Pressure Broadening of the Potassium Resonance Lines by Argon and Nitrogen*

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Broadening of the potassium resonance lines in absorption by argon and nitrogen pressures from 1 to 40 atmospheres has been observed. Half-widths and shifts of the lines, when plotted against "relative density," yield curves that are straight lines up to about relative density 14, indicating that in this pressure region Lorentz type of broadening predominates. At about relative density 14, the curves depart from linearity. The results are in accord with theory, and partly in agreement with previous work. Theoretical contours for pressure broadened spectral lines have been fitted to those of experiment. Agreement is quite satisfactory, considering the approximations made in evaluating the theoretical curves. Three independent methods of calculation yield for the constant b (measure of van der Waals forces) the values $24(10)^{-32}$ and $18(10)^{-32}$ cm^6 sec.$^{-1}$ for argon and nitrogen, respectively.

INTRODUCTION

PRESSURE effects of nitrogen on the potassium resonance lines in absorption have already been investigated by Watson and Margenau.[1] However, they were able to obtain only three spectrograms between relative density 12 and 20. It is in this higher pressure region where departure of the linear relation between relative density and broadening occurs. In order to establish more definitely this point of departure, and to observe the broadening at higher relative densities, the present work was undertaken. Since the publication of the paper by Watson and Margenau, the latter[2] has extended further the theory of pressure broadening and given a theoretical contour for broadened spectral lines. Consequently in the present work it was possible to compare theoretical with experimental contours.

EXPERIMENTAL PROCEDURE

A detailed description of apparatus is given elsewhere.[3] It consisted of a steel absorption tube 87 cm long, fitted with 1 cm thick Pyrex glass windows. A three-section electric furnace served to vaporize the potassium in the absorption tube. Argon and nitrogen were used as perturbing gases up to relative density 28 (40 atmospheres). Above this the potassium doublet coalesces making measurements of half-width inaccurate. Pressures were reduced to relative densities by the law for perfect gases. The more exact van der Waals law was not used, since for even the highest pressures the correction term was found to be negligible. Correction was not made for thermal transpiration, as was done by Watson and Margenau.[1] Both experiment and theory have shown[4] that no correction for this phenomenon is necessary if the diameter of the outlet to the pressure gauge is many times greater than the molecular mean free path. In the apparatus used, the diameter of the outlet was several mm and the mean free paths of the order of $(10)^{-4}$ mm or less.

Spectrograms of the resonance lines (7665A and 7699A) were taken on Eastman type 144-N plates in the first order of a 21-foot concave grating in a stigmatic mounting. A Pointolite lamp was used as continuous light source, and second order Fe lines served for the comparison spectrum. The characteristic log I vs. D curve of the spectrograms was obtained from the blackening marks produced by a step filter. This consisted of a quartz disk on which were deposited five strips of platinum of different densities and had been previously calibrated for $\lambda7650$. The filter was placed directly in front of the plate and just to one side of the resonance lines. Both blackening marks and potassium lines were recorded simultaneously on the photographic plate, thus insuring the same continuous spectrum as well as the same exposure time for each. This method of obtaining the characteristic curve has the advantage of not relying on the reciprocity law. Microphotometer traces of the spectrograms were made on a Koch-Goos self-recording instrument, and those line contours which did not lie on

[1] W. W. Watson and H. Margenau, Phys. Rev. **44**, 748 (1933).
[2] H. Margenau, Phys. Rev. **48**, 755 (1935).
[3] H. Margenau and W. W. Watson, Phys. Rev. **44**, 92 (1933).
[4] L. B. Loeb, *Kinetic Theory of Gases* (1927), p. 283.
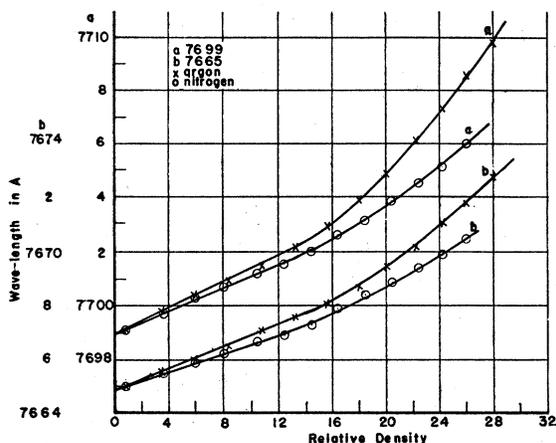
FIG. 1. Wave-lengths of the maxima of the potassium resonance lines vs. relative density of argon and nitrogen.

the straight line part of the characteristic curve were corrected to give true absorption contours. The wave-length of the maximum of each absorption curve as well as its half-width was calculated from the dispersion on the microphotometer trace as determined by interpolation between Fe lines.

RESULTS

The results are shown graphically in Figs. 1 and 2. In Fig. 1 the wave-lengths of the maxima of the potassium resonance lines are plotted against relative densities of argon and nitrogen, and in Fig. 2 the averaged half-widths of the doublet are plotted. (No significant difference between the half-widths of the doublet components was detected.) Curves have been drawn through the "mean" of the plotted points. The points in Fig. 1 lie more closely on the curves than do those in Fig. 2, which is to be expected, since wave-lengths of the maxima can be determined with greater accuracy than half-widths. The latter depend upon corrections for nonlinear plate characteristics, which do not affect the line maximum. Extrapolating the curves back to the axis of ordinates, the values 7664.84A and 7698.96A are obtained for the maxima of the potassium doublet at zero relative density, and 0.25 cm^{-1} for the half-widths. It is seen that argon produces a greater half-width and shift of the maximum than nitrogen, and the shift of $\lambda 7699$ is slightly greater than $\lambda 7665$. The curves up to relative density 14 are straight lines, indicating that in this pressure region "velocity"
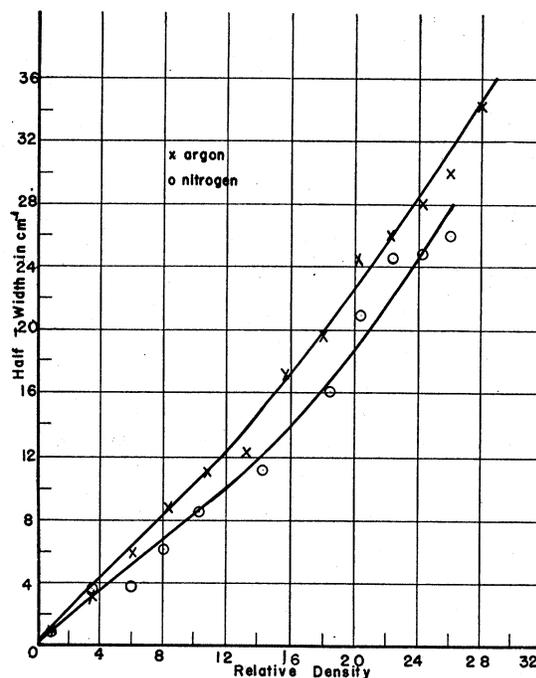
FIG. 2. Half-widths of the potassium resonance lines vs. relative density of argon and nitrogen. Points are averaged values for the two components of the doublet.

broadening[5] predominates. At about relative density 14, the curves depart from linearity, showing that "statistical" broadening[5] is becoming effective. This is in accordance with Margenau's theory.[2] and also with the previous work done by Watson and Margenau[1] using nitrogen as the perturbing gas. However, shifts and half-widths obtained for nitrogen in the present work are nearly twice as great as their values. Half this discrepancy can be accounted for by the fact that they made correction for thermal transpiration in reducing pressures to relative densities. In Table I are listed shifts and

TABLE I. Summary of shifts and half-widths of the potassium resonance doublet.

		Shift $\frac{\Delta \nu}{d}$	Half-Width $\frac{\Delta \nu_{\frac{1}{2}}}{d}$
Argon	7665A	0.360 cm^{-1}	1.01 cm^{-1}
	7699	0.420	
Nitrogen	7665	0.300	0.82
	7699	0.360	

[5] H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).
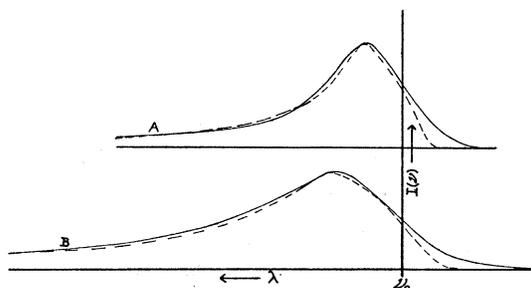
FIG. 3. Experimental (solid) and corresponding theoretical (dashed) contours of λ7699 perturbed by nitrogen (curves A), and by argon (curves B), relative densities 3.5 and 5.9, respectively.

half-widths per unit relative density as determined by the slope of the straight line part of the curves. According to theory, the half-width should be approximately twice as great as the shift when velocity broadening predominates. From Table I, we obtain $\Delta\nu_{\frac{1}{2}}/\Delta\nu = 2.6$ for argon and 2.5 for nitrogen.

To compare experimental with theoretical line contours, two microphotometer curves in the lower pressure range were chosen which did not need correction for the characteristic of the photographic plate. These were λ7699 contours for argon and nitrogen, relative density 5.9 and 3.5, respectively. In this pressure range, Margenau gives for an approximate theoretical contour:[2]

$$I(\nu') = \frac{1}{\Delta}\left[\phi\left(\frac{\pi\lambda^2}{\nu'-\Delta/2}\right)^{\frac{1}{2}} - \phi\left(\frac{\pi\lambda^2}{\nu'+\Delta/2}\right)^{\frac{1}{2}}\right], \quad (1)$$

where $\phi(x) = (2/\pi^{\frac{1}{2}})\int_0^x e^{-y^2}dy.$

Here, ν' is the frequency measured from the line origin ν_0, Δ the half-width, and $\lambda = \frac{2}{3}\pi|b|^{\frac{1}{2}}n$ where n is the number of perturbers per unit volume and b a constant, which is a measure of van der Waals forces. Eq. (1) was evaluated by numerical integration for various values of Δ and $\pi\lambda^2$. The best fit with the experimental contour for argon was obtained with $\pi\lambda^2 = 0.5\Delta$ where $\Delta = 4.28$ cm^{-1} and for nitrogen $\pi\lambda^2 = 0.4\Delta$, $\Delta = 2.50$ cm^{-1}. In Fig. 3 experimental (solid) and theoretical (dashed) contours are shown fitted together; curves A are for nitrogen, B for argon. Agreement is good on the long wave-length side of the maximum, but on the short wave-length side the theoretical curves fall off too rapidly. This is to be expected,

TABLE II. Values of the van der Waals constant b calculated by three different methods.

Calculation by Eq.	van der Waals Constant b	
	Argon	Nitrogen
(1)	24(10)$^{-32}$	18(10)$^{-32}$ cm^6 sec.$^{-1}$
(2)	24	17
(3)	23	18

however, because of the approximations made in deriving Eq. (1).

The relation between $\pi\lambda^2$ and Δ for the theoretical contours which best fit those of experiment, affords a means of calculating the van der Waals constant b. The values of b obtained in this manner are given in Table II. As a check on these values, two other methods of calculating b are available. The first is to apply Lorentz' formula as modified by Weisskopf:[6]

$$\Delta\nu_{\frac{1}{2}} = 2.2b^{2/5}(V)^{3/5}n, \quad (2)$$

where V is the molecular root mean square velocity, and where we shall take for $\Delta\nu_{\frac{1}{2}}$ the half-widths of the theoretical curves. Secondly Margenau's theory states[2] that the curves of half-width and shift versus relative density depart from linearity when the velocity broadening half-width becomes approximately equal to the statistical half-width; i.e., when

$$\Delta\nu_{\frac{1}{2}} \cong \pi\lambda^2. \quad (3)$$

Experimentally this point of departure is at about relative density 14, and the half-widths of the potassium doublet perturbed by argon and nitrogen at this relative density are 12.34 cm^{-1} and 11.29 cm^{-1}, respectively. Values of b calculated from (2) and (3) are also given in Table II. The results in Table II are in excellent agreement among themselves, but b for nitrogen does not agree with the value [$7(10)^{-32}$ cm^6 sec.$^{-1}$] calculated by Margenau[2] from the previous work on the broadening of the potassium resonance lines.[1] The reason for this discrepancy has already been noted; the half-widths obtained by Watson and Margenau are about half as large as obtained in the present work.

The author wishes to thank Professor W. W. Watson for suggesting this problem and for his helpful criticism during the course of the work, and also Professor H. Margenau for his advice in the theoretical interpretation of the results.

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