the entrance slit of a Jarrel-Ash model 82-000 half-meter Ebert scanning spectrometer. The spectrometer was used in first order to study the wavelength range of 8000 to 9000 Å with a dispersion of 32 Å/mm. A glass filter (Corning No. 2403, C.S. 2-58) was used to absorb radiation at wavelengths below 6400 Å, and so eliminate radiation transmitted by the spectrometer in higher orders. With a curved slit and a 590 grooves/mm grating (52 × 52 mm ruled area and blazed for 7500 Å) the spectrometer has the expected resolution of approximately 0.4 Å in the first order at a 10-μ-slit setting. The resolution of the monochromator was checked in first order with a low-pressure mercury discharge lamp at 3131 and 5460 Å and with a helium-neon gas laser at 6328 Å. The instrument function $K(\delta\lambda)$ determined with the laser⁵ is shown in Fig. 2, and has a full width at half maximum of 0.4 Å. Here $\delta\lambda$ is the difference between the monochromator setting and the wavelength of the incident monochromatic radiation. The instrument function⁶ at 3131 and 5460 Å had the same full width at half maximum. The function shown in Fig. 2 is assumed to be independent of the monochromator setting⁶ and will be used later in interpreting and analyzing the measured absorption line profile. A selected low-noise⁷ photomultiplier (Dumont

1430) with S1 photocathode is located at the exit of the spectrometer. The signal is fed to a vibrating reed electrometer, and then to a recorder. In order to record the absorption line profile, a variable-ratio speed reducer has been coupled to the driving mechanism of the spectrometer and, together with the recorder, gives a dynamic range of 0.02–20 Å/in. scanning rate at the first order.

The design of the absorption cells is similar to that used by Pollock and Jensen.³ The main body of the absorption cell is made of 304 stainless steel. Two 1-in. diam sapphire windows are brazed to Kovar cups which, in turn, are heliarc-welded to the stainless-steel body. The inner surfaces of the two windows are made parallel, and their separation is measured with a micrometer. Four cell lengths, 0.317, 0.635, 5.89, and 6.1 cm, were used in the present experiments. No evidence of Cs absorption by the sapphire was observed.

The vacuum system is processed according to conventional high-vacuum technology.⁸ A few grams of doubly distilled cesium (initial purity 99.98%) in a Pyrex capsule are loaded into a crusher mechanism attached to the cell. The system is evacuated and outgassed at ~380°C for 12 to 18 hours. A vacuum of the order 10^{-9} Torr is achieved with a rate of rise of $\sim 10^{-10}$ Torr per minute at room temperature with the system closed-off from the pump. The cesium capsule is crushed, and the cesium is distilled into the reservoir directly below the cell. The absorption cell and the cesium reservoir are housed in two separately controlled ovens, and their temperatures are monitored by nine Chromel-Alumel thermocouples at strategic locations. Both the cell and the reservoir are enclosed by a heavy copper heat reservoir, and their temperatures remain constant to within 1°C over a period of a few hours. The temperature of the absorption cell varied from 550 to 610°K as the cesium reservoir was varied from 427 to 561°K.

The cesium vapor pressure was calculated from the expression given by Taylor and Langmuir,⁹ i. e.,

$$\log_{10} p = 11.0531 - (4041/T_r) - 1.35 \log_{10} T_r, \quad (1)$$

where p is the equilibrium cesium vapor pressure over the liquid in Torr, and T_r is the temperature of the cesium reservoir in °K. Equation (1) has been checked recently at relatively low cesium densities by Marino *et al.*¹⁰ using surface ionization method and by Rozwadowski *et al.*¹¹ using optical absorption techniques. Pressure equilibrium is assumed throughout the system so that the density of cesium vapor in the absorption cell N is

$$N = 9.66 \times 10^{19} p / T_c, \quad (2)$$

where T_c is the temperature of the cell in °K. In the present experiment the presence of dimers (Cs_2) can be ignored since the dimer concentration is estimated¹² to be always less than 0.7% that of the atomic Cs.

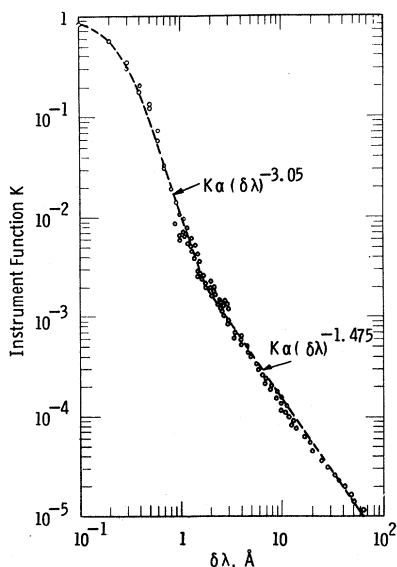


FIG. 2. Un-normalized instrument function of the Jarrel-Ash half-meter Ebert scanning spectrometer measured with helium-neon laser at 6328 Å and at 10-μ-slit setting. The spectrometer has a 590 groove/mm grating which is blazed for 7500 Å. The relatively large scatter in the experimental data at $\delta\lambda$ near 1.5 Å is due in part to oscillatory structure in $K(\delta\lambda)$. We have used smooth curves through the data in our calculations.

III. THEORY OF EXPERIMENT

If a parallel light of continuous spectrum with intensity $I_0(\lambda)$ is sent through an absorption cell of length L containing a homogeneous gas, the transmitted light intensity $I(\lambda)$ is given by the expression¹

$$I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)L}, \quad (3)$$

where $\alpha(\lambda)$ is the absorption coefficient. In the pressure region where collisional broadening is the dominant line-broadening mechanism,¹³ the absorption coefficient of the medium, neglecting the effect of hyperfine structure, can be represented by a dispersion relationship,¹

$$\alpha(\lambda) = (Ne^2f/mc)(\frac{1}{2}\gamma)/[(c/\lambda_0^2)^2(\lambda-\lambda_0)^2 + (\frac{1}{2}\gamma)^2]. \quad (4)$$

Here γ is the collisional half-width, f is the oscillator strength of the absorption line, m and e are the mass and charge of an electron, respectively, c is the velocity of light, and λ and λ_0 are the wavelengths of the incident light and the center of the absorption line, respectively. Under the condition

$$(c/\lambda_0^2)^2(\lambda-\lambda_0)^2 \gg (\frac{1}{2}\gamma)^2, \quad (5)$$

i. e., far from the line center, Eqs. (3) and (4) give

$$\frac{1}{N} \left[\frac{1}{L} \ln \frac{I_0}{I} \right]^{1/2} = \frac{e\lambda_0^2}{\sqrt{2m}c^{3/2}} \left(\frac{\gamma f}{N} \right)^{1/2} \frac{1}{(\lambda-\lambda_0)}. \quad (6)$$

The left-hand side of this equation is the square root of the apparent absorption coefficient divided by the gas density. This quantity varies inversely with $(\lambda-\lambda_0)$ if $\gamma f/N$ is a constant. Theoretical considerations¹³ predict that γ is proportional to the gas density if natural broadening is unimportant. This will be the case when¹ $\gamma \gg 5 \times 10^6 \text{ sec}^{-1}$ or $\gamma/N \gg 5 \times 10^6/N$ for the cesium resonance lines. This condition is readily satisfied in our experiments. Therefore, according to Eq. (6), a log-log plot of $N^{-1}[L^{-1} \ln I_0/I]^{1/2}$ versus $(\lambda-\lambda_0)$ should yield a straight line with a slope of -1 . The value of $\gamma f/N$ can be calculated from any point of this line.

The value of $\gamma f/N$ for an absorption line can also be determined from the total fractional absorption A , which is defined as the integral of the fractional absorption over the whole line. That is,

$$A = \int_0^\infty (1-I/I_0)d\lambda, \quad (7)$$

which, under the same conditions as for our application of Eq. (6), can be shown to be given by

$$A = (2\pi/mc^3)^{1/2} e\lambda_0^2 (\gamma f/N)^{1/2} NL^{1/2}. \quad (8)$$

According to Eq. (8), a plot of A against $NL^{1/2}$ for various Cs densities and cell lengths should give a straight line, and the value of $\gamma f/N$ can be deter-

mined from the slope of such a line. Equation (8) is a slight modification of one used previously¹ when the half-width of the dispersion broadened line is determined by natural broadening, and has been used recently¹⁴ to determine collisional widths. The quantity A in Eqs. (7) and (8) is also known as the equivalent width.¹⁵

The relations given by Eqs. (6)–(8) are derived under the assumption that the effective width of the transmission function of the monochromator is so small as to be negligible. However, the data of Fig. 2 shows that the monochromator transmission is measurable to wavelengths up to 60 Å from the center of a strong line. The measured spectral response of the instrument to monochromatic radiation $K(\delta\lambda)$ is related to the measured absorption line profile $I_m(\Delta\lambda)$ and the incident radiation $I_0(\lambda)$ by the equation

$$I_m(\Delta\lambda) = \int_0^\infty K(\lambda-\lambda_0-\Delta\lambda)I_0(\lambda)e^{-\alpha(\lambda)L}d\lambda, \quad (9)$$

where $\Delta\lambda$ is the setting of the monochromator relative to the center of the line. If Eqs. (6)–(8) are used for analysis of data, one effectively assumes that, for $\lambda-\lambda_0$ values of interest, $K(\delta\lambda)$ is narrow enough so that $\lambda-\lambda_0$ in Eqs. (6)–(8) can be replaced by $\Delta\lambda$. In the present discussion $K(\delta\lambda)$ is an even function of $\delta\lambda$, and is normalized such that

$$\int_{-\infty}^\infty K(\delta\lambda)d(\delta\lambda) = 1. \quad (10)$$

This normalization of K means that variations in the monochromator efficiency and the detector sensitivity are included in $I_0(\lambda)$. Fortunately, our conditions are such that the effective $I_0(\lambda)$ may be assumed to be constant for λ values near the lines of interest.¹⁶ This condition allows us to take I_0 out of the integral in Eq. (9). The differences between $I(\lambda)$ and $I_m(\Delta\lambda)$ have been investigated by Broderson¹⁷ and by Kostowski and Bass,¹⁸ but only for very idealized instrument functions or for small absorption at the line center.

The total fractional absorption of a line, taking the instrument function into account, is given by

$$A = \int_{-\infty}^\infty \int_0^\infty K(\lambda-\lambda_0-\Delta\lambda)(1-e^{-\alpha(\lambda)L})d\lambda d\Delta\lambda. \quad (11)$$

DePrima and Penner¹⁹ have shown that Eq. (11) reduces exactly to Eq. (7) when $K(\delta\lambda)$ and $\alpha(\lambda)$ are different from zero for only a limited range of $\delta\lambda$ and λ , and when the range of $\Delta\lambda$ is large enough to include all contributions to A . There does not appear to be any general investigation of the errors in A resulting when $\Delta\lambda$ is finite, but $\alpha(\lambda)$ and/or $K(\delta\lambda)$ approach zero slowly.²⁰

IV. RESULTS

Figure 3 shows several absorption profiles obtained for the 8521 Å and 8944 Å lines. We note that the lines are very symmetrical, and show no evidence of structure due to molecule formation such as found at higher Cs densities by Gregory.²

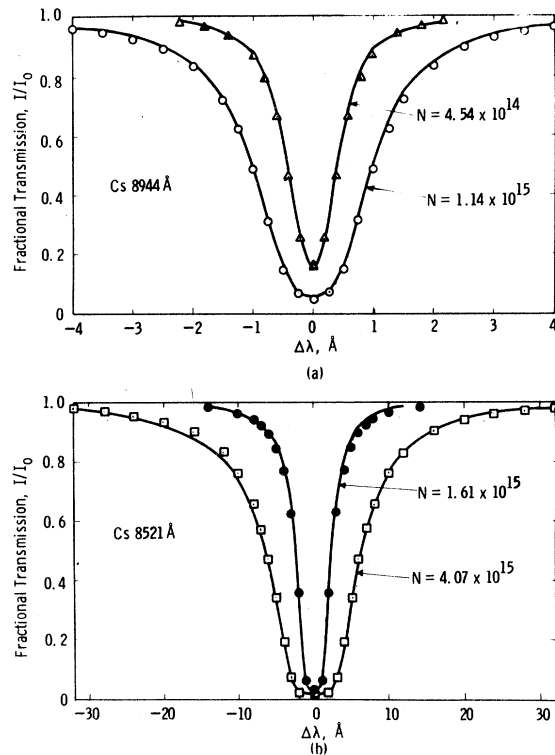


FIG. 3. Typical absorption curves for the (a) 8944 and (b) 8521 Å lines of Cs. The Cs densities are as marked and the cell length was 5.89 cm. The points are the results of calculations using Eq. (9).

The simplest way to check our hypothesis of dispersion broadening is to analyze data such as shown in Fig. 3, using Eq. (8). Our results will show that for $N \leq 10^{16} \text{ cm}^{-3}$ and $\Delta\lambda \geq 0.2 \text{ Å}$, $(c \Delta\lambda / \lambda_0)^2 \geq 100(\frac{1}{2}\gamma)^2$, so that the significant contributions to the integral in Eq. (7) come from portions of the line for which Eqs. (6) and (8) are valid. Figure 4 is a plot of the total fractional absorption versus $NL^{1/2}$ for four cell lengths and a range of cesium densities. The linear variation of A with $NL^{1/2}$ is considered as an experimental verification of the assumed Lorentzian line profile with a half-width proportional to the Cs density. The values of $\gamma f/N$ derived from the slope of these curves are: $1.04 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ for Cs 8521 Å ($6^2P_{3/2} - 6^2S_{1/2}$) and $0.30 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ for Cs 8944 Å ($6^2P_{1/2} - 6^2S_{1/2}$). A mean square precision of $\pm 4\%$ is assigned to these values and includes the effects of scatter in the data, uncertainties in reservoir temperature, and possible errors in the determination of A due to the finite scanning range.²⁰

A detailed examination of the wings of the line profiles can be made using Eq. (6), which shows that the square root of the absorption coefficient divided by the vapor density is inversely proportional to the difference of wavelength from the line center. Figures 5 and 6 are log-log plots of $N^{-1} \times [L^{-1} \ln(I_0/I)]^{1/2}$ versus $\Delta\lambda$ for Cs 8521 Å and for Cs 8944 Å lines, respectively. It can be seen that all data from the wings merge together to form a single line having a slope of -1 as predicted

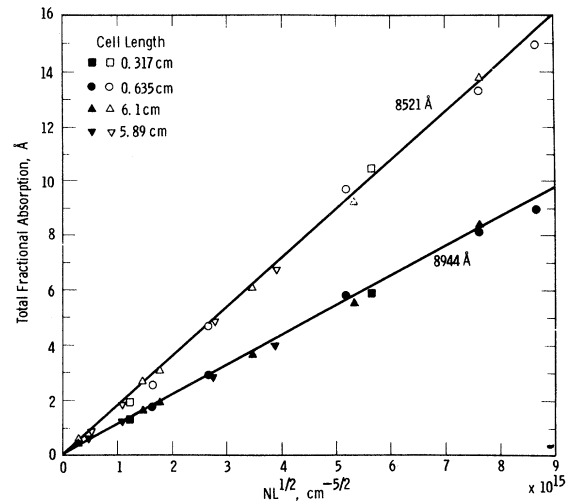


FIG. 4. Total fractional absorption versus $NL^{1/2}$ for Cs 8521 Å and Cs 8944 Å resonance lines at four cell lengths (0.317, 0.635, 5.89, and 6.1 cm) and a range of cesium density.

These results are also a confirmation of the assumed Lorentzian line profile for large $\lambda - \lambda_0$ and of the linear dependence of γ on N . The values of $\gamma f/N$ calculated from these lines are: $1.13 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ for Cs 8521 Å and $0.31 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ for Cs 8944 Å. On the basis of the scatter of the data, we assign a mean square precision to these $\gamma f/N$ values of $\pm 4\%$. The reason for the 8% difference between the $\gamma f/N$ values determined for the 8521 Å line using the data of Figs. 4 and 5 is unknown.

The departures of the experimental data²¹ from the straight lines of Figs. 5 and 6 at small values of $\Delta\lambda$ appear to be inconsistent with the assumption

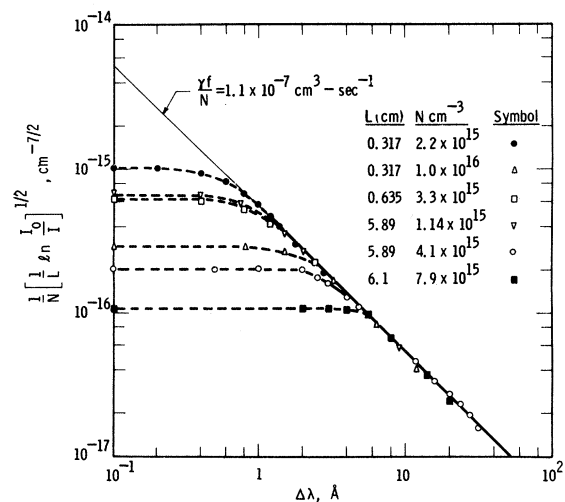


FIG. 5. The square root of the effective absorption coefficient per atom as a function of $\Delta\lambda$ for Cs 8521 Å. The data shown includes points from both sides of the absorption profile.

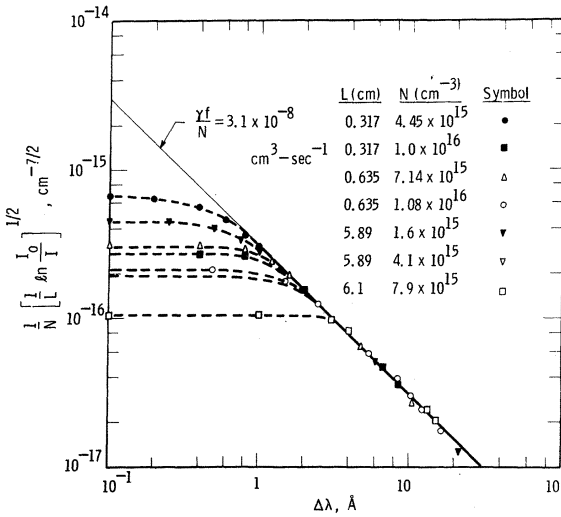


FIG. 6. The square root of the effective absorption coefficient per atom as a function of $\Delta\lambda$ for Cs 8944 Å. The data shown includes points from both sides of the absorption profile.

that our observations apply to the wings of the spectral line, i. e., that the condition represented by Eq. (5) is satisfied. The source of this apparent discrepancy can be understood by a consideration of the data shown in Fig. 7. The solid curve is the experimental absorption line profile for the Cs 8521 Å resonance line at a cesium density of 1.14×10^{15} cm^{-3} and a cell length of 5.89 cm. The absorption line profile, calculated from Eqs. (3) and (4) using the value of γ/N determined in Sec. V, is labeled as the idealized I/I_0 . At the line center, the discrepancy between the ideal curve and the experimental data is about 10^5 orders of magnitude.²¹ The circles are the results of the computer calculations for the convolution of the instrument function and the idealized I/I_0 curve using Eq. (9). Here we are concerned with wavelengths which are far enough from the line center so that the effects of hyperfine structure¹¹ on the calculation are small. The agreement between the calculated and the experimental curve is good. The points of Fig. 3 also show the results of sim-

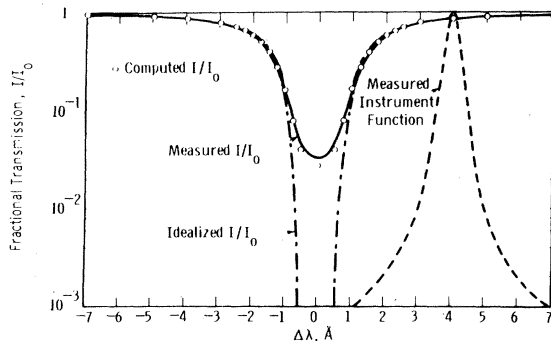


FIG. 7. Theoretical and experimental absorption line profile of Cs 8521 resonance line at a cesium density of 1.14×10^{15} cm^{-3} and a cell length of 5.89 cm.

ilar calculations using the same instrument function and the $\gamma f/N$ values determined from Figs. 5 and 6 for various cesium densities. The agreement in the wings, i. e., for $\Delta\lambda$ in the straight-line portion of Figs. 5 and 6, is usually better than 2% and always better than 4%, and at the line center is within 15% for the densities and cell lengths studied.⁶ It should be noted that for reasonably large NL values, i. e., the lower curves in Figs. 3, 5, and 6, the major contribution to the observed intensity at the line center arises from portions of the instrument function which are greater than 1 Å from the nominal monochromator setting, and significant contributions occur²² at wavelength differences out to 100 Å.

V. DISCUSSION

The results presented above show that for Cs densities below 2×10^{16} cm^{-3} , and for measurements at wavelengths greater than about 0.5 Å from the line center one can determine the absorption characteristics of only the wings of the line. Therefore, one can obtain values of $\gamma f/N$ but cannot separate γ/N and f . The values from our measurements of $\gamma f/N$ are compared with values calculated from Gregory's results² in Table I. Our values are about 12% higher than Gregory's values. The source of this small discrepancy is unknown. In our experiments, the largest source of error is in the determination of the Cs density. Uncertainties in Cs vapor pressure due to uncertainties in reservoir temperature are expected to be less than 3%. As a check on the cesium density values, we have examined the change in specular reflection²³ caused by the Cs vapor and find²⁴ agreement between theory and experiment for $\Delta\lambda > 0.8$ Å to within about 15%, i. e., the Cs densities given by Eq. (1) appear to be correct to within 15%. In view of the uncertainties in f values and the present incomplete state of the analysis of the specular reflection data,²⁴ we will assume that the Cs densities given by Eqs. (1) and (2) are correct to $\pm 3\%$ as claimed by Taylor and Langmuir.⁹

The $\gamma f/N$ value for the 8521 Å line calculated from the data of one-half of the absorption half-width ($\frac{1}{2}\gamma$) versus Cs density given in Pollock and Jensen's paper (i. e., their Fig. 2) is approximately 3.0×10^{-5} cm^3/sec , or more than two orders of magnitude larger than our result. The explanation of at least part of this discrepancy²⁵ can be seen by noting that the analysis of the "apparent absorption coefficient" used by Pollock and Jensen is equivalent to turning our Fig. 7

TABLE I. The product of oscillator strength and collisional half-width per atom for Cs 8521 and Cs 8944 resonance lines.

$(\gamma f/N)_{8521}$	$(\gamma f/N)_{8944}$	Author
0.96×10^{-7}	0.27×10^{-7}	Gregory ²
$(1.08 \pm 0.04) \times 10^{-7}$	$(0.30 \pm .01) \times 10^{-7}$	Present

upside down and using a linear ordinate scale to determine the width at half maximum for the solid curve. If one were to use this procedure for the data of Fig. 7, one would obtain a full width at half maximum of about 2 \AA , whereas the value of the width $\gamma\lambda^2/c$ calculated for the conditions of Fig. 7 from our results is only $4 \times 10^{-3} \text{ \AA}$. This latter value is much smaller than the Doppler width of 0.012 \AA or the hyperfine separation¹¹ of about 0.21 \AA . Although the resolution of the spectrometer used by Pollock and Jensen was comparable to that of our instrument, the distortion of the apparent absorption coefficient curve²⁶ due to the instrument function accounts for only a part of the discrepancy between our results and those of Pollock and Jensen. Thus the values of $\gamma f/N$ obtained from the wings of their line profiles, where the distortion due to the instrument function should be small, are roughly a factor of 30 larger than our $\gamma f/N$ values. The source of this discrepancy is unknown.

A comparison of our experimental results with theory is difficult because of the low spectral resolution of our apparatus and the effects of the hyperfine structure of the Cs resonance lines. Our apparatus, as well as that of Pollock and Jensen, does not resolve the line center or the hyperfine components of the absorption spectra. Therefore these experiments give no information regarding the collisional half-width at small wavelength shifts appropriate to theories based on the impact approximation,²⁷⁻²⁹ the possible differences in the behavior of different hyperfine components, or the possible departures from simple dispersion line shapes at the line center.^{4,29,30} In order to compare our values of γ/N for the wings of the lines with the theoretical values, we have used f values determined from recent lifetime measurements. Thus Link³¹ obtained the lifetime of the $6^2P_{3/2}$ state to be $(30.5 \pm 0.6) \times 10^{-9}$ sec, which gives $f = 0.718$. Similarly Gallagher³² has determined the lifetime of the $\text{Cs}6^2P_{1/2}$ level to be 34×10^{-9} sec so that $f_{8944} = 0.353$. Using these results and the mean of our determinations of $\gamma f/N$, the collisional half-widths per atom are

$$(\gamma/N)_{8521} = 1.51 \times 10^{-7} \text{ cm}^3/\text{sec}$$

$$\text{and } (\gamma/N)_{8944} = 0.86 \times 10^{-7} \text{ cm}^3/\text{sec}.$$

The fit to experimental data obtained with the assumed Lorentzian line shape and the assumed linear variation of γ with N show that γ/N is constant for each of the lines for Cs densities between 2×10^{14} and $2 \times 10^{16} \text{ cm}^{-3}$ and for $\Delta\lambda$ between 0.5 and 30 \AA . Our results are compared with the results obtained by Reck, Takebe and Mead⁴ in Table II. The agreement with these authors is good for the 8944 \AA line. However, the discrepancy for the 8521 \AA line would appear to be well outside our experimental error. If we had used the larger theoretical f values of Stone³³ to calculate γ/N from $\gamma f/N$, we would obtain comparable agreement with theory for each of the two lines. For comparison purposes we have shown the results of theoretical calculations using the impact approximation. This approximation is expected to be valid²⁹ only for $\Delta\lambda$ less than about 0.2 \AA . As pointed out previously,¹³ the two theoretical approaches give approximately the same result.

In view of the possibility of severe distortion of the apparent absorption coefficient data by the instrument function, it is suggested that several recent³⁴⁻³⁶ determinations of self-broadening absorption widths should be re-examined. A common characteristic of these studies is that these authors determine the half-widths from apparent absorption coefficient data near the line center, and obtain self-broadening collision coefficients which are much larger than expected from theory.^{4,27-30} The use of apparent absorption coefficients can also lead to errors in the determination of f values.³⁷ However, f values are usually¹⁴ determined from total fractional absorption (equivalent width) treatments of the data at low gas densities for which the errors due to the instrument function are small.

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TABLE II. Collisional half-widths per atom and their ratio for Cs 8521 and Cs 8944 resonance lines.

	$(\gamma/N)_{8521}$	$(\gamma/N)_{8944}$	$\gamma_{8521}/\gamma_{8944}$	Author
Experimental	1.34×10^{-7}	0.76×10^{-7}	1.77	Gregory ²
	3.0×10^{-5}			Pollock and Jensen ³
	1.51×10^{-7}	0.86×10^{-7}	1.76	Present
Statistical theory	1.29×10^{-7}	0.836×10^{-7}	1.54	Reck, Takebe, and Mead ⁴
Impact theory	1.1×10^{-7}	0.576×10^{-7}	1.91	Furssow and Wlassov ²⁷
	1.38×10^{-7}	0.712×10^{-7}	1.91	Bryon and Foley ²⁸
	1.12×10^{-7}	0.814×10^{-7}	1.35	Ali and Griem ²⁹

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¹A. Mitchell and M. Zemansky, Resonance Radiation and Excited Atoms (Cambridge University Press, Cambridge, England, 1961).

²C. Gregory, Phys. Rev. **61**, 465 (1942).

³D. H. Pollock and A. O. Jensen, J. Appl. Phys. **36**, 3184 (1965).

⁴G. P. Reck, H. Takebe, and C. A. Mead, Phys. Rev. **137**, A683 (1965). The numbers quoted in Table I correct an apparent arithmetic error in this reference.

⁵The instrument function has also been measured with a Varian-type cesium rf discharge lamp at 8944 Å. Beyond 0.6 Å from the line center, the instrument function so determined coincides with that measured with helium-neon gas laser at 6328 Å. Between 0 and 0.6 Å the shape of the apparent instrument function is wider in the case of cesium rf discharge lamp than the instrument function obtained with the He-Ne laser. This distortion of the instrument function probably results from the fact that the Cs $6^2P_{1/2}$ state has two hyperfine groups separated¹¹ by 0.246 Å. Our assumption that the central portion of the instrument function measured at 6328 Å with He-Ne laser is a good representation at 8521 and 8944 Å may be partly responsible for the small discrepancy between calculated and observed profiles as shown in Fig. 7.

⁶Figure 2 is strictly applicable only to the data obtained with cell lengths of 0.317 and 5.89 cm since the grating, incorrectly installed by the manufacturer, was reversed after completion of the measurements with the other cells. This change does not affect the analyses of data in Figs. 4-6. The comparison of measured and calculated profiles covered the density range $(2-40) \times 10^{14} \text{ cm}^{-3}$ for $L=5.89 \text{ cm}$ and $(3-40) \times 10^{14} \text{ cm}^{-3}$ for $L=0.317 \text{ cm}$.

⁷At liquid nitrogen temperature and at 980 V, the photomultiplier has an output dark current of $\sim 3 \times 10^{-13} \text{ A}$.

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²¹The observation of significant fractional transmission near the line center was independent of the intensity of the source and was qualitatively the same when interference filters ($\sim 180 \text{ Å}$ full width at 50% transmission) centered near either 8520 or 8940 Å were placed in front of the detector.

²²The reason for the large contribution of the instrument function at large wavelength differences $\delta\lambda$ is that, from Fig. 2, $K(\delta\lambda)$ varies as $(\delta\lambda)^{-n}$ where $1.3 < n < 1.8$ for $\delta\lambda > 2 \text{ Å}$, so that the integral from a given wavelength difference to some very large value of $\delta\lambda$ varies only as $(\delta\lambda)^{-(n-1)}$, e.g., $(\delta\lambda)^{-1/2}$.

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Antisymmetrization of Geminal Wave Functions. III. Calculations of the Density Matrix and Energy of a Three-Electron Atom

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The conditions, which have been discussed in two previous papers, for the antisymmetrization of a geminal-sum wave function have been applied, in a numerical example, to the calculation of the density matrix and energy of the three-electron ion Be^+ . The consequences of imposing spin symmetry upon the wave function and the effects of relaxing the antisymmetrization procedure are both discussed. A ground-state energy of -14.3024 a. u., some 0.2% above the "experimental energy," is obtained, and the corresponding density matrix given.

I. INTRODUCTION

Considerable interest has arisen, during the last few years, in techniques involving the second-order reduced density matrix (2-matrix) and in wave functions containing geminals. Theoretical considerations of the density matrix have shown that the N -representability problem at present remains intractable; even the derivation of useful necessary conditions for N -representability proves difficult. Concern with geminals has largely centered around calculations using a rather limited wave function, the antisymmetrized product of strongly orthogonal geminals. This wave function is essentially expanded in an orthonormal set of orbitals; the set is partitioned into $\frac{1}{2}N$ non-intersecting subsets, and each geminal expanded in one of these subsets. The wave function is written

$$\Psi = ANg_1(12)g_2(34)\cdots g_{\frac{1}{2}N}(N-1, N). \quad (1)$$

The author believes that an investigation of the geminal-sum wave function

$$\Psi = \sum_{n_1 \cdots n_{\frac{1}{2}N}} a_{n_1 n_2 \cdots n_{\frac{1}{2}N}} g_{n_1}(12) \cdots g_{n_2}(34) \cdots g_{n_{\frac{1}{2}N}}(N-1, N) \quad (2)$$

for even N , or

$$\Psi = \sum a_{n_1 n_2 \cdots n_{\frac{1}{2}(N+1)}} \Phi_{n_1}(12) \Phi_{n_2}(34) \cdots \Phi_{n_{\frac{1}{2}(N-1)}}(N-2, N-1) d_{n_{\frac{1}{2}(N+1)}}(N), \quad (3)$$

where $\{\Phi\}$ and $\{d\}$ are complete orthonormal sets

for odd N , may prove useful, since the properties of the vector $\{a_{n_1 \cdots n_M}\}$ that determines this function are intimately connected with N -representability conditions. In the first paper of this series¹ (hereafter referred to as Paper I), the conditions upon the $\{a_{n_1 \cdots n_{N/2}}\}$ due to the requirement of total antisymmetry of the wave function were imposed as

$$a_{n_1 n_2 \cdots n_{\frac{1}{2}N}} + \sum_{m_1 m_2 \cdots m_{\frac{1}{2}N}} a_{m_1 m_2 \cdots m_{\frac{1}{2}N}} \times Q_{n_1 n_2 \cdots n_{\frac{1}{2}N} m_1 m_2 \cdots m_{\frac{1}{2}N}} = 0 \quad (4)$$

(for even N), where

$$Q_{n_1 n_2 \cdots n_{\frac{1}{2}N} m_1 m_2 \cdots m_{\frac{1}{2}N}} = \delta_{n_3 m_3} \cdots \delta_{n_{\frac{1}{2}N} m_{\frac{1}{2}N}} \int \Phi_{n_1}^*(12) \cdots \Phi_{n_2}^*(34) \phi_{m_1}(13) \phi_{m_2}(24) \quad (5)$$

and the requirement of symmetry of $\{a_{n_1 \cdots n_{\frac{1}{2}N}}\}$ under interchange of n_i and n_j was also imposed. In the case of odd N , the conditions become, in addition to conditions (4) and (5),

$$P(ij)a_{n_1 n_2 \cdots n_{\frac{1}{2}(N+1)}} = a_{n_1 n_2 \cdots n_{\frac{1}{2}(N+1)}}, \quad i < j \leq \frac{1}{2}(N-1), \quad (6)$$

where $P(ij)$ interchanges n_i and n_j , and

$$a_{n_1 n_2 \cdots n_{\frac{1}{2}(N+1)}}$$