Absorption Coefficients for the Wings of the First Two Resonance Doublets of Cesium Broadened by Argon[*]

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Measurements are reported of the absolute absorption coefficients in the wings of the 8944-, 8521-, 4593-, and 4555-Å resonance lines of cesium in the presence of argon at densities between about 6×10^{18} and 2×10^{19} atom cm^{-3}. The data extend from about 0.7 Å to as much as 600 Å from the line center and were obtained using cesium densities between 7×10^{11} and 2×10^{15} atom cm^{-3} and temperatures between 390 and 470 °K. The measured absorption coefficients are proportional to the product of the cesium and argon densities as expected from line broadening produced by binary collisions between cesium and argon atoms. Using the quasistatic theory as a guide for interpretation, the line profiles for wings of the first resonance doublet show a transition from a wavelength dependence determined by long-range van der Waals forces to a dependence determined by the short-range internuclear potentials discussed by Hedges, Drummond, and Gallagher (HDG). The far-wing absorption profiles obtained in the present experiments are in good agreement with those calculated from the fluorescence data of HDG.

I. INTRODUCTION

Most experimental studies[1,2] of the broadening of the resonance lines of alkali metals by the rare gases have been concerned with the change in the half-width and with the shift in the wavelength of maximum absorption or emission caused by the rare gas. Recent comparisons[3,4] of such data with theory lead to the conclusion that the portions of the interaction potential at small internuclear separations must be taken into account when describing the broadening theoretically. Information concerning the excited-state and ground-state interaction potentials at small internuclear distance can be obtained most readily from analysis of the wings of the spectral lines.[1,5-8] One possibility is to use the very weak fluorescence profiles obtained using low-alkali-metal densities.[5] A second approach, i.e., the one used in this investigation,[9] is to measure absorption profiles at relatively large alkali densities.[10-12] Because of the difficulties of determination of the alkali-metal-atom density, previous absorption measurements have (a) yielded only relative values for the absorption coefficients at low perturber densities[6] and have differed significantly as to the magnitude of structure such as satellites,[11,12] or have (b) been made at large enough perturber densities[11,12] such that binary and multiple collisions[1,13-15] result in a profile that is sufficiently broadened so that the line center as well as the wings can be observed on a single absorption trace. In this paper we extend previous work to the determination of absolute ab-

sorption coefficients for the wings of the first-two resonance doublets of cesium at relatively low perturber densities, i.e., less than 1 atm, where the binary collision models are found to be valid.[1,2,11,12] Experimental conditions are chosen such that absolute values for the cesium-atom density are given by the equilibrium-vapor-pressure curve.

The experimental apparatus and the evidence supporting our use of the equilibrium-cesium-vapor data are discussed in Sec. II. The results of the measurements are given in Secs. III and IV and a comparison with the available theory is made in Sec. V.

II. EXPERIMENT

Except for the absorption cell to be described below, the apparatus used for the 8944- and 8521-Å lines in these experiments was the same as that used in our previous measurements of absorption in pure cesium.[16] For measurements of the 4593 and 4555 absorption profiles the photomultiplier with a $S1$ photocathode was replaced with a photomultiplier with a $S11$ photocathode and the filter was replaced with a Corning 7740 glass filter. The refillable absorption cell used in the earlier pure-cesium experiments[16] yielded highly variable results with the Cs-Ar mixtures used in these experiments. This behavior was apparently caused by a failure of the cesium pressure in the high-temperature region of the cell to attain equilibrium with the cesium pressure in the low-temperature region.[17] The absorption cells used in the final mea-

surements were fabricated from Corning 1720 alkali-metal-resistant glass. In these cells the side-arm reservoir for the liquid cesium was shortened to less than 1 in. length, so that it was not possible to control the cesium density and temperature separately. The cell lengths were 7.0 ± 0.1 and 20.0 ± 0.1 cm. Cell temperatures were determined by a set of nine strategically placed chromel-alumel thermocouples. The oven was designed such that the windows were operated at about 10 °C higher temperature than the central portion of the cell for central temperatures between 390 and 490 °K. Reasons for believing that the vapor pressure of the cesium throughout the cell reached its equilibrium value at the temperature of the central portion of the cell are (i) the results obtained with the cells described were independent of the temperature cycling and of the cell used; (ii) no cesium deposits were observed in the vicinity of the cell windows; (iii) no discoloration of the glass was observed; (iv) dielectric-constant measurements in pure cesium[18] using cells fabricated from Corning 1720 glass show that the cesium density in the cell is consistent with that expected from the equilibrium-vapor-pressure curve; and (v) the oscillator strengths derived from total absorption data of Sec. IV are in satisfactory agreement with other determinations.

The absorption cells were filled on a conventional high-vacuum system[19] which, after outgassing at about 400 °C for 12–18 h and upon cooling to room temperature, reached a pressure of about 10^{-9} Torr with a rate of rise of about 10^{-10} Torr/min when isolated from the pumps. Approximately half a gram of cesium was then distilled into the cell from a Pyrex capsule containing previously doubly distilled cesium obtained from 99.98% pure cesium.[20] Reagent grade argon[21] was then admitted to the cell to pressures between about 200 and 700 Torr as determined with a null-reading capacitance manometer system accurate to 0.1 Torr. Pressure variations during the sealoff procedure were monitored and introduced less than a 5% uncertainty in the final density of the argon in the cell. The cold-region temperatures were constant to within ± 1 °C during a 12-h period preceding and during the measurements so that the vapor pressure is constant to $\pm 5\%$.

The requirements on the data recording system are that position of the chart recorder pen be a linear function of the photon flux and that the chart drive operate at constant speed relative to that of the monochromator drive. The photomultipliers were operated at peak output currents of less than 10^{-9} A and the currents were measured by an electrometer. Linearity of the detection system was determined to be better than $\pm 2\%$ using calibrated neutral-density filters. The wavelength calibration

was checked by placing a narrow-line cesium resonance lamp in front of the monochromator during the period of large absorption and by noting the positions of the rubidium impurity absorption lines. The intensity of the radiation from the current regulated filament[16] used as a light source and the gain of the voltage-regulated photomultiplier were sufficiently constant so that during a given run the measurements of fractional transmission should be accurate to 0.5% for near unity transmission. A gradual change in the spectral dependence of the output of the incandescent source over a period of several weeks led to difficulties in the initial interpretation of the data obtained at wavelengths far from line center.[9] We are indebted to Gallagher for discussions of the data of Ref. 5 which led to resolution of these problems.

III. RESULTS FOR 8944- AND 8521-Å LINES

Figure 1 shows the wavelength dependence of the intensity arriving at the photomultiplier for wavelengths in the vicinity of the 8944-Å ($6^2S_{1/2}-6^2P_{1/2}$) and 8521-Å ($6^2S_{1/2}-6^2P_{3/2}$) resonance lines of cesium. Data are shown for two widely different cesium densities in the absorption cell. The signal-to-noise ratios indicated by these traces are typical of the data used to obtain the absorption coefficients cited in this paper. At low cesium densities the data were also recorded using a slower wavelength drive speed. In the analysis which follows the results are presented in terms of an absorption coefficient $k(\lambda)$ defined by the relation

$$k(\lambda) = (1/L)\ln[I_0(\lambda)/I(\lambda)], \qquad (1)$$

where $I_0(\lambda)$ and $I(\lambda)$ are the wavelength-dependent intensities of radiation incident on the photomultiplier in the absence of[22] and in the presence of cesium in the absorption cell, respectively, and L is the length of the absorption cell. As in the case of the pure cesium measurements,[16] no attempt has been made to correct the absorption coefficient data for the effect of the instrument transmission function. Because of the distortion of the absorption profile by the instrument function,[16] we use only data for which the wavelength shift from the line center is significantly greater than the instrumental full width at half-maximum of 0.4 Å and for which the measured transmission is greater than about 15%. Data meeting these conditions are indicated by the solid points in Figs. 2–5.

Absorption coefficient data for the red and blue wings of the 8944- and 8521-Å lines are shown in Figs. 2–5. In these figures the reduced absorption coefficient, which is defined as the measured absorption coefficient divided by the product of the cesium and argon densities, is plotted as a function of the measured wavelength shift from the line center. Here the cesium and argon densities are
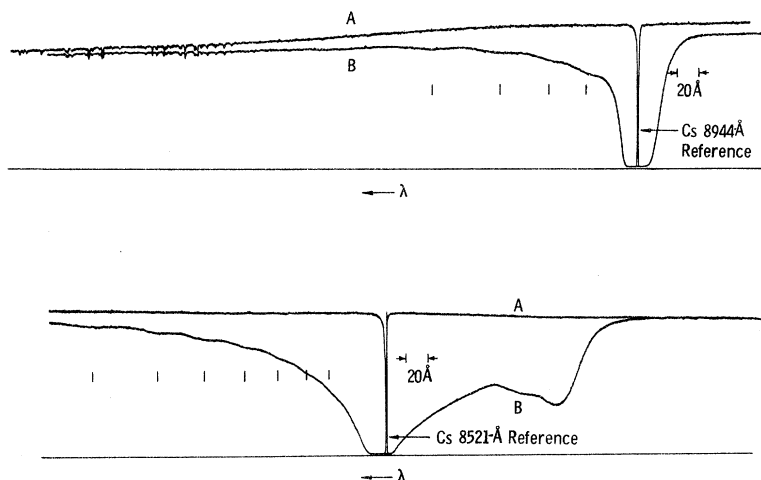
FIG. 1. Experimental absorption
profiles for the 8944- and 8521-Å lines
in a cesium-argon mixture for [Cs]
$= 1.8 \times 10^{15}$ atom/cm^3, [Ar] $= 2.17 \times 10^{19}$
atom/cm^3, and $T = 490\,°K$, $L = 20$ cm.
The two traces were taken one day apart.
The recorder traces have been broadened
so as to allow reproduction. The ver-
tical lines indicate the positions of the
maxima of the "red bands." The left-
hand side of the lower trace is a con-
tinuation of the right-hand side of the
upper trace.

represented by [Cs] and [Ar], respectively. We see
that this procedure results in a narrow spread in
those data points, i.e., the solid points, which are

expected to be reasonably free of distortion caused
by the instrument function.[23] The range of the ce-
sium densities covered by the data of these figures
is from 7.2×10^{11} to 1.8×10^{15} atom/cm^3 and the
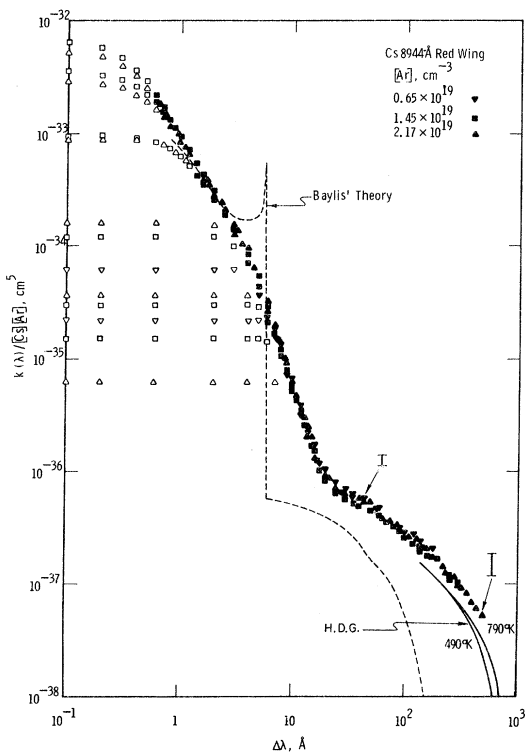range of argon densities is from $0.65 - 2.2 \times 10^{19}$

FIG. 2. Reduced absorption coefficients for the red
wing of the 8944-Å line in cesium-argon mixtures. The
solid points are believed to be free of significant instru-
mental distortion. The dashed curves are from the theo-
retical calculations of Baylis discussed in the text. The
solid curves are calculated from the fluorescence data
of HDG as discussed in the text. The wavelength dif-
ferences are measured from the center of the line emitted
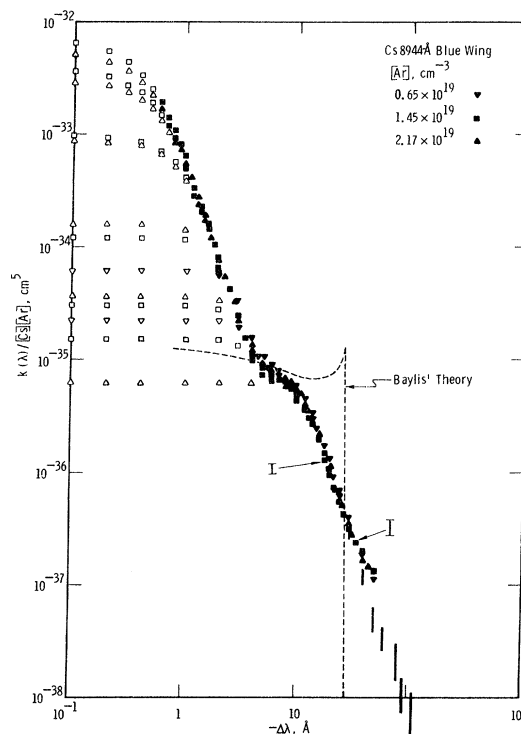by a low-density radio-frequency cesium lamp.

FIG. 3. Reduced absorption coefficients for the blue
wing of the 8944-Å line in cesium-argon mixtures. The
length of the vertical bars for $| \Delta \lambda | \geq 40$ Å indicates the
uncertainty introduced in the differenced absorption co-
efficients (see text) by the spread in our measured ab-
sorption coefficients and does not allow for uncertainty
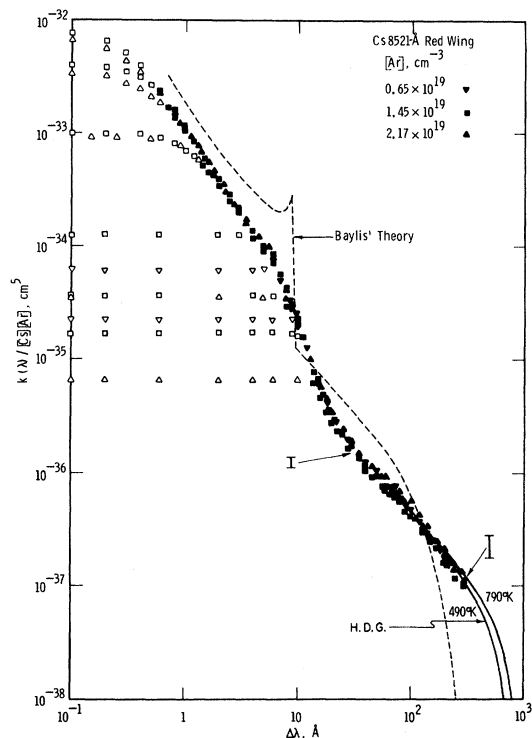in the results of HDG. See Fig. 2 for additional com-
ments.

FIG. 4. Reduced absorption coefficients for the red wing of the 8521-Å line in cesium-argon mixtures. See Fig. 2 for comments.

FIG. 5. Reduced absorption coefficients for the blue wing of the 8521-Å line in cesium-argon mixtures. See Fig. 2 for comments.

atom/cm^3. The proportionality between the absorption coefficient in the wings of the line and the product of the cesium and argon densities is characteristic of both the impact and statistical models for line broadening as the result of binary interactions between the cesium and argon atoms. The error bars shown are estimates of our ability to determine $k(\lambda)$ from the absorption profiles. The spread in the data is indicative of the determination of the cesium and argon densities and, at low wavelength shifts, the effect of the instrument function. The vertical bars shown for the blue wing of the 8944-Å line at $\Delta\lambda \equiv \lambda - \lambda_0 < -40$ Å were obtained by subtracting from the measured values the absorption coefficients for the red wing of the 8521-Å line as shown in Fig. 4 and as calculated from the fluorescence data of Hedges, Drummond, and Gallagher[5] (HDG) for the red wing of the 8521-Å line at $8904 > \lambda > 8824$ Å

A quantitative comparison of these results with most previous experiments is possible only with regard to the location of the peak in the absorption coefficient for the blue wing of the 8521-Å line, i.e., the blue "satellite." More detail regarding this portion of the line can be seen in Fig. 6, where the reduced absorption coefficient calculated from a single absorption trace is shown.[24] Here we see a relatively broad peak at about 153 Å from the
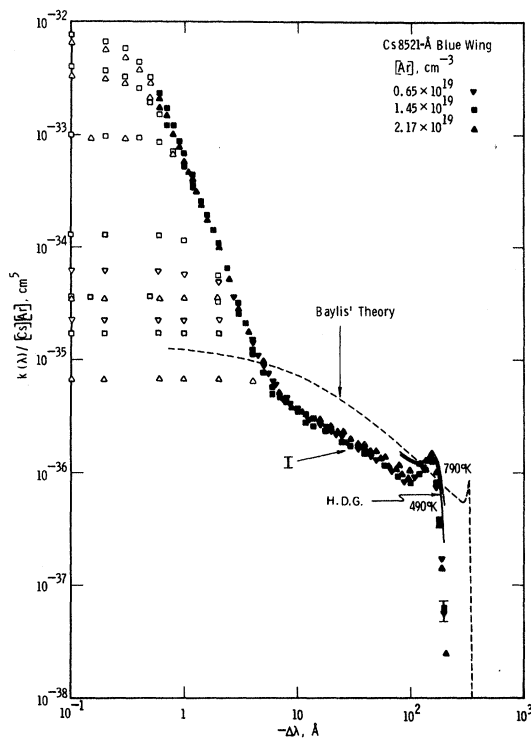
line center with an indication of additional structure near 125 Å from the line center. The location of the principal peak is in good agreement with the re-
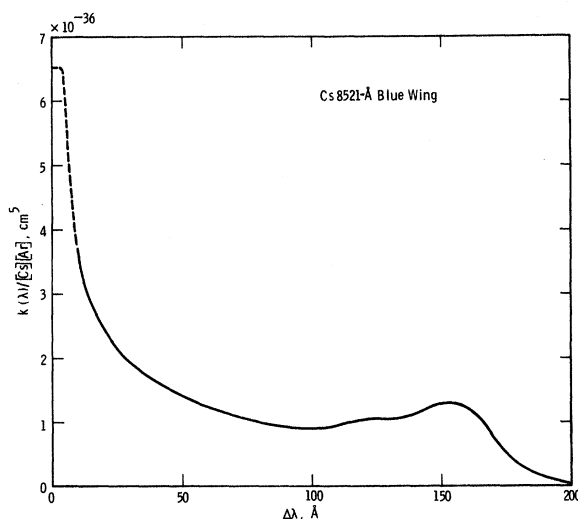
FIG. 6. Reduced absorption coefficients from a single absorption profile for the far violet wing of the 8521-Å line in a cesium-argon mixture. This curve shows details of the absorption coefficients in the vicinity of the violet satellite which are obscured by scatter among the various profiles of Fig. 5.

sults obtained by Jefimenko and Ch'en and by Gilbert and Ch'en.[12] From our results and data obtained at the line center,[1,2] the absorption coefficient at the peak of this satellite is about 5×10^{-5} of that at the line center at an argon density of one amagat, i. e. , 2.69×10^{19} atom/cm^3.

Figures 2, 4, and 5 show comparisons of our reduced absorption coefficients with values obtained by converting the fluorescence data of HDG[5] into reduced absorption coefficient values. The differences are less than the scatter of our data at $|\Delta\lambda| > 100$ Å for the red and blue wings of the 8521-Å line. For the red wing of the 8944-Å line our values are a factor of 1.4 ± 0.1 larger than those of HDG at $\Delta\lambda$ between 200 and 300 Å. This discrepancy is slightly larger than the sum of the scatter of our data and the 30% uncertainty estimated by HDG. The slow variation with temperature of the absorption coefficients calculated from the data of HDG for the wavelengths covered by our experiment confirms theoretical predictions[25] and justifies our use of an absorption cell without separate control of density and temperature.

The absorption profiles of Fig. 1 show additional structure in the form of a series of 4 and 7 broad maxima which tend to converge toward the 8944- and 8521-Å resonance lines, respectively. The maxima between the 8944- and 8521-Å lines appear to have characteristics similar to the "high-temperature " bands observed by Jefimenko and Ch'en.[12] As yet there is no unique interpretation of this structure. One possibility is that the maxima correspond to transitions from the continuum ground states[5,26] to a series of vibrational levels of the $A\,^2\Pi_{1/2}$ and $A\,^2\Pi_{3/2}$ states.[25,27] Because of the large ratio of kT to the apparent vibrational spacing, many rotational levels are excited and the vibrational bands are barely detectable. A second source of this structure is from the oscillatory nature of the Franck–Condon factors between the continuum ground states and the upper bound states.[28,29]

Figure 7 shows values of the integrated or total absorption[16,30] A_T for the 8944- and 8521-Å line plotted as a function of the product of the cesium and argon densities and the absorption path length. The uniqueness of such a plot is consistent with the scaling of the absorption coefficient data of Figs. 2–5 based on binary collisions. Thus, according to the data of Fig. 2–5 the absorption coefficients for the 8944- and 8521-Å lines can be written $k(\lambda, [Cs], [Ar]) = \alpha(\lambda)[Cs][Ar]$ for wavelength shifts greater than some $\Delta\lambda_1$ which is less than about 0.8 Å. Furthermore, if the value of $k(\lambda)\,L$ is large enough the absorption will be essentially complete at wavelength shifts less than $\Delta\lambda_1$ and the total absorption A_T is given by

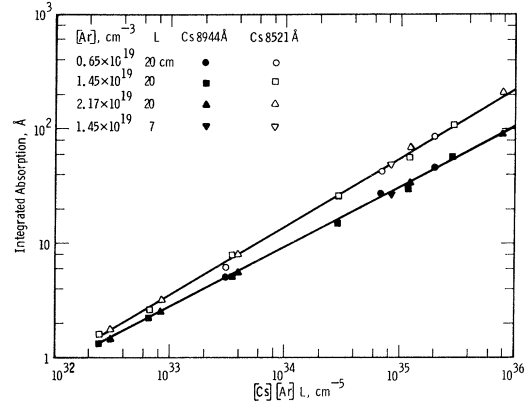$$A_T \equiv \int_0^\infty (1 - e^{-k(\lambda)L})\,d\lambda$$

Fig. 7. Total absorption data for the 8944- and 8521-Å line in cesium–argon mixtures. The smooth curve is drawn through an average of the points.

$$= \int_0^{\lambda_0 - \Delta\lambda_1} \{1 - \exp(-\alpha(\lambda)[Cs][Ar]L)\}\,d\lambda + 2\Delta\lambda_1$$
$$+ \int_{\lambda_0 + \Delta\lambda_1}^\infty \{1 - \exp(-\alpha(\lambda)[Cs][Ar]L)\}\,d\lambda. \quad (2)$$

For sufficiently large values of A_T the $2\Delta\lambda_1$ term is negligible and A_T is a function of $[Cs][Ar]L$ only. Because of uncertainties in the measured half-widths[2] at low densities, we can only set an upper limit to $\Delta\lambda_1$, i. e. , $\Delta\lambda_1 < 0.7$ Å.

There appear to be no previous published measurements of total absorption for the resonance lines of cesium broadened by argon with which we can compare our results. Gilbert and Ch'en[12] give relative values of the integrated absorption coefficient at an unspecified cesium density. We have not attempted to compare with their integrated absorption coefficients for the satellite because neither theory[5] nor experiment provides a quantitatively significant basis for doing so. We have not calculated the integrated absorption coefficient for the whole resonance line because our measured absorption coefficients do not extend to line center.

Data such as those in Fig. 7 are useful for the determination of cesium-atom densities in an argon atmosphere and are expected to be useful in the calculation of the energy radiated by cesium seeded, argon plasmas, e. g. , in magnetohydrodynamic generators.[31] For these purposes we note that the data of Fig. 7 is given approximately by

$$A_T(8521) = 0.90(10^{-32}[Cs][Ar]L)^{0.60} \text{ Å} \quad (3)$$

and

$$A_T(8944) = 0.83(10^{-32}[Cs][Ar]L)^{0.53} \text{ Å} \quad (4)$$

for $2 \times 10^{32} < [Cs][Ar]L < 10^{36}$ cm^{-5}. Contributions to $k(\lambda)$ and to A_T as the result of broadening by cesium will be less than 10% for $[Cs]/[Ar] < 1.7 \times 10^{-4}$ and the above range of $[Cs][Ar]L$. The far-wing fluorescence profiles of HDG[5] could be used to ex-

tend the curves of Fig. 7 to larger $[Cs][Ar]L$ values and the pure Cs profiles of Chen and Phelps[16] could be used to calculate sets of A_T curves for higher $[Cs]/[Ar]$ ratios.

IV. RESULTS FOR 4593- AND 4555-Å LINES

The reduced absorption coefficients for the 4593-Å $(6\,{}^2S_{1/2} - 7\,{}^2P_{1/2})$ and 4555-Å $(6\,{}^2S_{1/2} - 7\,{}^2P_{3/2})$ lines are shown in Figs. 8–11. These data are obtained from absorption profiles and are analyzed using Eq. (1). The solid points are those for which instrumental corrections[16] are expected to be small. The range of cesium and argon densities investigated was the same as for the 8944- and 8521-Å lines but because of the much lower oscillator strength the range of wavelengths and of reduced absorption coefficients investigated was much smaller than for the first doublet.

Figure 12 shows the values of the total absorption for the 4593- and 4555-Å lines plotted as a function of the product of the Cs and Ar densities and of the cell length. As in the case of the total absorption data for the 8944- and 8521-Å lines shown in Fig. 7, we expect all of the data for a given line to lie on a single curve provided that Eq. (2) is applicable, i.e., that the transmission is significant only at $\Delta\lambda$ which are large compared to the half-width of

FIG. 9. Reduced absorption coefficients for the violet wing of the 4593-Å line in cesium-argon mixtures. See Fig. 8 for comments.
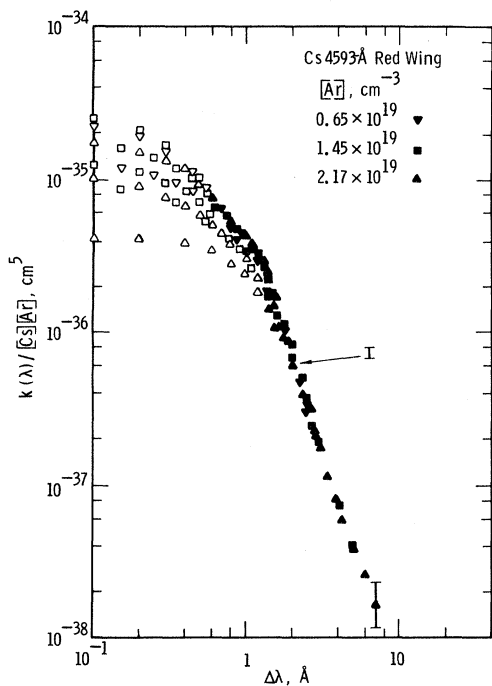

FIG. 8. Reduced absorption coefficients for the red wing of the 4593-Å line in cesium-argon mixtures. The solid points show the data for which there should not be significant instrumental distortion. The wavelength differences are measured from the center of the line emitted by a low-density cesium lamp.
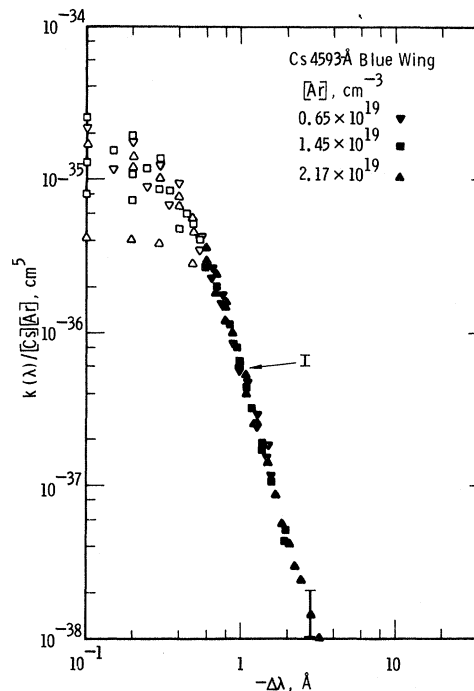
the line. However, when the absorption at the line center is small enough such that the measured absorption profile approaches the true line shape, the total absorption is proportional to the integrated absorption coefficient. Thus, as $A_T \rightarrow 0$,

$$A_T \rightarrow L \int k(\lambda)\, d\lambda = (\lambda^2 \pi e^2/mc^2) f[Cs]L , \qquad (5)$$

where e and m are the electron charge and mass, c is the velocity of light, and f is the oscillator strength. Unfortunately, our measurements of A_T for the second doublet included only a few measurements at low A_T values, i.e., the solid points of Fig. 12. However, we can make use of measurements of A_T values for the first and second doublets under stable but apparent nonequilibrium-vapor-pressure conditions to obtain additional values of A_T for the second doublet,[32] i.e., the open points of Fig. 12. In view of the approximately linear variation in A_T with $[Cs]L$ for an argon density of 2.35 $\times 10^{19}$ atom/cm^3 at low A_T in Fig. 12, Eq. (5) has been used to test our assumption that the cesium densities in the cell are given by the equilibrium-vapor-pressure curve. For convenience the results of the application of Eq. (5) are expressed in terms of the apparent oscillator strength, i.e., (2.8 ± 0.6) $\times 10^{-3}$ and $(8.5 \pm 0.5) \times 10^{-3}$ for the 4593- and 4555-Å lines, respectively.

These f values inferred from the data of Fig. 12, are to be compared with values of 2.8×10^{-3} and
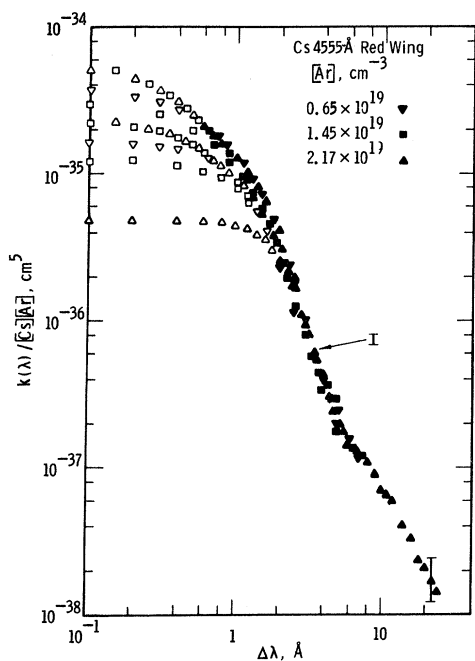
FIG. 10. Reduced absorption coefficients for the red wing of the 4555-Å line in cesium-argon mixtures. See Fig. 8 for comments.

1.2×10^{-2} from experiment[33] and of $(2.2 \pm 0.2) \times 10^{-3}$ and 1.04×10^{-2} from theory.[33] The agreement between our result and previous experiment for the 4593-Å line supports our assumption of an equilibrium vapor pressure. The approximately 20% discrepancy with previous experiment for the 4555-Å line is not understood. The combined results suggest that in the cesium density range between 2×10^{12} and 7×10^{13} atom/cm^3 the equilibrium vapor pressure assumption is good to significantly better than 20%.

V. COMPARISON WITH THEORY

A detailed theoretical interpretation of the experimental data presented in this paper is not possible at this time. In part, this is because none of the available theories[1] of line broadening is completely valid over the wavelength range covered in our experiments. Experimental evidence for the inapplicability of the impact theory is the failure of the reduced absorption coefficients to follow the wavelength dependence of the wings of a Lorentzian profile, i.e., $1/\Delta\lambda^2$, over a significant range of wavelengths about line center. In spite of the evidence[3,4] that the use of only the long-range van der Waals interaction does not allow a good description of the impact broadened portion of the line, the available criteria[4,34] for estimating the wavelength of the transition from the impact to the statistical regions are stated in terms of the long-range potentials. In our cases the transitions are estimated

to occur at $\Delta\lambda$ of about 2 and 0.3 Å from line center for the first and second doublets, respectively. This means that comparisons with statistical theory are the most nearly valid of the limiting theories in the wavelength range for which our data should be free of instrumental and hyperfine structure effects.

The first comparison with theory is in the range from about 1–6 Å from the line center for the 8944- and 8521-Å lines. In this spectral range the reduced absorption coefficients for the red wings vary as $(\Delta\lambda)^{-3/2}$ as predicted by a number of authors[1,34−36] for the statistical limit of large $\Delta\lambda$ and for a van der Waals interaction only. The value of the van der Waals constant derived from these data using the statistical theory is 1×10^{-31} cm^{6}sec^{-1} for the 8944-Å line. This value is to be compared with a value of 8×10^{-32} cm^{6}sec^{-1} calculated from the difference in potential energy curves given by Baylis[26] for the 8944-Å line. For the violet wings our data vary approximately as $(\Delta\lambda)^{-3}$, which is a more rapid variation than the $(\Delta\lambda)^{-7/3}$ variation predicted by Lindholm[35] and more in line with that predicted by Holstein[36] and by Tvorogov and Fomin.[37] According to these theories, the violet wings arise from nonstatic effects caused by the relative motion of the cesium and argon atoms. The reduced absorption coefficients calculated for the violet wing of the 8944-Å line using
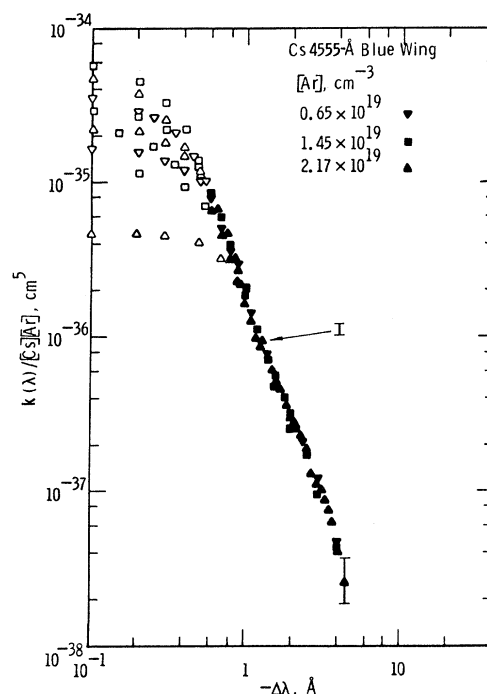

FIG. 11. Reduced absorption coefficients for the blue wing of the 4555-Å line in cesium-argon mixtures. See Fig. 8 for comments.
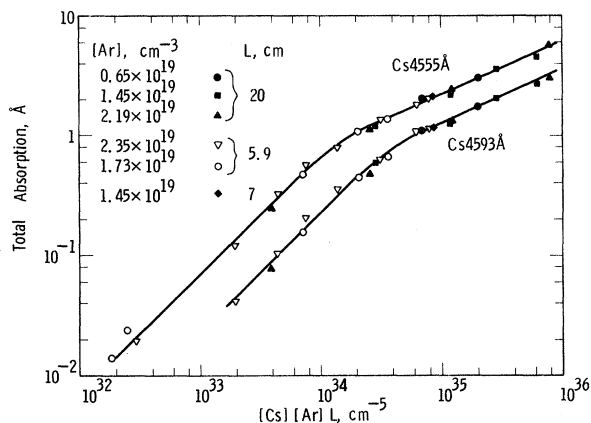
FIG. 12. Total absorption data for the 4593- and 4555-Å lines in cesium-argon mixtures. The values of [Cs] [Ar]L for the data shown for L = 5.9 cm (open points) were obtained using measured values of the total absorption for the 8944- and 8521-Å lines and the smooth curves through the data of Fig. 7. See Sec. IV. The solid points were obtained under conditions of apparent vapor-pressure equilibrium using the sealed off absorption cells. Note that the data at low values of total absorption are not expected to lie on a single curve when plotted as in the figure but instead should be a unique function of [Cs]L. See Sec. IV.

the van der Waals constant from the red wing and the formula given by Holstein[36] are about a factor of 3 smaller than the observed values at a wavelength of 2 Å from line center. The discrepancy increases with increasing $\Delta\lambda$.

A second comparison of theory and experiment is indicated by the relationship of the theoretical dashed curves of Figs. 2–5 to the solid experimental points. The theoretical curves were calculated by Baylis[38] using revised values of his semiempirical potential energy curves[26] and a quasistatic model[1,5] for the determination of the line shape. The magnitude and the wavelengths of prominent structures of these curves, e.g., the violet satellite of the 8521-Å lines, are in qualitative agreement with experiment. As pointed out by Hindmarsh and Farr,[6] the sharp maxima which occur as the result of parallel potential-energy curves for the ground and excited states are expected to be smoothed out when motional, i.e., nonstatic, effects are taken into account. Because of the apparent importance of motional effects in the wavelength range of much of our results, we have not attempted to construct a set of Cs-Ar potentials using, for example, the quasistatic model.[5] Such potential curves have been constructed by HDG [5] using fluorescence data obtained at generally larger wavelength shifts. Their results indicate that some

modifications should be made to the potential energy curves used by Baylis[26] to obtain the solid curves of Figs. 2, 4, and 5. The general agreement shown in these figures would seem to argue strongly for an explanation of the blue satellite in terms of parallel potential-energy curves[6,8,10–12,14] rather than a breakdown of the Born–Oppenheimer approximation.[39]

The rapid decrease in the reduced absorption coefficients for the red wings of the 4593- and 4555-Å lines suggests that short-range portions of the interaction potentials determine the wavelength dependence of the wings of the lines. The red wing of the 4555-Å line shows some evidence of structure at about 7 Å from line center.

VI. SUMMARY

The experimental results reported in this paper show that it is possible to make quantitative absorption coefficient measurements in mixtures of metal-vapor–rare-gas interactions and theories of these results with theory show that the absorption coefficient data can be used to test models of metal vapor-rare gas interactions and theories of the spectral distribution in the wings of the collision-broadened lines. The general agreement and detailed differences between theory and experiment using a quasistatic model for the line shape should encourage theoreticians to carry out more accurate calculations of the line shape using realistic interaction potentials and experimentalists to measure other combinations of absorbing and perturbing gases.

The principal source of error in these experiments is in the measurement of the metal vapor density. The data of Fig. 12 suggest that in future experiments the cesium density can be determined more accurately by making more accurate measurements of the total absorption by weakly absorbing resonance lines. Another possibility is to determine the cesium density through use of measurements of the real part of the index of refraction in the wings of the line. Both of these techniques require an improvement of our knowledge of the oscillator strength of the observed transition and the latter requires an investigation of the practical aspects of the relation between the real and imaginary parts of the index of refraction for non-Lorentzian spectral lines.[40]

[1]For a review of experiment and theory prior to 1957 see the article by S. Y. Ch'en and M. Takeo [Rev. Mod. Phys. 29, 20 (1957)].

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[22]Since the $I_0(\lambda)$ and $I(\lambda)$ traces were often taken several days apart, the $I_0(\lambda)$ curve sometimes changed during a series of runs. In these cases the $I_0(\lambda)$ was obtained from the wings of absorption data obtained at lower cesium density as in Fig. 1.

[23]As shown in detail in Ref. 16, the abnormally small apparent absorption coefficients observed at the line center are caused by the leakage of light at wavelengths far from that of maximum transmission through the monochromator.

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In addition, the values of [Cs][Ar]L were divided by the [Ar] values as determined from the filling pressure of argon to yield values of [Cs]L appropriate to each measured value of A_T. The ratio of A_T for the lines of the second doublet to [Cs]L was then used to calculate the respective oscillator strengths. The accuracy of these oscillator strengths is directly proportional to the accuracy of the [Cs][Ar]L values of Fig. 7 and, therefore, to the assumption of an equilibrium vapor pressure in the experiments using the sealed-off absorption cell. Because of the numerous sources of error present in this comparison, e.g., drift in cesium density and errors in planimeter determination of A_T values, we do not regard this as a measurement of the cesium density, but only as a consistency check on the assumption of an equilibrium vapor pressure.

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absorption coefficient for the line (Ref. 30). $\Delta\nu$ is the absolute value of the difference between the frequency of interest and that at line center, N is the perturber density, $\beta = 12\pi\,\Delta\nu^{5/6}C_6^{1/6}/5v$, C_6 is the van der Waals constant defined by setting the intermolecular potential equal to $\Delta\nu = C_6/R^6$ and v is the relative velocity of the collision. Note that in this notation the absorption coefficient for the red wing is $k(\Delta\nu) = \kappa N C_6^{1/2}(3\Delta\nu^{3/2})^{-1}$, i.e., the violet wing is lower by $(7/3\beta)^{-1}e^{+\beta}$. Also, Holstein's result is lower than Lindholm's (Ref. 35) by $0.23\,e^{(\beta)}$, i.e., by a large factor in the range of validity of the theory. Holstein (private communication) has averaged this result over a thermal distribution of velocities to obtain $\langle k(\Delta\nu)\rangle \approx \kappa\,(7/15)N C_6^{1/2}(\Delta\nu^{3/2}\beta^{2/3})^{-1}\exp(-\frac{3}{2}\beta^{2/3})$, where here $v = (2kT/\mu)^{1/2}$, k is Boltzmann's constant, T is the gas temperature, and μ is the reduced mass. Note that since the expansion parameter in Holstein's theory, $\frac{5}{6}\beta$, is only about unity at 2 Å from line center, we should not be too surprised as to the discrepancy between theory and experiment. Unfortunately, the shoulder in the absorption curve for the blue wing of the 8944-Å line at about 10 Å caused by the minimum in the ground-state potential[25,26] prevents a test of Holstein's theory at larger wavelength differences from line center.

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Second-Order Corrections to the Fine Structure of Helium. III. Improved Calculation of Some ^3P Contributions

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Spin-dependent perturbations from intermediate ^3P states are calculated by expanding the perturbations to the wave function in terms with one negative power of one of the electron or interelectron coordinates, in addition to standard Hylleraas terms. The nonstandard terms reflect singularities of the Breit operators. A method for solving linear equations with "almost-singular" coefficient matrices is devised. Significant improvement in accuracy is achieved for five contributions, but the procedure does not work well in all cases where the coefficient matrix is unsymmetrical.

I. INTRODUCTION

In an earlier paper,[1] referred to as I, the contributions to the fine structure of the 2^3P level of helium from second-order perturbation theory with intermediate ^3P states were calculated, and in a subsequent paper,[2] referred to as II, the contributions from ^1P and ^3D intermediate states were

also calculated. However, many of the results of I did not have the desired numerical accuracy, which was to match the absolute experimental precision of the two fine-structure separations of the $2\,^3P$ level (10^{-6} cm^{-1} for the large interval and 10^{-7} cm^{-1} for the small interval). In this paper, we present a method which dramatically increases the accuracy for those contributions that come