Pressure Broadening of the Violet Triplet of Manganese in the Presence of Argon and Helium*

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The λ4030 triplet of Mn ($3d^54s^2$, $^6S-3d^54s4p$, $^6P°$) was studied in absorption under various pressures of argon and helium ranging in relative density from 1 to 30. Helium produced no shift while argon produced a linear red shift of 0.12 cm^{-1}/r.d. In the presence of both helium and argon, the half-widths were found to increase directly with increasing relative density of the perturbing gas. The $j=\frac{3}{2}$, $\frac{5}{2}$ and $\frac{7}{2}$ components are broadened in helium by 0.46, 0.50, and 0.47 cm^{-1}/r.d., respectively, while the same components are broadened in argon by 0.33, 0.36, and 0.30 cm^{-1}/r.d. The result for Mn/Ar indicates that the interatomic energies are proportional to the inverse sixth power of the interatomic distance, and that the difference in the interaction constants for the ground state ^6S and the excited states ^6P of Mn in argon is 3×10^{-58} erg cm^6.

INTRODUCTION

EXCEPT for the resonance lines (λ3280 and λ3382) of Ag[1] and the first sharp series doublet (λ4101 and λ4511) of In,[2] all observations of the pressure broadening and shift of atomic absorption lines due to the presence of foreign gases have been performed with the alkali metals and Hg because their spectra are particularly easy to obtain. To extend such studies to atoms belonging to many-electron systems with spectral terms of high multiplicity, the violet triplet of Mn λ4034.489, λ4033.074, and λ4030.760 which corresponds to the transitions $3d^54s^2$, $^6S_{5/2}-3d^54s4p$, $^6P_{3/2,5/2,7/2}°$, were chosen. Fine structure pressure effects[3] can also be studied with these Mn lines.

EXPERIMENTAL

An absorption cell (4.9 cm long and $\frac{5}{8}$ in. in diameter) and its heating unit were placed inside the pressure chamber (8 in. in diameter) with zirconia blocks as insulation. Sapphire windows and fused quartz rods were used in the optical path to minimize the adverse effects of convection currents and the coating of the windows by Mn. The inner surface of the chamber was water cooled, so that the elevated temperature of the cell did not decrease the tensile strength.

The heating unit consisted of segments of tungsten wire mounted on an alundum core (parallel to the axis of the system) and connected in series by short nickel tubes. This heating unit was found to be much superior to the conventional spiral wound units with respect to uniformity in the temperature distribution. Furthermore, it was easy to replace a defective segment without replacing the whole unit as had been the case when using spiral windings. Observations were made on a 35-ft grating spectrograph in Wadsworth mounting[4] with a dispersion of 1.59 A/mm in the second order and a theoretical resolving power of 160 000. Figure 1 shows the broadening of the Mn triplet by helium as a function of the relative density. The temperature of the absorption tube was normally operated at 1030°C.

A. The Shift

The positions of the maxima of the broadened lines were determined with a recording microphotometer having a magnification of 25 and a reproducibility within a few tenths of an angstrom. It was found that in the presence of helium there was no observable shift for any of the three components of the λ4030 triplet for relative densities up to 30. Because of the relatively large broadening in the presence of helium, the line shift would have had to be greater than 0.05 cm^{-1}/r.d. in order to be measurable.

Preliminary observations on the Mn 2794 triplet in the presence of helium gave no indication of a shift either, although a pronounced broadening was noticed.

Argon was found to produce a red shift which varied linearly with the relative density. The data are shown in Fig. 2. The slopes of the best fitting curves are −0.11, −0.13, and −0.12±0.01 cm^{-1} per unit relative density for the $j=\frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$ components, respectively.

B. The Half-Widths

The half-widths obtained for each of the three components of the manganese λ4030 triplet broadened by

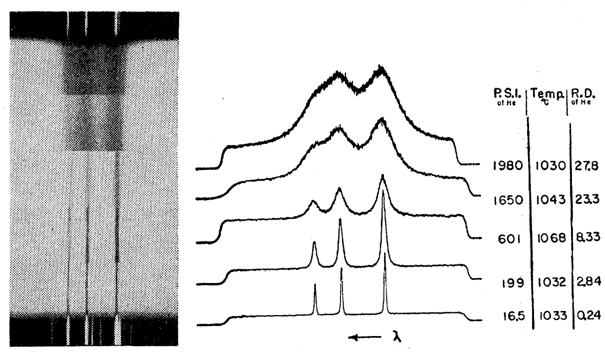

FIG. 1. The microphotometer traces of Mn triplet (4034.760, 4033.074, and 4030.760) when broadened by helium.

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[1] E. D. Clayton and S. Y. Ch'en, Phys. Rev. 85, 68 (1952).
[2] S. Y. Ch'en, A. Smith, and M. Takeo, Phys. Rev. 117, 1010 (1960).
[3] S. Y. Ch'en and M. Takeo, Revs. Modern Phys. 29, 57 (1957).
[4] The spectrograph was constructed with the support of a research grant from the Graduate School of the University of Oregon.

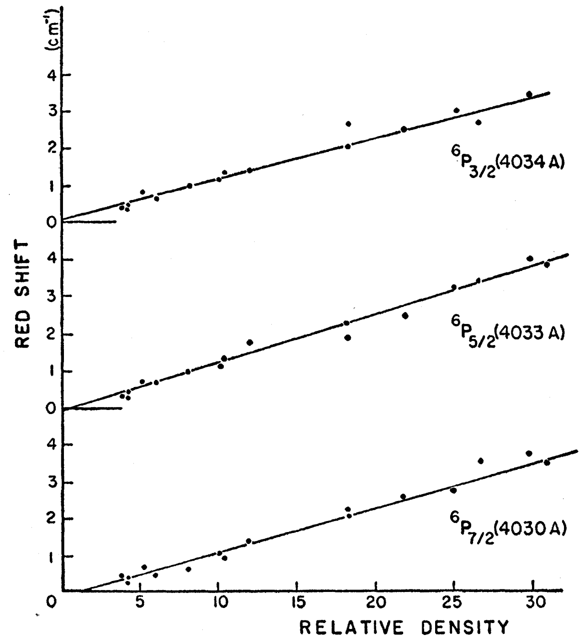

FIG. 2. Shift vs relative density of argon. The origin has been translated along the ordinate in order to separate the curves for the various components.

helium are plotted in Fig. 3. The overlapping of the spectral lines broadened by helium was so pronounced that the half-widths of the individual components of the multiplet were not measurable at relative densities greater than 10. For argon the half-widths were measurable for relative densities up to 20. The dependence of the half-width on the argon relative density is shown in Fig. 4. Since the ratio of the red to the violet half of

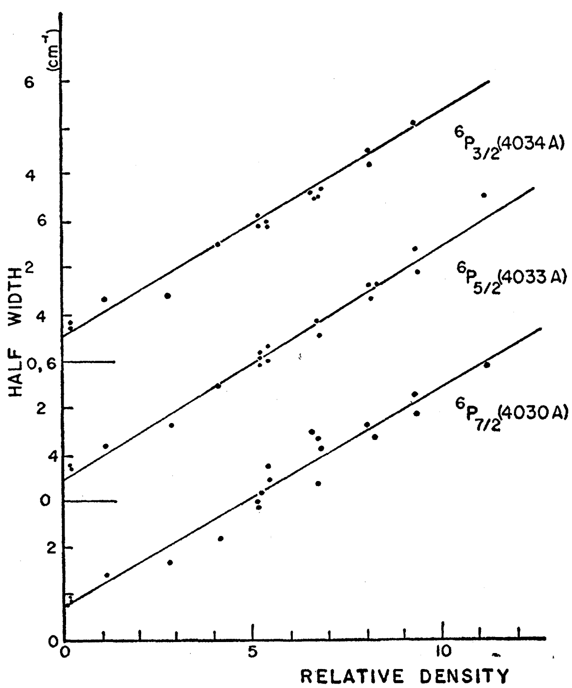

FIG. 3. Half-width vs relative density of helium.

the linewidth was found to be one in the relative density range 1–20, the curve for the $j=\frac{7}{2}$ component has been extended from relative density 20 to 30 by using twice the violet width. For low relative densities of helium the half-widths of the $j=\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$ components were found to increase by 0.46, 0.50, and 0.47 ± 0.05 cm^{-1}/r.d., respectively. In the same relative density region (r.d. =1–20) for argon the rate of change of the half-width is 0.33, 0.36, and 0.30 ± 0.02 cm^{-1}/r.d. for the $j=\frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$ components, respectively. The precision of the measured value of the change in the half-width per unit change in relative density was somewhat higher in the case of argon since the greater relative density range permitted a more precise determination of the slope.

DISCUSSION

The observations reported above show that the gross effect of argon as the foreign gas on the width and shift

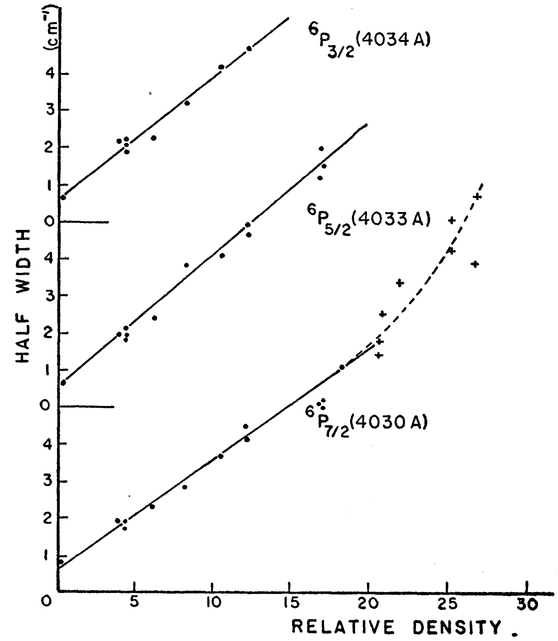

FIG. 4. Half-width vs relative density of argon.

of the spectral lines of a many-electron system with sextet multiplicity is of the same nature, although less pronounced, as the effects observed for the alkalies and In. Both the shift and broadening are between a half and a quarter as large as the corresponding phenomena in the alkali metals[3] and In.[2]

By inserting the experimental mean value of the half-width ($\Delta\nu_{\frac{1}{2}}$) and shift ($\Delta\nu_m$) for Mn and argon in Foley's relation[5]

$$\Delta\nu_{\frac{1}{2}}/|\Delta\nu_m|=2\cot\pi/(p-1).$$

The value of p was found to be 5.95 indicating there is an inverse sixth power interaction between manganese and argon. The observed linear dependence of the shift and half-width on the density is in accord with the Foley theory, although it is not a conclusive proof of

[5] Equation (58) of reference 3.

the Foley theory since practically all line-broadening theories yield a nearly linear relation. The Fourier integral theory predicts, for interactions with $p=6$ [Eq. (57) of reference 5], that the difference in interaction energy constant for the ground state ^6S and the excited states ^6P of Mn in argon is 3×10^{-58} erg cm^6.

An extension of the theory of the fine structure pressure effect[6] is applied to this triplet. A rather elaborate theoretical calculation of the broadening of the three fine structure components has been presented as a separate paper.[7] The results lead to the relative values of half-widths or shifts of the lines in the ratio

$$\text{Mn } (j=\tfrac{3}{2}):(j=\tfrac{5}{2}):(j=\tfrac{7}{2})=0.36:0.36:0.34.$$

(Experimentally the ratio is 0.33:0.36:0.30.) Although not perfect, the agreement is quite good.

The difference in the behavior of the shift for argon and helium may be of theoretical significance. The lack of shift in Mn lines broadened by helium is evidently very fascinating. According to Foley there should be a shift related in a definite way to the width. However, subsequent theoretical developments have shown that the shift is generally smaller than that predicted by adiabatic theories of the Foley type. The effect of collision-induced (real or virtual) nonadiabatic transitions is to cause interferences which can result in a very small shift even though the broadening is appreciable. Under the present experimental conditions the collision-induced transitions between discrete states were not likely to occur.

One should bear in mind that the theoretical assumptions for the analysis of pressure effects produced by light gases are somewhat open to question. The interaction force between He and Mn could be of the type $1/r^p$, p being a large value. Consequently, the short-range force may give a very small shift. Another cause may be the velocity effect. The important force is probably repulsive. The motion of the He atom passing by the Mn atom will probably be slowed down at close collisions but will not be appreciably affected if the collision takes place at large parameters.

[6] M. Takeo and S. Y. Ch'en, Phys. Rev. **93**, 420 (1954).
[7] M. Takeo, (to be published).

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Nonlocal Optical Model for Nucleon-Nuclear Interactions*†

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An attempt is made to achieve a unified potential description of the gross structure of the nucleon-nuclear interactions in bound states and in states of scattering. A model is employed with a nonlocal complex diffuse potential with spin-orbit coupling and surface absorption. This represents a relatively simple nonlocal generalization of the usual static models which might reasonably be expected to describe the nucleon-nuclear interaction in the low-energy range (say from −25 Mev to 25 Mev). Choosing the range of the nonlocal forces as suggested by considerations of the properties of infinite nuclear matter, the real parameters are fixed largely on the basis of neutron and proton separation energies. Two absorption parameters are then adjusted to provide agreement with total reaction and differential elastic cross-section data for neutrons. It is found that the successes of local optical models with energy-dependent parameters are largely preserved. Contrary to expectations, it is found that nonlocality tends to accentuate rather than wash out diffraction patterns. Although a diverse variety of experimental phenomena are treated, a range of parameter choices remains. Because of theoretical uncertainties as to the size of the "rearrangement energy," an effort is made to establish limits as to its magnitude on phenomenological grounds. The influence of several choices upon the physical phenomena used in adjusting the parameters of this model are shown. It would appear that this study does allow for a rearrangement energy but that it is rather small (<6 Mev) and comparable to the probable fluctuations of the potential from element to element.

I. INTRODUCTION

In recent years, considerable success has been achieved in accounting for the gross features of neutron and proton cross sections with the aid of a complex potential well model. During the same period,

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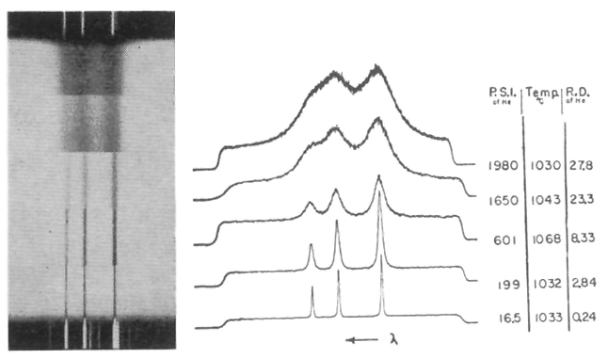
† This work is based in part on a dissertation (by P. J. Wyatt) submitted to the Graduate School of the Florida State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.



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