mation with respect to the position of the maxima and minima. The lack of quantitative agreement of our theoretical calculations with experiment may be due to the neglect of other excited states, especially the $2p$ states. Further the determination of the impact parameter for various incident energies corresponding to the fixed scattering angle should take proper account of the dependence of the trajectory on the electron state.

The calculations of Bates and Williams employing the 3-state approximation with the hydrogen molecular-ion states $1s_\sigma$, $2p_\sigma$, and $2p_\pi$ give the positions of the maxima and minima in close agreement with experiment, and also the maximum and minimum values are different from unity and zero in qualitative agreement with experiment; however, the damping of the oscillation in capture probability is too small at low energies. Smith[15] has attributed this discrepancy to the failure of the impact-parameter treatment for calculations of differential capture probability at low energies and small angles. He has shown that, even for the two-state approximation employing the $1s_\sigma$ and $2p_\sigma$ states, the wave treatment leads to considerable damping of the oscillations in the electron capture probability in H^+-H collisions at small angles and low energies. His wave treatment with two-state approximation, when suitably corrected for the coupling of the extra $2p_\pi$ state, gives satisfactory agreement with the experimental results of Lockwood and Everhart for a 3° angle of scattering. This correction, however, has been incorporated in a very indirect manner. Further, the wave treatment demands a tedious calculation with a large number of phases. To save such labor, approximations are often necessary, the effect of which is difficult to estimate, whereas the calculation in impact-parameter treatment is elegant and simple. It is to be noted that for the total cross section both the wave treatment and the impact-parameter treatment give nearly the same result.[7]

Recently Helbig and Everhart[16] have made an extensive study on the differential measurements of the electron capture probability in H^+-H collisions covering an energy range from 0.130 to 150 keV with different values of the scattering angle. In view of the very interesting results obtained by them, further theoretical investigations in this capture problem are being made.

ACKNOWLEDGMENTS

The authors wish to thank the authorities of the Tata Institute of Fundamental Research, Bombay, India, for their great help in computation of the numerical results on the computer CDC 3600.

[16] H. F. Helbig and E. Everhart, Phys. Rev. 140, A715 (1965).

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Pressure Effects of Foreign Gases on the Absorption Lines of Cesium. I. The Effects of Argon on the First Two Members of the Principal Series*

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The effect of Ar on both fine-structure components of the first two members of the Cs principal series is described. Experimental procedures are outlined. Cs(1)/Ar and Cs(2)/Ar measurements are reported up to 300 and 30 atmospheres, respectively. Special emphasis was given to obtaining precise data in the low-pressure region. This emphasis revealed structure heretofore unsuspected. In particular, the plot of half-widths versus argon density is nonlinear at low pressures, in contradiction to the present theory. Also, it is found that similar plots for shifts, although linear initially, deviate sharply from the original line at quite low pressures. After a transition region the shift curves are all observed to have a second linear region. The observed anomalous shift and broadening may be due to the effect of unresolved satellite bands of the lines.

I. INTRODUCTION

When an atom or a molecule is surrounded by a foreign substance, its natural frequencies and the breadth of its natural frequencies are modified. The well-known pressure effects are shift, broadening, asymmetry, and the appearance of satellites of spectral lines. A voluminous theoretical and experimental study of the phenomena[1] has shown that the effects are of very important significance, though much is not yet understood. It has been the general impression of theoretical investigators that experimental results, though numerous, have been quite fragmentary. For experimental convenience experimentalists have observed the effects

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[1] Such as R. G. Breene, Jr., *The Shift and Shape of Spectral Lines* (Pergamon Press, Inc., New York, 1961); H. Margenau and M. Lewis, Rev. Mod. Phys. 31, 569 (1959); S. Y. Ch'en and M. Takeo, *ibid.* 29, 20 (1957), etc.

for only certain lines of an atom. Employing different foreign gases, certain measurements were restricted to only high pressures and certain ones were limited to a very short pressure range in the low-pressure region. Theoretical work can be compared only with spotty sets of data with varying degrees of accuracy and completeness. Consequently, the theory is often regarded as confirmed when the theoretically derived relationship is in agreement with some experimental observations, even though it disagrees with others.

This paper is the first of an expected series of papers reporting the results of a current experimental program to furnish a complete set of observations of the effects of various foreign gases on all the spectral lines of cesium. It is hoped that the observations will serve as a basis for promoting theoretical understanding of the effects.

Cesium was chosen for study because it has a high vapor pressure which allows the absorption tube to be operated at relatively low temperatures. Since cesium is massive, in certain cases (for light perturbers) its motion can be neglected. The doublet separation of cesium lines is large so that the difference in the behavior of the two fine-structure lines can be measured more easily than for other alkalis. Also, the absorption series is located in such a region that light from a tungsten-ribbon lamp can serve as the background of the absorption spectrum throughout the series.

Previous data on the pressure effects on cesium lines consist primarily in the work of Füchtbauer and coworkers[2] who made shift and broadening measurements only on the $^2P_{3/2}$ component of Cs(2),[3] Cs(3), and Cs(4) perturbed by He, Ne, Ar, and N_2 and upon higher series members perturbed by methane, ethane, and propane. This data was obtained at only a single foreign-gas pressure in the low-pressure region near relative density (r.d.) 1. In addition, Ch'en and Parker[4] made shift and broadening measurements on both the $^2P_{1/2}$ and the $^2P_{3/2}$ components of Cs(2) perturbed by He and Ar. These measurements extended from r.d.$=4$ up to r.d.$=35$ and 80, respectively. No work has been reported on the cesium resonance lines.

This paper reports the pressure effects (primarily shift, broadening, and asymmetry) of argon on both fine-structure components of Cs(1) and Cs(2). For Cs(1) and Cs(2) the pressures ranged from a small fraction of an atmosphere up to 300 and 30 atmospheres, respectively. The results for Cs(2) above r.d.$=10$ are in satisfactory agreement with the earlier work of Ch'en and Parker,[4] so no need was seen to repeat still higher pressure measurements.

II. EXPERIMENTAL

The shifts in the low-pressure region were measured directly from photographic plates by means of a David Mann comparator fitted with a scanning, oscilloscope attachment[5] which provided reliable line positions within 2 μ on the plate. The plate factor was 1.54 Å/mm for the second order. Each of the data points in Figs. 2 and 4 was the average value of results from 6 to 8 spectrograms. The error estimate associated with each point is a root-mean-square computation of the 6 to 8 deviation measurements. For data points where no error mark is shown, the estimate was less than the size of the symbol being used. For the cesium resonance lines this method was used up to r.d. 10 above which the line had broadened enough to make direct measurements with the photomultiplier more accurate than the measurements from the plates. The plates used were Kodak type I-N with neon emission lines at 8495.36 and 8919.50 used for reference points. For the Cs(2) lines the corresponding limit was r.d. 4. Kodak type 103-0 plates were used with iron arc reference lines in general. Argon emission lines at 4510.73 and 4628.44 were used as reference for a few repeated points.

To obtain line-shape data in all pressure regions and to obtain shift data at higher pressures, a photomultiplier scanner with a 30-μ exit slit was used in place of the plate holder. An RCA type 7102 photomultiplier was used in the red region and an R.C.A. 6199 photomultiplier was used in the blue region. Typical signal currents were in the range of 10^{-9} to 10^{-10} A. The signal was amplified with a Kiethley Model 410 picoammeter and displayed on an *L* and *N* Speedomax "*G*" recorder. A recent improvement, which was not installed when this paper was being prepared, is the addition of a logarithmic converter between the amplifier and the recorder. Shift, asymmetry, and half-width measurements were all made directly from the chart paper after correction had been made for a sloping background. The chief source of error in the photomultiplier data was due to rapid fluctuation of the background intensity. This noise was typically 3–4% of the signal. The error flags reflect the resultant measurement uncertainty.

As many data points as possible were obtained at constant temperature. However, throughout the wide range of foreign-gas pressures, the cesium absorption line widths changed considerably. To maintain an intensity level for accurate photometrical measurements, the temperature of the absorption cell had to be higher for higher pressures. Beginning at the highest pressure, measurements were made at constant temperature until the line peak was reaching total absorption and a temperature decrease was required. The foreign-gas density was held constant from the lower end point of one interval to the upper end point of the next in order

[2] C. Füchtbauer and F. Gössler, Z. Physik **87**, 89 (1934); F. Gössler and H. E. Kundt, *ibid.* **89**, 63 (1934); C. Füchtbauer and H. J. Reimers, *ibid.* **97**, 1 (1935).
[3] The numeral in the parentheses represents the ordinal number of the member of the principal series.
[4] S. Y. Ch'en and W. J. Parker, J. Opt. Soc. Am. **45**, 22 (1955).
[5] E. G. Ebbighausen, Publ. Astron. Soc. Pacific **74**, 488 (1962).

to moniter possible temperature effects. Only a large effect could be detected in this way because a typical temperature change was only 5% with 7% being a maximum change. The measurement uncertainty was typically about 3%.

It is noted that no attempt was made to correct any of the shift or width values for the effect of satellite-band overlap or overlap from the wing of the other doublet component which became serious at high pressures. Because of the lack of knowledge of the shape of the lines and the satellite bands, it is considered appropriate to avoid semiquantitative corrections.[6]

III. RESULTS

A. Cs(1)/Ar and Cs(2)/Ar Shifts

The red shift of Cs(1) in the presence of Ar [hereafter abbreviated Cs(1)/Ar] is shown in Fig. 1. Figure 2 is an enlargement of the low-pressure region where very careful and precise measurements were made. The temperature of the absorption tube ranged from 31–200°C with corresponding cesium vapor pressures of 2×10^{-6} to 3×10^{-2} mm Hg.

The shift ($\Delta\nu_m$) is initially linear for both components up to r.d. = 2.2. The $^2P_{1/2}$ component (λ 8943) shift has a slope of -0.238 ± 0.005 cm^{-1}/r.d. (the negative sign means red shift) and the $^2P_{3/2}$ component (λ 8521) shift has a slope of -0.215 ± 0.005 cm^{-1}/r.d. From r.d. = 2.2 to r.d. = 28 the $^2P_{1/2}$ component graph follows a slight "*S*" shaped curve and then becomes linear again with a slope of -0.51 ± 0.01 cm^{-1}/r.d. From r.d. = 2.2 to r.d. = 25 the $^2P_{3/2}$ component shift increases more rapidly and surpasses the $^2P_{1/2}$ component shift at r.d. = 23. It then becomes linear with a slope of -0.94 ± 0.01 cm^{-1}/r.d.

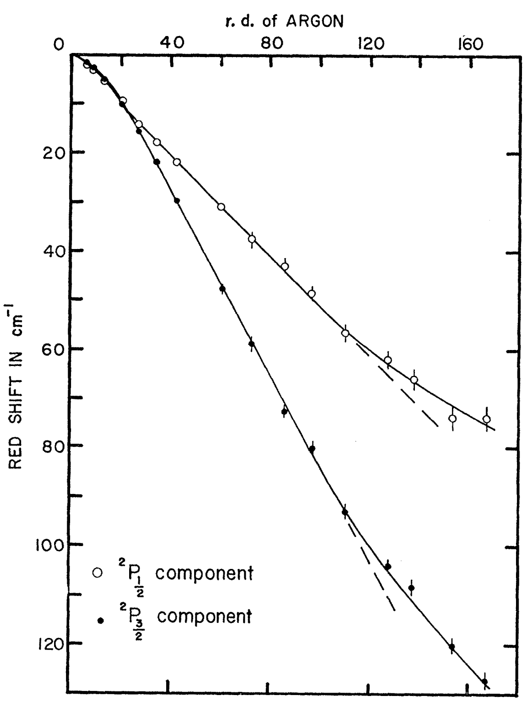

FIG. 1. Red shift of Cs(1)/Ar fine-structure lines in cm^{-1}. Dashed lines show a linear extension of the curve in the region where overlap effects may be responsible for the deviation from a linear curve. r.d. ≡ relative density.

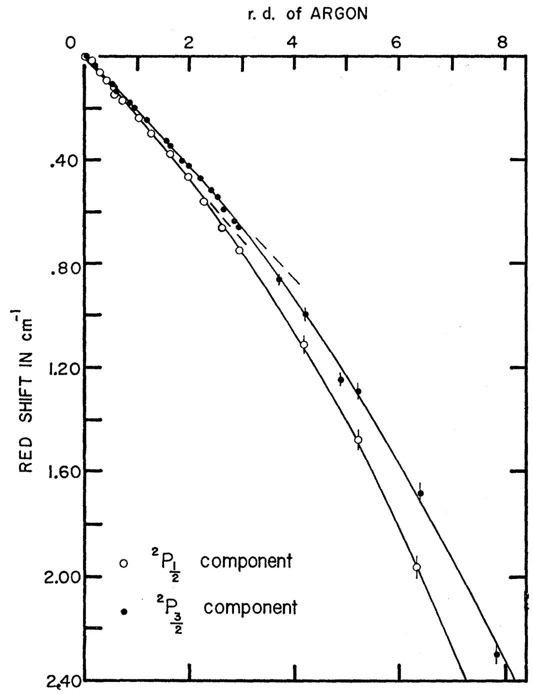

FIG. 2. Low-pressure-region enlargement of the red shift of Cs(1)/Ar fine-structure lines in cm^{-1}. Dashed lines show end of first linear region.

Above r.d. = 100 the experimental graphs deviate from linearity, but this may be due in part to the effect of overlapping of the lines and of the violet satellite band. The very large red asymmetry of the $^2P_{3/2}$ component tends to make the peak of the $^2P_{1/2}$ component absorption curve shift toward the violet. Similarly, the violet satellite band tends to make the peak of the $^2P_{3/2}$ component absorption curve shift toward the violet. As shown in Figs. 3 and 4.

The shift curves for both components of Cs(2) are linear up to r.d. = 0.9 with slopes of -0.70 ± 0.02 cm^{-1}/r.d. for the $^2P_{1/2}$ component (λ 4593) and -0.63 ± 0.02 cm^{-1}/r.d. for the $^2P_{3/2}$ component (λ 4555). A transition exists up to r.d. = 2.5 above which point both curves are again linear. The $^2P_{1/2}$ component slope is -2.75 ± 0.02 cm^{-1}/r.d. and the $^2P_{3/2}$ component slope is -2.83 ± 0.02 cm^{-1}/r.d. The curves cross at r.d. = 10±2.

It is evident that the slope of the curve for Cs(2)/Ar reported by Ch'en and Parker[4] was that of the second linear region whereas the value reported by Füchtbauer and Gössler was that of the first linear region. Two

[6] For more experimental details see R. O. Garrett, Ph.D. thesis, University of Oregon, 1964 (unpublished).

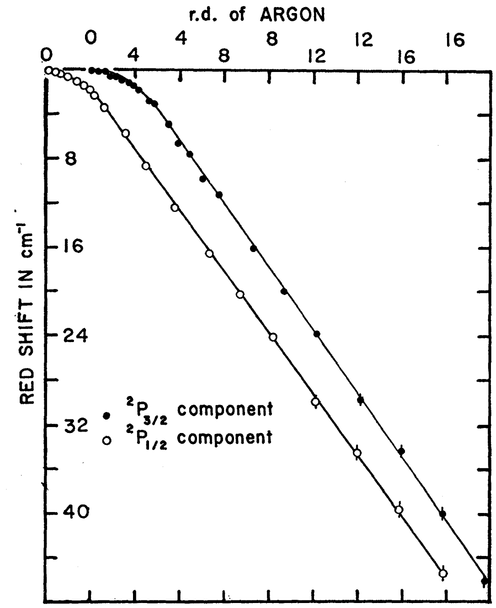

FIG. 3. Red shift of Cs(2)/Ar fine-structure lines in cm^{-1}. $^2P_{3/2}$ data are shifted 2 r.d. divisions for clarity.

linear regions separated by a transition region appear to be general for the shifts of all members of the cesium principal series perturbed by argon with the transition region occurring at lower pressures the higher the member. Preliminary work with Cs(3)/Ar and Cs(4)/Ar suggests this conclusion.

B. Cs(1)/Ar and Cs(2)/Ar Broadening

The half-width ($\Delta\nu_{1/2}$) of Cs(1)/Ar is shown in Fig. 5. Figure 6 is an enlargement of the low-pressure measurements. Figure 6 shows that there is no difference in broadening for the two doublet components until the relative density was increased to 8.5. The initial slope

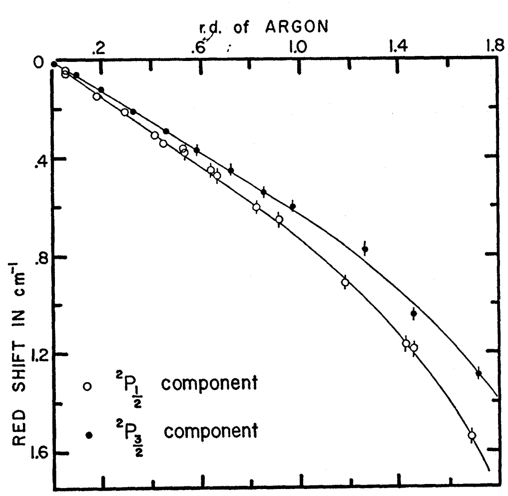

FIG. 4. Low-pressure-region enlargement of the red shift of Cs(2)/Ar fine-structure lines in cm^{-1}.

of the curve (below r.d. = 1) is 0.30 ± 0.02 cm^{-1}/r.d., but the curves are conspicuously nonlinear. Above r.d. = 8.5 both curves follow somewhat S-shaped paths until a linear region is attained (Fig. 5). The curve for the $^2P_{1/2}$ component becomes linear above r.d. = 20 with a slope of 0.53 ± 0.03 cm^{-1}/r.d. and that for the $^2P_{3/2}$ component becomes linear above r.d. = 26 with a slope of 0.84 ± 0.02 cm^{-1}/r.d. Above r.d. = 100 the overlap of the lines and of the violet satellite bands tends to artificially broaden each line.

The hyperfine structure of each component line[7] was not observable until the relative density of foreign gas was decreased to below r.d. = 0.1. Then the hyperfine

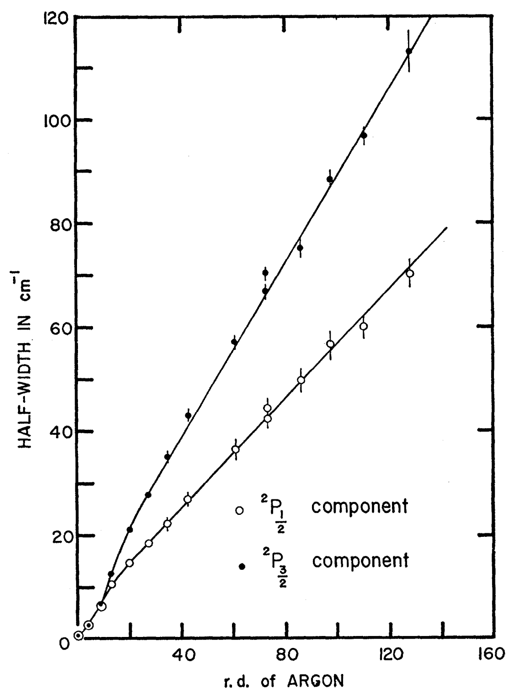

FIG. 5. Half-width of Cs(1)/Ar fine-structure lines in cm^{-1}.

lines were narrow enough to be resolved. These are 0.30-cm^{-1} apart. The experimentally measured width of 0.20 ± 0.02 cm^{-1} for each of the hyperfine lines is just 0.30 cm^{-1} less than the 0.50 ± 0.02 cm^{-1} width obtained by extrapolating the half-width curve of the unresolved lines to r.d. = 0. The dotted line on Fig. 6 is the experimental measurement after subtracting the 0.30 cm^{-1} hyperfine splitting correction.

In addition to the hyperfine-splitting effect, a further correction should be made to each of the experimental half-widths to take into account slit-width effects. This is not an easy correction to make as the line is not a single line but a double one as noted above. Also, the effects of two slits must be taken into account, the entrance and the exit slits. A close estimate suggests

[7] H. Kleiman, J. Opt. Soc. Am. 52, 441 (1962).

that near r.d. = 0 the additional slit-width correction should be about 0.20 cm^{-1} (both entrance and exit slits were 30 μ wide and the dispersion was such that 50 μ corresponded to 0.20 cm^{-1}). Thus, the half-width of the lines at r.d. = 0 would become less than 0.01 cm^{-1}.

Figure 7 shows the broadening of Cs(2)/Ar with Fig. 8 being the low-pressure enlargement. The experimental half-width at r.d. = 0 is 0.66±0.03 cm^{-1} for both components. However, the 0.30 cm^{-1} hyperfine split of the ground state and the effect of two 30-μ slits must again be taken into account. In the neighborhood of Cs(2) the dispersion of the spectrograph is such that

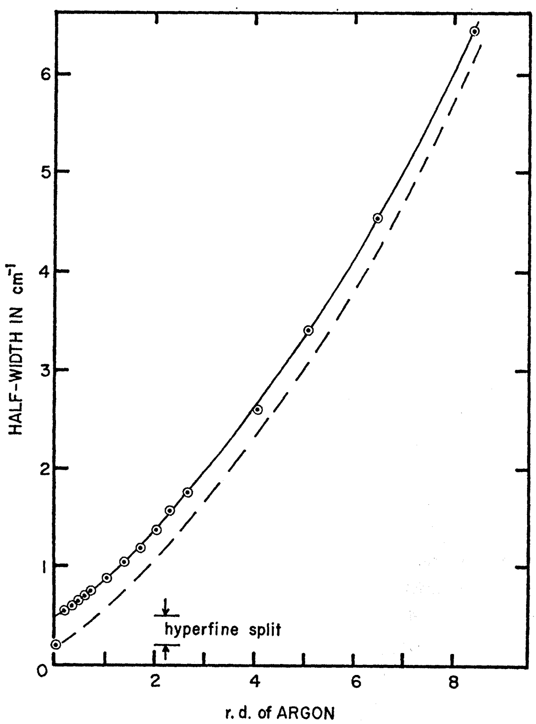

FIG. 6. Low-pressure enlargement of the half-width of Cs(1)/Ar fine-structure lines in cm^{-1}. Both $^2P_{1/2}$ and $^2P_{3/2}$ component points are coincident. The dashed line shows the half-width curve corrected for the hyperfine split effect but not corrected for slit width effects.

50 μ corresponds to 0.36 cm^{-1} so the true line width is again probably less than 0.01 cm^{-1} at r.d. = 0. Only uncorrected measurements are shown in the figures.

From Fig. 7 one can see that the $\Delta\nu_{1/2}$-versus-r.d. curves are not linear in the low-pressure region and follow pronounced S curves up to r.d. = 4.5. The curves cross at r.d. = 3.2. Above r.d. = 4.5 the $^2P_{1/2}$ component graph becomes linear with a slope of 1.86±0.02 cm^{-1}/r.d. The $^2P_{3/2}$ component graph continues to curve slightly to r.d. = 10 above which it becomes linear with a slope of 2.00±0.05 cm^{-1}/r.d.

C. Asymmetry

Figures 9 and 10 show the asymmetry ratios for Cs(1)/Ar and Cs(2)/Ar, respectively. The ratios were

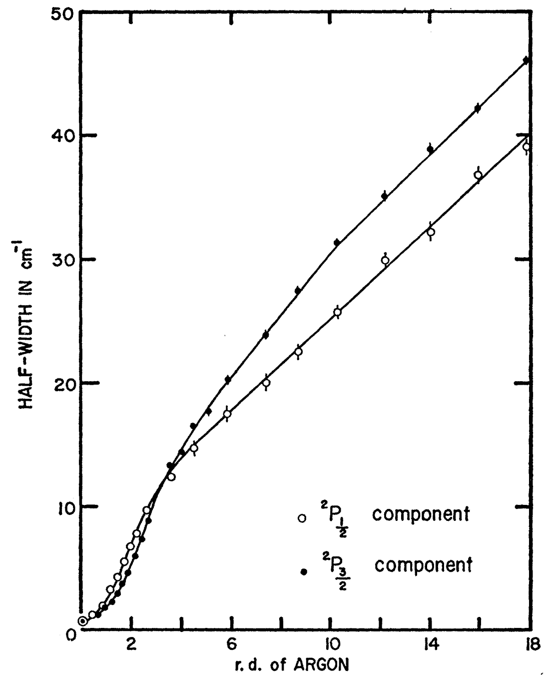

FIG. 7. Half-width of Cs(2)/Ar fine-structure lines in cm^{-1}.

obtained by taking the ratio of the red semi-half-width, i.e., the width at half-maximum of the red side of the line, to the violet semi-half-width directly from the chart paper. The accuracy in the low-pressure region is not

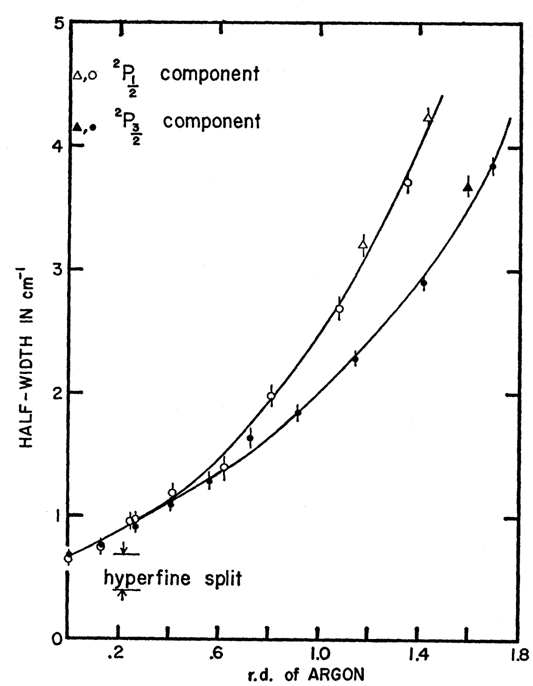

FIG. 8. Low-pressure enlargement of the half-width of Cs(2)/Ar fine-structure lines in cm^{-1}. Triangular symbols are higher temperature points described in the text.

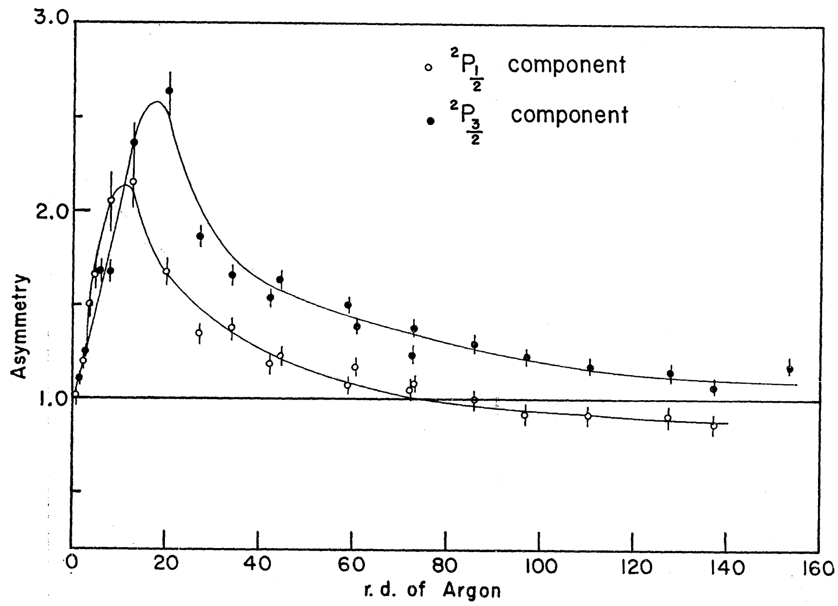

FIG. 9. Asymmetry ratio at half-intensity points for Cs(1)/Ar fine-structure lines.

as high as on the shift and half-width curves covering the same region due to the difficulty in determining the peak position with respect to the half-intensity points for a narrow line.

The Cs(1)/Ar and Cs(2)/Ar asymmetry curves both show similar features. The asymmetry rises rather quickly to a maximum and then decays more slowly, approaching a nearly constant value near unity at high relative densities. In both cases the $^2P_{1/2}$ component curve reaches its maximum before the $^2P_{3/2}$ component curve and the asymmetry for the $^2P_{1/2}$ component is in general less than that of the $^2P_{3/2}$ component except at very low pressures. For Cs(1)/Ar the $^2P_{1/2}$ component asymmetry rises to a value of about 2.1 at r.d. = 12 and then decays to a value near 0.8 or 0.9 at high r.d.'s while the $^2P_{3/2}$ component asymmetry rises to a value of about 2.6 at r.d. = 18 and then decays to a value near 1.1 at high r.d.'s. For Cs(2)/Ar the $^2P_{1/2}$ component asymmetry rises to a value of about 2.9 at r.d. = 2.2 and then decays to a value near 1.3 at higher r.d.'s while the $^2P_{3/2}$ component asymmetry rises to a value of about 3.1 at r.d. = 2.8 and then decays to a value near 1.45 at higher r.d.'s. Ch'en and Parker[4] extended these measurements to r.d. = 80 for Cs(2)/Ar and found that above r.d. = 30 the asymmetry increased up to values near 6 and 5 for the $^2P_{1/2}$ and $^2P_{3/2}$ components, respectively. However, overlapping effects become important above r.d. = 20 and these measurements may have little significance.

It should be noted that the asymmetry ratio is quite a misleading quantity for argon-broadened lines. For high relative densities the asymmetry ratio was seen to be close to unity and, in one case, was even observed to be less than unity. However, the line, while nearly symmetric at the half-intensity point, is strongly asymmetric in the wings. The red wing is more intense and extends to a greater extent than the violet wing.

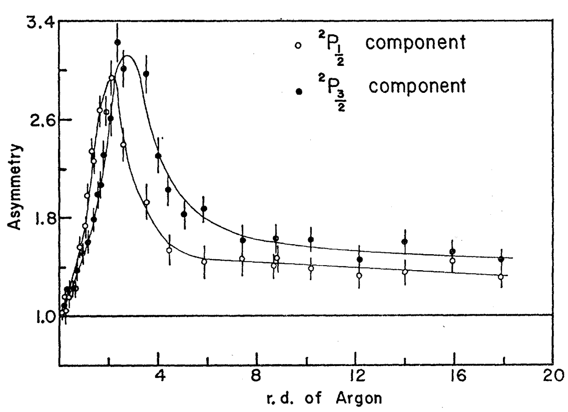

FIG. 10. Asymmetry ratio at half-intensity points for Cs(2)/Ar fine-structure lines.

D. Temperature Effects

No shift measurement showed any noticeable temperature effect. There was some indication of an increase in the width of a line as the temperature was increased but the evidence was not sufficient to draw any definite conclusions. The double points shown on each of the curves of Fig. 5 at r.d. = 73 represent data at 165°C and 137°C, the upper point being obtained at a higher temperature in each case. However, other temperature changes up to 181°C and down to 123°C and to 101°C did not show positive effects so that any temperature effect for Cs(1)/Ar must be assumed to be small. In Fig. 8 the three triangular points were obtained at temperatures higher than those of the nearby data points. The two points on the $^2P_{1/2}$ component curve were obtained at 160°C with the adjacent points obtained at 139°C. The one point on the $^2P_{3/2}$ component curve was obtained at 139°C with the adjacent points on both sides obtained at 115°C. No significant higher pressure evidence was observed for a temperature effect with Cs(2)/Ar. The largest effect that would be possible is a 3% increase in half-width as the result of a 5% increase in temperature which is about a $T^{1/2}$ dependence. Any temperature effect on shifts of the argon perturbed lines must be less than $T^{1/2}$ which is about the minimum observable effect. All curves in this paper were drawn assuming no temperature effect at all.

IV. DISCUSSION

The original purpose of this work was to obtain more accurate and more reliable data than are presently available to allow a strict comparison between theory and experiment. Substantial agreement with theory was expected, as has been the case with data reported previously. Unexpectedly, the present detailed experimental study of shifts and broadening in the low-pressure region has revealed more complex behavior than the earlier data. The most remarkable discrepancies with respect to previous data as well as previous theoretical work are the nonlinear relationship between the half-widths and the argon density and the linear shift over two different pressure ranges with slopes that are dissimilar in the two ranges.

Granier, Granier, and de Croutte[8] recently observed the shift and broadening of Rb(1)/Ar. Except for the fact that their pressure range is only one-third of ours, their Figs. 1 and 2 have features similar to our Figs. 1 and 5. We both observed that the broadening of the two components of the resonance lines is the same when the r.d. of argon is low [below 10 for Rb(1)/Ar; 8.5 for Cs(1)/Ar]. The disagreement is that they reported a linear relationship between half-width and r.d. while our results show an unmistakenly upward curvature (cf., Fig. 6). They missed this observation mainly due to the lack of data points at low r.d.

For a qualitative and phenomenological description the observed anomalous shift and broadening may be due to the effect of unresolved satellite bands.[9] The intensity of these satellites increases with either the increase in the temperature of the absorption tube (thus, the vapor pressure of the absorber) or the increase of the r.d. of the perturber. For Cs(1)/Ar the violet satellite should not affect our results because it is quite far (220 cm^{-1}) from the shorter wavelength component of Cs(1) lines and is very faint under the experimental conditions. But, an unresolved red satellite for each component of Cs(1) is possible. As the r.d. of argon is increased, the rise in intensity of a red satellite will cause the observed half-widths to increase more rapidly than linearly as is shown in Figs. 6 and 8. Also, the increase should be primarily on the red side of the line as is shown by the strong peak of the asymmetry ratios, Figs. 9 and 10. A plot of the blue semi-half-width for Cs(1)/Ar shows only a slight deviation from linearity whereas the red semi-half-width shows a large deviation.

Likewise, the growth of unresolved red satellites may affect the observed shift as follows: When the r.d. was very low (and temperature was also low) the satellite intensity was negligibly small. Under these conditions the first linear region was observed. As the r.d. became larger, the intensity increase of the red satellite caused a shift of the peak toward the position of the satellite. This gave the transition region. The second linear region obtained upon further increase in r.d. may be due to the increase in satellite intensity at the same rate as the line is shifting, since the slope differs from that in the first linear region.

For Cs(2)/Ar the corresponding violet satellite becomes close (<20 cm^{-1}) and the red satellite is again not resolved. The relative intensity of these satellites with respect to the associated lines is stronger than in the case for Cs(1)/Ar. Thus, a plot of blue and red semi-half-widths does not show such sharp differences as it does for Cs(1)/Ar. Also, Fig. 8 shows a much faster increase than does Fig. 6.

For a refinement of the theoretical assumptions of the existing theories, two comments may be pertinent: (1) Correlations between radiating and perturbing atoms might affect a change in the probability distributions of the perturbers. Further, the distribution with respect to internuclear distance may be affected by pressure, by temperature, and by the nature of the colliding pairs. (2) The nature of the collision-induced satellite bands is not yet well understood.[10] These bands, in general, overlap with the broadened lines. Can the observed line contour be considered as a superposition of the pressure-broadened line and the pressure-induced satellite or should the two be considered together as one absorption process? Detailed theoretical treatment must be postponed until the observations are completed and the phenomena are studied with many foreign gases.

[8] R. Granier, Mme. J. Granier, and E. de Croutte, J. Phys. (Paris) **24**, 349 (1963).

[9] S. Y. Ch'en and R. A. Wilson, Physica **27**, 497 (1961); S. Y. Ch'en and C. W. Fountain, J. Quant. Spectry. Radiative Transfer **4**, 323 (1964).

[10] So far, there are at least three different ideas on satellites. The satellite is considered as (1) due to temporary, loosely bound molecules, (2) due to the relative shape of the potential curves for the upper (excited) and the lower (ground) states at various collision distances, and (3) due to plasma oscillations at the time of collision.