

Absorption of Light by Potassium Vapor between 2856 and 1150 Å

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The continuous atomic and molecular cross sections of potassium vapor have been measured using photoelectric techniques from the $4s^2S \rightarrow np^2P^0$ series limit at 2856 to 1150 Å. The bandwidth of the monochromator was 0.75 Å and values of the cross sections were obtained at 2-Å intervals. The value obtained for the atomic absorption cross section at the series limit was 0.010 ± 0.003 Mb or 0.012 ± 0.003 Mb, depending on which vapor-pressure formula was used in the analysis of the results. A minimum of 0.002 ± 0.002 Mb was observed between 2730 and 2600 Å. This latter result disagrees with previous experimental results but is in agreement with theoretical predictions.

I. INTRODUCTION

THIS paper is the third in a series of investigations of the absorption cross sections of the alkali metals, following measurements in sodium¹ and lithium² vapors.

Ditchburn, Tunstead, and Yates³ obtained experimental values of the atomic absorption cross section of potassium between 2856 and 1600 Å which show a finite minimum at 2725 Å of 0.008 Mb (1 megabarn = 10^{-18} cm²). Bates⁴ calculated the atomic absorption cross section of potassium semiempirically employing a variable polarizability and found that when a polarizability was selected to yield a cross section at the spectral head which agreed with that obtained by Ditchburn, Tunstead, and Yates, a zero rather than a finite minimum was predicted. Burgess and Seaton⁵ have also completed a theoretical calculation of the atomic absorption cross section of potassium as a function of wavelength using the quantum-defect method. Their results are extremely sensitive to the quantum defects employed, and vary widely in both magnitude and slope. However, the curve which fits the experimental data of Ditchburn *et al.* at the spectral head also predicts a zero minimum. Seaton,⁶ who performed a detailed analysis of this minimum taking into account spin-orbit splitting, obtained a finite, although small (0.0003 Mb) cross section.

The work presented in this paper has been undertaken in an effort to dispel the uncertainty regarding a possible zero minimum in the atomic absorption cross section and to obtain an accurate photoelectric measurement of the absorption cross sections of potassium for comparison with theoretical calculations.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

Details regarding the basic theory and experimental arrangement have been discussed previously by

- ¹ R. D. Hudson, *Phys. Rev.* **135**, 1212, (1964).
- ² R. D. Hudson and V. L. Carter, *Phys. Rev.* **137**, 1648 (1965).
- ³ R. W. Ditchburn, J. Tunstead, and J. G. Yates, *Proc. Roy. Soc. (London)* **A181**, 386, (1943).
- ⁴ D. R. Bates, *Proc. Roy. Soc. (London)* **A188**, 350 (1947).
- ⁵ A. Burgess and M. J. Seaton, *Monthly Notices Roy. Astron. Soc.* **120**, 121, (1960).
- ⁶ M. J. Seaton, *Proc. Roy. Soc. (London)* **A208**, 418, (1951).

Hudson.¹ Hudson and Carter² describe several modifications to the instrumentation incorporated prior to their work on lithium; these have been retained for the present potassium measurements.

Figure 1 shows the basic configuration of the apparatus employed in this laboratory in measuring atomic and molecular absorption cross sections in potassium vapor. The apparatus consists essentially of a 2.2-m normal-incidence scanning monochromator, behind the exit slit of which is a temperature-regulated furnace serving as an absorption chamber. Light is generated in a hydrogen Hanovia lamp operated at approximately 1200 W. The 600 lines per mm Bausch and Lomb replica grating, combined with 100- μ slits, resulted in a spectral bandwidth of 0.75 Å.

Continuous and simultaneous recordings of incident and transmitted light intensities were obtained over the wavelength interval from 3000 to 1150 Å. Two complete sets of incident and transmitted intensities were taken at each of 25 temperature settings in the range from 300 to 500°C.

III. VAPOR PRESSURE

Four recent publications⁷⁻¹⁰ summarizing thermochemical data have been considered in selecting the vapor-pressure figures for this work. Table I lists the

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

Paper	Vapor pressure, mm Hg			
	500°K	600°K	700°K	800°K
JANAF ^a	2.38×10^{-2}	6.96×10^{-1}	7.57	44.44
Nesmeyanov ^b	2.06×10^{-2}	6.18×10^{-1}	6.88	40.99
Hultgren <i>et al.</i> ^c	2.12×10^{-2}	6.35×10^{-1}	7.12	43.62
Honig ^d	2.33×10^{-2}	6.20×10^{-1}	6.71	41.85

^a See Ref. 7.

^b See Ref. 8.

^c See Ref. 9.

^d See Ref. 10.

⁷ JANAF Thermochemical Tables, The Dow Chemical Company, Michigan (unpublished).

⁸ A. N. Nesmeyanov, in *Vapor Pressure of the Chemical Elements*, edited by Robert Gary (Elsevier Publishing Company, New York, 1963).

⁹ 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).

¹⁰ R. E. Honig, *RCA Rev.* **23**, 567, (1962).

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

Paper	Vapor pressure, mm Hg			
	500°K	600°K	700°K	800°K
JANAF ^a	3.20×10^{-5}	3.40×10^{-3}	8.95×10^{-2}	9.95×10^{-1}
Nesmeyanov ^b	2.71×10^{-5}	3.01×10^{-3}	8.10×10^{-2}	9.57×10^{-1}

^a See Ref. 7.

^b See Ref. 8.

estimated vapor pressure of the potassium atom at the appropriate temperatures, obtained by JANAF⁷ and Nesmeyanov⁸; and the total vapor pressure (i.e., the sum of both atomic and molecular vapor pressures), estimated by Hultgren *et al.*⁹ and Honig.¹⁰ Table II lists the vapor pressure of the potassium molecule estimated by JANAF⁷ and Nesmeyanov.⁸ Of the four references, Nesmeyanov⁸ and Honig¹⁰ summarize both experimental and calculated findings, Hultgren *et al.*⁹ report experimental data, and JANAF⁷ presents the results of calculation.

Because none of these works quotes errors, it is difficult to select for use one above any other. The data was therefore reduced for both the JANAF⁷ and the Nesmeyanov⁸ vapor-pressure formulas.

IV. 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

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

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 a column of vapor with atomic and molecular concentrations C_a and C_m , and effective path lengths L_a and L_m .

A. Molecular

A smooth curve has been fitted to the molecular data in the wavelength interval from 2975 to 1150 Å. The

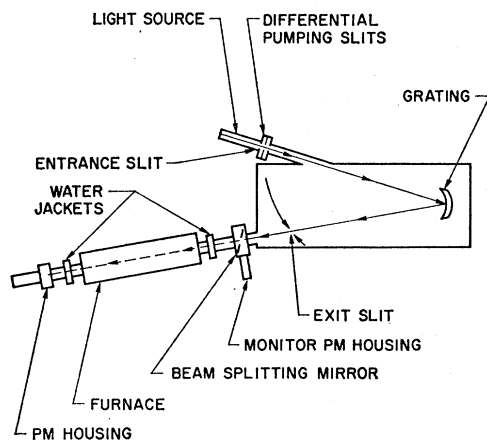


FIG. 1. 2.2-m monochromator and associated equipment.

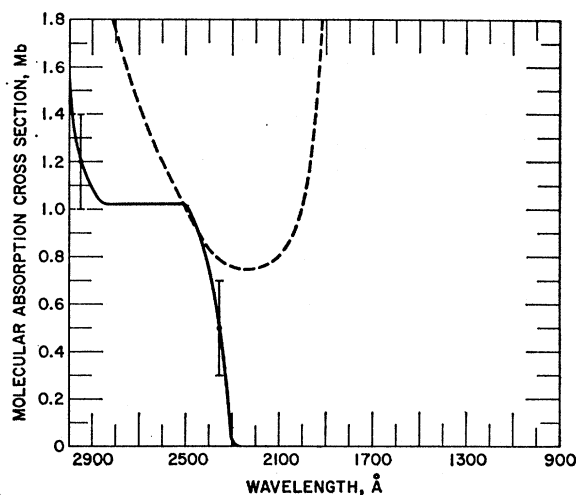


FIG. 2. Molecular absorption cross section versus wavelength. The solid curve presents results of this experiment with error bars defining random scatter of data points. The dashed curve shows the result of Ditchburn, Tunstead, and Yates.

resultant curve is the same using either the JANAF⁷ or Nesmeyanov⁸ vapor-pressure data, and is shown in Fig. 2. As the concentration of the molecule is approximately 100 times less than that of the atom, separation of the effect of molecular absorption is difficult. An approximately constant error of ± 0.2 Mb was apparent in the scatter of the molecular results. The molecular absorption cross section observed through this random error decreases rapidly below 2975 Å, passing smoothly through the atomic series edge at 2856 Å and assumes a constant value of 1.0 ± 0.3 Mb down to 2400 Å. Here

TABLE III. Comparison of the results obtained for the atomic absorption cross section using the JANAF and the Nesmeyanov vapor-pressure data.

λ Å	JANAF σ_a Mb	Nesmeyanov σ_a Mb
2856	0.010	0.012
2800	0.004	0.005
2750	0.002	0.003
2700	0.002	0.003
2650	0.002	0.003
2600	0.002	0.003
2550	0.005	0.006
2500	0.010	0.012
2450	0.018	0.021
2400	0.030	0.034
2350	0.045	0.051
2300	0.060	0.068
2200	0.092	0.103
2100	0.125	0.140
2000	0.157	0.176
1900	0.188	0.211
1800	0.218	0.244
1700	0.250	0.280
1600	0.280	0.314
1500	0.313	0.351
1400	0.338	0.379
1300	0.358	0.401
1200	0.370	0.414

the cross section drops sharply to 0.0 ± 0.2 Mb and remains so to the short-wavelength limit of these measurements.

In addition to the random error, systematic errors estimated at $\pm 5\%$ in the vapor pressure, $\pm 2\%$ in the temperature calibration, and $\pm 3\%$ in the path-length determination must be assigned.

B. Atomic

Table III compares the results obtained for the atomic absorption cross section of potassium using the JANAF⁷ and the Nesmeyanov⁸ vapor-pressure data. Figure 3 presents a curve of the variation of the atomic absorption cross section with wavelength from the $4s^2S \rightarrow np^2P^0$ ionization edge to 1150 Å assuming the JANAF⁷ vapor-pressure data. The results are subject to the same systematic errors as the molecular data and have a random error of ± 0.002 Mb over the entire wavelength range. In Fig. 4 the region from 2856 to 2400 Å has been redrawn on a larger scale; and cross sections, assuming both the JANAF⁷ and the Nesmeyanov⁸ data, are presented.

V. DISCUSSION OF RESULTS

A. Molecular

The only experimental results to which this data can be compared are those obtained by Ditchburn, Tunstead, and Yates³ using photographic techniques. The two sets of molecular data fall within the combined experimental error of one another over the common wavelength interval from 2975 to 2000 Å (Fig. 2). Ditchburn *et al.* report that the uncertainty in their measurement could be as high as ± 1 Mb with the result that the molecular absorption cross section could be as low as zero from 2500 to 2000 Å. This possibility supports the present observations. A marked divergence

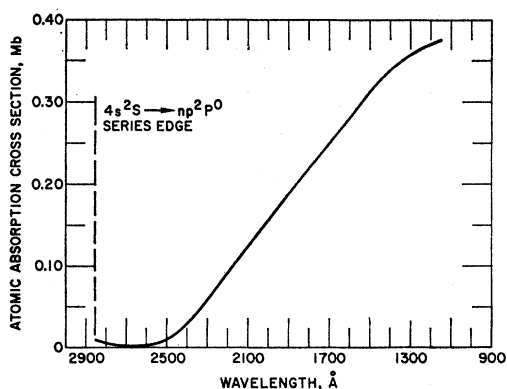


FIG. 3. Atomic absorption cross section versus wavelength. These results were obtained using the JANAF vapor-pressure data.

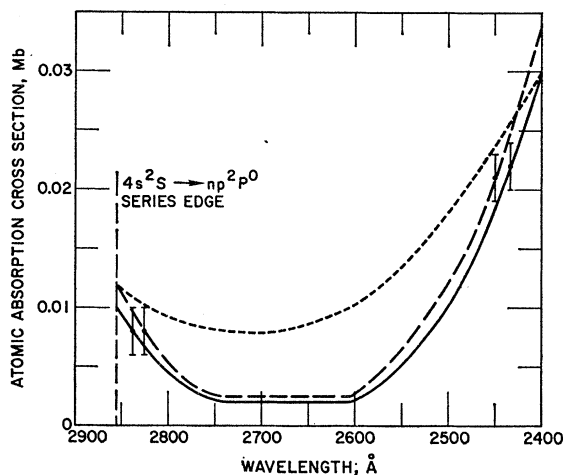


FIG. 4. Atomic absorption cross section versus wavelength. The solid and dashed curves were obtained in the present experiment using the JANAF and Nesmeyanov vapor-pressure data, respectively. The error bars denote random error. The dotted curve was obtained by Ditchburn, Tunstead, and Yates.

in the two sets of molecular data occurs at 1900 Å, however, for here Ditchburn *et al.* observed a large increase in absorption down to the short-wavelength limit of their experiment at 1625 Å, whereas no molecular absorption was detected in the present experiment from 2250 to 1150 Å. The shape of the curve that is obtained in this experiment is similar to that obtained recently for the sodium molecule.¹

B. Atomic

Comparison of the two experimental sets of atomic data shows good agreement at the series edge and at wavelengths shorter than 2400 Å. Between these two regions the data do not agree (Fig. 4). The disparity between the two curves may be the result of the method of separation of the atomic and molecular absorption used by Ditchburn *et al.*,³ for as discussed by Hudson,¹ their method of separation will always give a finite value to $\sigma_a(\lambda)$, if $\sigma_m(\lambda) \neq 0$, even if $\sigma_a(\lambda)$ is in fact zero. As the value obtained for the atomic absorption cross section at the minimum, 0.002 Mb, is equal to the limit of measurement of this experiment, it is felt that the existence of a zero minimum in this region is not precluded.

The theoretical curve obtained by Bates,⁴ assuming a polarizability of 1.55×10^{-24} cm³, is in best agreement with the results presented in this paper.

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