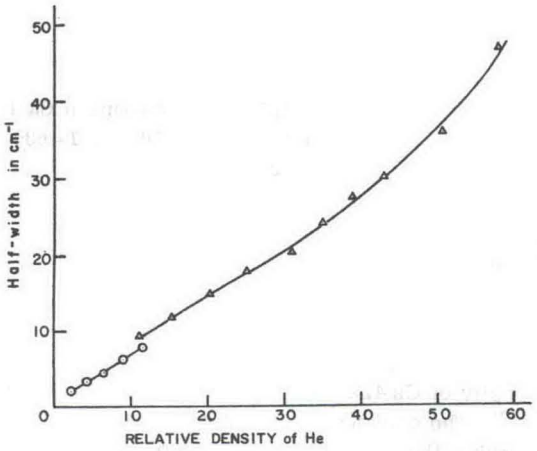


FIG. 3. Half-width of Ca 4227 in He. Open triangle for $T = 638$ °C, open circle for $T = 571$ °C.

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 $T = 2860 \pm 150$ °C), implying a slope of 0.71 $cm^{-1}$/rd.

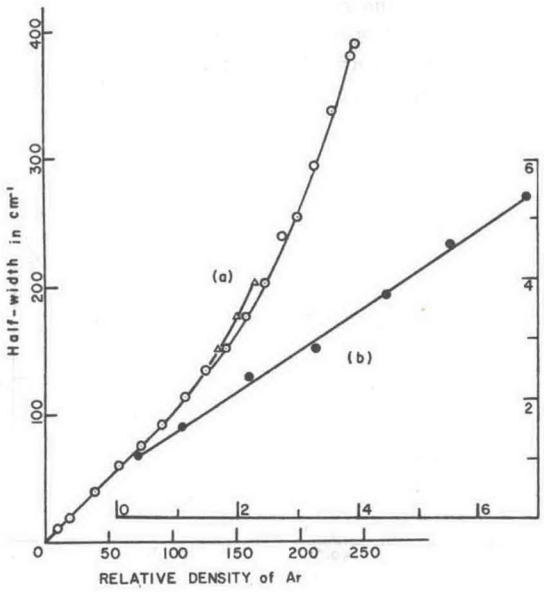


FIG. 4. Half-width of Ca 4227 in Ar. Curve (a): For high rd at 637 °C. Use the ordinate at the left and the abscissa at the bottom, where open circles are rd values computed with Beattie-Bridgeman equation; open triangles, those according to Lecocq. Curve (b): For low rd at 556 °C. Use the ordinate at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

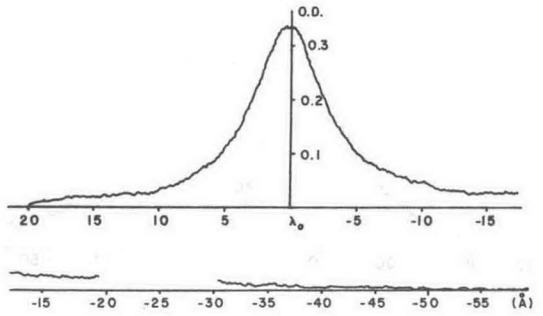


FIG. 5. Line shape of Ca 4227 in He. $P = 2563$ psi, $T = 638$ °C, rd = 50.7.

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. $\lambda_0$ 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-

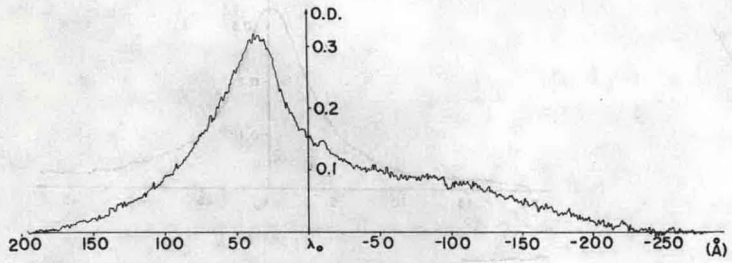


FIG. 6. Line shape of Ca 4227 in Ar. $P=15$, 450 psi, $T=638\,^{\circ}C$, rd = 245.

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]

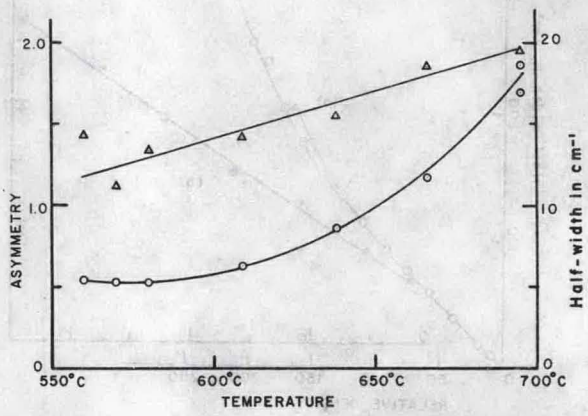


FIG. 7. Effect of the temperature of the absorption column containing an excess of Ca metal vs the observed half-width of Ca 4227 and the asymmetry at constant argon rd of 6.8. Open triangle for asymmetry; open circle for half-width.