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Pressure Effects of Foreign Gases on the Absorption Lines of Cesium. IV. The Effects of Neon*

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The effect of Ne on the fine-structure components of the first four members of the Cs principal series is described. Less detailed information is provided for higher series members up to Cs(20)/Ne, with the emphasis on the shift of the ${}^2P_{3/2}$ component. Both components of Cs(1)/Ne shift toward the red for relative density (r.d.) <24, above which point the ${}^2P_{1/2}$ component shifts to the violet. For Cs(2)/Ne the ${}^2P_{1/2}$ component has almost zero slope initially and shifts to the violet. The ${}^2P_{3/2}$ component shifts to the red initially, but above r.d.=14 it is also violet-shifted. The Cs(2)/Ne shift curves are both linear above r.d.=25. Both components of all higher members are observed to be violet-shifted in all regions, with fine-structure effects becoming less apparent. Half-widths are observed to be nonlinear with density in all regions studied. Temperature effects are described for Cs(1)/Ne and Cs(2)/Ne, with an increase in temperature causing a large increase in violet shift (or decrease in red shift) at low pressures. The possible existence of a violet satellite for the long-wavelength component of Cs(2)/Ne as well as the short-wavelength component is reported.

I. INTRODUCTION

THIS paper is the fourth in a series of papers reporting results of a detailed study of the effects of various foreign gases on the absorption lines of cesium. Reference is made to our earlier papers[1] for experimental details and nomenclature. The neon employed was 99.99% pure with some impurities of He and N_2.

The pressure effects of neon for the Cs resonance lines have not been investigated previously. Füchtbauer and his associates[2] studied Cs(2) and Cs(3) up to 4700 mm of Ne. Other observations[3] were concerned with only the high-series lines with neon at a low pressure.

In the present work, the broadening, shift, and asymmetry effects of Ne for Cs resonance lines were measured up to 113 atm [relative density, (r.d.)=74.7]; up to 93.5 atm (r.d.=55.0) for Cs(2); up to 42.8 atm (r.d.=22.5) for Cs(3); and up to 19 atm (r.d.=11.1) for Cs(4). The shift of the ${}^2P_{3/2}$ component of the high-series lines up to Cs(20) is also provided. The strikingly characteristic behavior of shift and broadening of these Cs lines in Ne reported here will be information of importance in checking theoretical results on the pressure broadening of spectral lines.

II. RESULTS

A. Shifts

1. The Shift of the Doublet Components of Cs(1)/Ne

Figure 1 shows the shift in cm^{-1} of the doublet components of Cs(1) versus the relative density (r.d.) of Ne. A low-pressure-region enlargement is shown in Fig. 2. Several interesting results should be pointed out: (a) One should note the much smaller shift produced by neon in comparison with the shift produced by other gases. (b) While the short-wavelength (${}^2P_{3/2}$) component (λ8521) shifted towards red for r.d. up to 74 or more, the long-wavelength (${}^2P_{1/2}$) component (λ8943) shifted first toward the red, reaching a maximum at around r.d.=12, then the shift reversed, and became

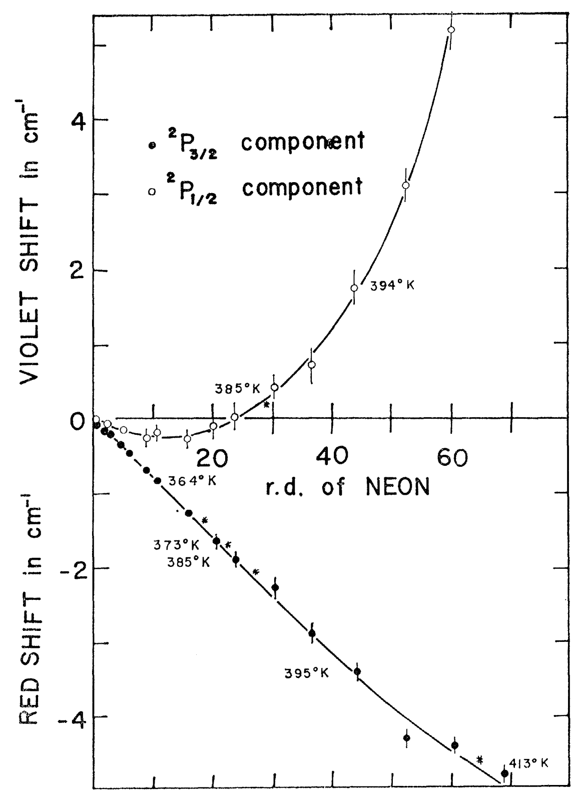

FIG. 1. The shift of Cs(1)/Ne fine-structure lines. The asterisks mark the boundaries of different temperature values of the absorption tube.

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[1] S. Y. Ch'en and R. O. Garrett, Phys. Rev. 144, 59 (1966) (Paper I); R. O. Garrett and S. Y. Ch'en, *ibid.* 144, 66 (1966) (Paper II); S. Y. Ch'en, E. C. Looi, and R. O. Garrett, *ibid.* 155, 38 (1967) (Paper III).

[2] C. Füchtbauer and F. Gossier, Z. Physik 87, 89 (1933).

[3] Such as C. Füchtbauer, P. Schulz, and A. F. Brandt, Z. Physik 90, 403 (1943); C. Füchtbauer and H. J. Reimers, *ibid.* 95, 1 (1935).

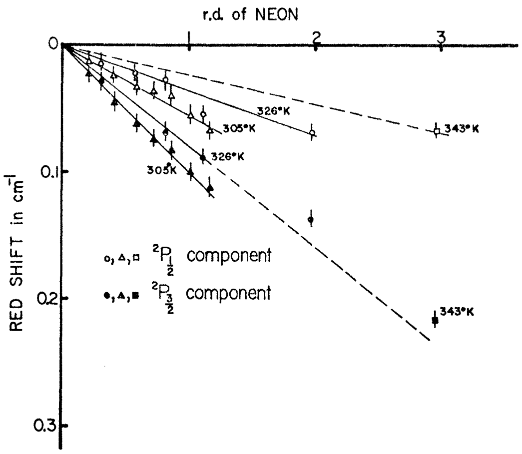

FIG. 2. Low-pressure region enlargement of Cs(1)/Ne fine-structure lines. Effect of temperature change on the shift is shown.

violet when the r.d. was higher than 24. (c) The data indicate a strong temperature dependence at low pressures. An increase in temperature will cause an increase in shift (i.e., more towards violet). Because the shift is small and the points have relatively large uncertainties, and the experimental apparatus was not designed to allow large temperature variations for a constant r.d., it is uncertain as to how large the effect is. The initial slope of the $^2P_{1/2}$ component shift is approximately -0.05 cm^{-1}/r.d. for 305°K and appears to increase to about -0.035 cm^{-1}/r.d. for 326°K. Similarly, the $^2P_{3/2}$ component has a slope of -0.10 cm^{-1}/r.d. at 305°K which appears to increase to about -0.08 cm^{-1}/r.d. at 326°K. The vapor pressure of Cs changes from 2×10^{-6} mm Hg to 1×10^{-5} mm Hg at these temperatures. (d) At "high" pressures (say r.d. above 9), the shift is not appreciably affected by temperature changes. This is clearly seen by the linear slope of the $^2P_{3/2}$ component which has a constant slope of -0.080 ± 0.002 cm^{-1}/r.d.

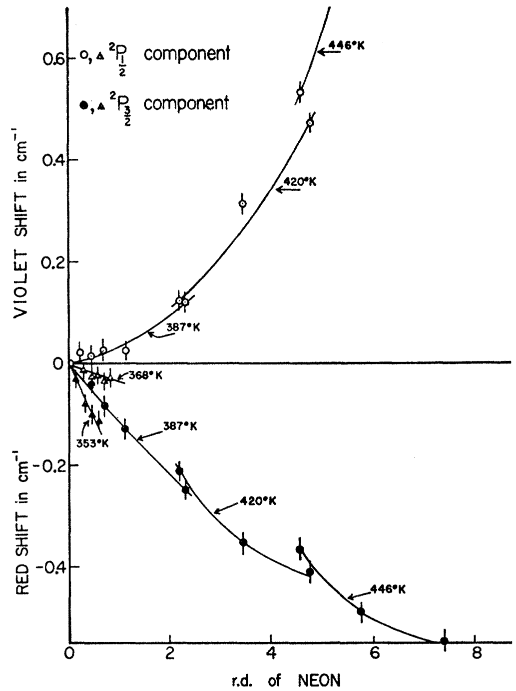

FIG. 4. Low-pressure region enlargement of Fig. 3. Effect of temperature changes on the shift is shown.

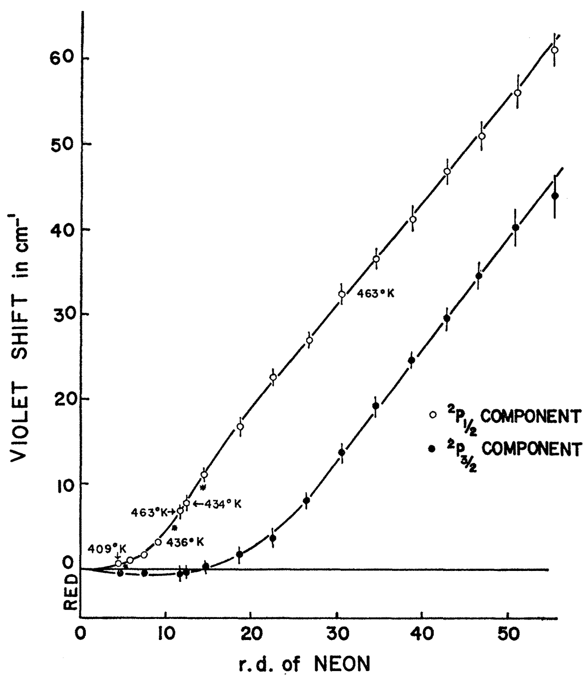

FIG. 3. The shift of Cs(2)/Ne fine-structure lines. The temperature of the absorption tube is indicated and is the same for both components at a given r.d.

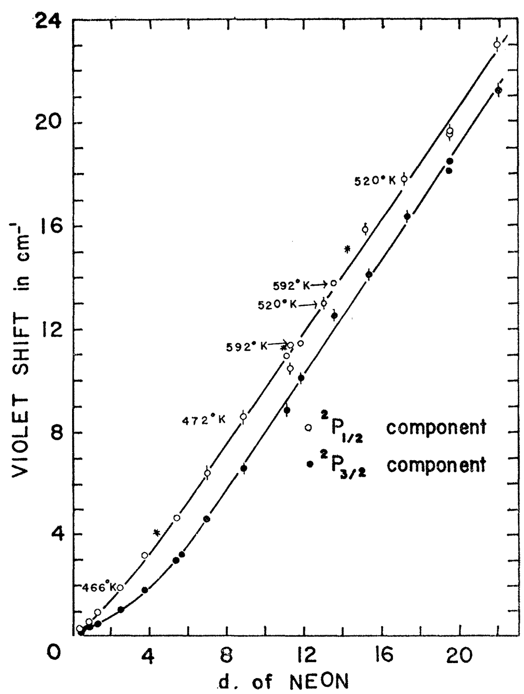

FIG. 5. The violet shift of Cs(3)/Ne fine-structure lines. The asterisks mark the boundaries of different temperature values of the absorption tube.

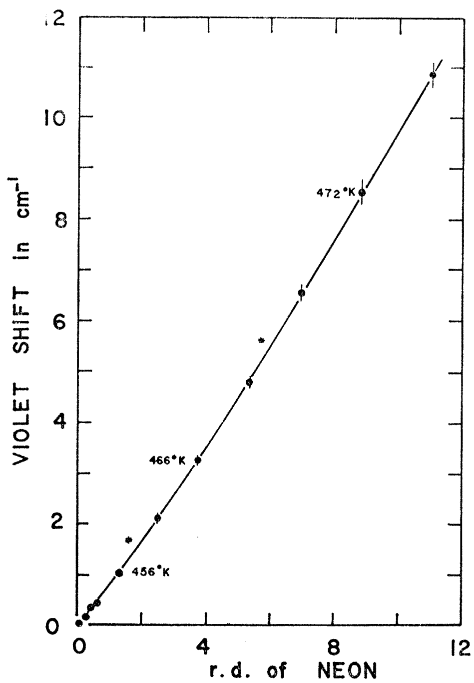

FIG. 6. The violet shift of the short-wavelength component ($^2P_{3/2}$) of Cs(4)/Ne. The asterisks mark the boundaries of different temperature values of the absorption tube.

This slope is the same as the low-pressure 326°K data, but includes points taken at 348, 356, and 395°K with all points above r.d. = 28 being obtained at the latter temperature.

2. *The Shift of the Doublet Components of Cs(2)/Ne*

Figures 3 and 4 shows the shift of Cs(2)/Ne up to r.d. = 54.8 and the more accurate measurements in the low-pressure region, respectively. It is of interest to note the difference of the behavior of the shift for this doublet in comparison to that of Cs(1)/Ne. The $^2P_{1/2}$ component graph is generally violet shifted, the slope of which becomes constant above r.d. = 20 with a value 1.19 ±0.02 cm^{-1}/r.d. The $^2P_{3/2}$ component graph is initially red shifted (as for Cs(1)/Ne), but at about r.d. = 14 it becomes violet shifted. Above r.d. = 25 it becomes linear with a slope of 1.31±0.02 cm^{-1}/r.d.

At low pressures (Fig. 4) the shift of both components again seems to exhibit definite temperature effects—the higher-temperature data point shifted more towards the violet in every instance. The $^2P_{1/2}$ component points initially have almost zero slope, but data points obtained at 368°K are shifted towards the red, whereas data points obtained at 387°K are shifted towards the violet. Data points taken for the $^2P_{3/2}$ component at 387, 420, and 446°K seem to lie on a single smooth curve. However, 353°K data do not lie on this curve, and the double points taken at the higher temperature changes seem to indicate a definite effect.

3. *The Shift of the Doublet Components of Cs(3)/Ne*

Figure 5 shows that both components of Cs(3)/Ne shift towards the violet. The $^2P_{1/2}$ component graph is initially linear with a slope of 0.65±0.02 cm^{-1}/r.d. The graph curves gradually upward above r.d. = 1.5, be-

TABLE I. Summary of results for the shifts of all the lines of cesium (up to the 20th member) in neon.

Member		Initial linear region Range of r.d.	Slope[a] of shift versus r.d. (cm^{-1}/r.d.)	Second linear region Range of r.d.	Slope of shift versus r.d. (cm^{-1}/r.d.)
1	$^2P_{1/2}$	0–2	−0.05 to −0.035 (temp. effect)		
	$^2P_{3/2}$	0–60	−0.080±0.002 (temp. effect)		
2	$^2P_{1/2}$	...	...	20–54 (or more)	1.19±0.02
	$^2P_{3/2}$	0–2	−0.11 or less (temp. effect)	25–54 (or more)	1.31±0.02
3	$^2P_{1/2}$	0–1.5	0.65±0.02	4.5–22 (or more)	1.10±0.02
	$^2P_{3/2}$	0–1.5	0.33 to 0.42 (temp. effect)	6–22 (or more)	1.10±0.02
4	$^2P_{1/2}$	0–2	0.83±0.02 (temp. effect)	...	...
	$^2P_{3/2}$	0–2	0.84±0.02 (temp. effect)	5–9 (or more)	1.08±0.04
5	$^2P_{3/2}$	0–0.7 (or more)	0.82±0.05		
6	$^2P_{3/2}$	0–0.7 (or more)	0.86±0.05		
7	$^2P_{3/2}$	0–0.7 (or more)	0.83±0.05		
8	$^2P_{3/2}$	0–0.7 (or more)	0.82±0.05		
9	$^2P_{3/2}$	0–0.7 (or more)	0.74±0.05		
10	$^2P_{3/2}$	0–0.7 (or more)	0.72±0.05		
11	$^2P_{3/2}$	0–0.7 (or more)	0.72±0.05		
12	$^2P_{3/2}$	0–0.7 (or more)	0.67±0.05		
14	$^2P_{3/2}$	0–0.7 (or more)	0.65±0.05		
16	$^2P_{3/2}$	0–0.7 (or more)	0.55±0.05		
18	$^2P_{3/2}$	0–0.7 (or more)	0.61±0.05		
20	$^2P_{3/2}$	0–0.7 (or more)	0.56±0.05		

[a] Minus sign means red shift.

coming linear again above r.d.$=4.5$ with a slope of 1.10 ± 0.02 cm^{-1}/r.d. Some data points below r.d.$=0.9$ were obtained at both 408 and 458°K, with no evidence of any shift differences due to temperature effects. The vapor pressure of Cs changes from 4×10^{-3} mm Hg to 4×10^{-2} mm Hg at these temperatures.

The $^2P_{3/2}$ component graph does appear to be affected by temperature in the low-pressure region. At 380°K, the slope up to r.d.$=0.9$ is approximately 0.33 ± 0.03 cm^{-1}/r.d., but at 438°K the slope in the same region is approximately 0.42 ± 0.03 cm^{-1}/r.d. Above r.d.$=1.5$ the graph curves upward, becoming linear again above r.d.$=6$ with a slope identical to that for the $^2P_{1/2}$ component (1.10 ± 0.02 cm^{-1}/r.d.). Thus, at higher pressures the shift slope of both components is the same, but the two curves are displaced from one another so that the shift of the $^2P_{1/2}$ component is constantly higher than that of the $^2P_{3/2}$ component by about 1.6 cm^{-1}.

4. *The Shift of the Doublet Components of Cs(4)/Ne*

Both the $^2P_{1/2}$ and the $^2P_{3/2}$ components of Cs(4)/Ne are initially linear up to r.d.$=2$ with nearly identical slopes of 0.83 ± 0.02 cm^{-1}/r.d. As shown in Fig. 6, above r.d.$=2$ the $^2P_{3/2}$ graph curves slightly upward. Data were only taken to r.d.$=11$, so the existence of a second linear region cannot be confirmed, but the graph may be linear above r.d.$=5$ with a slope of 1.08 ± 0.04 cm^{-1}/r.d.

It happened that the shift of both components was measured at two different temperatures, thus supplying some information of temperature effect. For the $^2P_{1/2}$ component, a run was performed at 458°K for r.d. up to 1.8 and another at 421°K for r.d. up to 0.9. The plots of shift versus r.d. are linear with a slope of 0.83 and 0.72 cm^{-1}/r.d., respectively. Likewise, for the $^2P_{3/2}$ component, runs with 458°K for r.d. up to 1.8 and 408°K for r.d. up to 0.8 were made. The plots are also linear with slopes of 0.84 cm^{-1}/r.d. and 0.80 cm^{-1}/r.d., respectively.

5. *The Shift of the $^2P_{3/2}$ Components of Cs(5)/Ne–Cs(20)/Ne*

Data on the $^2P_{3/2}$ components of Cs/Ne for the 5th through the 20th members were obtained from r.d.$=0$ to r.d.$=0.7$ only. In this region, all shift graphs appeared to be linear with the slopes shown in Table I. The data on these latter members were all obtained at 465°K.

Figure 7 is a plot of the data contained in Table I. The initial slopes are depicted by solid circles and are connected by a line on the graph. One will note that this figure is quite different from that obtained for Cs/Kr (Fig. 8 of Paper III). For Cs/Kr, the only observed linear region of the red shift for the high-member lines may correspond to the second-linear region of the red shift for lower-member lines in interatomic interaction. For Cs/Ne the only observed linear region of the violet shift of the high-member lines appears to relate closely with the first linear region of the violet shift of the lower member lines.

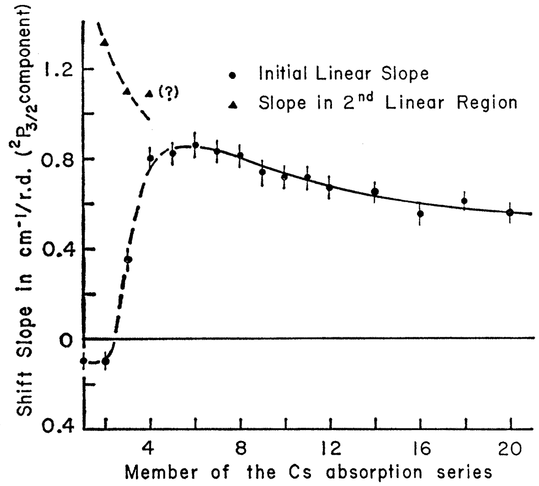

FIG. 7. The slopes of the shift versus r.d. curves for the $^2P_{3/2}$ components of various series lines at low pressures. Solid triangles show slopes of linear regions reached at higher pressures for Cs(2)/Ne, Cs(3)/Ne, and Cs(4)/Ne.

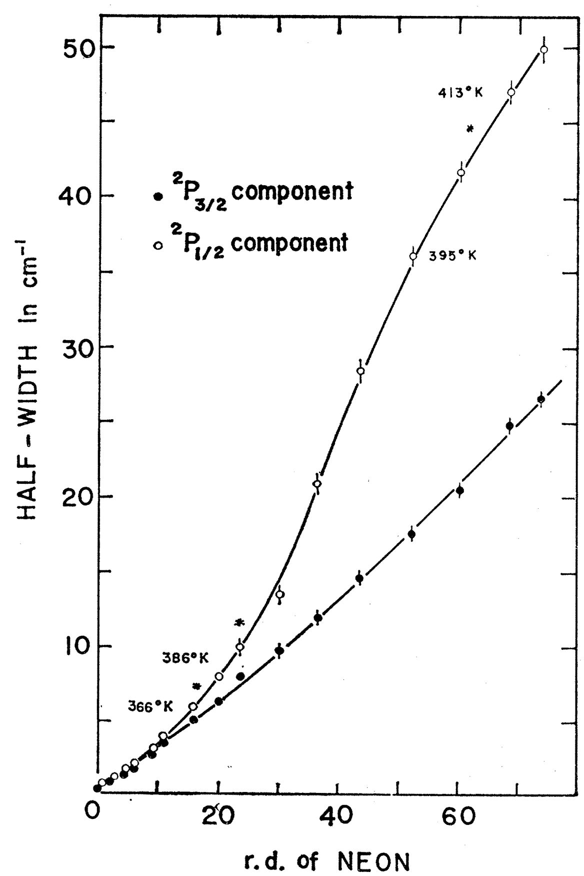

FIG. 8. The half-width of Cs(1)/Ne fine-structure lines. The asterisks mark the boundaries of different temperature values of the absorption tube.

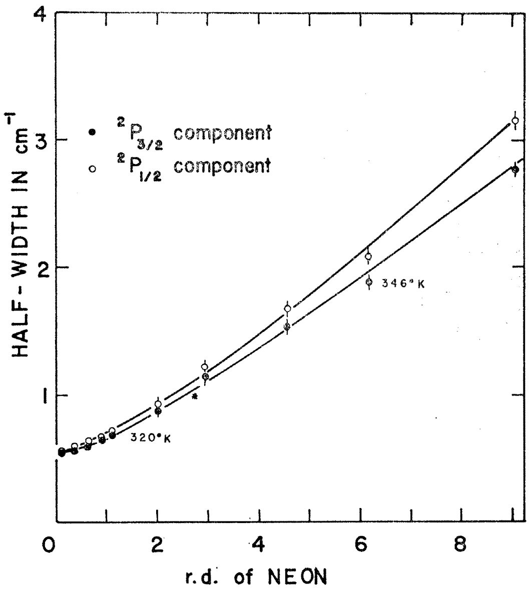

FIG. 9. Low-pressure region enlargement of Fig. 8.

B. Broadening

Figures 8 and 9 represent the half-widths of Cs(1)/Ne for the high-pressure range (r.d. up to 75) and the low-pressure range, respectively. The graphs deviate slightly from linearity at low pressures, but the deviation is a real one. At higher pressures, the $^2P_{3/2}$ component curve continues to deviate only slightly from a straight line whereas the $^2P_{1/2}$ component graph exhibits much more curvature. Because of the lack of linearity anywhere, no slopes should be reported. However, for the sake of comparison with the broadening of other lines, the rate of broadening with r.d. within r.d. = 3 may be put as approximately 0.2 cm^{-1}/r.d. for both components. As noted in Paper I, the half-width at r.d. $\rightarrow$ 0 has not been corrected for the 0.30 cm^{-1} hyperfine splitting nor for the 0.20 cm^{-1} slit width effect, so the true half-width is near zero on the scale of Fig. 9 at r.d. $\rightarrow$ 0.

Figures 10 and 11 show the corresponding graphs for Cs(2)/Ne. The effect of temperature on the half-width of the $^2P_{1/2}$ component was not detectable. However, a very conspicuous effect was observed for the $^2P_{3/2}$ component. A temperature increase of 12% (25 out of 400°K) appears to result in a half-width increase of 20–30%. The approximate slopes within r.d. = 1 of the graphs are approximately 0.6 cm^{-1}/r.d. for both components.

Figure 12 shows the half-width of the $^2P_{3/2}$ component of Cs(3)/Ne and Cs(4)/Ne. These curves are very similar in shape to those for Cs(2)/Ne. The graph for Cs(3)/Ne is straight within r.d. = 1, with an identical slope of 1.14 cm^{-1}/r.d. for both components. The initial slope of the $^2P_{3/2}$ component of Cs(4)/Ne is 1.0 cm^{-1}/r.d. One sees that Cs(3) has the highest broadening of all Cs lines in the presence of neon.

C. Asymmetry

Figure 13 is a plot of the red half to the blue half of the half-width for Cs(1)/Ne. The $^2P_{1/2}$ component exhibits blue asymmetry in all regions attaining a maximum of about 0.30 at r.d. = 52. The $^2P_{3/2}$ component is initially asymmetric to the red side reaching a maximum in this direction of about 1.10 at r.d. = 12 and then becoming asymmetric to the blue above r.d. = 43.

Figure 14 shows the asymmetry ratio of Cs(2)/Ne. The $^2P_{1/2}$ component reaches a maximum blue asymmetry of 0.29 at r.d. = 9 and then becomes considerably less asymmetric above this value of r.d. The $^2P_{3/2}$ component reaches a maximum blue asymmetry of 0.24 at r.d. = 22 and gradually becomes less asymmetric above this point.

Up to r.d. = 9 the asymmetry of the $^2P_{3/2}$ component of Cs(3)/Ne and Cs(4)/Ne are not so extreme as for Cs(1)/Ne and Cs(2)/Ne. The maximum blue asymmetry of Cs(3)/Ne appears to be reached at r.d. = 9 with a value of 0.47. The measurements on Cs(4)/Ne show that it is nearly symmetrical at the half-intensity point in the low-pressure region.

III. DISCUSSION

Two very interesting phenomena about the behavior of the shift of Cs lines produced by Ne are exposed in this work: (1) The very striking difference of shift of the fine-structure component lines for a given lower-member doublet, and (2) changes of the difference in shift of the fine structure lines as one goes to higher doublets in the

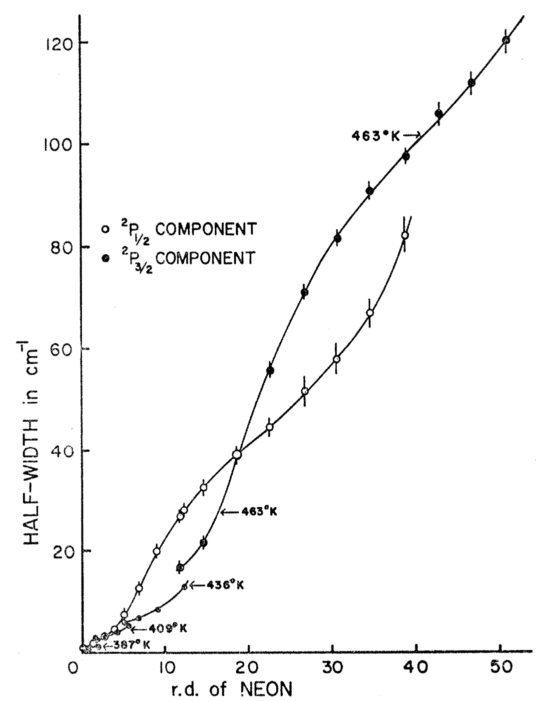

FIG. 10. The half-width of Cs(2)/Ne fine-structure lines. Temperature effect for $^2P_{3/2}$ component is shown by broken segments.

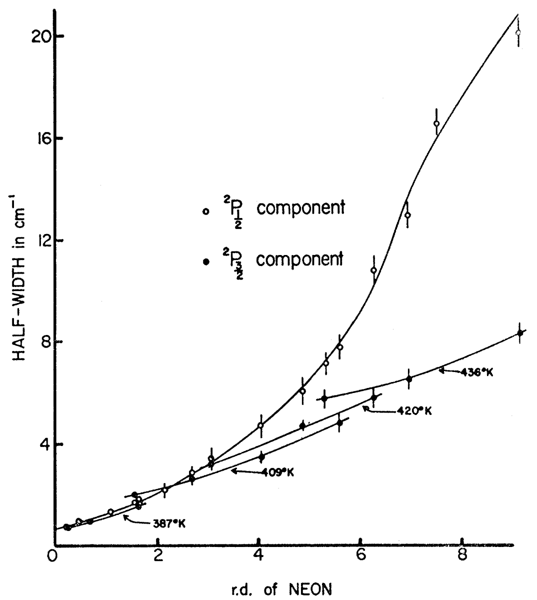

FIG. 11. Low-pressure region enlargement of Fig. 10, showing the temperature effect in more detail.

series. Figure 1 shows the very startling result of the shift of the two doublet components of Cs(1)/Ne as the number density of neon perturbers is increased. Below Ne r.d.$=24$ both components shifted towards red, beyond which the red shift of the $^2P_{3/2}$ component continued to increase while that of the $^2P_{1/2}$ component was shifting towards violet. With reference to the observations by Robin and Robin[4] and the data observed here for Cs(2)/Ne (Fig. 3), it is expected that the shift of the $^2P_{3/2}$ component would turn back towards blue as the r.d. of Ne is further increased above r.d.$=150$. For the second member of the Cs series lines (Fig. 3), the initial red shift of the $^2P_{1/2}$ component disappeared. The red shift of the $^2P_{3/2}$ component decreased quickly as the r.d. of Ne was increased, and then turned to a violet shift at a much lower r.d. of 14. If one reviews Fig. 5 also, one would be led to the conclusion that, for Ne, the shift of the higher doublet components behaves very differently from that for Cs(1). As the member of the series lines is higher, it is observed that (a) the difference became smaller very rapidly, and (b) the shifts of the doublet components are both pushed towards the violet as shown in Fig. 7.

It is evident here that, for Ne, the shift and broadening of the $^2P_{1/2}$ component is in general greater than those of the $^2P_{3/2}$ component for the low-member doublets observed. This relative shift and broadening of the fine structure components is similar to those observed for He in Paper II.

Also, within the same range of r.d., the general shape of asymmetry curves for Cs(2)/Ne is very similar to those for Cs(2)/He. In general, the shape of the Cs(1)/Ne and Cs(1)/He asymmetry curves is also alike, except that the asymmetry of the $^2P_{1/2}$ component is much larger for Cs(1)/Ne.

It is to be noted that while the $^2P_{1/2}$ component of Cs(1) was shifting towards "red" for r.d.<24, and the $^2P_{3/2}$ component of Cs(2) was shifting towards "red" for r.d.<14, both lines always had a "violet" asymmetry.

The present experiment was not designed to study temperature effects. The maximum temperature change that caused a given line to change from almost too much absorption to almost too little absorption was about 25°K. Since a typical temperature was 400°K, this amounts to a typical temperature change of 6%. Each datum point is typically subject to an error of approximately 3% so that a $T^{1/2}$ temperature dependence would probably be just barely detectable. Some very low pressure data points were obtained with a tube six times as long as the one used for higher-pressure points so that a larger range of temperatures was obtained. The very strong temperature effects noted in Figs. 2 and 4 were obtained in this way, and hence resulted from different experimental arrangements. Both used saturated vapor pressures of cesium.

The relatively slight shifts observed for neon-perturbed lines of cesium at low pressures together with corresponding measurement uncertainties, which, as noted by the error flags, were rather large, suggest that the magnitude of the temperature effect as reflected in the data should be accepted only with great caution. However, the effect was always in the same direction so that it is beyond experimental error to state that at

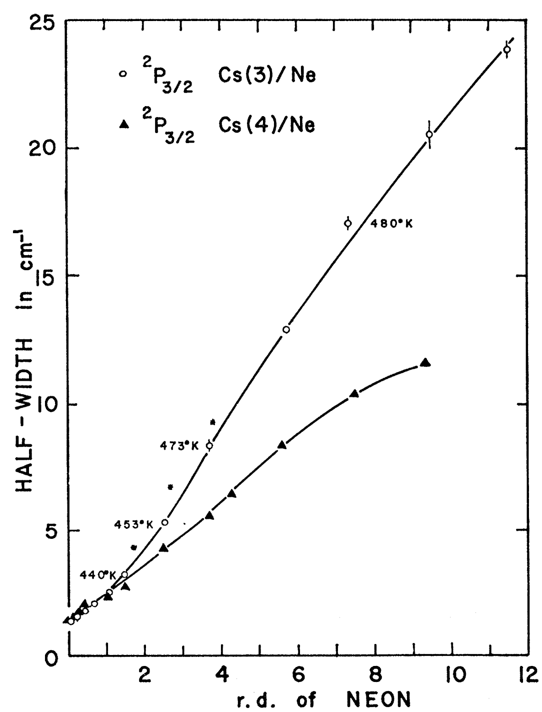

FIG. 12. The half-width of the $^2P_{3/2}$ components of Cs(3)/Ne and Cs(4)/Ne.

[4] J. Robin and S. Robin, Compt. Rend. 233, 1019 (1951).

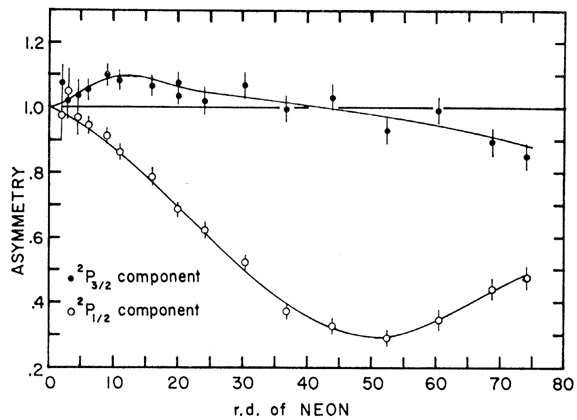

FIG. 13. Asymmetry at half-intensity points for Cs(1)/Ne fine-structure lines.

low pressures of neon, cesium lines are shifted toward the blue (less negative or more positive shift) as the result of an increase in temperature.

Granier and Granier[5] have reported a similar temperature effect on the resonance lines of rubidium perturbed by hydrogen and also deuterium. Their experiment was made to check part of Schuller's[6] theory on the shifts of spectral lines perturbed by foreign gases. Schuller determined that the attractive part of the interaction potential acting between the active and the perturbing atom should cause a red shift which should have little or no temperature dependence. The repulsive part of the interaction potential should cause a violet shift which has a large temperature dependence

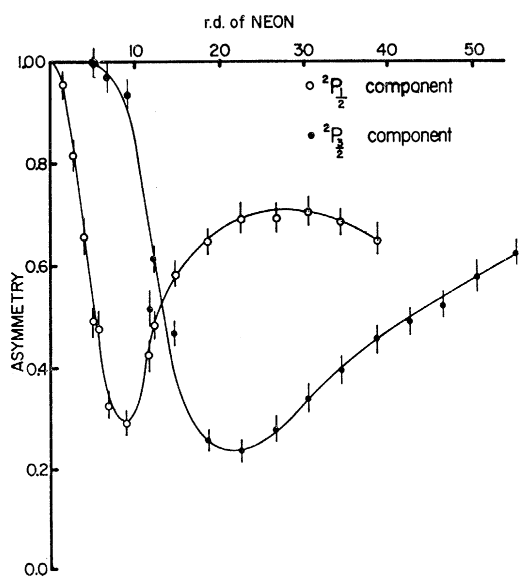

FIG. 14. Asymmetry at half-intensity points for Cs(2)/Ne fine-structure lines.

[5] R. Granier and J. Granier, Compt. Rend. **257**, 2627 (1963).
[6] F. Schuller, J. Rech. Centre Nat. Rech. Sci. Lab. Bellevue (Paris), **61**, 281 (1962).

in certain situations. A detailed check of Schuller's theory is not possible with the present experimental data, since the information on the magnitude of several parameters which describe the potential of the neon-cesium interaction is not known.

No temperature effect on shifts was observed in Paper III which reported krypton-perturbed lines of cesium. Since krypton causes strong red shifts, presumably the attractive term in the interaction potential dominates so that little or no temperature effect would be observed. Neon-perturbed lines of cesium are observed to blue shift, usually, so that the repulsive part of the interaction potential is not negligible. Thus, a temperature dependence in the shift would be predicted. On the other hand, helium-perturbed lines of cesium reported in Paper II were measured in much the same way and observed to shift to the blue, so that the repulsive term is a strong one, and yet the lines were not observed to have a large temperature dependence. These results should be re-checked with apparatus capable of controlling the cesium vapor pressure independently of the temperature.

Schuller's theory does not discuss half-widths of lines and possible temperature dependences. The strong temperature dependence observed for the half-width of the $^2P_{3/2}$ component of Cs(2)/Ne is probably due to the growth of the violet-satellite band which partially overlaps the line and is enhanced more than the line by temperature increases. The corresponding violet-satellite band for Cs(1)/Ne is well resolved and hence has little effect on the line.

All previous experiments which have revealed the existence of violet satellite bands when alkalis are perturbed by foreign gases have detected only one satellite band for each doublet, not for each member of the doublet. The present experiment has revealed the possible existence of a violet satellite for both the long and the short wavelength components of Cs(2)/Ne. Although a violet satellite was never resolved for the $^2P_{1/2}$ component (λ4593 Å), many of the traces had a shape which had a constant slope region on the blue side of the line unlike the bell-shaped curve one normally associates with a single line. The behavior of the asymmetry ratio curve lends further evidence to the conclusion, since it is qualitatively very similar to that of the corresponding $^2P_{3/2}$ component which is known to have a violet satellite. At low pressures the satellite grows, and, it it overlaps the line as for Cs(2)/Ne, it causes an apparent increase in violet asymmetry of the line. After the violet satellite has grown large, the relative increase in violet asymmetry of the line is reduced, since the measurement is made on the combination of line plus satellite. Granier and Granier[7] also reported a violet satellite associated with the $^2P_{1/2}$ component of Cs(1)/Ne.

[7] R. Granier and J. Granier, Compt. Rend. **262**, 1502 (1966).