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Relative photoionization cross sections of Cs, Cs_2, Rb, and Rb_2

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The relative photoionization cross sections of atomic and molecular cesium and rubidium have been measured between 2300 and 3400 Å. The variations of the atomic cross sections with wavelength are in excellent agreement with published semiempirical calculations.

I. INTRODUCTION

Photoionization cross sections for atomic cesium and rubidium have been measured by several methods since the pioneering work of Foote and Mohler in 1929.[1,2] However, until recently there have been serious differences between experimental values[3-7] of the atomic cross sections and theoretical calculations.[8-17] Traditionally, experimental data have been obtained by measuring the attenuation of radiation passing through long absorption tubes suitably heated to produce vapor pressures of several Torr. Unfortunately, the vapor is a mixture of atomic and molecular species and it is difficult to separate the effect of molecular absorption from that of the total absorption. The only absolute measurements of the molecular cross sections of cesium and rubidium are those by Creek and Marr.[18] Relative measurements were made on Cs_2 by Popescu *et al.*[19] down to the atomic ionization threshold at 3184 Å.

Most *ab initio* calculations have failed to predict the magnitude and form of the atomic cross sections. However, recently, Johnson and Soff[17] have developed a relativistic many-body method that takes into account correlation effects in open-shell atoms and the strong spin-orbit effects found in cesium. The results still differ considerably from the experimental data.

Absolute cross sections are difficult to obtain with a high degree of accuracy. One reason is the uncertainty in the absolute vapor pressure of cesium and rubidium. Because of this the present work has concentrated on establishing accurate relative cross sections for both the atomic and molecular species. A mass spectrometer was used to identify the atomic- and molecular-absorption processes separately.

II. EXPERIMENTAL

When ionizing radiation passes through a low-pressure gas, the number of ions produced (N) per incident photon (I) is given by

$$N_j/I=\sigma_j n_j l \ , \tag{1}$$

where the subscript j represents a specific atom or molecule, n_j is the number density, l is the path length for collecting the ions, and σ_j is the ionization cross section for the jth species. For Eq. (1) to be valid, $\sigma n l \ll 1$.

When collecting the ions we have to be concerned about the efficiency (Y_j) of the detector to ions of different types (for example, atomic or molecular ions). If a constant fraction f_j of the ions produced are collected, then the actual signal (S_j) observed is given by

$$S_j=Y_j f_j N_j \ , \tag{2}$$

and Eq. (1) becomes

$$\sigma_j=S_j/(Ilf_j n_j Y_j) \ . \tag{3}$$

Because l, f_j, n_j, and Y_j are independent of wavelength, relative values of the atomic and molecular cross sections can be obtained from measurements of the ratio S_j/I. In addition, the ratio of the molecular to atomic cross section can be obtained by applying Eq. (3) separately to atoms and molecules and solving for σ_m. That is, substitute the subscripts a and m for j to identify the atomic and molecular quantities, then

$$\sigma_m=\sigma_a(S_m/S_a)(n_a/n_m)(f_a/f_m)(Y_a/Y_m) \ , \tag{4}$$

where Y_a/Y_m is the relative response of the detector to atomic and molecular ions, n_a/n_m is the ratio of the atomic to molecular number densities produced in the oven at a given temperature, and f_a/f_m is the ratio of the fraction of the atomic to molecular species that is extracted from the oven. To a first approximation this ratio should be equal to the relative conductances for the two species. If the flow of particles is purely molecular flow then the conductance is inversely proportional to the square root of the atomic (or molecular) weight. Thus, $f_a/f_m=\sqrt{2}$. For viscous flow $f_a/f_m \sim 1$. Because of the vapor pressures used (about 1–2 Torr) and the diameter of the exit hole in the oven, the flow rate was in the transition region between molecular and viscous flow. Thus, f_a/f_m lies between 1 and 1.4.

The detector efficiency for the atomic and molecular ions was not measured. However, Peart and Harrison[20] have measured efficiency data for atomic species with different velocities. Applying their data to the present results, a ratio of $Y_a/Y_m=1.3$ was obtained for cesium and 1.25 for rubidium. A similar ratio was obtained by Tuithof and Boerboom[21] for 3-kV molecular ions of masses 131 and 164, which are similar to the masses of Cs and Cs_2.

The ratio n_a/n_m for cesium and rubidium is not known

TABLE I. Vapor pressure of Cs. Summary of results published between 1962 and 1977. Numbers in parentheses are powers of ten.

T (K)	Honig[a] 1962	Nesmeyanov[b] 1963	Volyak[c] 1968	Ewing[d] 1969	JANAF[e] 1971	Hultgren[f] 1973	Gushchin[g] 1975	Behrens[h] 1977
400	2.5(−3)	2.9(−3)		2.9(−3)	3.0(−3)	3.5(−3)		2.4(−3)
500	2.0(−1)	2.4(−1)		2.4(−1)	2.4(−1)	2.6(−1)	2.2(−1)	
600	3.8	4.3	4.0	4.3	4.3	4.4	4.1	
700	27.0	33.0	32.0	32.8	32.8	32.8		

[a] See Ref. 25.
[b] See Ref. 22.
[c] See Ref. 26.
[d] See Ref. 28.
[e] See Ref. 23.
[f] See Ref. 29.
[g] See Ref. 30.
[h] See Ref. 31.

accurately. This is primarily caused by our poor knowledge of the molecular vapor pressures. The only source of tabulated molecular vapor pressures is that given by Nesmeyanov.[22] The JANAF tables[23] give the thermochemical data necessary to calculate the vapor pressures of Cs and Cs_2, whereas the compilation by Evans *et al.*[24(a)] gives values suitable for Cs_2 and Rb_2. The molecular vapor pressure P_m is derived from the equilibrium constant K by use of the relation

$$P_m = P_a^2 / K \ ,$$

where P_a is the atomic vapor pressure of the species. K is derived, in turn, from the value of the Gibbs free energy for the reaction (tabulated in the JANAF tables). However, the uncertainty in the value of the free energy is about ± 1 kcal.[24(b)] This value produced an uncertainty in the molecular vapor pressure of Cs_2 by factors of 3—20 at 500 K and by comparable factors for Rb_2. Thus, absolute values of the molecular cross sections have little meaning until more accurate vapor-pressure data are available. Tables I and II list the atomic vapor pressures for Cs and Rb, respectively, that have been reviewed between 1962 and 1973, in addition to some recent measurements.[22–32] For cesium, at a temperature of 573 K, Nesmeyanov gives the ratio $n_a / n_m = 153$, whereas the JANAF tables yield a value of 60. For rubidium, Nesmeyanov's tables give a value of $n_a / n_m = 375$ at 493 K. The Evans *et al.* compilation only allows the Rb_2 vapor pressure to be calculated. Thus, in addition it is necessary to use the atomic vapor pressures quoted in Table II. We find the ratio n_a / n_m varies from 270 to 502. Because of the large uncertainty in the value of n_a / n_m, only relative values of σ_m can be obtained at this time.

The atomic and molecular ions were separated by a time-of-flight (TOF) mass spectrometer.[33] A schematic of the system used is shown in Fig. 1. Photoionization takes place between two parallel plates separated by 30 mm. A voltage of 6 kV is placed across the plates driving the electrons and positive ions in opposite directions as shown. The charged particles pass through screened holes in the center of the plates and are detected by electron multipliers. When an electron-ion pair is produced, the detected electron signal starts a time-to-amplitude converter (TAC). The timing interval is stopped when the ion arrives at the TAC. Thus, a mass spectrum is built up.

A stainless-steel oven was used to evaporate Cs and Rb. Oven temperatures ranged from 493 to 573 K providing vapor pressures of Cs from 0.2 to 2.2 Torr, respectively,

TABLE II. Vapor pressure of Rb. Summary of results published between 1962 and 1973. Numbers in parentheses are powers of ten.

T (K)	Honig[a] 1962	Nesmeyanov[b] 1963	Volyak[c] 1968	Ewing[d] 1969	Hultgren[e] 1973	Piacente[f] 1973
400	1.0(−3)	1.03(−3)		1.18(−3)	1.21(−3)	1.72(−3)
450		1.39(−2)		1.56(−2)		2.32(−2)
500	1.0(−1)	1.10(−1)		1.22(−1)	1.23(−1)	1.86(−1)
550		5.88(−1)		6.49(−1)		10.20(−1)
600	2.20	2.37	2.59	2.59	2.61	
700	20.0	20.6	23.0	22.3	22.7	

[a] See Ref. 25.
[b] See Ref. 22.
[c] See Ref. 27.
[d] See Ref. 28.
[e] See Ref. 29.
[f] See Ref. 32.

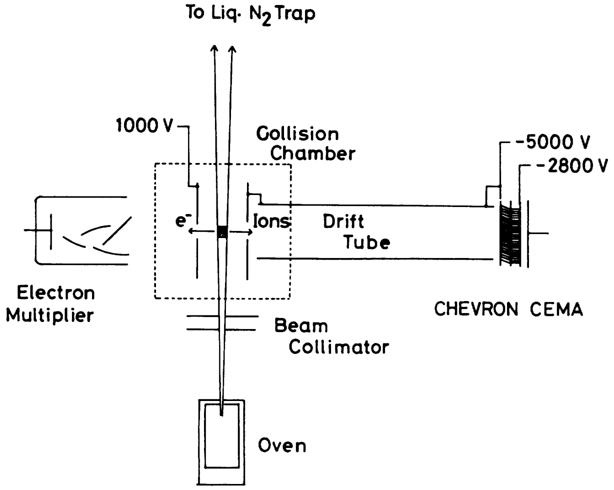

FIG. 1. Schematic diagram of experimental arrangement.

and vapor pressures of Rb from 0.09 to 1.1 Torr, respectively. The beam emerged from the oven through a small tube of inner diameter 1 mm and length 10 mm. The tube was maintained at a temperature a few degrees above that of the oven to prevent any condensation within the tube. The path of the beam was determined by a series of collimating apertures ranging in diameter from 2 to 4 mm. After passing through the center of the ionization region, the vapor passed over a hot tungsten filament, which ionized any atom that made contact.[7] The ion current was used to monitor the stability of the atomic number density within the beam. The remaining vapor was trapped on a liquid-N_2 cooled surface. The Rb and Cs used were of high purity (99.9%) and were supplied in glass capsules. The capsules were broken in the oven under an argon atmosphere.

The light source employed was a 1-kW xenon-mercury arc lamp with high-quality quartz optics. The output of the lamp was a continuum superimposed with some intense emission lines. The source was used in conjunction with a 50-cm Czerny-Turner–type monochromator. Data were taken with spectral band passes of 16 and 48 Å, full width at half maximum (FWHM). The relative intensity of the radiation was measured after it passed through the ionization region. The detector was a photomultiplier which had a coating of sodium salicylate deposited on its window. Because sodium salicylate has a nearly constant fluorescent quantum efficiency,[34] the output of the photomultiplier is proportional to I, the intensity of the incident radiation, and could be used directly in Eq. (3).

III. RESULTS AND DISCUSSION

A. Photoionization of Cs (threshold 3184.1 Å)

The relative photoionization cross sections for atomic cesium are plotted in Fig. 2 (solid circles). A smooth fit to the data points was drawn (solid line) and normalized to 10 at the ionization threshold. The statistical errors in the present data were less than ±2%. To compare the present data with the previously published experimental results of Mohler and Boeckner[2] (open squares), and Marr and Creek[6] (open triangles), we normalized their quoted threshold cross sections to 10. We normalized the data of Cook *et al.*[7] (open circles) to our smoothed curve at 3150 Å.

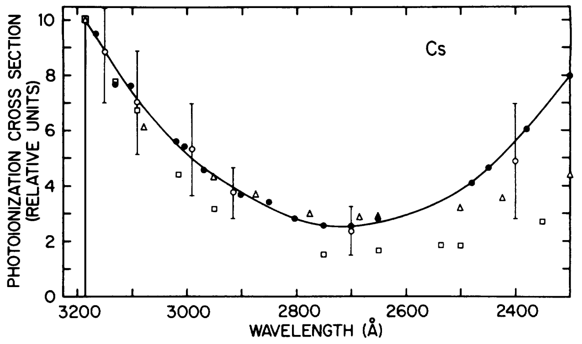

FIG. 2. Relative photoionization cross sections of Cs. Present data, ●; Mohler and Boeckner, □; Marr and Creek, △; Cook *et al.* ϕ; the solid line represents the best fit to the present experimental data.

The relative cross sections are all in good agreement down to 2650 Å with the exception of Mohler and Boeckner's data. All the data begin to diverge at wavelengths shorter than 2650 Å.

Mohler and Boeckner did not consider the effect of Cs dimers that were present in their experiments. In addition, they used an indirect method to measure the presence of ions. This was a space-charge neutralization technique developed by Kingdon.[35] These factors may account for the different shape in their cross-section curve. Marr and Creek, however, did make corrections for the presence of molecular ions. In their work they used photographic techniques to measure the attenuation of radiation through a cesium absorption cell.

The experimental cross-section measurements of Cs by Cook *et al.*[7] were taken at very low oven temperatures, typically about 340 K. The ratio of molecular to atomic cesium decreases rapidly with the oven temperature. For example, according to Nesmeyanov the percentage of dimers present at 340 K is $\sim 10^{-3}\%$, whereas at 600 K, it is 1%. Thus, their cross-section measurements should be free from any molecular effects. Both the present experimental arrangement and that of Cook *et al.* used atomic beams and measured the number of ions directly with electron multipliers.

Mohler and Boeckner, and Marr and Creek quote absolute values at thresholds of 0.23 and 0.20 Mb, respectively ($1\ \text{Mb} = 10^{-18}\ \text{cm}^2$). However, different vapor pressures were used by each group. When their results are adjusted to the values calculated from the JANAF tables[23] their theshold values become 0.15 and 0.18 Mb, respectively. Cook *et al.* did not use the published vapor-pressure data, but instead measured the Cs number density directly using a hot tungsten filament as a detector. Extrapolating their absolute data to the ionization threshold a cross section of approximately 0.1 Mb is obtained. This value is in good agreement with the semiempirical calculations of Weisheit[12] and Norcross.[13] Both authors obtain a value for the cross section at the ionization threshold of 0.1 Mb. The semiempirical calculations, along with the *ab initio*

TABLE III. Relative photoionization cross sections for Cs and Cs$_2$.

	Cross sections			Cross sections	
λ (Å)	Cs	Cs$_2$	λ (Å)	Cs	Cs$_2$
3383		0.23	3020	0.056	
3338		0.36	3003	0.054	0.72
3330		0.40	2968	0.046	0.49
3300		0.74	2900	0.037	0.38
3285		0.78	2850	0.034	0.87
3265		0.63	2802	0.028	0.35
3235		1.00	2749	0.025	0.34
3210		1.53	2698	0.025	0.50
3180	0.10	0.84	2651	0.028	0.53
3165	0.095	0.71	2480	0.041	0.36
3130	0.077	0.66	2448	0.047	0.38
3100	0.076	0.90	2378	0.060	0.35
3050		0.58	2300	0.080	0.38

calculations of Huang and Starace,[15] and Johnson and Soff,[17] are shown in Fig. 3. The present data, normalized to a threshold value of 0.1 Mb by the method described in Fig. 2, are also included in Fig. 3 and listed in Table III. The two semiempirical calculations are in close agreement with each other over most of the spectral range down to 2300 Å. Their maximum deviation is about 16% at the cross-section minimum. Further support for these calculations have been obtained by Sander *et al.*[36] who measured the relative cross sections of potassium by isolating the atoms with a mass spectrometer. The semiempirical calculations have pointed out the importance of including core-polarization effects in any calculation in addition to the inclusion of spin-orbit interactions, which are known to influence strongly the value of the cross section.

Our normalized data are in excellent agreement with the semiempirical calculations except at the shortest wavelengths. This could be caused by the perturbing effect of the inner 5*p* subshell, which was not taken into account by the semiempirical calculations. Huang and Starace[14] have shown that by including interchannel coupling between the 6*s* and 5*p* subshells the photoionization cross section increases more rapidly at shorter wavelengths beyond the minimum in the cross-section curve.

The recent calculations by Johnson and Soff,[17] and by Huang and Starace[15] have produced the best agreement between an *ab initio* calculation and experiment. Huang and Starace took into account the effect of final-state spin-orbit interaction and examined the effect of core relaxation, but omitted polarization and correlation effects. Johnson and Soff used a relativistic many-body calculation that treated both spin-orbit and correlation effects. However, they also omitted polarization effects. Figure 3 shows their results using the dipole length approximation. Their velocity results (not shown) are very similar but lie approximately 1.0×10^{-2} Mb lower. For comparison, the results of Huang and Starace are shown only for their frozen core calculation in the dipole velocity approximation. They have a much larger spread between their length and velocity calculations than those of Johnson and Soff.

B. Photoionization of Cs$_2$

The relative value of the cesium molecular photoionization cross section was obtained by measuring the number

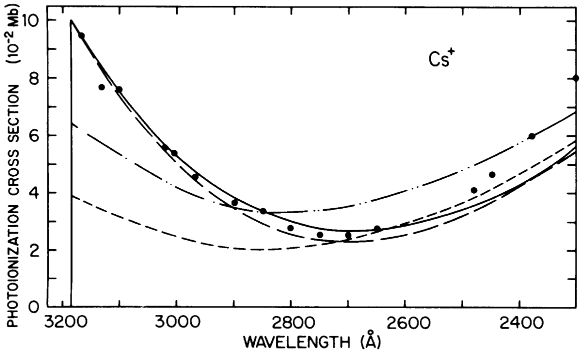

FIG. 3. Photoionization cross sections of Cs. Semiempirical calculations are by Norcross (——) and by Weisheit (— — —). The *ab initio* calculations are by Johnson and Soff (—··—··), and Huang and Starace (-----). Present results (●) were normalized to the semiempirical results at threshold.

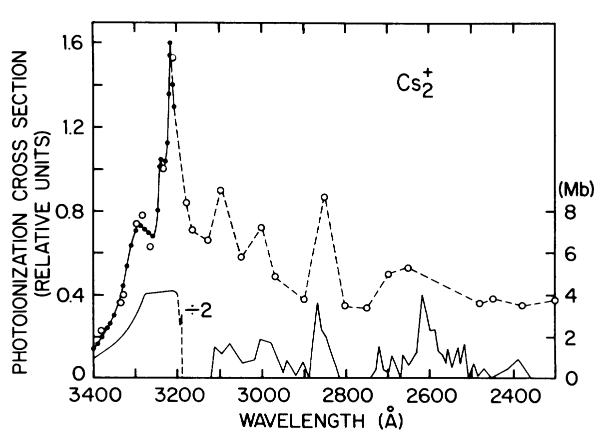

FIG. 4. Relative photoionization cross sections of Cs$_2$. Present results, ○; Popescu *et al.* ●; Creek and Marr, solid line. Note the scale for the data of Creek and Marr is given on the right side of the figure and their major peak at 3250 Å is divided by 2.

of molecular ions per photon (S_m/I) as a function of wavelength, see Eq. (3). The results are shown in Fig. 4 and the numerical values are tabulated in Table III. The data points in Fig. 4 are joined by a dashed curve to indicate the trend of the cross section as a function of wavelength. Clearly, structure could exist between the data points. The solid line with solid data points represent the relative cross-section data between 3200 and 3400 Å reported by Popescu *et al.*[19] Their data have been normalized to give a "best fit" to the present data. There is excellent agreement between the two sets of data. Care was taken with the present data to make measurements between the atomic Rydberg lines in this region, otherwise indirect molecular ions would be produced from the reaction,

$$\mathrm{Cs}^* + \mathrm{Cs} \rightarrow \mathrm{Cs}_2{}^+ + e \ . \qquad (5)$$

The absolute values of the molecular cross section obtained by Creek and Marr[18] are also plotted in Fig. 4 (right-hand scale). There is qualitative agreement between the two sets of data on the position and general shape of the molecular band structure.

The process of dissociative photoionization could affect the present molecular cross section at wavelengths shorter than the dissociative photoionization threshold at approximately 2850 Å.[37] Thus, below 2850 Å the present data represents the relative cross section for producing $\mathrm{Cs}_2{}^+$ ions. This will be somewhat less than the total photoionization cross section and will depend upon the degree of dissociation at these wavelengths. The production of atomic ions by this process should not affect the atomic cross section appreciably owing to the large atomic-to-molecular concentration.

If we apply Eq. (4) to the present data, then the actual numbers given in Table III and shown in Fig. 4 represent the absolute molecular cross sections in Mb for the following values of the various parameters, namely, $\sigma_a = 0.10$ Mb at the threshold for atomic ionization, $n_a/n_m = 153$ at 573 K from Nesmeyanov's tables, $Y_a/Y_m = 1.3$, and $f_a/f_m = \sqrt{2}$. The actual ratio of the molecular- to atomic-ion signal obtained in our experiment at 573 K is given by

$$S_m/S_a = 0.003\,56(\sigma_m/\sigma_a) \ ,$$

where σ_m/σ_a is the ratio of the relative cross-section data for molecules and atoms given in Table III.

Popescu *et al.* normalized their results by use of the threshold value of the atomic cross section as quoted by Marr and Creek (namely, 0.20 Mb). This gave them a maximum molecular cross section at 3214 Å of 21 Mb. However, Creek and Marr obtained a value of 8.4 Mb at this wavelength. Our sample calculation above, using Eq. (4), yields a value of about 2.4 Mb at 3214 Å if we adjust our data to Creek and Marr's vapor pressure and threshold atomic cross sections. Thus, there is a wide discrepancy in the absolute values of the molecular cross section obtained by three quite different techniques. With the present method there is a major uncertainty in the value of the ratio f_a/f_m. Earlier we pointed out that the ratio must depend on the relative conductances for the two species. However, this ratio may be further modified. For example, it is known that when atomic or molecular cesium reevaporates from a metal surface of high work function there is a probability that it does so as a positive ion.[38] On the other hand, there is a copious supply of thermal electrons produced in a cesium oven. Thus, the production of negative ions becomes a possibility. In either case, any ions formed and entering into the mass spectrometer will be swept away by the field in the ionization chamber and hence lost. Thus, the number of atoms and molecules in the ionization chamber will depend strongly on the probability of each species being ionized in the oven. Of course, there are also uncertainties in the vapor pressure and in the ion-detector efficiency. The point of this discussion is to emphasize the large uncertainty in the absolute value of the Cs_2 cross section, but at the same time show the agreement in the relative values.

C. Photoionization of Rb (threshold 2968.15 Å)

The relative photoionization cross sections for atomic rubidium are shown in Fig. 5. Numerical values are tabulated in Table IV. The solid line in Fig. 5 represents the best fit to our data points. These results have been normalized to the semiempirical calculations of Weisheit[12] at 2850 Å. This provides a perfect fit between the two sets of data in the range 2425–2900 Å. Outside these limits the continuation of Weisheit's curve is represented by the dashed line. These results are compared with the values obtained by Mohler and Boeckner[2] and by Marr and Creek.[6] The absolute values of Mohler and Boeckner were plotted because they effectively provided a best fit to

TABLE IV. Relative photoionization cross sections for Rb and Rb_2.

	Cross sections			Cross sections	
λ (Å)	Rb	Rb_2	λ (Å)	Rb	Rb_2
3130		0.32	2749	0.027	0.58
3050		0.91	2698	0.018	0.90
3021		0.83	2651	0.001	0.80
3000		0.69	2500	0.007	0.85
2968		0.56	2480	0.004	1.23
2956	0.105	1.39	2450	0.004	1.66
2900	0.062	0.94	2400	0.006	0.77
2850	0.049	0.58	2378	0.006	
2802	0.038	0.39	2300	0.010	0.39

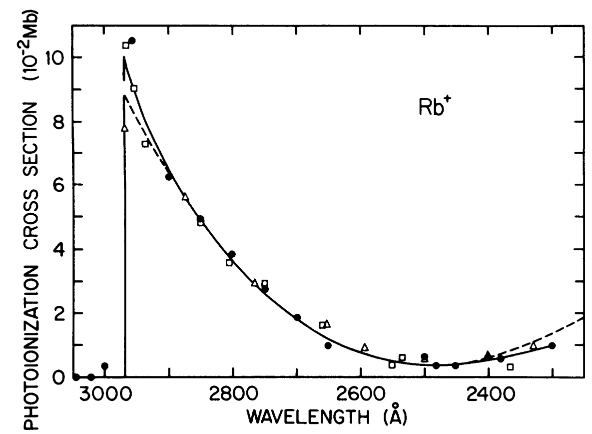

FIG. 5. Normalized photoionization cross section of Rb. The solid line indicates the best fit to the present experimental data (●). These results were normalized to the semiempirical calculations of Weisheit (---) at 2850 Å. In the region between 2450 and 2900 Å the solid and dashed lines overlap. Other experimental data points are Mohler and Boeckner, □; Marr and Creek, △. Both sets of data were also normalized to Weisheit's results.

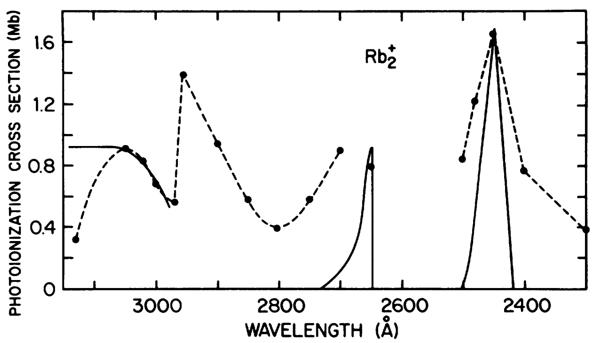

FIG. 6. Relative photoionization cross sections of Rb$_2$. The present data (●) have been normalized to Creek and Marr's absolute data (——) between 3000 and 3050 Å.

Weisheit's data. They, of course, have used different vapor-pressure results from those used by Marr and Creek. Marr and Creek's absolute data were reduced by about 22% to normalize their data to Weisheit's curve at 2765 Å in order to produce a good fit.

As can be seen from Fig. 5, the normalized experimental data follow the semiempirical calculations very closely. Weisheit quotes an absolute threshold cross section of 0.089 Mb. Although both Mohler and Boeckner and Marr and Creek used different values for the vapor pressure of Rb, their results can be standardized to a common value. Standardizing to the vapor-pressure data of Nesmeyanov, threshold cross sections of 0.072 and 0.09 Mb were obtained, respectively, from the data of Mohler and Boeckner and Marr and Creek. The present status of the variously quoted Rb vapor pressures are given in Table II. As can be seen from the table, a variation of up to 1.86 is possible ($T=500$ K).

D. Photoionization of Rb$_2$

The relative values of the rubidium molecular photoionization cross section were also obtained by measurements of ions per photon. Data were taken at 493 and 536 K for two sets of monochromator slit widths, representing band passes of ±16 and ±48 Å, respectively. The results were averaged to give a relative cross-section curve. The results are tabulated in Table IV and shown in Fig. 6 along with the data of Creek and Marr.[18] As in the case of Cs$_2$, the values listed (in Mb) were calculated by use of Eq. (4). However, the same criticism applies, namely, the uncertainty in the values of the parameters used. The actual ratio $S_m/S_a=0.54$ at 2450 Å for a temperature of 493 K.

The good agreement between the two sets of data from 2970 to 3050 Å is accidental because different values of the vapor pressure were used. Adjusting the present data to the vapor pressure and atomic cross sections used by Creek and Marr, we find the present data should be increased by a factor of 1.4. However, for comparison between the two sets of data it is sufficient to consider the present data simply normalized to that of Creek and Marr between 2790 and 3050 Å. This shows qualitative agreement at the 2450-Å peak. However, it also shows a large amount of absorption between 2700 and 2970 Å that has not been reported.

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