ture $[(295/90)^{3/10}=1.43]$. The measurements in krypton (Table I) show good agreement with these results. In particular the precision measurements on λ 7601 Å give width-to-shift ratios of −2.93 and −2.96±0.2 and a temperature coefficient of 1.48±0.12. This result and an investigation of foreign-gas broadening of krypton lines are discussed at greater length in the following paper.[23]

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ACKNOWLEDGMENTS

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Interpretation of Foreign-Gas Broadening and Shift in Krypton

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Collision broadening and shift due to low pressures of He, Ne, Ar, and Kr have been measured for two emission lines of krypton at temperatures of 80 and 295°K. Different perturbing gases are found to produce widely different temperature dependencies of line shift and line broadening. These results are interpreted in terms of the Lindholm-Foley "impact theory" of collision broadening, assuming a Lennard-Jones (12-6) interaction between radiating and perturbing atoms. Semiquantitative agreement of theory and experiment is found in the case of helium perturbers; the results for neon perturbers are described with striking accuracy. Agreement in the case of argon perturbers is less good. As expected, for the line with a metastable lower level, the krypton-krypton broadening data are consistent with the extreme of a Van der Waals r^{-6} interaction.

I. INTRODUCTION

It is well known that the phenomena of collision broadening and shift in spectral lines are related to the interaction potentials between radiating and perturbing atoms. However, any such investigation of interaction potentials has been hampered by lack of both accurate experimental data and a fully confirmed theory of collision broadening and shift. A recent paper[1] has analyzed measurements of collision broadening and shift of a number of alkali lines perturbed by low pressures of inert gases. This work has shown that the results may be interpreted in a consistent manner by means of the semiclassical impact theory due to Lindholm[2] and Foley[3], developed for a Lennard-Jones (12-6) potential; that is, a potential having attractive r^{-6} and repulsive r^{-12} components.

Until recently all the experimental data suitable for interpretation by this treatment have referred to measurements made at a single temperature. A check on the temperature dependence predicted for both broadening and shift has thus been impossible. However, the techniques developed at the Clarendon Laboratory for studying self-broadening in the rare gases[4–7] provide a suitable means for precision measurements of collision broadening and shift due to low pressures of foreign gases over a wide temperature range. This paper presents an analysis of the results of such measurements. Two red krypton lines have been examined in emission when perturbed by low pressures of He, Ne, Ar, and Kr at temperatures of 80 and 295°K; widely different temperature coefficients and shift-to-broadening ratios were found for the different perturbers. It is shown that these results can be interpreted in a semiquantitative manner by the theoretical treatment outlined above and described in the following section.

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II. THEORETICAL BACKGROUND

The Lennard-Jones interaction potential produces angular frequency perturbations given by

$$\Delta\omega = C_{12}'r^{-12} - C_6'r^{-6}, \tag{1}$$

where C_{12}', C_6' are constants and r is the distance between two interacting atoms. Our notation is consistent with that of the first reference where the complete theoretical treatment will be found. The Lindholm theory predicts a Lorentzian line profile $I(\omega)$ of half half-width γ (angular frequency), shifted with respect to the unperturbed line by an amount β.

$$I(\omega) = \frac{\gamma}{\pi}\frac{1}{(\omega-\omega_0-\beta)^2+\gamma^2}. \tag{2}$$

The constants β, γ are proportional to the perturbing particle density, N, and may be expressed in the form

$$\beta/N = 2\pi(\tfrac{3}{8}\pi)^{2/5}(\bar{v})^{3/5}|C_6'|^{2/5}S(\alpha), \tag{3}$$

$$\gamma/N = 4\pi(\tfrac{3}{8}\pi)^{2/5}(\bar{v})^{3/5}|C_6'|^{2/5}B(\alpha), \tag{4}$$

where $(\bar{v})$ is the mean relative velocity between radiating and perturbing atoms, and the functions $S(\alpha)$, $B(\alpha)$ are defined, for a Lennard-Jones interaction, by the integrals

$$S(\alpha) = \int_0^\infty x \sin(\alpha x^{-11} - x^{-5})dx, \tag{5}$$

$$B(\alpha) = \int_0^\infty x \sin^2[\tfrac{1}{2}(\alpha x^{-11} - x^{-5})]dx. \tag{6}$$

Here, x is proportional to the impact parameter ρ being given by

$$x = \rho[\tfrac{3}{8}\pi|C_6'|/(\bar{v})]^{-1/5}, \tag{7}$$

and the parameter α expressing the relative magnitude of C_{12}' and C_6' is given by

$$\alpha = 0.536(\bar{v})^{6/5}C_{12}'/|C_6'|^{11/5}. \tag{8}$$

The functions $S(\alpha)$, $B(\alpha)$ have been evaluated numerically[1] and are shown in Fig. 1 together with the ratio $S(\alpha)/2B(\alpha)=\beta/\gamma$. In the limit of a pure van der Waals interaction ($C_{12}'\to 0$, left-hand side of Fig. 1), $S(\alpha)$ and $B(\alpha)$ reduce to the constant quantities -0.438 and 0.301, respectively. Hence in this case the ratio β/γ is -0.728 independent of temperature, and both β and γ should vary with temperature only through the velocity factor $(\bar{v})^{3/5}$. In general, however, there will be an additional temperature dependence of β and γ through the factors $S(\alpha)$ and $B(\alpha)$ since α is also velocity-dependent.

III. EXPERIMENT AND RESULTS

The following lines arising from transitions between the $4p^55s$ and $4p^55p$ levels were examined in emission:

λ 7587 Å: $4p^5(^2P_{3/2})5s[\tfrac{3}{2}]_1 - 4p^5(^2P_{3/2})5p[\tfrac{1}{2}]_0$,

λ 7601 Å: $4p^5(^2P_{3/2})5s[\tfrac{3}{2}]_2 - 4p^5(^2P_{3/2})5p[\tfrac{3}{2}]_2$.

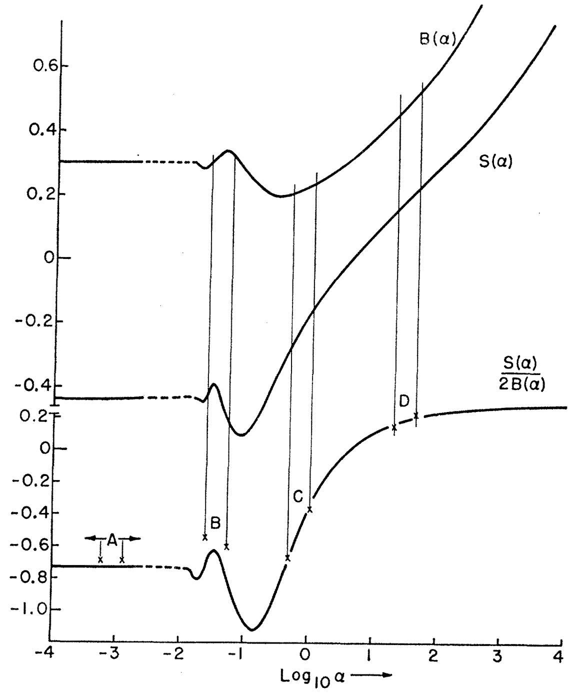

FIG. 1. The shift integral $S(\alpha)$, the broadening integral $B(\alpha)$, and the ratio $S(\alpha)/2B(\alpha)$ plotted against $\log_{10}\alpha$. The regions A, B, C, D show the best fit to the experimental data for Kr, Ar, Ne, and He, respectively.

The apparatus used in these experiments has already been described in a report on self-broadening in krypton.[7] The gas discharge was cooled either by liquid nitrogen or by oil at room temperature. The discharge current was maintained at less than 0.5 mA so that

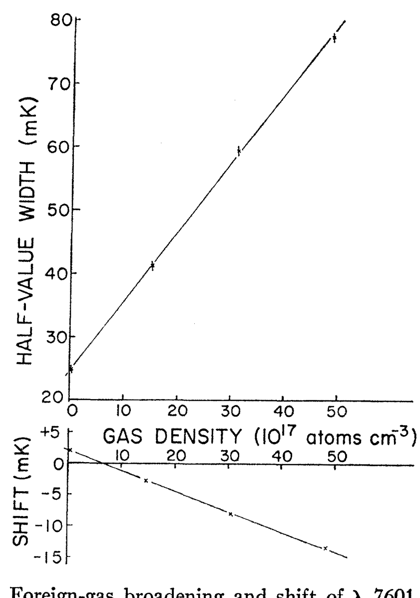

FIG. 2. Foreign-gas broadening and shift of λ 7601 Å due to argon, liquid nitrogen coolant (~80°K). The half-value width (the whole line width at half the peak intensity) is plotted against foreign-gas density.

Stark broadening would be negligible. Complications due to the presence of more than one isotope were avoided through the use of separated Kr^{86}. Shifts were measured relative to lines from a Geissler tube of natural krypton (mainly Kr^{84}). A krypton density of about 0.1×10^{17} atoms/cm^3 was initially established in the discharge. The perturbing gas was then leaked in from a high-pressure source and four or five traces of broadening and shift were made at densities in the range of about 1 to 50×10^{17} atoms/cm^3. A discharge through such a mixture exhibits spectral lines almost exclusively due to the component of lower excitation potential.

In the derivation of final results the technique of full Voigt profile analysis was combined with that of comparison of half-value width (see Ref. 7). The profiles were found to be of pure Voigt form and showed no

TABLE I. Coefficients of broadening $(\frac{1}{2}\pi c)(2\gamma/N)$ and shift $(\frac{1}{2}\pi c)(\beta/N)$ in krypton (cm$^{-1}\times10^{-20}$ atoms^{-1} cm^3).

	Temperature ~80°K Broadening	Shift	Temperature ~295°K Broadening	Shift
	Broadening by helium			
7587 Å	1.44	+0.141	2.73	+0.350
7601 Å	1.38	+0.108	2.57	+0.283
	(0.1–60×10^{17} atoms cm^{-3})		(0.1–27×10^{17} atoms cm^{-3})	
	Broadening by neon			
7587 Å	0.73_5	-0.23_7	1.20	-0.22_6
7601 Å	0.68_3	-0.22_7	1.14	-0.21_1
	(0.1–70×10^{17} atoms cm^{-3})		(0.1–42×10^{17} atoms cm^{-3})	
	Broadening by argon			
7587 Å	1.25	-0.32_1	2.66	-0.75_5
7601 Å	1.18	-0.32_1	2.44	-0.73_5
	(0.1–50×10^{17} atoms cm^{-3})		(0.1–20×10^{17} atoms cm^{-3})	
	Self-broadening by krypton			
7587 Å	12.8[a]	+0.2[a]	13.1	~+0.2
7601 Å	1.30_4[a]	-0.44_5[a]	1.93_5	-0.65_2
	(0.1–20×10^{17} atoms cm^{-3})		(0.1–20×10^{17} atoms cm^{-3})	

[a] Temperature ~90°K.

asymmetry. Both broadening and shift increased linearly with gas density as predicted by the Lindholm theory. A specimen set of results is shown in Fig. 2. Previous experience with these low-current gas discharges combined with estimates of the Gaussian contribution to the line profiles established that the effective gas temperatures were very close to 80 and 295°K. The gas densities were derived from the measured pressures on the basis of these values. In the case of self-broadening by Kr, where liquid-oxygen coolant was used, the lower temperature was about 90°K. The small uncertainty in these temperatures contributes significantly to the final errors in (β/N) and (γ/N) but not to the ratio (β/γ). Total errors in each of these quantities are estimated to be less than 7%. Coefficients of broadening and shift, including self-broadening data, are given in Table I together with the density ranges over which the

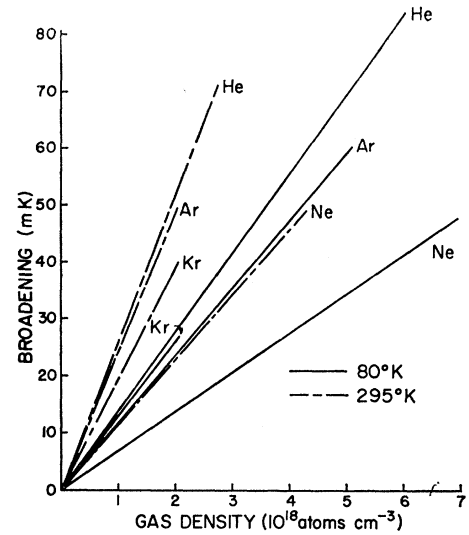

FIG. 3. Foreign-gas broadening (Lorentzian half-value width) of krypton λ 7601 Å at two temperatures. The density range of each experiment is indicated but for clarity individual data points (which establish the linearity within a few percent—see, e.g., Fig. 2) are not shown.

measurements were made. These final results are expressed graphically for λ 7601 Å in Figs. 3 and 4.

IV. DISCUSSION

The two lines show very similar behavior when perturbed by inert gases other than krypton itself. This is to be expected since both lines involve similar transitions and corresponding states must therefore have similar radial wave functions. Krypton itself perturbs the λ 7601 line just like a foreign gas but produces the large broadening and near zero shift characteristic of resonance interactions in the λ 7587 line. These latter effects are the subject of a separate paper[7]. Only the interpretation of the results for the λ 7601 line will be considered in detail. It may be assumed that the

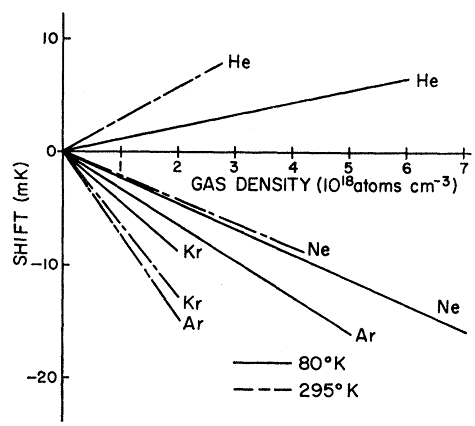

FIG. 4. Shift of λ 7601 Å due to foreign gases at two temperatures. Note the reduced red shift at the higher temperature for neon.

conclusions apply equally well to foreign-gas perturbations of the λ 7587 line.

A. Temperature Dependence of the Broadening and Shift Coefficients

The widely different temperature dependence of β and γ from one foreign gas to another shows that an interpretation in terms of a compound interaction potential is necessary. We may therefore attempt to apply the theory outlined in Sec. II. The value of α corresponding to measurements of broadening and shift at the same temperature can easily be found from the curve of β/γ against α (Fig. 1). Because of the approximate proportionality between the C_6 interaction constant and polarizability, it is to be expected that the value of α will decrease markedly with perturbing gas in the order He, Ne, Ar, Kr. A crucial test of the theory is to examine whether the α values obtained for a particular gas at the two temperatures show the temperature dependence predicted by Eq. (8); from 80 to 295°K, the expected change in $\log_{10}\alpha$ is 0.34. Table II shows that the agreement is satisfactory for He ($\Delta\log_{10}\alpha = 0.47\pm0.23$) and Ne ($\Delta\log_{10}\alpha=0.28\pm0.10$) though in the former case the evidence is hardly convincing because of the slow variation of β/γ with α in region D of Fig. 1. An alternative test, however, is provided by the individual variations in β and γ. The experimental ratios for β/γ have been fitted as closely as possible to the theoretical curve with the restriction that the two α values thus obtained should show the correct temperature dependence. The resulting points are shown in Fig. 1. The corresponding values of $S(\alpha)$ and $B(\alpha)$ may then be used to predict the temperature effects in β and γ individually. These are compared with the observed effects in Table III and are discussed in turn.

1. Helium

The observed change in the broadening γ by a factor 1.87 is close to the value 1.92 which would be predicted by a hard-sphere model. From the table it is clear that the Lennard-Jones potential comes close to explaining the temperature dependence for both broadening γ and β; the remaining discrepancy between theory and experiment would appear to lie slightly outside the experimental error.

TABLE II. Temperature dependence of the shift (β) to broadening (γ) ratio for the Kr λ 7601 line perturbed by inert gases.

Perturber	He	Ne	Ar	Kr
$(\beta/\gamma)_{80°K}$	0.156	−0.664	−0.545	−0.684[a]
$(\beta/\gamma)_{295°K}$	0.220	−0.371	−0.602	−0.678
$(\log_{10}\alpha)_{80°K}$	1.23±0.08	1.70±0.06	indeterminate	
$(\log_{10}\alpha)_{295K°}$	1.70±0.15	1.98±0.04		
$\Delta(\log_{10}\alpha)_{expt.}$	0.47±0.23	0.28±0.10		
$\Delta(\log_{10}\alpha)_{theory}$	0.34	0.34		

[a] The low-temperature Kr result refers to a temperature of 90°K.

2. Neon

This is a particularly interesting case in which the broadening increases strongly with temperature whereas the magnitude of the shift slightly decreases. Table III shows that these temperature effects in both β and γ are predicted with striking accuracy by the theory.

3. Argon

A direct application of the theory to the argon ratios β/γ would place these along with neon in region C of Fig. 1. This is unacceptable, however, since the argon results do not show the steep temperature dependence of the neon results and experimental errors are too small to permit such a discrepancy. Because of the higher polarizability of argon, the argon results would be expected to approach the van der Waals limit much more closely than the neon results, and therefore to lie to the left of C. In addition, the individual values for β and γ both show temperature effects significantly greater than van der Waals's. Thus the absolute magnitudes of both $S(\alpha)$ and $B(\alpha)$ must increase with temperature and hence with α, a condition which is only satisfied in region B. Although the shape of the theoretical curves can account qualitatively for the observed variations in β and γ, it must be admitted that the theory is unable to provide a quantitative explanation within the experimental error. Possible reasons for this will be examined later.

TABLE III. Comparison between observed and predicted temperature dependence of shift (β) and broadening (γ) for the Kr λ 7601 line perturbed by inert gases.

Perturber	$(\beta_{295°K})/(\beta_{80°K})$ Observed	Predicted	$(\gamma_{295°K})/(\gamma_{80°K})$ Observed	Predicted
Helium	2.62	2.16	1.87	1.73
Neon	0.93	0.84	1.67	1.70
Argon	2.29	1.79	2.07	1.64
Krypton	1.47	1.43	1.48	1.43

4. Krypton

The observed values of β and γ show almost exactly the temperature increase by a factor of 1.43 (Table III) which would be expected for a pure van der Waals interaction; also the ratios β/γ (Table II) agree with that predicted for a van der Waals interaction (−0.728, see Sec. II) to within the experimental error. The krypton results may thus be assigned to region A in Fig. 1.

B. Constants C_6 and C_{12}

Mean values of the constants C_6 and C_{12} have been calculated for each interaction with the use of the measured β, γ and the α values derived as above. Theoretical C_6 values may be estimated with the use of the expression[8]

$$C_6 = e^2\sigma(\langle r_i^2\rangle - \langle r_f^2\rangle)\text{erg cm}^6\,,$$

where $\langle r_i^2\rangle$, $\langle r_f^2\rangle$ are the average values of r^2 for upper and lower states in the transition and σ is the dipole polarizability of the perturbing atoms. The validity of this relation depends on the assumption that the energy separation between the ground level and the other levels of the perturbing atoms is large compared with the separation between the levels i and f and other levels in the radiationg atom. This is a reasonable assumption for inert-gas perturbers. For $\langle r^2\rangle$ we may use the approximate expression

$$\langle r^2\rangle = \tfrac{1}{2}a_0^2(n^*)^2[5(n^*)^2+1-3l(l+1)]\,,$$

where n^* is the effective quantum number, l the orbital quantum number, and a_0 the Bohr radius. Table IV shows a comparison between C_6 values calculated as above and C_6 values derived with the use of the Lindholm theory. The agreement is satisfactory in view of the approximations involved.

It was suggested by Hindmarsh *et al.*[1] that the repulsive force constants C_{12} could be simply related to atomic properties by

$$C_{12} = qR^{12}\text{erg cm}^{12}\,,$$

where q is a constant and R is given by $R = r_A + r_B$, r_A (or r_B) being the distance from atom A (or B) at which the unperturbed radial charge density has fallen to 0.012 atomic units (a.u.). With the use of their best-fit value for q, $0.9\pm0.3\times10^{-16}$ ergs, and C_{12} values derived from experiment, we obtain R values of 18.3 and 18.2 a. u. for He and Ne, respectively. These are in good agreement with corresponding values of 17.7 and 18.3 a. u. derived from radial integrals kindly computed for us by Dr. B. Warner with the use of scaled Thomas-Fermi-Dirac potentials.[9]

C. Conclusion

The experimental work described in this paper provides by far the most exacting test yet available for the interpretation of collision broadening and shift proposed by Hindmarsh *et al.*[1] This interpretation is able to show in a qualitative way how the irregular temperature effects, which are observed when the Kr λ 7587 and λ 7601 lines are perturbed by low pressures of inert gases, can be related to different interatomic potentials.

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[9] J. C. Stewart and M. Rotenberg, Phys. Rev. **A140**, 1508 (1965).

TABLE IV. Comparison between theoretical C_6 values and those derived from broadening and shift measurements on the Kr λ 7601 line.

Perturber	$(C_6)_{\text{expt}}$ 10^{-58}erg cm^6	$(C_6)_{\text{theor}}$ 10^{-58}erg cm^6
Helium	0.45	0.47
Neon	1.59	0.86
Argon	2.45	3.54
Krypton	5.46	5.38

In particular, the interpretation provides a convincing quantitative explanation of the very unusual temperature effects which occur with neon perturbers. Only in the case of argon perturbers does a serious discrepancy arise.

Failure of the interpretation might arise from two causes—use of the Lindholm impact approximation and wrong choice of interaction potential. The impact approximation would appear to be well satisfied at the low perturbing particle densities of the experiment. However, a comparison with recent studies of resonance broadening[10] suggests that the Lindholm theory may not deal adequately with the close collisions which give rise to large phase changes. This drawback is not likely to be very important for broadening by helium and neon where the potential well is very shallow and is cut off by a steeply rising repulsive wall. Kr-Kr interactions produce a deep well so that only the van der Waals region is important. The simple Lindholm theory may well be inadequate for the Ar-Kr interaction which is an intermediate case. In order to check the sensitivity of the functions $S(\alpha)$ and $B(\alpha)$ to the form of the interaction potential, calculations have been made for (10-6) and (18-6) potentials. The former has the desired effect of increasing the gradient of the β/γ curve in the region of importance to helium. Both potentials satisfy the neon results but make little difference in the argon region. A more severe change in the shape of the well is necessary to affect the argon region but it would not seem worthwhile to pursue this approach until yet more accurate experimental results are available. The nature of the temperature effect in the region where the theoretical curves appear to oscillate (region B and to the left) would thus seem to require more thorough investigation since the present results do not provide conclusive evidence for these oscillations.

ACKNOWLEDGMENTS

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