The Displacement of Principal Series Lines of Rubidium by the Addition of Rare Gases

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The positions of the principal series lines of Rb displaced by spectroscopically pure helium, neon and argon are measured. The constant shift of the high terms reaches 37.24 cm^{-1} towards violet under 12.75 atmospheres (at 570°K) for helium; 2.08 cm^{-1} towards violet under 13.59 atmospheres (at 590°K) for neon; and 33.4 cm^{-1} towards red under 7.12 atmospheres (at 563°K) for argon. The effective cross sections for all the atoms in 1 cm^3 at 1 mm pressure calculated by Fermi's equation is 15.47 cm^2/cm^3 for helium, 0.24 cm^2/cm^3 for neon, and 23.7 cm^2/cm^3 for argon in good agreement with the results of Füchtbauer from his experiment with Na and K, and of Wahlin by direct electrical method. In the range of rare gas pressures above relative density 5 the mean shifts of the high members of the Rb principal series increases more rapidly than linearly with density.

THE effects of foreign gases upon spectral lines, such as displacement, broadening and asymmetry, has opened up a new way for investigating the perturbations of the energy levels of the absorbing atom and consequently attracted the attention of many experimental and theoretical physicists. V. Weisskopf[1] and H. Margenau and W. W. Watson[2] have given a general review on the subject with an adequate bibliography. In the present research the displacements of the principal series lines of rubidium by the addition of helium, neon, and argon are studied. The results for the high series members are in agreement with those of other experimenters[3] using sodium and potassium as the absorbing atoms, and verify again Fermi's theory.

[1] V. Weisskopf, Physik. Zeits. **34**, 1 (1933).
[2] H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

APPARATUS AND EXPERIMENTAL PROCEDURE

A nickel steel tube 100 cm long, 2.6 cm inner diameter, with two quartz windows, one right-

[3] E. Amaldi and E. Segrè, Nature **133**, 141 (1934); Nuovo Cimento **11**, 145 (1934); C. Füchtbauer, P. Schulz, and A. F. Brandt, Zeits. f. Physik **90**, 403 (1934).

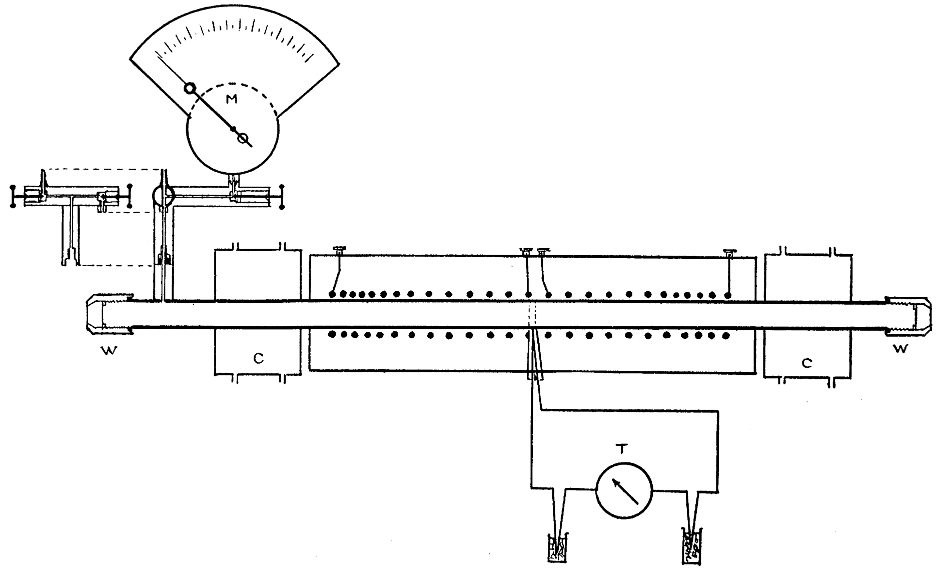

FIG. 1. Absorption tube. C, water coolings; M, pressure gauge; T, steel constantan thermocouple; W, quartz windows.

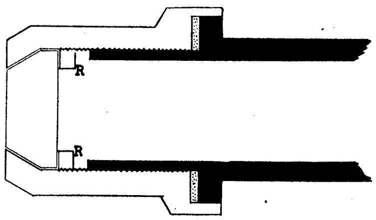

FIG. 2. The quartz window.

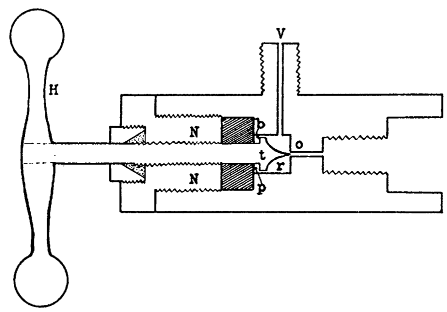

FIG. 3. The valve.

handed and one left-handed, on its ends was used as an absorption tube. The absorption tube was heated by an electrical furnace so wound that the central part of the absorption tube about 40 cm long was at uniform temperature. Water cooling was used near the two ends of the tube to prevent the rubidium vapor from being deposited on the windows. The general arrangement of the absorption tube, which could stand high vacuum and moderate pressure, is shown in Fig. 1. The quartz window W was held by a steel frame threaded on to the main tube (Fig. 2). Lead rings were employed in the gaskets. The steel ring R was to hold the quartz in position when the tube was evacuated.

Near one end of the absorption tube, a side tube led to the rare gas tank, the vacuum system, and the manometer through three separate valves. The manometer M, read to 0.01 atmosphere, was carefully calibrated both before and at the end of the experiment.

The construction of the valves is shown in Fig. 3. The opening O could be closed or opened by a steel tip t which was located in a small chamber enclosed by a strong nut N, so that no gas could leak out from the outer screw. When the valve O was closed, only the gas in the enclosure r could leak out very slowly through the inner screw; but when O was opened the flat part b of the tip will be in firm contact with the surface p, thus the leakage was stopped immediately. Only a fraction of a turn of the handle H would be sufficient to open or close the opening O, thus there was no appreciable leakage due to the closing and opening of the valve. V was an opening for admitting a foreign gas or to be connected to the manometer or the pump.

The temperature of the absorption tube was measured by a steel constantan thermocouple. The temperature was sufficiently uniform over a 40 cm length at the central part of the tube to justify the assumption that within this column the concentration of the perturbing gas had a constant value.

The absorption spectrum was photographed with a Hilger E-1 quartz spectrograph which gives a dispersion of 5.2A to 4.6A per millimeter from the 7th member to the end of the rubidium principal series. Carbon arc light was used as the background of the absorption spectrum, and the plate used was Kodak's type 0-IV spectroscopic plates.

The absorption tube was carefully cleaned, and the contained gas in the tube wall was removed by long pumping and heating. Metallic rubidium was inserted from the window into the tube in a current of CO_2. The tube was then pumped again immediately. The absorption spectrum of rubidium was taken when the tube was heated to a certain temperature. Then the spectroscopically pure foreign gas (He, Ne, or A) was introduced into the tube, and spectra were taken at convenient steps under different pressures. For the determination of the displacement of the low members the tube was heated to a lower temperature (about 220°C) in order to avoid too much broadening of the lines.

An iron arc spectrum was used as a comparison spectrum. The wave-length of the absorption lines were measured by Hilger L-1 comparator. In determining the wave-length of the lower members, a Moll type A microphotometer was used.

RESULTS AND DISCUSSION

Our spectrogram contained all rubidium principal lines except the first member. When the pressure of a foreign gas is pretty high, the

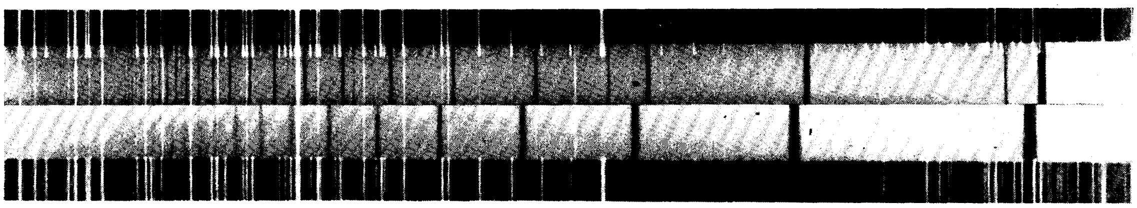

FIG. 4a. Spectra showing the violet shifts of the high members of Rb principal series perturbed by helium. Above: without He; below: under 12.75 atmos. (570°K).

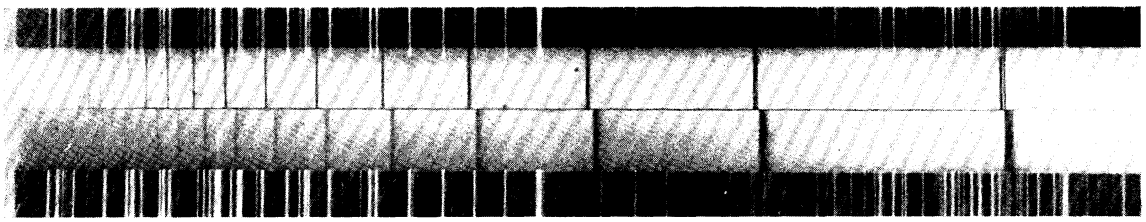

FIG. 4b. Spectra showing the red shifts of the high members of Rb principal series perturbed by argon. Above: without A; below: under 5.79 atmos. (566°K).

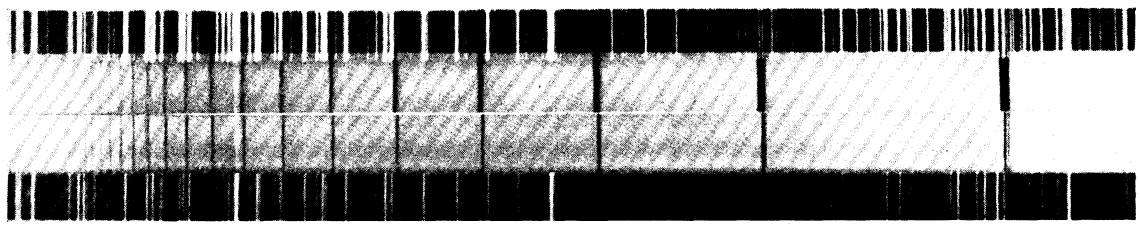

FIG. 4c. Spectra showing the slight violet shifts of the high members of the Rb principal series perturbed by neon. Above: under 13.59 atmos. (590°K); below: without Ne.

low members of the absorption lines become very broad and the high members are much diffused, especially in the case of argon. By the addition of helium or neon all the lines shift towards the violet, while by the addition of argon they shift towards the red (Figs. 4a, b, and c). For helium, the shift first increases with the ordinal number of the lines in the series, then attains a weak maximum at the line 5S-13P, and finally approaches a constant value for the lines near the limit of the series. For argon, the shift continuously increases from the second member and approaches also a constant value for the high members. The shift for neon is very small and practically constant for the high members. The results for the three gases under different pressures are shown in Figs. 5, 6, and 7. The shift of a given line increases with the concentration of the perturbing gas.

According to Fermi's theory,[4] the displacement of the high terms of the series is due to the superposition of two effects: the polarization of the foreign atoms in the field of the core of the alkali atom, and the perturbation of the valence electron by the foreign atoms. The first corresponds always to a displacement towards the red and is given by

$$\nabla_\epsilon = 20e^2(\epsilon_0-1)n^{4/3}/8\pi hcN$$
$$=0.000922(\epsilon_0-1)n^{4/3}/N \text{ cm}^{-1},$$

where N is the Loschmidt's number, ϵ_0 the dielectric constant of the foreign gas under normal conditions, and N the number of atoms per cc.

The second depends upon the collision cross section, σ, of slow electrons in the gas and is

[4] E. Fermi, Nuovo Cimento **11**, 157 (1934).

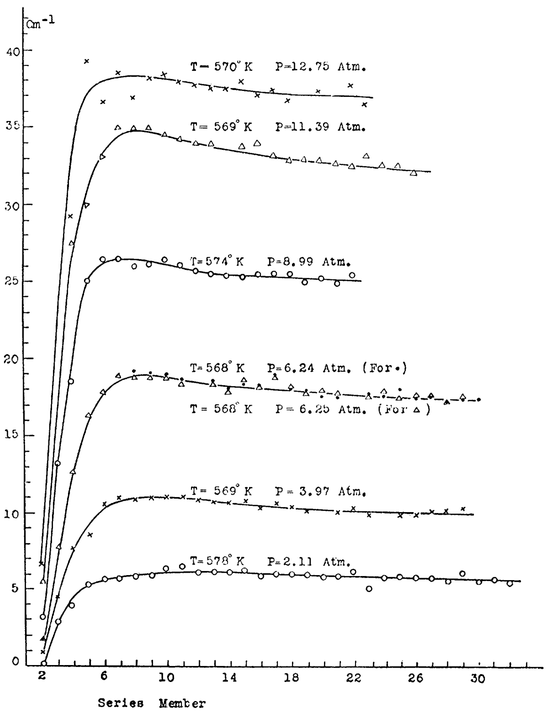

FIG. 5. The displacement of the Rb principal series lines perturbed by helium. (Violet shifts in cm^{-1} against series members.)

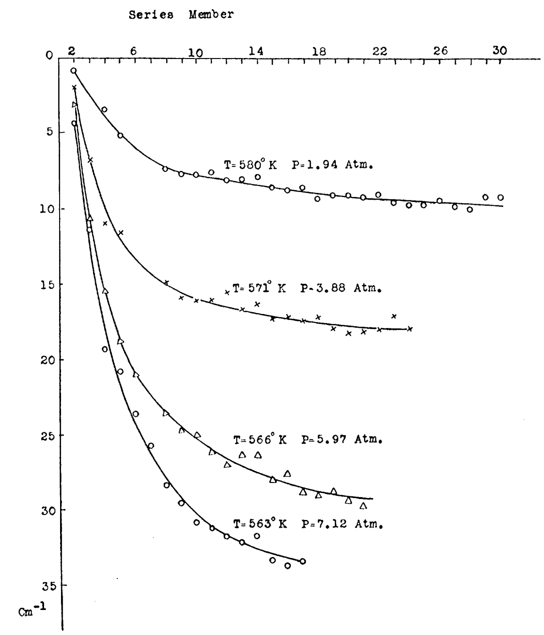

FIG. 7. The displacement of the Rb principal series lines perturbed by argon. (Red shifts in cm^{-1} against series members.)

given by

$$\nabla_\sigma = \pm hn\sigma^{\frac{1}{2}}/4\pi^{\frac{3}{2}}mc = \pm 1.09\cdot 10^{-11}n\sigma^{\frac{1}{2}}.$$

Tables I–III summarize the constant shifts ∇ of the high terms perturbed by He, Ne and A. In column 5 are given the calculated values ∇_ϵ. The differences between ∇ and ∇_ϵ give the values ∇_σ in the 6th column of the tables.

The shifts ∇_σ are plotted, in Fig. 8, against the relative densities d, the unit being the density of the same quantity of a foreign gas as that used in the experiment but at 0°C and 1 atmosphere. For relative densities less than 4, the relation between the shift ∇_σ and the concentration is linear which is in agreement with Fermi's theory. From the slopes of the straight parts of these curves, we deduce the cross sections for the single atom of perturbing gases. Multiplying these values by $N/760$, i.e., 3.553×10^{16}, we get the effective cross sections for all the atoms in 1 cm^3 at 1 mm pressure and 0°C. For comparison, they are listed in Table IV with the results of Amaldi and Segrè and Füchtbauer, Schulz, and Brandt from Na and K, and those of Wahlin[5] by direct electric method.

The agreement between the results of the present work using Rb as an absorbing gas and

[5] H. B. Wahlin, Phys. Rev. **37**, 260 (1931).

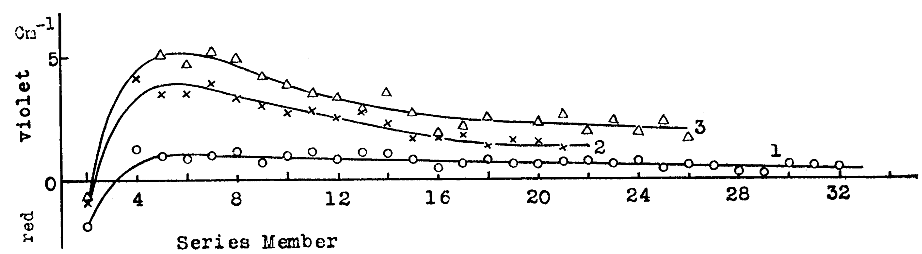

FIG. 6. The displacement of the Rb principal series lines perturbed by neon. (Shifts in cm^{-1} against series members.) Curve 1. $T=609$°K, $P=2.63$ atmos., curve 2. $T=584$°K, $P=11.25$ atmos., curve 3. $T=590$°K, $P=13.59$ atmos.

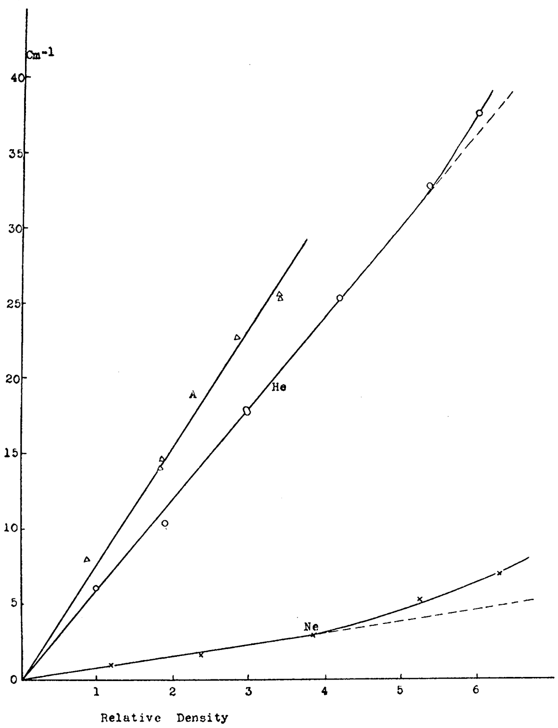

FIG. 8. Shifts ∇_σ *vs.* the relative density of perturbing gas.

those from Na and K confirms again that the shift is independent of the kind of absorbing atoms. The deviations of Amaldi and Segrè's results for He and A are chiefly due to the impurities of the perturbing gases they used. (Their helium contained 5 percent of N_2, and argon 25 percent of N_2 as impurity.)

It is to be noticed that when the relative density of the perturbing gas is above 5 the shift increases more rapidly than linearly with density. This has also been observed by Watson and Margenau in their experiment on the pressure shifts of the first three doublets of the principal series of potassium produced by nitrogen.[6] The departure from linearity of the shifts is to be expected as a regular occurrence, if the perturbing influences are of van der Waals type as pointed out by Margenau.[7]

[6] W. W. Watson and H. Margenau, Phys. Rev. **44**, 748 (1933).

[7] Margenau, Phys. Rev. **48**, 755 (1935).

TABLE I. *The mean shifts of the high terms of the rubidium principal series produced by helium.* (∇_ϵ *and* ∇_σ *are values calculated from Fermi's equations.*)

Pressure (atmos.)	Tempera-ture	Relative Density	∇ (cm^{-1})	∇_ϵ (cm^{-1})	∇_σ (cm^{-1})	Series Members
			(violet)	(red)	(violet)	
2.11	578°K	1.00	5.92	0.20	6.12	12–32
3.97	569	1.91	10.21	0.56	10.77	12–28
6.24	568	3.01	17.76	0.89	18.65	14–30
6.25	573	2.98	17.81	0.88	18.69	14–29
8.99	574	4.26	25.14	1.42	26.56	13–26
11.39	569	5.46	32.64	1.97	34.61	18–27
12.75	570	6.10	37.24	2.27	39.51	13–23

TABLE II. *The mean shifts of the high terms of rubidium principal series produced by argon.*

Pressure (atmos.)	Tempera-ture	Relative Density	∇ (cm^{-1})	∇_ϵ (cm^{-1})	∇_σ (cm^{-1})	Series Members
			(red)	(red)	(red)	
1.94	580°K	0.912	9.26	1.41	7.85	15–30
3.88	571	1.86	17.60	3.62	13.98	15–24
3.92	569	1.88	18.21	3.69	14.52	15–24
5.97	566	2.88	29.06	6.50	22.56	17–21
7.00	555	3.45	33.65	8.25	25.40	15
7.12	563	3.46	33.40	8.29	25.11	15–17

TABLE III. *The mean shifts of the high terms of rubidium principal series produced by neon.*

Pressure (atmos.)	Tempera-ture	Relative Density	∇ (cm^{-1})	∇_ϵ (cm^{-1})	∇_σ (cm^{-1})	Series Members
			(violet)	(red)	(violet)	
2.63	609°K	1.18	0.57	0.51	1.08	16–32
5.06	580	2.38	0.43	1.31	1.74	15–26
8.07	570	3.86	0.43	2.50	2.93	15–24
11.25	584	5.26	1.52	3.75	5.27	16–24
13.59	590	6.29	2.08	4.77	6.85	16–26

TABLE IV. *The effective cross sections of certain gases for electrons of very low velocity as measured by different authors.*

Gas	Amaldi, etc.	Füchtbauer, etc.	Wahlin	Ny & Ch'en
He	11.7 cm^2/cm^3	15.5 cm^2/cm^3	15.3 cm^2/cm^3	15.5 cm^2/cm^3
Ne	–	0.23	–	0.24
A	42	25.2	2.6	23.7

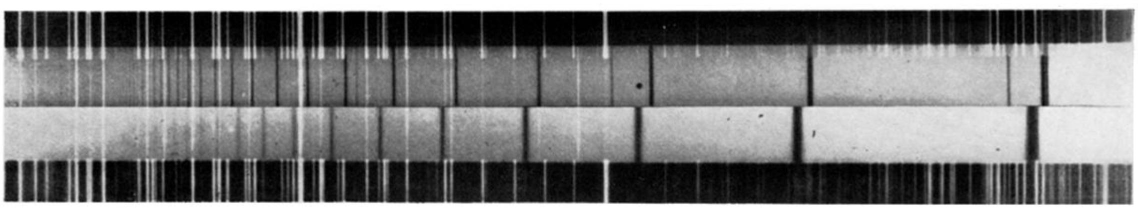

FIG. 4a. Spectra showing the violet shifts of the high members of Rb principal series perturbed by helium. Above: without He; below: under 12.75 atmos. (570°K).

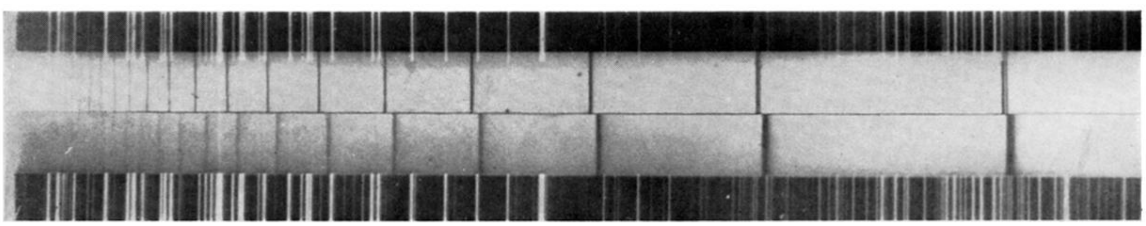

FIG. 4b. Spectra showing the red shifts of the high members of Rb principal series perturbed by argon. Above: without A; below: under 5.79 atmos. (566°K).

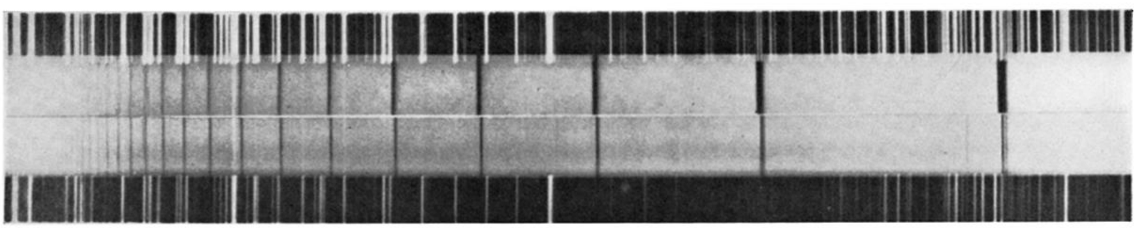

FIG. 4c. Spectra showing the slight violet shifts of the high members of the Rb principal series perturbed by neon. Above: under 13.59 atmos. (590°K); below: without Ne.