Pressure Effects of Homogeneous Rubidium Vapor on Its Resonance Lines

CH'EN SHANG-YI*
Norman Bridge Laboratory of Physics, California Institute of Technology, Pasadena, California
(Received September 23, 1940)

The broadening of the resonance lines of rubidium in absorption under pressures up to 150 mm of its own homogeneous vapor was studied by means of a 21-foot grating. Under pressures below 1 mm the broadening of the lines was very symmetrical and the line contours could be described by the dispersion formula, but when the pressure was high the lines exhibited asymmetrical broadening of van der Waals type. The $^2P_{1/2}$ component showed red, while the $^2P_{3/2}$ component showed violet asymmetry. Both lines showed the proportionality of the width with N, the concentration of Rb atoms. The experimental width at half-maximum is greater than that predicted by Houston's theory by a factor of 1.5 and the width of the transition from $^3P_{3/2}$ is greater than that from $^3P_{1/2}$ by a factor of 1.6. A narrow diffuse band was observed near the shorter wave-length side of the $^2P_{1/2}$ component and a similar one near the longer wave-length side of the $^2P_{3/2}$ component.

THE development of the new corrosion resistant MgO windows[1] has made feasible many experimental researches. Using the new windows Hughes and Lloyd[2] first made an experimental study of the resonance broadening of potassium resonance lines under pressures up to 20 mm. In the present research the corresponding problem for rubidium was studied and observations were made for Rb pressures up to 150 mm under which the two broadened component lines (with a separation of 147A) began to overlap.

EXPERIMENTAL

Absorption tubes of 1.5 cm inside diameter with MgO windows on both ends were used. Three tube lengths were employed, *viz.* 15, 7.5 and 0.2 cm. The construction of the 2-mm tube is shown in Fig. 1. The tube was made of steel. A small capsule containing rubidium was placed inside the hole A, and the end of the hole was closed by a copper tap screw whose coefficient of thermal expansion was higher than that of steel. Thus the hole was always tightly closed throughout the experiment. B was an annealed copper ring which served as a gasket when the tube C was compressed onto the tube D at high temperatures. The copper ring was too hard, but had the advantage over aluminum of not alloying with rubidium.[3] The length of the absorption tube could be easily determined from the thickness of the section S.

The absorption tubes were mounted in a vacuum furnace. By means of a sylphon it was possible to move the tube C and thereby seal off the absorption tube while a vacuum was maintained in the furnace. The entire tube was heated uniformly and its temperature was kept constant within 1°C as indicated by a Chromel-Alumel thermocouple in contact with the absorption tube.

Light from a tungsten filament lamp passed through the absorption tube and was photographed in the first order of a 21-foot grating in a Rowland mounting. Eastman type 1 R plates hypersensitized with ammonia were used, the second-order violet being eliminated with a Wratten F filter. The plates were calibrated by means of two step-weakeners mounted just in front of the plate on both sides of the absorption lines.

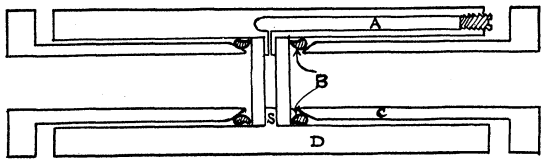

FIG. 1. The 2-mm tube.

* Research Fellow of the China Foundation for the Promotion of Education and Culture. Now at Yenching University, Peiping, China.

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

[2] D. S. Hughes and P. E. Lloyd, Phys. Rev. **52**, 1215 (1937).

[3] An aluminum ring was tried. When the tube was heated to 300°C or higher a large amount of silvery liquid alloy of rubidium and aluminum appeared and the tube gave no more absorption lines.

TABLE I. *The width at half-maximum of the two doublet components.*

Tube Length in cm x	Temperature Kelvin T	Vapor Pressure in mm P	Number of Atoms per cc N	Width at Half-Maximum ($\Delta\nu_{1/2}$) $\times 10^7$ Divided by N $(^2P_{3/2})$	$(^2P_{1/2})$	$\frac{(\Delta\nu_{1/2})(^2P_{3/2})}{(\Delta\nu_{1/2})(^2P_{1/2})}$
15.06	409	1.87×10^{-3}	4.42×10^{13}	1.84	1.41	1.3
15.06	445	1.14×10^{-2}	2.44×10^{14}	1.06	0.62	1.7
7.50	454	1.35×10^{-2}	2.88×10^{14}	1.04	0.63	1.7
7.50	491	9.80×10^{-2}	1.94×10^{15}	1.43	0.77	1.9
0.20	563	9.83×10^{-1}	1.69×10^{16}	0.72	0.42	1.7
7.50	575	1.183	1.99×10^{16}	1.51	0.84	1.8
7.50	601	2.361	3.89×10^{16}	1.09	0.60	1.8
0.20	600	2.32	3.75×10^{16}	1.06	0.61	1.7
0.20	621	3.84	5.67×10^{16}	1.19	0.79	1.5
0.20	651	7.57	1.14×10^{17}	0.76	0.54	1.4
0.20	660	9.18	1.34×10^{17}	1.80	0.63	1.7
0.20	664	9.98	1.45×10^{17}	0.52	0.36	1.4
0.20	699	19.9	2.75×10^{17}	0.29	0.19	1.5
0.20	721	29.6	3.97×10^{17}	0.16	0.12	1.3
0.20	766	62.2	7.87×10^{17}	0.11	0.09	1.2
0.20	797	98 ?	1.2×10^{18}	0.09 ?	0.07 ?	1.3
0.20	829	152 ?	1.8×10^{18}	0.07 ?	0.06 ?	1.2

The line contours were traced by a Kruss microphotometer and were compared with those given by the dispersion formula:

$$\alpha x=\frac{\rho\gamma}{2\pi\{(\delta\lambda)^2+(\gamma/2)^2\}} \tag{1}$$

in which ρ is the area under the absorption curve, γ is the width, in wave-length units, of the absorption line measured between points of half-maximum absorption coefficient, α is the absorption coefficient at wave-length $\delta\lambda$ from the central maximum, and x is the length of the absorption tube. If I/I_0 is the fraction of the light of wave-length $\lambda\pm\delta\lambda$ transmitted by the absorption tube, this yields

$$(\delta\lambda)^2=\frac{\rho\gamma\log_{10}e}{2\pi\log(I_0/I)}-\left(\frac{\gamma}{2}\right)^2. \tag{2}$$

Therefore a plot with $(\delta\lambda)^2$ as ordinate against $(\log_{10}I_0/I)^{-1}$ as abscissa is a straight line with slope $(\rho\gamma\log_{10}e)/2\pi$ and intercept $(\gamma/2)^2$. The intercept $(\gamma/2)^2$ was practically nil. However, since

$$\rho=\int_{-\infty}^{+\infty}\alpha x d(\delta\lambda)=\pi e^2\lambda_0^2Nf_{21}x/mc^2, \tag{3}$$

the width at half-maximum, γ, could be calculated from the experimentally determined slope, the number of Rb atoms per cc, N, the tube length, x and the oscillator strength f_{21} of the line components. N was found from the vapor pressure data

$$\log_{10}p=-52.23(76/T)+6.976, \tag{4}$$

where T is the temperature and p is the vapor pressure in mm. The width at half-maximum was then expressed in wave number units ($\Delta\nu_{1/2}$) by means of the relationship $\Delta\nu_{1/2}=c\gamma/\lambda^2$.

Results and Discussion

The lines were very symmetrically broadened when the vapor pressure was below about 1 mm Hg. But for plates taken when the temperature of the tube was raised to about 290°C or more, the lines exhibited more and more asymmetrical broadening of the van der Waals type, and a shadow of absorption was observed near the broadened line components.

A. Observations of the line broadening under low pressures

(*a*) *Theoretical formulas for resonance broadening.*—It is possible to compare the symmetric broadening at the lower pressures with that predicted by the theory. The Lorentz collision theory has been quantum theoretically modified by various persons, including Weisskopf[4] and Margenau and Watson.[5] The result given by Margenau and Watson is

$$\Delta\nu_{\frac{1}{2}}=e^2\lambda Nf_{12}/2\pi mc, \tag{5}$$

[4] V. Weisskopf, Zeits. f. Physik **75**, 287 (1932).
[5] H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

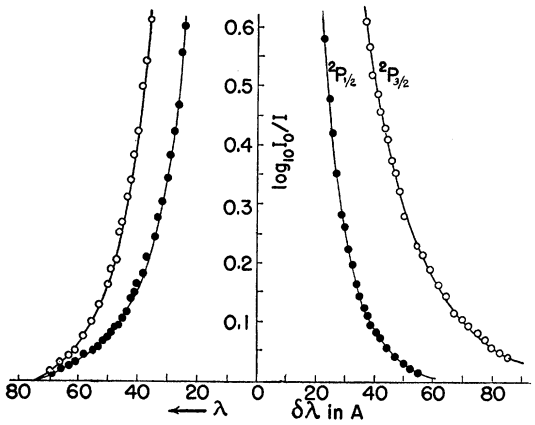

FIG. 2. The asymmetrically broadened lines. $T=766°K$; $p=62.2$ mm Hg; $x=0.196$ cm.

where f_{12} is the oscillator strength of the line in question. The numerical factor 2π is the result of a crude approximation and might be in error by as much as a factor 2.

The features of this expression that are subject to test are the dependence on N, the approximate correctness of the numerical factor, and the dependence on f_{12}. In Weisskopf's work no distinction is made between f_{12}, which is the same for both members of the doublet, and f_{21} which is twice as great for one member as for the other. The oscillator strength f_{12} is approximately $\frac{1}{3}$ in this case, and Margenau and Watson indicate clearly that f_{12} is to be used.

Another treatment of the problem, with special attention to the relative broadening of the members of a multiplet, has been given by Houston.[6] His result is

$$\Delta\nu_{\frac{1}{2}}=\frac{6^{\frac{1}{2}}S(1,2)N}{\hbar(2J_1+1)(2J_2+1)}=\frac{3\times 6^{\frac{1}{2}}}{2(2J_1+1)}\frac{e^2\lambda}{2\pi mc}Nf_{12}. \quad (6)$$

The quantity $S(1, 2)$ is the line strength as defined by Condon and Shortley,[7] while J_1 and J_2 are the inner quantum numbers of the ground and the excited states, respectively. This expression has the same dependence on N as has Eq. (5), it has a somewhat different numerical factor, and it definitely predicts that all members of a Russell-Saunders multiplet should have the same width, except for a factor equal to the ratio of the wave-lengths.

[6] W. V. Houston, Phys. Rev. **54**, 884 (1938).
[7] E. U. Condon and G. Shortley, *The Theory of Atomic Spectra* (Cambridge, 1935), p. 98.

(*b*) *Comparison of theory with experiment.*— In Table I are listed the experimental values of the width at half-maximum divided by N the number of absorbing atoms per cc. The ratios are listed separately for the two components of the resonance doublet corresponding to transitions from the $^2P_{3/2}$ and the $^2P_{1/2}$ states. In the range below 1 mm of vapor pressure, in which the lines are observed to be symmetrical and in which one may expect the theory to apply, the width at half maximum is found to be proportional to N as predicted by theory. In this range the average values of the ratio are

$$(\Delta\nu_{1/2})(^2P_{3/2})/N=1.22\times 10^{-7},$$
$$(\Delta\nu_{1/2})(^2P_{1/2})/N=0.77\times 10^{-7}.$$

In comparison Houston's formula (6) predicts the ratio

$$(\Delta\nu_{1/2})(^2P_{3/2})/N=0.65\times 10^{-7},$$
$$(\Delta\nu_{1/2})(^2P_{1/2})/N=0.66\times 10^{-7}.$$

The differences in the absolute values of the experimental and theoretical ratios are probably not greater than can be explained by the approximations used in the theoretical derivation. On the other hand, the great difference between the observed line widths of the two components at every pressure is definitely not predicted by the present theories.

B. Observational line broadening under higher pressures

When the temperature of the tube was raised to 290°C, corresponding to a Rb vapor pressure of 1 mm, the absorption lines began to show traces of asymmetry which became more pronounced as still higher pressures were reached. The $^2P_{1/2}$ component was asymmetrical towards the red and the $^2P_{3/2}$ component towards the violet. Figure 2 gives sample curves showing this asymmetry. Obviously the whole of these asymmetrical lines cannot be represented by the dispersion formula (1). If $(\delta\lambda)^2$ is plotted against $(\log I_0/I)^{-1}$ for each side of these lines separately it is found that a fairly straight line is obtained for the shorter wave-length wing of the $^2P_{3/2}$ component and the longer wave-length wing of the $^2P_{1/2}$ component while the opposite wings of these components yield strongly curved lines. The values of the width at half-maximum divided

by N listed in Table I for the pressures above 1 mm were calculated from the slopes of these straight lines. The values for these higher pressures do not therefore represent true widths at half-maximum. They are merely convenient parameters for indicating the form of one wing of each component in terms of formula (1).

The fact that the shorter wave-length wing of the $^2P_{1/2}$ component and the longer wave-length wing of the $^2P_{3/2}$ component deviate strongly from the dispersion formula (1) is not only due to the asymmetry but is also due to the appearance at these higher pressures of a faint structureless band near each of the component lines. Because the bands are diffuse and faint and are located near to the doublet lines the position of the bands could not be determined with great accuracy. The first of these bands extends for approximately 6A to the red of a fairly sharp edge at 7964.5A while the second extends about 10A to the violet of an edge at 7817.6A. While these bands have apparently not been observed before, similar bands have appeared in the absorption spectra of other alkalis.

In conclusion the author wishes to express his gratitude to Professors I. S. Bowen and W. V. Houston for their supervision and encouragement. He is also indebted to Dr. P. E. Lloyd for his generosity in discussing his experiences during research on K resonance lines.

NOVEMBER 15, 1940 PHYSICAL REVIEW VOLUME 58

The Energy Losses Attending Field Current and Thermionic Emission of Electrons from Metals*

G. M. FLEMING† AND JOSEPH E. HENDERSON
University of Washington, Seattle, Washington

(Received September 10, 1940)

The energy losses accompanying field emission and thermionic emission have been measured in the same experimental tube. This was accomplished by observing the thermal electromotive force in a junction from which the emission currents were drawn. No measurable temperature change was observed for field emission up to thermionic temperatures. For thermionic emission, temperature changes were observed which, when correlated with the power losses from the filament as a function of temperature, yield a calorimetric value for the work function of tungsten of 4.46±0.09 volts. A theoretical expression is given for the average net energy loss per electron emitted in thermionic and field current emission. The experiment gives strong additional evidence that in field emission the electrons escape by penetrating rather by surmounting the surface potential barrier as in thermionic emission.

INTRODUCTION

IT has frequently been observed that during the emission of large thermionic currents of electrons there is a very noticeable decrease in the temperature of the emitting body. This phenomenon provides direct evidence that the electrons furnishing the emission current partake of the thermal energy of the solid. Evidently the electrons leaving a metal at the high temperatures occurring in thermionic emission have more temperature energy than those which are supplied to replace them. The difference in the average energy of the electrons emitted by the cathode and of those supplied to the cathode results in a loss of power and in a corresponding decrease of temperature. The power loss producing the temperature change, when translated in terms of the average net energy loss per electron emitted, yields a value of the work function of the emitting metal in very satisfactory agreement with that obtained by independent methods.[1]

* Abstracts: J. E. Henderson and G. M. Fleming, Phys. Rev. **48**, 486 (1935); **54**, 241 (1938); **56**, 853 (1939).

† Now at Russell Sage College.

[1] Saul Dushman, Rev. Mod. Phys. **2**, 394 (1930).