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Resonance Broadening of the Sodium *D* Lines

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By direct measurement of the contours of the line wings, the resonance broadening of the sodium *D* lines in absorption was determined for vapor pressures of sodium ranging from 10^{-3} to 70 mm Hg with negligible amount of foreign gases. Over nearly the entire range, the half-intensity width varied linearly with the density of the absorbing atoms; i.e., $\Delta\nu_{\frac{1}{2}}/N=0.80\times10^{-7}$ sec.$^{-1}$ cm^{-3}—the constant being 1.6 times that predicted by theory but much less than the corresponding experimental results for potassium. Above 5 mm pressure, $\Delta\nu_{\frac{1}{2}}$ increased slightly faster than N; moreover, the contour for the absorption coefficient was more adequately represented by an inverse cube contour than by the inverse square. Somewhat in contradiction to theory, the relative width, $\Delta\nu_{\frac{1}{2},s}/\Delta\nu_{\frac{1}{2},l}$ was 1.12. No definite evidence of van der Waals force was observed at the higher pressures; likewise no appreciable shifts or asymmetries. The natural width measured was consistent with previous results.

PRIOR to the present investigation of sodium and Chen's simultaneous study of rubidium,[1] the only substantial experimental work on resonance broadening of spectral lines appears to be that by Hughes and Lloyd[2] on potassium resonance lines. They were able to overcome a major experimental difficulty by employing MgO windows[3] which resist alkali vapors to relatively high temperatures. In agreement with theory, their result showed a linear dependence on the half-intensity width, $\Delta\nu_{\frac{1}{2}}$, with the density of the absorbing atoms, N; however, the absolute value of the proportionality constant they obtained was several times larger than theoretical predictions. Particularly, a theoretical paper by Houston[4] raises some doubt as to the accuracy of their results. In addition to the inadequacy of the vapor pressure curve used for potassium, it is thought that their temperature determination involved some uncertainty and their photometry required large corrections. From these considerations, sodium was selected for the present investigation on resonance broadening.

PROCEDURE

The experimental procedure used in this investigation is essentially the same as that described by Hughes and Lloyd.[2] The most important improvement is the provision for a reproducible metallic contact for the Chromel-Alumel thermocouple which measured the temperature of the absorption cell. Repeated *in situ* calibration showed only a small consistent temperature gradient between the thermocouple junction and the absorption cell, whereas in the case of Hughes and Lloyd there was a relatively large gradient with considerable uncertainty and lack of reproducibility. The temperature of the absorption cell was kept constant to within one degree during an exposure and the saturation value of Na vapor was usually assured by the presence of liquid Na.

The following equation by E. Thiele[5] provided the vapor pressure of Na:

$$\log_{10} p(\text{Na}) = -26{,}244/(4.573T) - 1.178 \log_{10} T + 11.402, \quad (1)$$

where p is in mm Hg. This equation was considered sufficiently accurate in view of the uncertainties in the photometry. In contrast to the case of potassium, no extrapolation was necessary over the entire range investigated. For relatively high temperatures the vapor pressure of sodium molecules becomes appreciable. Thiele[5] gives

$$\log_{10} p(\text{Na}_2) = -7020/T + 8.149 \quad (2)$$

for the vapor pressure of sodium molecules.

The error in photometry was minimized by repeated *in situ* calibration of the step weakeners used by means of rotating sectors. The Eastman

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[1] S. Y. Chen, Phys. Rev. **58**, 884 (1940).

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

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

[4] W. V. Houston, Phys. Rev. **54**, 884 (1938).

[5] E. Thiele, Ann. d. Physik **14**, 970 (1932).

TABLE I. *Results on the resonance broadening of sodium D lines.*

	T	p	N	$\Delta\nu_{\frac{1}{2},l}/N$	$\Delta\nu_{\frac{1}{2},s}/N$	$\Delta\nu_{\frac{1}{2},s}/\Delta\nu_{\frac{1}{2},l}$
1	510	9.34×10^{-4}	1.78×10^{13}	?	?	0.97
2	550	5.50×10^{-3}	9.71	1.14×10^{-7}	1.25×10^{-7}	1.09
3	569	1.18×10^{-2}	2.02×10^{14}	0.79	1.02	1.05
4	570	1.22	2.10	0.73	0.75	1.03
5	601	3.81	6.16	0.73	0.77	1.05
6	601	3.81	6.16	0.57	0.68	1.19
7	$643\frac{1}{2}$	1.50×10^{-1}	2.27×10^{15}	0.80	0.97	1.20
8	645	1.57	2.37	0.80	1.03	1.28
9	669	3.14	4.56	0.90	1.14	1.29
10	701	7.29	1.01×10^{16}	0.93	0.96	1.04
11	719	1.13×10^{0}	1.53	0.63	0.74	1.18
12	783	4.62	5.73	0.59		
13	796	5.96	7.28	0.79		
14	840	1.33×10^{1}	1.54×10^{17}	1.06		
15	878	2.50	2.27	1.17		
16	951	7.23	7.38	1.1		

type I-D and type I-B plates used required for the most part very small corrections for varying sensitivity between the two members of the doublet. The exposure time was usually less than one hour without recourse to hypersensitization. The spectrograms were obtained by using a Rowland grating with 2.64A/mm dispersion in the first order and the traces of the lines and step weakener images were recorded by a Küss microphotometer.

The absorption tube lengths were 0.22 and 7.47 cm. The f values were taken to be $f_l=\frac{1}{3}$ and $f_s=\frac{2}{3}$ for the D_1 and D_2 lines, respectively, although there is some doubt as to the use of f values in the case of lines strongly broadened by resonance forces.

CALCULATION

For the most part the intensity distribution of the line was determined by measuring the transmission of the line wings with the aid of the step weakener traces. Usually the microphotometer traces required only small linear corrections for the varying sensitivity of the plates and the lines were as a rule symmetrical. Consequently when there was no overlapping of the lines, both wings of each line were averaged together.

The experimental intensity distribution was compared with the dispersion equation for the absorption coefficient,

$$\alpha x = -\ln (I/I_0) = \frac{Kx\Delta\nu_{\frac{1}{2}}/2\pi}{(\nu_0-\nu)^2+(\Delta\nu_{\frac{1}{2}}/2)^2}, \quad (3)$$

where $K=(\pi e^2/mc)Nf_i$ sec.$^{-1}$, x is the absorbing path length, e is the electronic charge in e.s.u. and I/I_0 is the transmission (about 0.35 to 0.95). This equation was usually adequate, except for the incompletely resolved lines and the lines corresponding to vapor pressure of Na above about 5 mm.

Equation (3) was transformed to

$$y=C_iz-C' \qquad i=1 \text{ or } 2$$

where $y=(\Delta\lambda)^2$, $z=[-\log_{10}(I/I_0)]^{-1}$ and $C_i=k_iNx\Delta\nu_{\frac{1}{2}}$, k_i being equal to $(\lambda_{0i}^4e^2f_i)/(2mc^3\log_e 10)$. The graph was usually linear and the value C_i gave the half-intensity width.

The incompletely resolved lines were measured by the area method.[6] Near the region of natural broadening the half-intensity widths for resonance broadening and for natural broadening were considered simply additive on the basis of the similarity of their dispersion equations. Hence the theoretical value of natural width was always subtracted from the measured width. Moreover calculation shows that Doppler broadening can be neglected.

For vapor pressure above 0.5 mm, the D lines overlapped partially or completely. For partial overlapping corrections were made according to the degree of overlapping. For completely overlapped lines the wings were treated as caused by a single line—taking into consideration the separation of the two lines. For vapor pressure above 20 mm, measurements become

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[6] R. Ladenburg and F. Reiche, Ann. d. Physik **42**, 181 (1913).

difficult because of the conspicuous appearance of the Na_2 bands.

THEORETICAL VALUES

Weisskopf,[7] Margenau and Watson,[8] and Furssow and Wlassow[9] have given similar theoretical values for the half-intensity width of resonance broadening,

$$\Delta\nu_{\frac{1}{2}} = k(e^2f/m\nu_0\pi)N \text{ sec.}^{-1}, \qquad (5)$$

where k equals $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{2}{3}$, respectively. Houston[4] has treated the problem in terms of fine structures and has given

$$\Delta\nu_{\frac{1}{2}} = 2\pi(6)^{\frac{1}{2}}S(J, J')N/\{h(2J+1)(2J'+1)\} \text{ sec.}^{-1}, \qquad (6)$$

where $S(J, J') = (2J'+1)e^2h/8\pi^2m\nu_0$ for the resonance lines of the alkalis, while J and J' are the inner quantum numbers for the ground and the excited states, respectively. Accordingly

$$\Delta\nu_{\frac{1}{2}} = (6)^{\frac{1}{2}}Ne^2/8\pi m\nu_0 \text{ sec.}^{-1} \qquad (7)$$

for each member of the alkali doublets. This gives

$$\Delta\nu_{\frac{1}{2}} = 0.49N \times 10^{-7} \text{ for Na.} \qquad (8)$$

The natural width for sodium is

$$\Delta\nu_{\frac{1}{2}} = 1.01 \times 10^7 \text{ sec.}^{-1}. \qquad (9)$$

RESULTS

The experimental results are summarized in Table I.

The mean value of $\Delta\nu_{\frac{1}{2}}/N$ is 0.80×10^{-7} sec.$^{-1}$ by taking the values 4–13 as being most reliable. This result is seen to be about 1.6 times the theoretical value given by Eq. (8). Since nearly all the experimental errors tend to broaden the lines, the values 0.80×10^{-7} sec.$^{-1}$ for Na is probably slightly too high and possibly too high by as much as twenty percent, the order of experimental error.

The natural width was measured for the narrowest lines by subtracting the resonance width obtained above from the total measured width. The results were consistent with previous measurement and in agreement with Eq. (10). This provided a rough check for the value of resonance broadening.

A serious discrepancy was the ratio of the half-widths, $\Delta\nu_{\frac{1}{2},s}/\Delta\nu_{\frac{1}{2},l}$, which was found to be 1.12 for Na, while the theory[4] gives unity. Since the more intense line is relatively wider and since the measurement of the ratio is comparatively easy, the experimental value cannot be very much in error.

The microphotometer traces of the *D* lines showed symmetry in nearly every plate. Slight asymmetries in some were of the order of the variation in the sensitivity of the plates. There were also no appreciable shifts in the lines even at the highest temperature. It was impossible to measure plates for vapor pressure above 70 mm, for there was hardly any measurable background because of the absorption of the Na_2 bands.

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[7] V. Weisskopf, Zeits. f. Physik **75**, 287 (1932).

[8] H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

[9] Furssow and Wlassow, Physik. Zeits. Sowjetunion **10**, 379 (1936).