Pressure Effects of Rare Gases on the Absorption Line Ca 4227. I. The Effects of Argon and Helium†

Shang Yi Ch'en and Arvid T. Lonseth
Physics Department, University of Oregon, Eugene, Oregon 97403
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The shift, broadening, and line shape of the absorption line Ca 4227 in the presence of Ar and He were observed under a wide range of pressures. The relative densities (rd) employed extended from 1 to about 245 (15 450 psi at 638 °C) for Ar and to 58 (2563 psi at 638 °C) for He. Both Ar and He produce a red shift, $-0.019\ \mathrm{cm^{-1}/rd}$ for He and $-0.23\ \mathrm{cm^{-1}/rd}$ for Ar. The dependence of the half-width on rd appears to adhere to linearity less than does the dependence of the shift on the rd. The broadening at low rd (< 10) is $0.64\ \mathrm{cm^{-1}/rd}$ for He and $0.74\ \mathrm{cm^{-1}/rd}$ for Ar. Some typical intensity profiles are given showing also the presence of a very extended blue wing due to He and a broad violet satellite due to Ar.

I. INTRODUCTION

An experimental study of the pressure broadening of the resonance line of neutral calcium at λ 4227, $4s^2\,{}^1S_0 - 4s4p\,{}^1P_1$ is highly desirable for several obvious reasons: (i) It is a singlet line, so that the determination of the shapes of the broadened line can be extended to wide pressure ranges without limitation due to the overlapping of fine-structure components which is observed in the case of alkali atoms. (ii) If satellites or other profile modifications are observed, an explanation of their origin need not include the hypothesis of the intracomponent coupling, which cannot be ruled out in the case of nonsinglet lines. And (iii) this line occurs very frequently in plasmas of both terrestrial and astronomical origin. A knowledge of the behavior of the line under various environmental conditions would provide useful information about the physical environment in which the line was emitted or absorbed.

Kusch[1] observed in a King's furnace at 2170 °K the broadening of Ca 4227 by molecular hydrogen at pressures up to 30 atm [3.3 relative density (rd)]. The slope of the broadening was $7.24\ \mathrm{cm^{-1}/rd}$. As mentioned in Sec. III, the broadening and shift of Ca 4227 produced by helium was measured by Hindmarsh[2] only at very low pressures (rd < 0.4). Holmes, Takeo, and Ch'en[3] measured the shift of Ca 4227 in emission due to Ar from 26 to 100 rd at a high temperature of 3230 ± 250 °K with a ballistic compressor.

In the present work the observation of shift, broadening, and line shape due to He and Ar was made from 0.4 rd, the maximum pressure Hindmarsh used, up to 2563 psi at 638 °C for He (rd ~ 57), and to about 15 450 psi at 638 °C for Ar (rd ~ 245).

II. EXPERIMENTAL

The experimental procedures have been described before.[4] The shift, broadening, and line shapes were determined with a 35′ grating spectrograph modified to function as a space-shared dual-beam spectrophotometer with phase-sensitive detection and log-ratio output. The sample beam and a reference beam (which traverses the ambient atmosphere of the laboratory) are presented alternately to the slit, at a 450-Hz rate, by means of a toothed chopper wheel. A photomultiplier (EMI 6256 SA), mounted behind a 30-μ exit slit, scans the spectrum slowly; its output is demodulated by a FET switch (synchronized to the chopper wheel) and detected by two phase-sensitive amplifiers (PAR JB-4). Their outputs (proportional to sample and reference channel transmittance, respectively) are fed to a log feedback operational amplifier module (Burr-Brown 1665) whose output is proportional to the log of the ratio of its two inputs, that is, to the absorption coefficient, when divided by the length of the absorption column ($l = 5.0$ cm). Hence this signal, when displayed on a chart recorder gives directly $\alpha(\lambda)$ vs λ. This method of compensating for the background results in much greater accuracy in the determination of the shape of the wings of a line. The instrumental width of a sharp line, from a He-Ne laser, is $0.5\ \mathrm{cm^{-1}}$.

Background traces made in the absence of an absorbing sample are flat to within 0.3 dB [optical density (OD) = 0.015], with noise levels around 0.2 dB. The temperature of the absorption column was maintained by a Leeds and Northrup temperature controller to within $\frac{1}{2}$ °C. Relative densities were obtained from the Beattie-Bridgeman equation[5] by computing the ratio of the molar volume under standard conditions to that under the experimental conditions. Solution of the equation was done by a computer program using Newton's method.

III. RESULTS AND DISCUSSION

A. Shift

Graphs of shift $\Delta\nu_m$ vs relative density, (rd), for He and Ar are presented in Figs. 1 and 2, respectively. It is to be noted that ours is the first experiment in which He produces a small "red" shift for Ca 4227. Though the readings are somewhat scattered, the least-square-fitted straight line gives a slope of $-0.019\ cm^{-1}/rd$ for the range of rd from 1 to 57 (2563 psi at 638 °C).

Hindmarsh[2] reported a mean value of a very small "blue" shift ($+0.0135\ cm^{-1}/rd$) at very low rd (under 0.4). His data points were very highly scattered (values from a blue shift of $15\times10^{-3}\ cm^{-1}$ to a red shift of $24\times10^{-3}\ cm^{-3}$).

The shift produced by Ar was observed for pressures from one to over a thousand atmospheres (15 450 psi at 637 °C). Figure 2 curve (b) is a plot of the portion of Fig. 2 curve (a) for rd < 7. It is obvious that the relationship is linear at low rd with a slope of $-0.23\ cm^{-1}/rd$ and also at high rd (rd > 50) with a slope of $-0.82\ cm^{-1}/rd$. The slope gradually increases from -0.23 to $-0.82\ cm^{-1}/rd$ between rd 10 and 50. No appreciable effect of temperature on the shift was seen in the temperature range of 500–640 °C.

The Beattie-Bridgeman equation was generally used to compute rd, but the equation becomes increasingly invalid as the pressure rises above 250 atm.[6] The empirical data of Lecocq[7] provide tabulated information on the rd of Ar at temperatures from 300 to 950 °C and pressures as high as 710 atm. His 650 °C isotherm approximates closely the argon temperature of 637 °C used in this work. For pressures below 300 atm the values of rd computed by the two equations agree well within 0.2%, but the discrepancy rises to 4.5% at 707 atm. Since the pressure effects of argon were

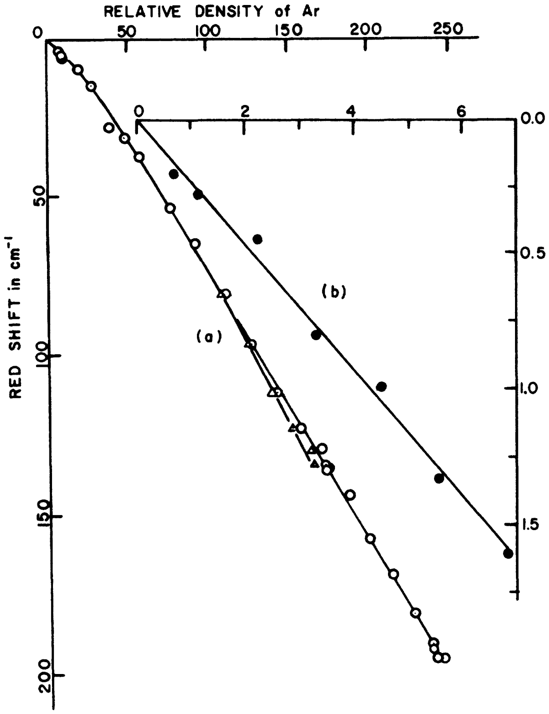

FIG. 2. Shift of Ca 4227 vs rd of Ar. Curve (a): For high rd at 637 °C. Use the ordinate at the left and the abscissa at the top, where open circles are rd values computed with Beattie-Bridgeman equation; open triangles, those computed according to Lecocq. Curve (b): For low rd at 556 °C. Read the ordinate at the right in cm^{-1}; the abscissa in rd.

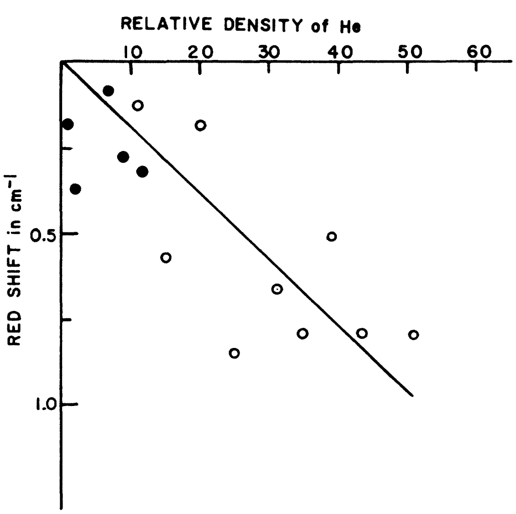

FIG. 1. Shift of Ca 4227 vs rd of He. Open circle readings taken at 638 °C; closed circle taken at 571 °C.

observed in the present work up to 1000 atm, empirical PVT data are lacking for the region between 707 and 1000 atm. Levitt[8] suggested that for a gas under pressures in excess of 1000 atm, the pressure is an exponential function of rd; however, this limiting relationship does not appear to be met in the pressure range in question.

Holmes, Takeo, and Ch'en[3] reported a shift of $-0.23\ cm^{-1}/rd$ for rd up to 50 (at 3230 ± 250 °K) increasing to about twice that value for rd 50 to 100. These results are in good agreement with those obtained in the present work.

B. Broadening

The dependence of the Ca 4227 half-width on the rd of He and Ar is shown in Figs. 3 and 4. For He, the slope of the plot, Fig. 3, is $0.64\ cm^{-1}/rd$ for rd 2.2–11.6 at 571 °C and 11–40 at 638 °C. For Ar, the slope is $0.67\ cm^{-1}/rd$ for rd 0.36–6.8 and $1.0\ cm^{-1}/rd$ for rd 10–100. The dependence of the half-width on rd appears to be less linear than that of the shift.

Hindmarsh[2] observed the broadening of Ca 4227 by He in a King's furnace and obtained a half-width of $0.224\ cm^{-1}$ for He at 600 °C and 750 Torr (rd

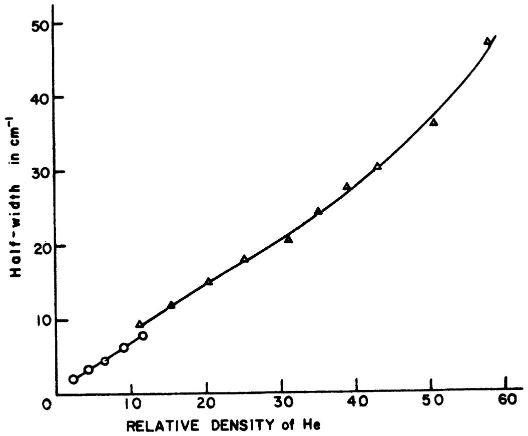

FIG. 3. Half-width of Ca 4227 in He. Open triangle for T= 638 °C, open circle for T= 571 °C.

about 0. 31). Assuming a linear relationship of half-width and rd, his results imply a slope of 0. 72 cm^{-1}/rd. His subsequent report[2(b)] gave a slope of 0. 463 cm^{-1}/rd for T = 400 °C. This temperature effect is also shown in Fig. 3.

By means of a ballistic compressor, Holmes, Takeo, and Ch'en found a half-width of 39. 2 cm^{-1} for rd = 55 (at T = 2860 ± 150 °C), implying a slope of 0. 71 cm^{-1}/rd.

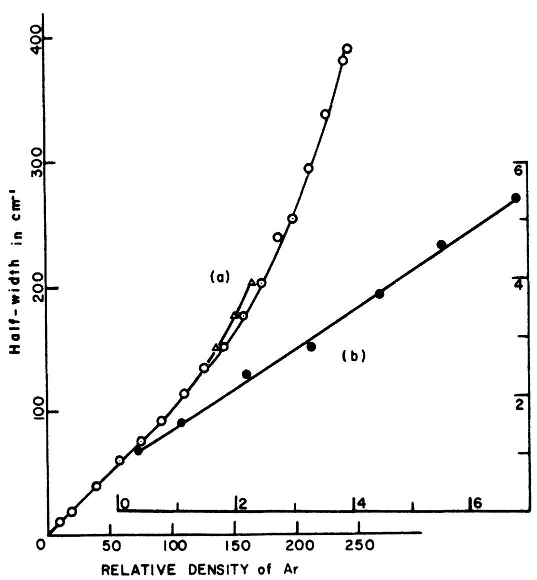

FIG. 4. Half-width of Ca 4227 in Ar. Curve (a): For high rd at 637 °C. Use the ordinate at the left and the abscissa at the bottom, where open circles are rd values computed with Beattie-Bridgeman equation; open triangles, those according to Lecocq. Curve(b): For low rd at 556 °C. Use the ordinate at the right in cm^{-1}; the abscissa in rd.

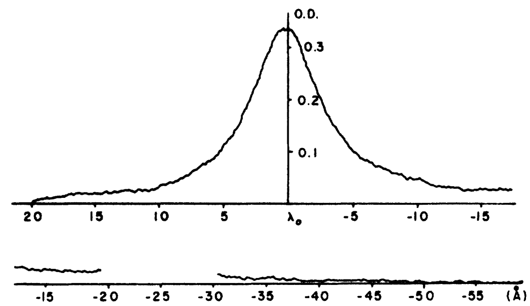

FIG. 5. Line shape of Ca 4227 in He. P = 2563 psi, T = 638 °C, rd = 50.7.

The ratio of half-width to shift at low rd for Ar is found to be 2. 9, which is only slightly greater than the predicted 2. 8 for $1/r^6$ interaction potential (Foley's relation).

C. Line Shape

An analysis of the complete line shape[9] will provide more significant information about the interaction potential between colliding particles than can be obtained from the traditionally measured parameters such as shift and half-width. The most useful methods of displaying this information have not yet been established. In the meantime, the observed line contours themselves are presented for a few representative conditions of pressure and temperature (Figs. 5 and 6). The line shapes are traced directly from the original data. The vertical coordinate is the optical density which, when divided by the length of the absorption column (5. 0 cm) yields the absorption coefficient. λ_0 represents the wavelength of the unshifted line.

One example of the additional information yielded by accurate line-shape determinations is immediately obvious in the case of He. If one measures the ratio of the red half to the blue half of the half-intensity-width of the broadened lines to obtain the "asymmetry parameter," the results imply that the lines are completely symmetrical for all He pressures. However, inspection of the line shape reveals that even at low pressures the otherwise perfect symmetry is destroyed by a weak blue wing of appreciable extent whose existence is not even suggested by the asymmetry parameter.

This new result is clearly shown in Fig. 5. In the presence of He the blue wing is over twice as long as the red wing when the helium density is increased to 50. 7 rd at 638 °C. While the broadened Ca line has a half-width at half-peak-intensity of 18 cm^{-1}, the blue wing is detectable as far as 308 cm^{-1} from the peak of the line.

In the case of Ar, when the pressure and the temperature of the absorption column are low (say, T = 556 °C and rd below 5), the line is quite sym-

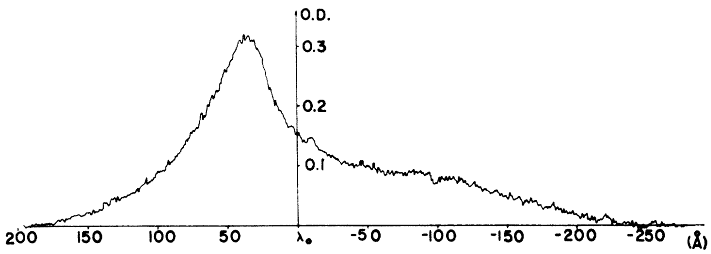

FIG. 6. Line shape of Ca 4227 in Ar. $P=15$, 450 psi, $T=638\,°C$, rd = 245.

metrical with some indication of a faint blue wing. The line becomes highly asymmetrical towards the red when the temperature is raised. The asymmetry parameters lie between 1.5 and 2.0 when the temperature is 638 °C and Ar rd 1–240. When the Ar rd is over 150, as in Fig 6, the line shape shows the presence of a broad blue satellite, with a half-intensity-width of about 670 cm^{-1} (120 Å), whose peak is roughly 700 cm^{-1} (125 Å) from the broadened line peak. There is also an indication that between the broad blue satellite and the line there is another weak blue satellite.

The red asymmetry and the width of the Ca line produced by argon are found to increase with an increase of temperature (Fig. 7). This is an indication that a red satellite due to Ca(1)/Ar overlaps the broadened line. When the temperature is raised the vapor pressure of Ca increases, causing a relatively rapid increase in the red satellite intensity with respect to the line intensity.

D. Integrated Intensity of the Line Contour

In the present work, an excess of Ca metal was placed in the absorption column. Since the integrated area under the absorption contour of Ca 4227 should totally depend on the Ca vapor concentration, it should not be affected by the pressure of foreign gas if the foreign gas caused no pressure-induced transitions and there was no appreciable effect on the vapor pressure of Ca. This consideration is confirmed for He. For argon the integrated intensity first increased steeply with rd, then mildly decreased with rd after passing a broad maximum.

In order to keep the Ca metal as pure as possible, the metal was introduced into the absorption column as soon as a fresh metal surface was obtained by cutting and filing the surface under oil, and then handling the sample in an argon atmosphere as much as possible. However, it was found empirically that the degree of purity of the surface of Ca metal could hardly be reproduced, as proved by the fact that no two separate runs from different Ca metal insertions produced the same integrated intensity of Ca 4227 for a given T and P of foreign gas.[10] The coating on the Ca metal changes considerably the rate of evaporation of Ca. Consequently saturated vapor pressure for a given temperature could hardly be reached within a finite length of time. This is to say that the concentration of Ca vapor in the absorption column at a given temperature is not equal to the empirically determined vapor pressure.

E. Estimation of Interaction Constants

The significance of the estimation of interaction constants depends on (a) the sophistication of the evaluation of the correlation function from the line profile and (b) the adequacy of the form of an effective interaction potential function assumed to account for the observed results. Considerable work[11] is being done to formulate a workable method of performing an inverse Fourier transform of the observed line shape for the correlation function. Before this is accomplished, if the rd is low enough, one can use the intensity-distribution function of the spectral line as[12]

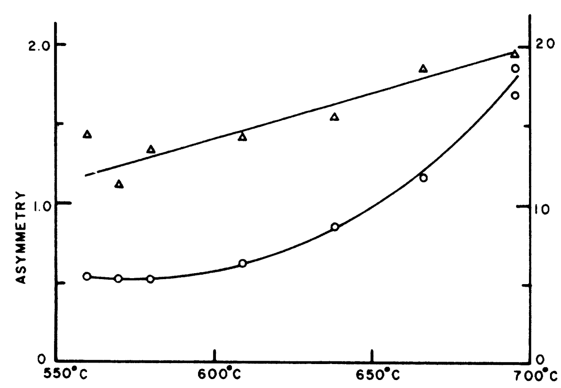

FIG. 7. Effect of the temperature of the absorption column containing an excess of Ca metal vs the observed half-width of Ca 4227 and the asymmetry at constant argon rd of 6.8. Open triangle for asymmetry; open circle for half-width.

TABLE I. Computed differences of interaction constants for upper and lower states of a potential function of Lennard-Jones type and other parameters from the observed half-width and shift at low pressures.

Colliding pairs	Ca 4227/Ar	Ca 4227/He
$\Delta\nu_m$	-0.23 cm^{-1}/rd	-0.019 cm^{-1}/rd
$\Delta\nu_{1/2}$	0.67 cm^{-1}/rd	0.64 cm^{-1}/rd
T	556 °C	571 °C
ΔC_6	8.72×10^{-31} cm^6/sec	8.38×10^{-32} cm^6/sec
	or 9.2×10^{-58} erg cm^6	or 9.2×10^{-59} erg cm^6
ΔC_{12}	7.22×10^{-73} cm^{12}/sec	1.04×10^{-74} cm^{12}/sec
	or 7.6×10^{-100} erg cm^{12}	or 1.09×10^{-99} erg cm^{12}
σ_r	2.51×10^{-14} cm^2	1.01×10^{-14} cm^2
ρ	8.94 Å	5.68 Å
r_{pm}	10.9 Å	7.93 Å
$\Delta\nu_s$	-1.40 cm^{-1}	-0.89 cm^{-1}
I_s/I_l	0.04	0.016

$$I(\Delta\omega) = \frac{2e^2\omega^4|x_0|^2}{3\pi c^3}\,\frac{nv\delta_r}{(\Delta\omega - nv\delta_i)^2 + (nv\delta_r)^2},$$

where the half-width $\Delta\omega_{1/2}$ and shift $\Delta\omega_m$ are related to the real and imaginary part of the Weisskopf collision cross section as

$$\Delta\omega_{1/2} = 2nv\delta_r = 4\pi nv \int_0^\infty \rho\, d\rho\, [2\sin^2(\tfrac{1}{2}\theta)],$$

$$\Delta\omega_m = nv\delta_i = 2\pi nv \int_0^\infty \rho\, d\rho \sin\theta,$$

where v is the relative velocity of collision, n the number density of perturbers, ρ the collision distance, and θ the phase change

$$\theta = \int_{-\infty}^{\infty} \Delta\omega(t)\, dt.$$

$\Delta\omega$ may be expressed with two parameters, such as those in the Lennard-Jones form

$$\Delta\omega(t) = \left(\frac{\Delta C_{12}}{\gamma^{12}} - \frac{\Delta C_6}{\gamma^6}\right),$$

where $\gamma = [\rho^2 + (vt+\epsilon)^2]^{1/2}$, ρ is the impact parameter, assuming a straight perturber path relative to the absorber, and the ΔC's are the differences-of-interaction constants for upper and lower states. Consequently, one can put $\Delta\omega_{1/2}$ and $\Delta\omega_m$ as functions of ΔC_{12} and ΔC_6, and the latter can be computed.[13] The results of computations are shown in Table I, where $\Delta\nu_m$ is the shift in cm^{-1}; $\Delta\nu_{1/2}$ is the half-width; T is the temperature of the absorption column; σ_r is the real part of the Weisskopf collision cross section; ρ is the optical collision diameter; r_{pm} is the interatomic distance at which the differences of potentials of upper and lower states have a minimum value; $\Delta\nu_s$ is the position of the satellite with respect to the line peak if the satellite position is related to the minimum of the differences of potentials; and I_s/I_l the estimated intensity of the "red" satellites with respect to that of the line peak under 1 rd of Ar or He from the probability density. Actually, the shapes of potential curves for the two states may be rather different, so that there is no simple connection between satellite position and potential minimum. These values will be revised as soon as the work mentioned in the first paragraph of this section becomes successful.

The ΔC_6 of Hindmarsh's[2] result for Ca 4227/He was $3\pm1\ 10^{-59}$ erg cm^6. Our value is about three times higher because we report a small red shift instead of blue shift and the broadening was measured under higher rd where the half-width per rd could be increased by the overlapping satellite.

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