Broadening, Asymmetry and Shift of Rubidium Resonance Lines under Different Pressures of Helium and Argon up to 100 Atmospheres

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A new absorption tube was constructed which made feasible the study of the pressure effects of foreign gases on the absorption lines of alkali vapors of homogeneous density and temperature. In addition to helium and argon at pressures up to 100 atmospheres, hydrogen was used up to 20 atmospheres. Up to relative density 46 the broadening is proportional to the concentration of helium or argon gas. The slopes of the half-width *vs.* relative density curves are 0.735 cm^{-1} and 0.594 cm^{-1} per unit relative density of helium for $^2P_{3/2}$ and $^2P_{\frac{1}{2}}$ components, respectively, and the corresponding values for argon are 0.855 cm^{-1} and 0.627 cm^{-1} per unit relative density. Helium produces a violet, argon a red asymmetry. The degree of asymmetry increases as the concentration of foreign gas increases, and is comparatively much greater for argon. For argon the asymmetry of the $^2P_{3/2}$ component is greater than that of the $^2P_{\frac{1}{2}}$ component, while for helium the reverse is true. Argon produces a greater shift than helium. The former produces a strong red shift, the latter a violet shift. For both gases the shift of the $^2P_{\frac{1}{2}}$ component is greater than that of the $^2P_{3/2}$ component. For helium the shift appears to be proportional to the relative density, and the shift of the longer wave-length component is about twice as great as that of the shorter wave-length component, while for argon the shifts for the doublet components are quite close, and the relation between shifts and relative densities obeys in general the 3/2 power relationship. Optical collision diameters as calculated from the half-width data are 13.37A and 7.753A for Rb–A and Rb–He, respectively. From the measurements of the amount of total absorption from the line contours, f values and the transition probabilities were evaluated.

INTRODUCTION

TO realize the advantages of the corrosion resistant MgO windows,[1] in absorption measurements on metallic vapors it is necessary to design a mounting for them which will remain pressure-tight during repeated heating and cooling of the tube. Margenau and Watson[2] made an absorption tube whose windows could be heated, but they confessed to only partial success at overcoming leakage. Prior to that time high pressure tubes were of the old form with water cooling at both ends.[3] Under such conditions it is impossible to determine many physical constants from the measurement of the absolute absorption coefficients because the optical path in the absorbing vapor is unknown and neither the absorbing nor the perturbing atom have a homogeneous concentration in the tube. In addition experimental troubles arise of the kind pointed out by Ny and the author[3] and later confirmed by Füchtbauer and Heesen.[3]

In the present research, an absorption tube was made which is perfectly pressure-tight both at low and at high pressures. The pressure effects of helium and argon on the resonance lines of rubidium were studied under pressures up to 100 atmospheres (also with hydrogen up to 20 atmospheres). Furthermore, MgO windows were used so that the length of the optical path in the rubidium vapor was known. The optical collision diameters, and the area under the absorption line contours, were determined, leading to the evaluation of the oscillator strength of the atom and of the transition probabilities.

APPARATUS AND EXPERIMENTAL PROCEDURE

The construction of the absorption tube is shown in Fig. 1. A is a steel pressure tube $1\frac{1}{2}$ inches in diameter with $\frac{3}{16}$ inch wall thickness. At the middle of the tube was connected very strongly by iron soldering a side tube S about 7 inches long whose end was ready to connect by a union with a cross tube. Inside the pressure tube was placed an inner absorption tube about 26 cm long with an MgO window $\frac{3}{4}$ inch in diameter and $\frac{1}{8}$ inch thick at each end. The ends were closed tightly by pressing the MgO windows on the sharp edges of the tube ends. At the central part of the tube there was a side-tube

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[1] J. Strong and R. T. Brice, J. Opt. Soc. Am. **25**, 207 (1935).

[2] H. Margenau and W. W. Watson, Phys. Rev. **44**, 92 (1933).

[3] For example: Ny Tsi-Zé and Ch'en Shang-Yi, Phys. Rev. **51**, 567 (1937); **54**, 1045 (1938); C. Füchtbauer and W. v. Heesen, Zeits. f. Physik **113**, 323 (1939).

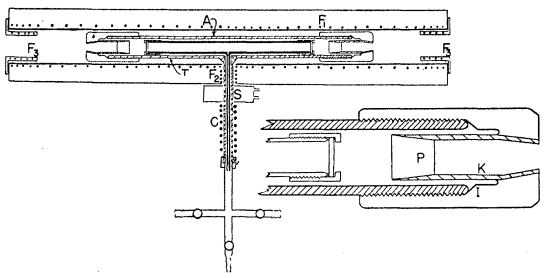

FIG. 1. The absorption tube.

thinner than S. This thinner side-tube was screwed to the inner absorption tube and could be taken off very easily.

The essential difficulty in constructing the pressure tube was to make the pressure-tight windows whose construction is shown in the insert of Fig. 1. The whole window frame was made of the same material as that of the main pressure tube except the Pyrex glass window P and the Kovar cone K which held the window. When the window frame is screwed on to the ends of the pressure tube, the inclined part, I, of the frame is pressed very tightly on the round and smooth end of the pressure tube. This serves as an excellent and permanent pressure seal because the tube end and the window frame contract or expand equally at various temperatures.

The thin Kovar cone was united with the steel frame by silver soldering. Before the glass window was put in position the Kovar cone was ground so that it fitted very nicely with the polished conical glass. Very thin aluminum rings were employed in the gasket.[4] The Pyrex glass was pressed into the Kovar cone while the whole was heated to about 250°C at which temperature the aluminum ring became soft. As Kovar metal has nearly the same coefficient of expansion as that of Pyrex glass, the window was tightly fitted in the cone at all temperatures. The slight difference between the expansion of the two materials was taken up by the elasticity of the thin cone.

The Pyrex glass window was 2 cm thick and $\frac{3}{4}$ inch in diameter and the angle of the cone was about 5°. If the angle was greater than 7° the window leaked even with the above method. Obviously, there will be no difficulty if the Pyrex glass is replaced by fused quartz when observations are to be made in the ultraviolet region.

The absorption tube was uniformly heated by the furnace F_1 which was made by winding Chromel wire on steel cyclinders covered by asbestos paper. The whole furnace, F_1, consisted of two sections which were connected at the position of the side tube. The windings were so made that when the side tube was heated by a small furnace, F_2, the main absorption tube could be heated uniformly to about 240°C as shown by the thermocouple probe. When the furnace had to be heated to still higher temperatures, additional furnaces, F_3, were added on both ends. They were used to compensate the heat loss of the ends to the surroundings.

The furnace F_2 was made by simply winding the resistance wire around the side tube protected by asbestos paper and mica. The furnaces F_3 were made by first winding the heating wire on a cylinder covered with asbestos then putting it inside another bigger cylinder forming a very compact and removable heating unit. The temperature of the absorption tube was measured by an Alumel-Chromel thermocouple, whose hot junction was fastened tightly by a steel ribbon on the pressure tube at the position T in the figure. The whole furnace was placed in a box full of asbestos powder. As the side tube had to be put below the absorption tube the box was placed on a table with a large hole in the center. In this way the cold gas in the side tube would not flow into the absorption tube on account of its density being higher than that of the hot gas in the main tube.

Water cooling was applied immediately outside of the heating box to cool the side tube. The upper jacket was composed of two semicylindrical vessels which could be applied and taken off much more conveniently than the copper coils below. The function of the water cooling was not only to keep the cross tube and the needle valves cooled but also to condense the rubidium vapor if it escaped from the absorption tube A. Thus this arrangement served to give a connection between the outer and the inner tubes for the foreign gas, but not for the alkali vapor.

[4] Copper rings were tried. They did not work because of the hardness of copper. Gold rings would be even better than aluminum because gold is softer and has a still higher melting point.

Three needle valves were used; one led to the pressure tank containing foreign gas, one to the pressure gauge, and one to the high vacuum pump. Between the valve and the gas tank was a thick-walled copper tubing and a condensing spiral to feed the foreign gas back into the tank after the experiment was completed. Three pressure gauges were used. They served to measure the pressure in three ranges, 1–300 lb., 1–600 lb., and 1–3000 lb. They were calibrated by means of a standard pressure gauge. The first two gauges were calibrated to read pressures accurately to 1 lb., while the third one could be read to 10 lb.

The helium gas[5] was obtained originally from evaporation of liquid helium, and was once more purified by an absorption method to eliminate contaminations by the sealing liquid during storage. The total impurity at the source is estimated to be smaller than 0.01 percent. The small trace of impurity would be hydrogen. The argon tank was supplied by the Ohio Chemical and Manufacturing Company, Cleveland. The purity was 99.6 percent. The impurity would be nitrogen. The hydrogen tank was supplied by the Cryogenic Laboratory of this Institute. The gas was claimed to be about 99.5 percent pure.

During experiment the absorption tube was first cleaned and the absorbed gas in the tube wall was removed by long pumping and heating. Then metallic rubidium, which was prepared by reducing RbCl with Ca, was introduced into the absorption tube in a current of nitrogen. With the 21-foot grating and a high intensity tungsten filament lamp the absorption spectrum of rubidium was taken when the pure foreign gas was admitted into the tube and the tube was heated to a certain temperature. The temperature was adjusted at each pressure of the foreign gas so that the absorption was less than total in the center of the resonance lines in order that true line contours could be registered.[6]

To measure the density gradations in the absorption lines, the plate (Eastman Type $I-R$) was calibrated by a step weakener placed in the plateholder just on one side of each absorption line. An iron arc spectrum was superposed on both sides of the main exposure as a comparison.

Results and Discussion

(a) Broadening

The half-widths of the Rb resonance lines broadened by different concentrations of helium, argon, and hydrogen are tabulated in Table I. As shown in Fig. 2 the half-widths turn out to be proportional to the relative densities of these gases, indicating the predominance of velocity broadening even in this high pressure range. The slopes of these curves are 0.735 cm^{-1} and 0.594 cm^{-1} per unit relative density of helium for $^2P_{3/2}$ and $^2P_{1/2}$ components, respectively, and the corresponding values for argon are 0.855 cm^{-1} and 0.627 cm^{-1} per unit relative density.

It is to be noted that the broadening by argon is greater than that by helium and the broadening of the shorter wave-length component is slightly greater than that of the longer wave-length one for both gases. Watson and Margenau[7] and Hull[8] have shown in their results for sodium (with H_2, N_2 and A) and potassium (with N_2 and A) that there is no significant difference between the half-widths of the doublet components for resonance lines and also for the second doublet of the K principal series. But Petermann[9] found that the blue Cs doublet and the corresponding K doublet show about 20 percent greater broadening for the shorter wave-length component when broadened by hydrogen. Ny and the author[10] found that for helium and neon the half-width of the $^2P_{1/2}$ component of the second doublet of Rb principal series is greater than that of the $^2P_{3/2}$ component, while for argon the half-width of the $^2P_{1/2}$ component is slightly greater. In the present research the results for argon are in harmony with

[5] Thanks are due to Professor A. Goetz, the Director of the cryogenic laboratory of California Institute, for his generous permission and help in using his pure helium.

[6] In order to approach as much as possible the theoretical assumptions it is certainly desirable to use low temperatures so that the influence of atomic motion of Rb be eliminated. But, since the area under the absorption line contour depends on the concentration of absorbing atoms, the line will be diffused out when it is broadened; therefore the temperature of the absorption tube had to be raised to a high value, so that the absorption of the line could be easily measureable.

[7] H. Margenau and W. W. Watson, Phys. Rev. **44**, 92 (1939).

[8] G. F. Hull, Phys. Rev. **50**, 1148 (1936).

[9] Petermann, Zeits. f. Physik **87**, 96 (1933).

[10] Ny Tsi-Zé and Ch'en Shang-Yi, Phys. Rev. **52**, 1158 (1937).

TABLE I. *Broadening, asymmetry and shift of the resonance lines of* Rb *produced by* He, A, *and* H_2.

P ATM.	T °K	RELATIVE DENSITY	HALF-WIDTH IN CM^{-1} 7947	7800	ASYMMETRY (7947) (1)	(2)	(7800) (1)	(2)	SHIFT 7947	7800
					(*a*) *Rubidium/helium*					
									(violet)	(violet)
3.95	447	2.41	1.61	1.79	0.95	0.911	1.00	0.988	0.39	0.19
8.98	455	5.39	3.07	3.69	0.98	0.967	1.01	0.990	1.85	0.95
20.48	461	12.13	7.86	9.18	0.97	0.843	0.98	0.961	2.89	1.52
41.10	463.5	24.21	16.95	17.08	0.78	0.772	0.88	0.874	5.76	2.26
77.29	569	37.08	21.74	27.80	0.83	0.782	0.90	0.832	7.54	2.62
96.62	579.5	45.52	27.80	33.21	0.86	0.777	0.99	0.748	10.88	4.40
98.79	581.5	46.36	—	34.46						
					(*b*) *Rubidium/argon*					
									(red)	(red)
2.72	440	1.69	1.30	1.21	1.07	1.128	1.41	1.538	0.82	0.36
6.12	515	3.24	2.76	3.16	1.39	1.588	1.50	1.654	1.03	0.48
10.21	517.5	5.39	3.37	3.42	1.56	1.661	1.50	1.702	1.69	1.33
19.94	527	10.33	7.22	7.29	1.79	1.975	1.71	1.912	4.63	3.99
41.16	552	20.36	15.10	19.46	1.42	1.387	1.60	1.641	11.01	9.64
71.44	569	34.28	22.65	32.39	1.38	1.374	1.80	1.825	20.23	19.63
85.73	576.0	40.63	24.99	34.48	1.33	1.395	1.58	1.658	24.17	26.04
97.98	576	46.44	28.00	39.02	1.36	1.352	1.63	1.568	29.90	29.85
					(*c*) *Rubidium/hydrogen*					
									(violet)	(red)
3.47	457	2.07	—	—	—	—	—	—	1.32	1.33
20.00	462	11.82	7.73	10.26	1.18	—	1.00	—	1.63	1.61

those of the author's former experiment for the second member of Rb principal series. The difference between the half-widths of the doublet components detected both by the former[11] and by the present researches suggests again that the perturbing effect of neighboring atoms (similar or dissimilar) may be different for different j values.

(b) Asymmetry

In the 6th–9th columns of Table I the asymmetry of the broadened Rb resonance lines produced by He, A and H_2 are given both in the ratios of the red half to the blue half of the half-widths as listed in the sixth and the eighth columns represented by (1) and in the ratios of the areas under the red half to those under the violet half of the line contour as represented by (2).

Helium produces a violet asymmetry, while argon produces a red asymmetry. The degree of asymmetry increases as the concentration of helium or argon increases. For helium the degree of asymmetry is a little greater for the longer wave-length component, while for argon the degree of asymmetry for the shorter wave-length component is greater. For argon the degree of asymmetry first increases very rapidly with the increase of concentration, then attains a weak maximum around relative density 10; finally the asymmetry drops slightly to a nearly constant value. The degree of asymmetry produced by helium is comparatively much lower than that produced by argon. The asymmetry was small when the relative density was below 10, but increased gradually with the increase of concentration. The asymmetry produced by the hydrogen is quite small.

The values listed under the columns numbered (1) and (2) permit interesting comparison of the two ways of describing the nature of the asymmetry of the line contours. The first way (the ratios of the halves of the half-widths as represented by (1)) gives in general the asymmetry at nearly the central portion of the line. The asymmetry at the far wings is not given. While the second way (the ratios of the areas under the line contour as represented by (2)) is a more sensitive way of measuring the asymmetry for the asymmetry of the line affects the area more conspicuously than it does the half-width. The asymmetries were most pronounced near the

[11] Ch'en Shang-Yi, Phys. Rev. **58**, 884 (1940).

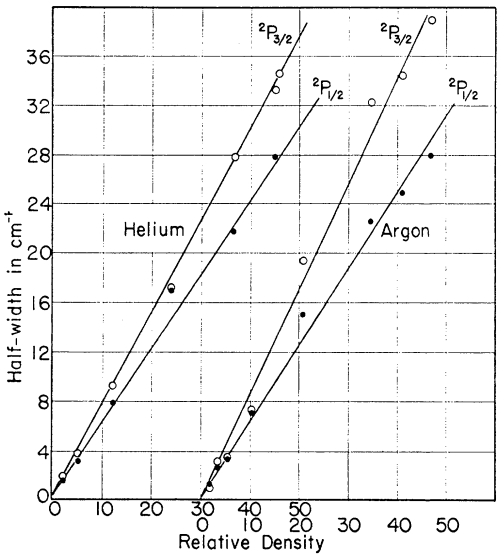

FIG. 2. Half-width *vs.* relative density.

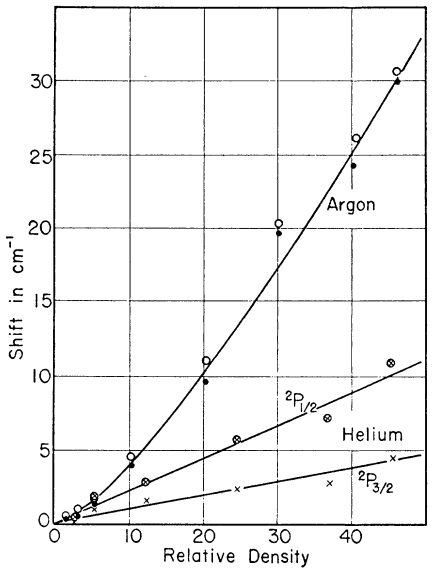

FIG. 3. Shift *vs.* relative density.

base of the line. The values of the eighth and the ninth columns for helium in the table give a good illustration.

Although three figures are recorded in expressing the degree of asymmetry, the last figure has very little significance as regards the accuracy of measurement. The chief source of error is in the planimetric measurement near the end of the wings. The wing stretched very far on both sides of the wings especially the side which showed asymmetry, a little error in tracing the line contour would affect the area by a considerable amount.

(c) Shift

The displacement of the central maxima of the Rb resonance lines produced by helium and argon are also given in Table I, and are plotted in Fig. 3. Argon produced a greater shift than helium. The former produces a strong red shift while the latter a violet shift. For both gases the shift of the $^2P_{1/2}$ (λ7947) component is greater than that of the $^2P_{3/2}$ (λ7800) component. This phenomenon is shown very obviously in Fig. 4.

In Fig. 4 is given a direct comparison of the positions of the Rb resonance lines, with and without the effects of foreign gases. Figure 4(a) is the spectra taken with the absorption tube containing pure rubidium vapor at very low pressure (10^{-2} mm Hg), Fig. 4(b) is that taken when the pure Rb vapor pressure was increased to about 4 mm Hg, and Figs. 4(c) and (d) are the spectra taken when foreign gases were introduced. As pointed out in the previous article,[11] and also shown here, the very small shift of Rb resonance lines caused by the pressure of its own vapor, and the large shift of the lines produced by foreign gases are strikingly illustrated.

It is well known that the shift of the resonance lines produced by foreign gases is the smallest among the series lines.[12] Thus it is easy to imagine that under so large a foreign gas pressure (100 atmospheres) the shift for higher series members would be as large as one hundred angstrom units.

It is to be noted from Fig. 3 that for helium the shift appears to be proportional to the relative density, while for argon there is a noticeable departure from the linear relationship. For argon the shifts for the two doublet components are very nearly the same, while for helium the shift of the longer wave-length component is about twice as great as for the shorter wave-length component. Hydrogen produces a violet shift on the longer wave-length component and a red shift on the shorter wave-length component.

The difference between shifts of the two components has already been pointed out by Mar-

[12] For instance, see Füchtbauer, Schulz and Brandt, Zeits. f. Physik **90**, 403 (1934); Ny Tsi-Zé and Ch'en Shang-Yi, Phys. Rev. **51**, 567 (1937); **54**, 1045 (1938).

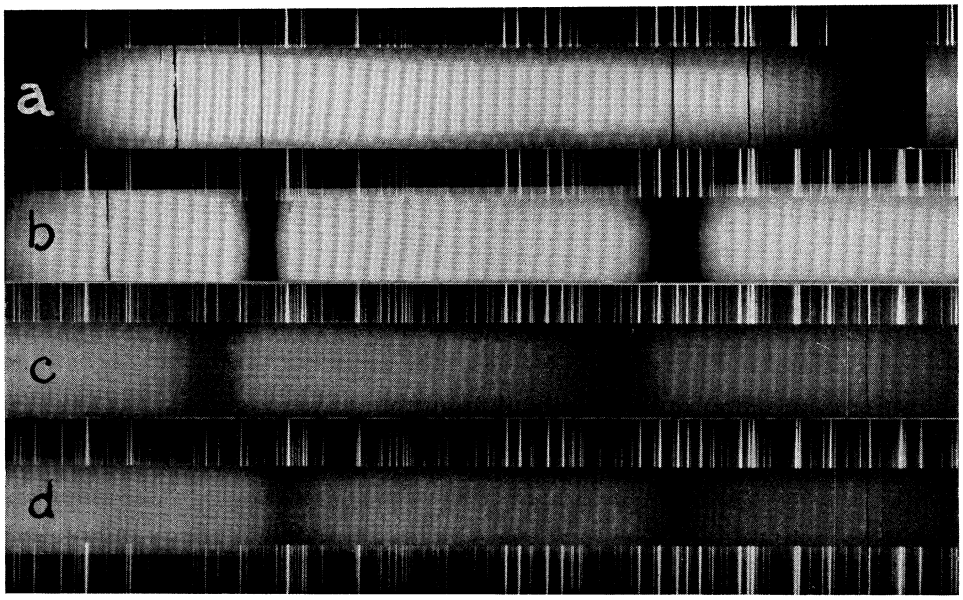

FIG. 4. Positions of rubidium resonance lines. (a) Under 10^{-2} mm pressure pure vapor ($T=190°C$). (b) Under 4 mm Hg pressure pure vapor ($T=347°C$). (c) Under 97.98 atmospheres argon ($T=303°C$). (d) Under 96.62 atmospheres helium ($T=306.5°C$).

genau and Watson[7] and Hull[8] in their experiments on effects of nitrogen and argon on potassium resonance lines and also by Ny and the author[10] in their experiment on the effects of rare gases on the second member of Rb absorption series.

The relation between the shift and the relative density is still an unsolved problem. Both the linear and the quadratic relations were predicted and observed. Ny and the author[10] found that for argon the shift of the second member of Rb principal series appears to be proportional to the square of the relative density in conformation with Kuhn's theory.[13] In the present case, however, the shift of the lines produced by helium is linearly proportional to the relative density, but for argon the relation between shift and relative densities obeys in general the 3/2 power relationship. The accuracy of locating the positions of the maxima of these lines was estimated; the greatest possible error should not be more than 2 percent. It is evident that, for low members, the relationship between shift and relative density depends on the nature of foreign gas added as well as the member of the series and

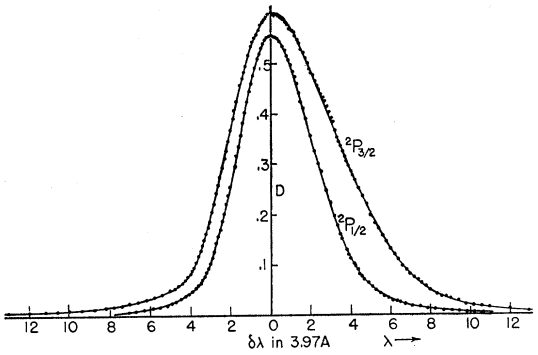

FIG. 5A. $\text{Log}_{10}\, I_0/I$ *vs.* δλ. Argon pressure 97.98 atmospheres; ($T=576°K$).

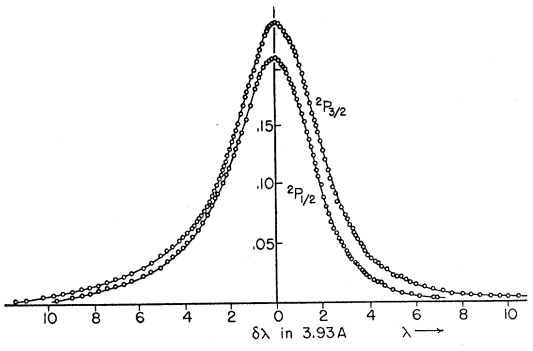

FIG. 5B. $\text{Log}_{10}\, I_0/I$ *vs.* δλ. Helium pressure 96.92 atmospheres; ($T=579.5°K$).

[13] H. Kuhn, Phil. Mag. **18**, 987 (1934); Phys. Rev. **52**, 133 (1937).

the nature of the absorbing atom. Further theoretical investigation seems very desirable.

(d) The evaluation of f values and transition probabilities

Oscillator strengths and transition probabilities were computed from the amount of the total absorption[14] $\int_0^\infty(n\kappa)d\nu$ which was obtained by graphical integration of the line contours as illustrated in Figs. 5*A* and 5*B*. Thus

$$\int_0^\infty(n\kappa)d\nu=(2.303\times3\times10^{10}/4\pi l\lambda)\int_0^\infty D\delta\lambda,$$

where $D=\log_{10} I_0/I$, and $n\kappa$ is the electron theory absorption coefficient. According to radiation theory the oscillator strength of the atoms, i.e., the f value, is

$$f=(4\nu m/ne^2)\int_0^\infty(n\kappa)d\nu$$

and the transition probability, A, is

$$A=(4\pi/cnh)\int_0^\infty(n\kappa)d\nu$$
$$=(\pi e^2/ch\nu m)f.$$

Substituting the numerical constants

$$f=(6.086\times10^6/n)\int_0^\infty(n\kappa)d\nu \quad \text{for } \lambda7800$$
$$=(5.974\times10^6/n)\int_0^\infty(n\kappa)d\nu \quad \text{for } \lambda7947$$

TABLE II. *The f values of* Rb *resonance lines under different pressures of foreign gases.*

$T°K$	p mm Hg	n	R.D.	f_s	f_l
		(*a*) *Rubidium/helium*			
447	1.25×10^{-2}	2.71×10^{14}	2.41	0.780	0.467
455	1.79×10^{-2}	3.81×10^{14}	5.39	0.614	0.323
461	2.32×10^{-2}	4.88×10^{14}	12.13	0.463	0.253
463.5	2.582×10^{-2}	5.404×10^{14}	24.21	0.307	0.186
569	1.00	1.70×10^{16}	37.08	0.202	0.152
579.5	1.337	2.238×10^{16}	45.52	0.0884	0.0742
		(*b*) *Rubidium/argon*			
440	9.00×10^{-3}	1.98×10^{14}	1.69	0.595	0.281
515	1.58×10^{-1}	1.98×10^{15}	3.24	0.582	0.301
517.5	2.023×10^{-1}	3.792×10^{15}	5.39	0.503	0.264
527	2.78×10^{-1}	5.12×10^{15}	10.33	0.511	0.253
552	6.08×10^{-1}	1.07×10^{16}	20.36	0.378	0.220
569	1.00	1.70×10^{16}	34.28	0.253	0.172
576.0	1.214	2.044×10^{16}	40.63	0.304	0.194
576	1.214	2.04×10^{16}	46.44	0.305	0.197

[14] Cf. H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 29 (1936).

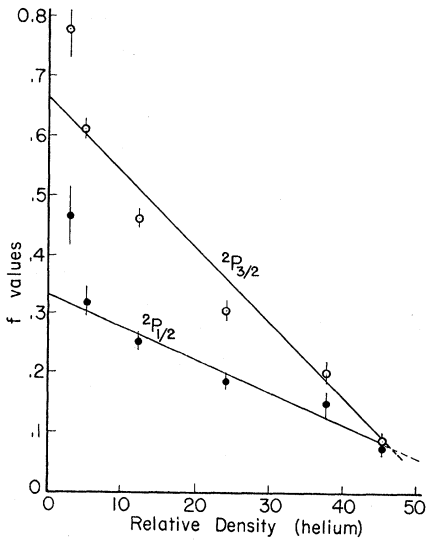

FIG. 6A. f values *vs.* relative density of helium.

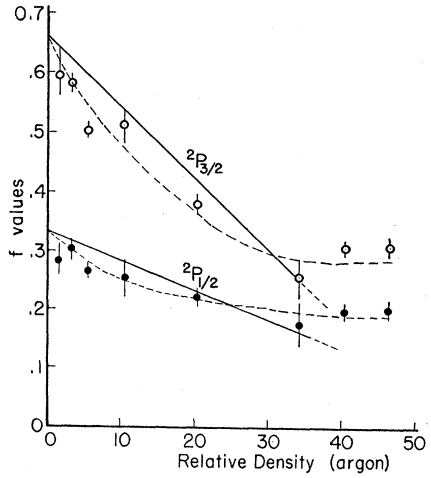

FIG. 6B. f values *vs.* relative density of argon.

and

$$A=1.050\times10^{10}f \quad \text{for } \lambda7800$$
$$=1.070\times10^{10}f \quad \text{for } \lambda7947.$$

In Table II are listed the f values when the lines were broadened by foreign gases. There p and n stand for the vapor pressure and the concentration of the alkali vapor and R. D. the relative density of foreign gas. The f values of the resonance lines without the presence of foreign gases were found by extrapolating to zero density of foreign gas as shown in Figs. 6*A* and 6*B*. The results are 0.33 and 0.66 for the $^2P_{1/2}$

and the $^2P_{3/2}$ components, respectively, and the corresponding transition probabilities are 6.93×10^9 and 3.53×10^9. These results agree with the results of Na, K and Cs resonance lines as measured by Minkowski, etc.[15] As shown in Figs. 6A and 6B readings for low foreign gas concentrations were not as accurate owing to the inaccuracy in obtaining $\int_0^\infty(n\kappa)d\nu$. Also the readings for argon in Fig. 6B are not as good as those for helium. This might be due to the fact that the argon was not as pure as the helium; impurities such as O_2, N_2 and H_2[16] would remove some Rb atoms causing a decrease in absorption. Great care was taken to heat the absorption tube for a long time after the foreign gas was inserted, in order to be sure that the saturation of the alkali vapor in the absorption tube was recovered after the vapor had been condensed by the cold foreign gas or caught by impurity atoms.

(e) The optical collision diameters

These can be computed from the observed half-widths, using the relation

$$\rho^2=[\pi\Delta\nu_{\frac{1}{2}}/2n(2\pi kT)^{\frac{1}{2}}][mM/(m+M)]^{\frac{1}{2}}$$

where m and M are the masses of the absorbing and of the perturbing atoms, respectively; taking

$$\Delta\nu_{\frac{1}{2}}/n=0.665 \text{ cm}^{-1} \text{ for helium}$$
$$=0.741 \text{ cm}^{-1} \text{ for argon,}$$

which are the mean values for the doublet components. Then for argon and Rb $\rho=13.37$A, while for helium and Rb $\rho=7.75$A.

Finally, the author takes pleasure in expressing his gratitude to Professor I. S. Bowen for his supervision throughout the research. He is also indebted to Messrs. J. Pearson and S. C. Lin for their help in various ways.

[15] Cf. A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Macmillan, 1934), p. 146.

[16] N_2 and H_2 will react with rubidium when the pressure is increased higher than about thirty atmospheres.

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Pressure Effects of Hydrogen and Nitrogen on the Second Doublet of Rb Principal Series

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Pressure effects of nitrogen and hydrogen on the second doublet of the rubidium principal series, were studied at pressures up to 13 atmospheres. Both for hydrogen and nitrogen the $^2P_{3/2}$ component broadens more conspicuously than the $^2P_{\frac{1}{2}}$ one, and the relationship between the half-width and the relative density is linear. Nitrogen produces a red shift for both components, while hydrogen has a weaker red shift for $^2P_{3/2}$ and a stronger violet shift for $^2P_{\frac{1}{2}}$. The departure from a linear relationship between shift and the density of the perturbing gases is quite manifest. Study of the line contours reveals marked asymmetry, toward the red in the case of nitrogen and slightly toward the blue for hydrogen. The relationship between the half-width and the shift is discussed.

INTRODUCTION

IN sequel to the previous observations on the pressure effects of rare gases on the second doublet of rubidium principal series,[1] the same problem was studied with hydrogen and nitrogen at pressures up to 13 atmospheres. The experimental procedure was essentially the same as that of the previous research. Commercially pure hydrogen and nitrogen (the purity was about 99.5 percent) were used. The results obtained in the present research were compared with those for other alkalis.

[1] Ny Tsi-Zé and Ch'en Shang-Yi, Phys. Rev. **52**, 1158 (1937).

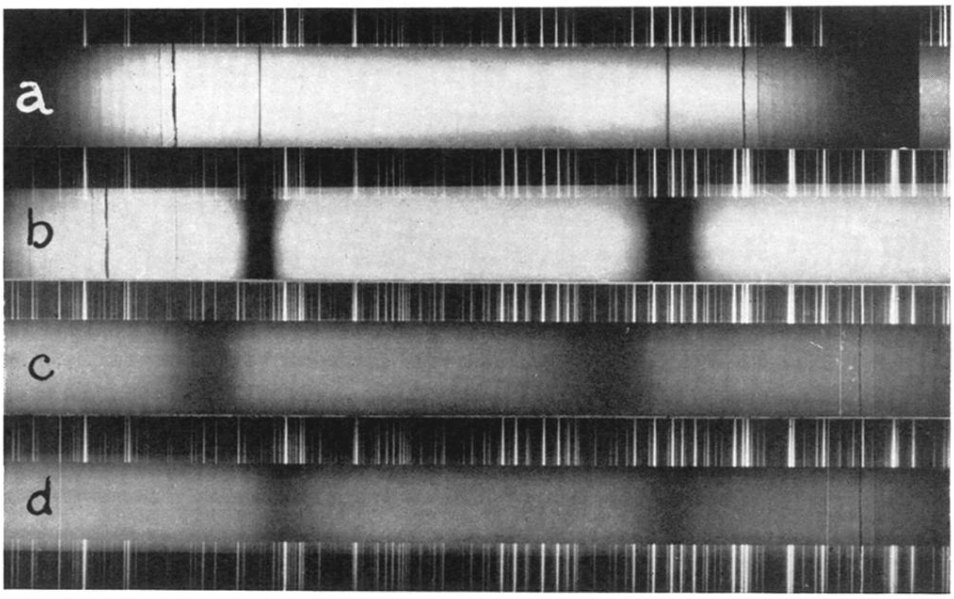

FIG. 4. Positions of rubidium resonance lines. (a) Under 10^{-2} mm pressure pure vapor ($T=190°C$). (b) Under 4 mm Hg pressure pure vapor ($T=347°C$). (c) Under 97.98 atmospheres argon ($T=303°C$). (d) Under 96.62 atmospheres helium ($T=306.5°C$).