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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 cm^{-1}/rd for He and -0.23 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 cm^{-1}/rd for He and 0.74 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 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 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 $-0.019\ \text{cm}^{-1}/\text{rd}$ 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 ($+0.0135\ \text{cm}^{-1}/\text{rd}$) at very low rd (under 0.4). His data points were very highly scattered (values from a blue shift of $15\times10^{-3}\ \text{cm}^{-1}$ to a red shift of $24\times10^{-3}\ \text{cm}^{-3}$).

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 $-0.23\ \text{cm}^{-1}/\text{rd}$ and also at high rd (rd > 50) with a slope of $-0.82\ \text{cm}^{-1}/\text{rd}$. The slope gradually increases from -0.23 to $-0.82\ \text{cm}^{-1}/\text{rd}$ 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

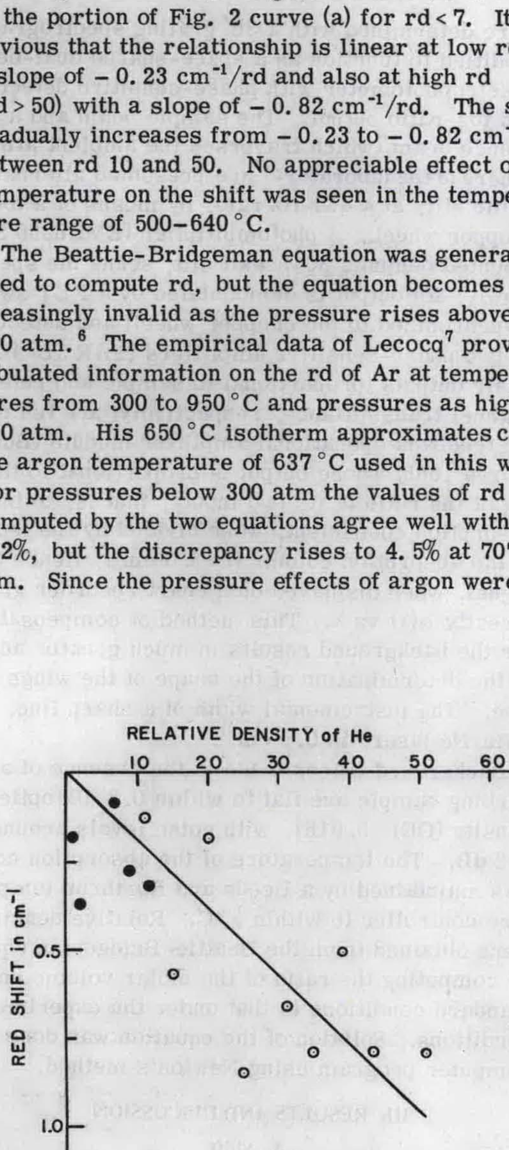

FIG. 1. Shift of Ca 4227 vs rd of He. Open circle readings taken at 638 °C; closed circle taken at 571 °C.

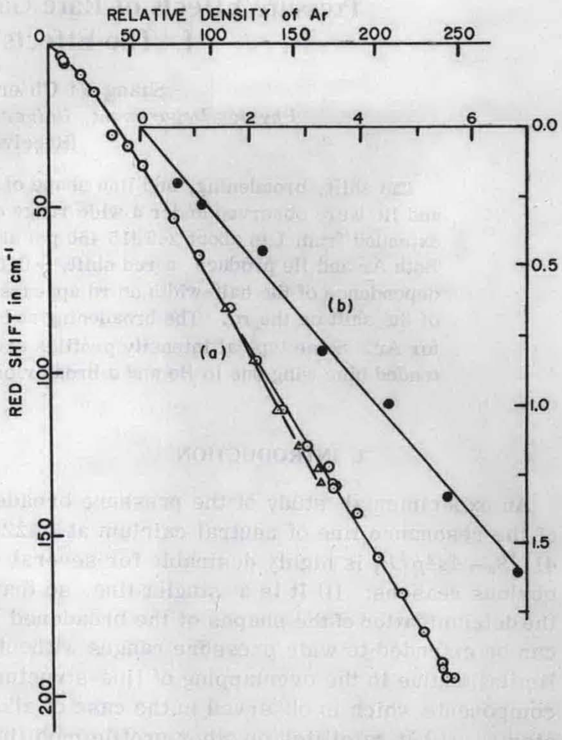

FIG. 2. Shift of Ca 4227 vs rd of Ar. Curve (a): For high rd at 637 °C. Use the ordinate at the left and the abscissa at the top, where open circles are rd values computed with Beattie-Bridgeman equation; open triangles, those computed according to Lecocq. Curve (b): For low rd at 556 °C. Read the ordinate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

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 $-0.23\ \text{cm}^{-1}/\text{rd}$ 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 $0.64\ \text{cm}^{-1}/\text{rd}$ for rd 2.2–11.6 at 571 °C and 11–40 at 638 °C. For Ar, the slope is $0.67\ \text{cm}^{-1}/\text{rd}$ for rd 0.36–6.8 and $1.0\ \text{cm}^{-1}/\text{rd}$ 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 $0.224\ \text{cm}^{-1}$ for He at 600 °C and 750 Torr (rd