Self-Broadening and the Resonance Oscillator Strengths in Krypton

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By means of a direct-recording Fabry-Perot interferometer, the emission profiles of five red lines in krypton were obtained under widely varying conditions of gas density and temperature. The profiles were analyzed in various ways, and the Lorentz components determined as functions of density. In two of the lines studied, 7587 and 7685 Å, the observed broadening coefficients could be attributed almost entirely to resonance interaction in the lower levels. From the measured broadening coefficients, the oscillator strengths of the resonance lines were calculated as ${}^1f(1164\text{ Å})=0.184$ and ${}^3f(1236\text{ Å})=0.204$ with estimated error limits of 10% (arising mostly from uncertainties in the broadening constant). These values are more than 30% larger than recent theoretical calculations. Linear extrapolation of the Lorentz width to zero gas density provides some evidence of the anomaly found in helium and neon, which has been attributed to an additional "coupling width" at very low density. The study of the strongly resonance-broadened line 7587 Å was extended up to pressures of 20 mm Hg at 90°K. It was found that the rate of self-broadening decreased at high pressure, where the line was symmetrical but not of the Voigt shape; also, the maximum was shifted towards higher frequencies. Possibilities of relating these effects to theoretical considerations are discussed. In the lines whose lower levels are metastable, the ratios and temperature coefficients of width and shift are consistent with broadening due to van der Waals forces obeying an r^{-6} potential law.

I. INTRODUCTION

In a series of recent experiments, the method of direct-recording interferometry has been used to measure self-broadening in the noble gases: helium,[1,2] neon,[3] and argon.[4] The experiments in helium have established an experimental value of the resonance-broadening constant $k_{JJ'}$ which is very close to recent theoretical values.[5–9] Measurements of emission-line profiles in krypton were thus undertaken with the primary aim of determining the oscillator strengths of the far ultraviolet resonance lines of krypton with the use of the known value of $k_{JJ'}$.

As in the work on the other noble gases, resonance effects were studied not in the resonance lines themselves, which are inaccessible to interferometric techniques, but in lines whose lower levels are resonance levels. Lines whose lower levels are metastable were also examined. The measurements of broadening and shift were carried out at two temperature ranges (90 and 295°K) and were extended over a wider range of density (0.025–20×10^{17} atoms cm^{-3}) than has been previously examined. It was thus possible to seek, at low pressure, the extrapolation anomaly found in helium and neon[10]; at high pressure one could investigate a region at and beyond the limits of applicability of the impact theory.

II. EXPERIMENTAL CONSIDERATIONS AND TECHNIQUES

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

Line	Transition
λ7587 Å:	$4p^5({}^2P_{3/2})5s[\frac{3}{2}]_1–4p^5({}^2P_{3/2})5p[\frac{1}{2}]_0$,
λ7685 Å:	$4p^5({}^2P_{1/2})5s[\frac{1}{2}]_1–4p^5({}^2P_{1/2})5p[\frac{1}{2}]_0$,
λ7601 Å:	$4p^5({}^2P_{3/2})5s[\frac{3}{2}]_2–4p^5({}^2P_{3/2})5p[\frac{3}{2}]_2$,
λ7694 Å:	$4p^5({}^2P_{3/2})5s[\frac{3}{2}]_2–4p^5({}^2P_{3/2})5p[\frac{3}{2}]_1$,
λ7854 Å:	$4p^5({}^2P_{1/2})5s[\frac{1}{2}]_0–4p^5({}^2P_{1/2})5p[\frac{1}{2}]_1$.

The first of these lines can be described as a transition to the ${}^3P_1$ resonance level, the second to the ${}^1P_1$ resonance level, and the others to metastable levels ${}^3P_{2,0}$. The choice of lines has been partly dictated by the spectral response of the best available photomultiplier (EMI9558A) which is not sensitive above 8000 Å.

The technique of direct recording of emission-line profiles using a Fabry-Perot etalon has been described in detail in earlier publications (e.g., Refs. 1 and 2). With the direct recorder of Kuhn and Lucas-Tooth[11] a trace is produced of light intensity plotted against wave number in which these scales are accurately linear. The technique has proved especially convenient for the study of line profiles; the present results are based on nearly 300 recordings.

Two sets of very high-quality etalon plates with imperfection profiles estimated at less than 1/90 of an order have been used with various spacers. The etalon spacer had to be adjusted to the linewidth to

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avoid appreciable overlap of orders. Spacers of 3.96, 0.998, and 0.226 cm were used. The plates have been coated with silver films which are very efficient in the red, are readily replaced to match a specific problem, and have therefore proved extremely convenient. Auxiliary dispersion was provided by a Littrow mounted Bausch and Lomb "precision-replica" grating blazed for 16 000 Å and used in the second order. With a 2.2-m spectrograph of effective aperture $f/16$ a dispersion of 0.31 mm/Å was obtained. At 7500 Å tests showed that the sensitivity of the tri-alkali EMI 9558A photomultiplier was increased by a factor of 3.5 by cementing a small prism on to its face as described by Grant *et al.*[12] In general, two or three orders were scanned.

To avoid complications due to the presence of more than one isotope, it was necessary to use enriched isotopes. Samples of krypton-86 were available in concentrations of >99.8% and have been used throughout this work. For economy in the use of the separated isotope the apparatus, including discharge tubes, cold traps, and McLeod and mercury thread manometers, was specially designed to keep the total volume small; it was approximately 35 cm³. Since the vapor pressure of krypton over liquid nitrogen (77°K) is only about 2 mm Hg, cooling with liquid oxygen (90°K) was used in most of the experiments. By means of a cold finger dipping into liquid nitrogen, the pressure in the apparatus could be adjusted without wastage of gas. Errors arising from pressure measurement were generally small in comparison with those from other sources. The dc discharge tube was similar to those described earlier,[2] and was designed with a view to reducing self-absorption; the depth of the gas column viewed was about 2 mm. Under suitable conditions a uniform, steady glow could be obtained at currents of less than 0.6 mA, corresponding to current densities of less than 5 mA/cm². Stark broadening due to ions and electrons can be neglected under these conditions.

Measurements of shifts were made relative to lines from a discharge tube containing natural krypton (mainly krypton-84), partially immersed in liquid nitrogen; the traces from both discharges were taken in quick succession and superimposed on the same paper.

III. MEASUREMENTS

A. 3.96-cm Etalon Spacer

Traces of λ7587 Å were made within the density range $0.25\text{–}9.5\times10^{16}$ atoms cm^{-3}. The profiles were completely analyzed in terms of Voigt profiles as fully described in Refs. 1 and 2. It was found that the component Gaussian widths averaged 9.1 ± 0.3 mK to be compared with the calculated Doppler width of 9.0 mK

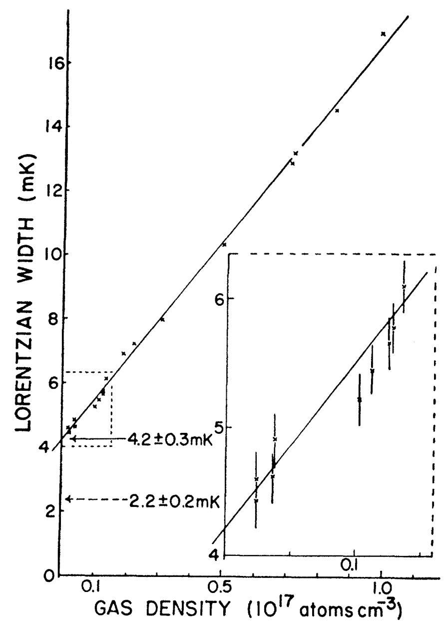

FIG. 1. Self-broadening of λ 7587 Å (∼80°K). The intercept at zero density is shown by the full arrow, the instrumental width is shown by the dotted arrow. The insert shows the low-pressure results.

at the bath temperature (liquid nitrogen ∼77°K). In Fig. 1 the component Lorentz widths are plotted against gas density, the latter being obtained from the measured gas pressure; a temperature was derived from the Gaussian width in each case. The indicated instrumental width was calculated from additional measurements with a smaller spacer (for technique see Ref. 1).

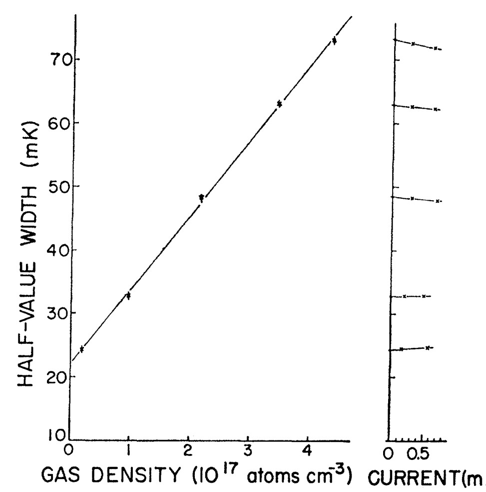

FIG. 2. Self-broadening of λ 7587 Å, liquid oxygen coolant (90°K). The right-hand side shows the current dependence of the half-value width (the whole linewidth at half the peak intensity) at various pressures. The points on the main graph are obtained by extrapolation to zero current.

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TABLE I. Coefficients of self-broadening and shift in krypton ($cm^{-1} \times 10^{-20}$ atom $^{-1}$ cm^3).

Line (Å)	Density range (10^{17} atoms cm^{-3})	Temperature ~90°K Broadening	Shift	Temperature ~295°K Broadening	Shift
7587	0.02– 1.0	12.6 ±0.7[a]	...	...	...
	0.1 – 4.0	12.8 ±0.5	+0.1 ±0.1	13.1 ±0.6	+0.2 ±0.2
	0.1 –10.0	12.7 ±0.7	+0.25 ±0.1	...	...
7685	0.1 – 4.0	10.8 ±0.5	0.0 ±0.5	11.0 ±0.5	−0.1 ±0.3
7601	0.1 –20	1.30±0.06	-0.44_5±0.03	1.93_5±0.1	−0.65±0.04
7694	0.1 –20	1.3 ±0.2	−0.5 ±0.1	2.4 ±0.4	-0.7_6 ±0.1
7854	0.1 –20	1.5 ±0.2	−0.5 ±0.2	2.3 ±0.4	−0.7 ±0.1

[a] Temperature ~80°K.

B. 0.998-cm Spacer

For experiments carried out over a larger range of pressure the technique of complete profile analysis could not provide the requisite accuracy for the Gaussian width owing to its relatively small size compared with the total width. However, on the basis of previous experience it could be safely assumed that the gas temperature approached the bath temperature at very low currents. Accordingly the following technique was used: The half-value widths of a series of traces were measured at different currents but constant pressure. The widths were extrapolated to zero current as shown on the right-hand side of Fig. 2. The extrapolated half-width was then plotted at the gas density corresponding to the bath temperature (liquid oxygen ~90°K). From this graph the Lorentz-broadening coefficients are easily calculated by allowing for the appropriate Doppler width. The results of similar experiments conducted over the indicated density ranges are shown in Table I. The quoted errors are estimated limits. Within the limits of accuracy of complete analysis the profiles were of true Voigt form and the broadening increased linearly with density.

C. 0.226-cm Spacer

The results of an examination of λ7587 Å at higher density are shown in Fig. 3. It did not prove possible to obtain reliable measurements of λ 7685 and λ 7587 Å at room temperature, owing to the very low intensity of these lines at high density. The measured shifts were such small fractions of the linewidth that, as a check for spurious effects, they were repeated with a larger spacer with similar results. At the highest density the tracings of λ 7587 Å were examined for any possible asymmetry but none was found. However, clear evidence was seen of a departure from the Voigt form. Profiles from the discharge maintained at densities larger than 8×10^{17} atoms cm^{-3}, where the measurements extended over a range greater than 0.15 cm^{-1} of the line center, showed increased intensity in the wings compared with a purely Lorentz shape; this effect increased with increasing pressure. As seen in Fig. 3 the rate of increase of width with density decreases above $\sim 15 \times 10^{17}$ atoms cm^{-3}.

IV. DISCUSSION AND CONCLUSIONS

A. Broadening Constants and *f* Values

In Table I the differences in the properties of the lines connected with the resonance levels (7587 and 7685 Å) and those connected with the metastable levels (7601, 7694, 7854 Å) are very striking: large broadening constants, no noticeable or slight violet shift, and no temperature dependence in the first group of lines; broadening an order of magnitude smaller, a distinct red shift, and a marked increase of broadening with temperature in the second group of lines. These facts establish that resonance is the dominating effect in the broadening of the first group; the question arises as to whether it is permissible to assume a pure resonance interaction. The broadening in the lines of the second group must be due to second-order interactions, mainly dispersion forces, the magnitude of which must be similar for both groups. The theoretical analysis of Lewis[13] leads to the conclusion that the correction

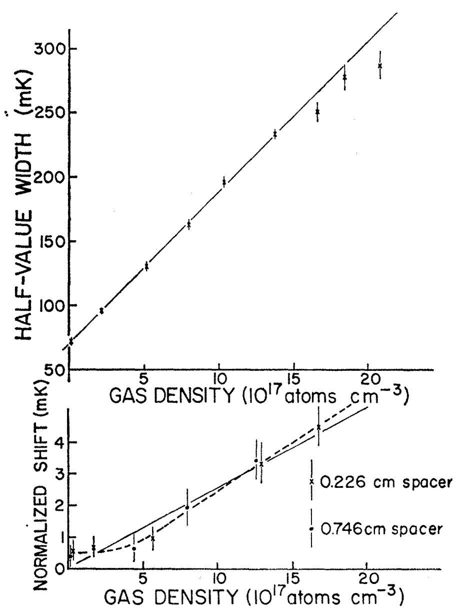

FIG. 3. Self-broadening and shift of λ 7587 Å at high pressure, liquid oxygen coolant (90°K).

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necessary to take account of such small second-order effects is negligibly small.

The f values of the resonance lines of krypton (1236 and 1164 Å) can thus be derived directly from the broadening coefficients of the lines 7587 and 7685 Å. These broadening coefficients are related to the resonance frequencies, oscillator strengths, and universal constants by the numerical broadening constant $k_{JJ'}$, for which the experimental value 1.44±0.09 derived from measurements in helium can be used[2,5]; similar values are derived from various forms of theory.[6–8] The oscillator strengths are thus found to be: ^1f (1164 Å) $=0.184\pm0.02$ and ^3f (1236 Å) $=0.204\pm0.02$. The errors quoted are largely due to the experimental error in $k_{JJ'}$. Recently, from solutions of nonrelativistic Hartree-Fock equations, Dow and Knox[14] have calculated the values $^1f=0.136$ and $^3f=0.138$ for which an accuracy better than 15% would probably be expected. The absorption measurements of Wilkinson[15] give the results $^1f=0.135$ and $^3f=0.158$, although errors are not quoted. From a study of radiative decay Turner[16] has obtained the value $^3f=0.166$. The present results are thus considerably larger than these values, but are not inconsistent, however, with Geiger's electron-scattering measurement of $\Sigma(^1f+^3f)=0.346\pm0.06$.[17]

B. Extrapolation Anomaly

The measurements on the krypton line λ 7587 Å shown in Fig. 1, in particular in the inset, show that linear extrapolation leads to a total Lorentz width of 4.2±0.3 mK or, after subtraction of the instrumental width of 2.2±0.2 mK, to a spectral Lorentz width 2.0±0.5 mK. This is to be compared with the natural width of 1.6 mK calculated for the free atom from the above f value. The result points to the existence of an extrapolation anomaly similar to that found in helium[1,2] and neon.[3] A possible explanation of the latter results in terms of an additional coupling width[10] would suggest that extension of the measurements to sufficiently low density should eventually show a downward trend in the broadening curve. Simple estimates[3] would lead one to expect that such a trend would be evident well above the minimum densities examined in this work, and similarly in helium and neon. However, no such trend is apparent, although in the present case the limits of error are too large to allow any definite conclusion.

C. Resonance Effects at High Density

For resonance interaction in krypton the optical collision radius at 90°K may be calculated as about 50 Å and the duration of an optical collision as about $t_d=4\times10^{-11}$ sec (see, e.g., Ref. 18). The impact approximation may therefore be expected to hold within a wave-number range of $\pm(2\pi c t_d)^{-1}=\pm0.14$ cm^{-1} of the line center. At gas densities up to 4×10^{17} atoms cm^{-3} the profiles analyzed were well within these limits and the time between optical collisions ($\sim2\times10^{-10}$ sec) was considerably greater than t_d. The usually accepted conditions for the validity of the impact theory (see e.g., Ref. 19) were thus fulfilled within this range; the above derivation of f values from broadening constants is thus justified. An examination according to the criteria discussed by Mead[9] similarly shows that the two-body and classical path approximations should hold within this range.

At densities approaching 20×10^{17} atoms cm^{-3} these conditions are no longer fulfilled. It is therefore not surprising that the profiles deviate from the Lorentz shape and the broadening density relation is no longer linear. The latter result is consistent with the calculations of Reck *et al.*[20] who show that the broadening varies with the square root of the density at high pressure.

A further effect not predicted by the impact theory of resonance broadening is the small violet shift found in the line 7587 Å, and this begins to appear even at moderate densities. It can certainly not be explained by higher-order (dispersion) interactions which would shift the line towards lower frequencies. The fact that the experimental points (Fig. 3) tend to lie more closely on the dotted curve (which rises faster than a linear increase with density) might indicate that the shift must be ascribed to resonance interactions involving more than two atoms. A reliable theory which could be applied directly to these experimental conditions does not appear to exist, but it is interesting that some theories of resonance broadening lead to an effect qualitatively similar to that observed. The classical treatment of Weisskopf[21] and quantum treatment of Mead[22] predict a small red shift of the resonance line which implies a violet shift of the line whose lower level is the resonance level. Neither of these treatments takes the effect of atomic motion properly into account so that quantitative comparison is not possible.

D. Nonresonant (Dispersion) Effects

For the heavier rare gases, self-broadening effects in the lines with metastable levels should be well described by means of attractive r^{-6} potentials. The impact theories make two definite predictions in this case: The ratio of broadening to shift should be -2.8 and the temperature coefficient of the broadening should be given by $(T_1/T_2)^{3/10}$, where T is the absolute tempera-

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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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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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