roughly proportional to the magnitude of the off-diagonal parameters. When these are large, the Hartree-Fock equations can no longer be interpreted as representing an electron in a potential field.

The ionized neon configuration has already been investigated by Garstang.[18] He compared the one-electron energies of self-consistent Hartree wave functions with observed energies and found a considerable difference; in each case the observed energies were larger. He also compared the transition integrals with those derived from the Coulomb approximation of

Bates and Damgaard.[19] Again a significant difference occurred when the Coulomb approximation was based on observed energies. It is interesting to note that the Hartree-Fock energies agree more closely with the observed than with the Hartree energies; in fact, a difference of about 10% between observed and Hartree energies is reduced to 2% with Hartree-Fock energies. Even so, the transition integrals are about half-way between those of the Coulomb approximation based on observed energies, and those from the Hartree wave functions.

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[19] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. London A242, 101 (1949).

Atomic Absorption Cross Section of Lithium Vapor Between 2300 and 1150 Å

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The continuous atomic absorption cross section of lithium vapor has been measured using photoelectric techniques from the $2s^2S \to np^2P^0$ series limit at 2300 to 1150 Å. The bandwidth of the monochromator was 0.75 Å and values of the cross section were obtained at 2-Å intervals. The best value for the atomic absorption cross section at the series limit was 1.54 ± 0.23 Mb. The shape of the curve near the series limit is in close agreement with some recent theoretical predictions. There is an apparent disagreement with recent experimental results.

I. INTRODUCTION

CONSIDERABLE interest exists in experimentally obtained absorption cross sections of the alkali metals at energies greater than that at their ionization edge. Apart from the immediate quantitative need for these data, comparison with the theoretically predicted absorption curves can lead to an insight into the nature of the alkali metal wave functions themselves.[1] Lithium is of particular interest because of the relatively straightforward nature of its configuration and the singular absence of a predicted absorption zero minimum near its ionization edge.

Theoretical estimates have been made by Stewart,[2] and Burgess, and Seaton,[3] of the variation with wavelength of the atomic absorption cross section of lithium from the ionization edge at 2300 to 1800 Å. Within this wavelength range, both curves show a gradual increase of the cross section with energy, but differ in their absolute magnitude. Tait's recent theoretical results[4] in the dipole velocity formulation agree in magnitude with the former works, but his dipole

length formulation yields results approximately 50% higher. Both curves indicate a slight decrease in cross section with decreasing wavelength. The recent experimental results obtained by Marr[5] using photographic techniques agree in magnitude, within experimental error, with Tait's dipole length data. This agreement is considerably improved if Marr's results are adjusted for more recent vapor pressure data.

Marr's results show a maximum at 1900 Å which is not apparent in any of the theoretical curves. Thus, although the agreement between theoretical and experimental magnitudes is good, the shape of the curve of atomic absorption cross section versus wavelength remains in doubt.

This paper is an account of the determination of the atomic absorption cross section of lithium from 2300 to 1150 Å in which photoelectric techniques and the most recent vapor pressure data are employed.

II. EXPERIMENTAL APPARATUS

The basic theory and experimental arrangement employed in this laboratory in the measurement of the cross sections of alkali metal vapors have been discussed previously by Hudson.[6] Certain modifications to the instrumentation were incorporated prior to the work on

[1] R. W. Ditchburn and V. Öpik, *Atomic and Molecular Processes* (Academic Press, Inc., New York, 1962).

[2] A. Stewart, Proc. Phys. Soc. (London) 67, 917 (1954).

[3] A. Burgess and M. J. Seaton, Monthly Notices Roy. Astron. Soc. 120, 121 (1960).

[4] J. H. Tait, in *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland Publishing Company, Amsterdam, 1964), p. 586.

[5] G. V. Marr, Proc. Phys. Soc. (London) 81, 9 (1963).

[6] R. D. Hudson, Phys. Rev. 135, A1212 (1964).

lithium, chief of which was the positioning of the furnace immediately behind the exit slit (Fig. 1). The experiment was performed on a 2.2-m normal-incidence scanning monochromater. A 600-lines/mm-grating blazed at 1500 Å provided an inverse dispersion of 7.5 Å/mm in first order. The effective bandwidth of the instrument was 0.75 Å. A dc hydrogen discharge lamp was employed as the light source.

The photomultiplier tube at the far end of the furnace was used to measure the absorbed radiation. The incident radiation was monitored by diverting a portion of the beam with a plane mirror into an auxiliary photomultiplier as shown in Fig. 1. For measurements above 1500 Å the mirror was coated with aluminum; but in order to avoid the deterioration in reflectivity below 1500 Å (as observed by Hudson[6]), a gold coating was employed.

The difficulties encountered in measuring ultraviolet radiation in a high infrared background were avoided through the use of EMR 541F photomultipliers which
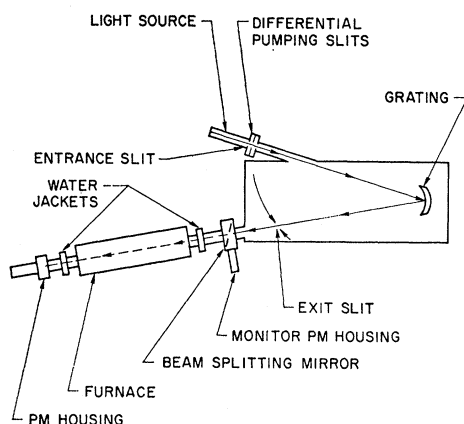

FIG. 1. 2.2-m monochromator and associated equipment.

are insensitive to radiation longer than 3200 Å. These photomultipliers are limited on the short wavelength side by the cutoff of their window material, in this case LiF. They could not be inserted directly into the furnace tube because an electrical breakdown between cathode and ground occurred due to the presence of the inert filling gas. To avoid this problem, the photomultipliers were placed in a vacuum housing separated from the inert gas by LiF windows. No breakdown was detected provided a pressure of less than 10^{-4} mm Hg was maintained within the vacuum housing.

To prevent variations in transmission or reflectivity resulting from infrared heating, both the mirror and the window at the far end of the furnace tube were water cooled.

III. EXPERIMENTAL PROCEDURE

Freshly cut lithium washed in alcohol was placed in the furnace tube and the system was evacuated to

TABLE I. Comparison of recent compilations of thermochemical data for atomic lithium vapor.

Paper	Vapor pressure, mm Hg			
	800°K	900°K	1000°K	1100°K
JANAF[a]	0.00677	0.0878	0.674	3.547
Hultgren et al.[b]	0.00722	0.0897	0.722	3.876
Honig[c]	0.00751	0.100	0.708	3.692
Honig[d]	0.00838	0.109	0.834	4.485
Nesmeyanov[e]	0.00739	0.0952	0.717	3.858

[a] See Ref. 8.
[b] See Ref. 11.
[c] See Ref. 9.
[d] See Ref. 10.
[e] See Ref. 7.

10^{-5} mm Hg. The furnace was then heated to 181°C, the melting point of lithium. Following degassing in the liquid phase, the system was sealed off, and 2 mm Hg of helium were added. The furnace was then raised to 750°C for several hours, cooled, and again evacuated to 10^{-5} mm Hg. This procedure removed organic impurities.

The calibrating runs[6] were taken at 450°C. Individual runs differed from the average by no more than 2%. The temperatures at which this experiment was performed ranged from 750 to 630°C at 20° intervals. The absorbed and monitoring signals were recorded twice at each temperature over the wavelength interval from 2300 to 1150 Å.

IV. VAPOR PRESSURE

Four recent publications[7-10] summarizing thermochemical data have been considered in selecting the vapor pressure figures for this work. Table I lists the estimated vapor pressure of the lithium atom at the appropriate temperatures, obtained by JANAF[8] and Nesmeyanov[7]; and the total vapor pressure (i.e., the sum of both atomic and molecular vapor pressures) estimated by Hultgren et al.[11] and Honig.[9,10] Table II lists the vapor pressure of the lithium molecule estimated by JANAF[8] and Nesmeyanov.[7] Of the four references, Nesmeyanov[7] and Honig[9,10] report both experimental and calculated findings, Hultgren et al.[11]

TABLE II. Comparison of recent compilations of thermochemical data for molecular lithium vapor.

Paper	Vapor pressure, mm Hg			
	800°K	900°K	1000°K	1100°K
JANAF[a]	5.115×10^{-5}	1.306×10^{-3}	1.702×10^{-2}	1.357×10^{-1}
Nesmeyanov[b]	6.056×10^{-5}	1.516×10^{-3}	2.043×10^{-2}	1.623×10^{-1}

[a] See Ref. 8.
[b] See Ref. 7.

[7] A. N. Nesmeyanov, Vapor Pressure of the Chemical Elements (Elsevier Publishing Company, Inc., New York, 1963).
[8] JANAF Thermochemical Tables, The Dow Chemical Company, Midland Michigan, 1962 (unpublished).
[9] R. E. Honig, RCA Rev. 23, 567 (1962).
[10] R. E. Honig, RCA Rev. 18, 195 (1957).
[11] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys (John Wiley & Sons, Inc., New York, 1963).
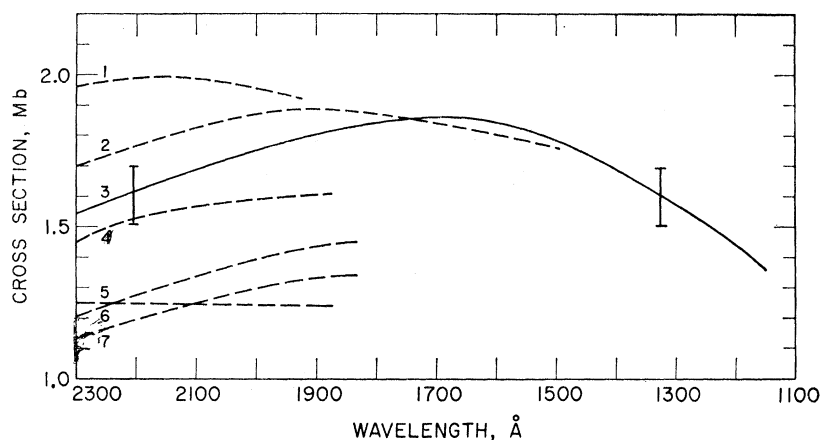
reports experimental data, and JANAF[8] presents the results of calculation. Honig's 1962 data is approximately 15% less than the 1957 data employed by Marr.[5]

It should be noted that Nesmayanov's results for the total pressure are generally higher than the total vapor pressure estimated by Honig and Hultgren *et al.* The results of JANAF however are consistent with the total vapor pressure data obtained by Hultgren *et al.* (based entirely on experimental results), and have therefore been employed in the present work.

V. RESULTS

Values of the atomic and molecular cross sections, σ_a and σ_m, were obtained at 2 Å intervals on a computer by solving the equation

$$\ln[I_0(\lambda)/I(\lambda)] = C_a\sigma_a(\lambda)L + C_m\sigma_m(\lambda)L,$$

by the method of least squares at more than 25 different concentrations. $I_0(\lambda)$ and $I(\lambda)$ are, respectively, the intensity incident on and transmitted through the column of vapor of length L, with atomic and molecular concentrations C_a and C_m. A smooth curve has been fitted to the atomic data in the wavelength interval from 2300 to 1150 Å (Fig. 2). All of the data points fall within the error bars ($\pm 6\%$) shown in Fig. 2. It is estimated that the error introduced in the temperature calibration is $\pm 1\%$ and in the path-length determination, $\pm 3\%$. Inaccuracies in the vapor pressure formulas adopted could result in a further error of the order of $\pm 5\%$. Thus the experiment has a combined random and systematic error of $\pm 15\%$.

The best value obtained for the atomic absorption cross section at the series limit of the $2s^2S \rightarrow np^2P^0$ series was 1.54 ± 0.23 Mb (1 megabarn $= 10^{-18}$ cm²). This value increases to a maximum of 1.85 ± 0.28 Mb at 1700 Å, beyond which it decreases gradually to 1.36 ± 0.21 Mb at 1150 Å, the wavelength limit of these measurements.

The cross section of the lithium molecule was 4.8 ± 0.7 Mb in the region from 2400 to 2300 Å where the atomic absorption cross section is zero. No reliable molecular cross sections were obtained at wavelengths shorter than the series edge. The separation of the effect of molecular absorption was subject to a large error (of the order of $\pm 100\%$), because the molecular concentration in the temperature range employed was one hundred times lower than the atomic concentration while the molecular and atomic cross sections were of the same order.

VI. DISCUSSION OF RESULTS

Figure 2 presents the most recent theoretical and experimental results for the atomic absorption cross section of lithium.

As discussed in Sec. IV, the vapor pressure data employed by Marr is approximately 15% higher than that employed in this work. Hence, the apparent agreement in magnitude between the two sets of experimental results is somewhat misleading.

The shape of the curve obtained in this experiment is in close agreement with those of Stewart using Hartree-Fock wave functions, and Burgess and Seaton using the quantum defect method, but not with that of Tait, who used a wave function containing correlation terms which allow for the effect of inter-shell polarization. The magnitudes of the results obtained are in best agreement with those of Burgess and Seaton.

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