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Cross-Section Ratios for K* + Rb Electronic Excitation Transfer*

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Cross-section ratios have been determined for the collisional transfer of electronic energy from the resonance levels of K to those of Rb. The results obtained were

$$\frac{Q(\mathrm{K}\,^2P_{3/2}\rightarrow\mathrm{Rb}\,^2P_{1/2})}{Q(\mathrm{K}\,^2P_{1/2}\rightarrow\mathrm{Rb}\,^2P_{1/2})}=1.1\pm0.2,\qquad \frac{Q(\mathrm{K}\,^2P_{3/2}\rightarrow\mathrm{Rb}\,^2P_{3/2})}{Q(\mathrm{K}\,^2P_{3/2}\rightarrow\mathrm{Rb}\,^2P_{1/2})}=2.2\pm0.2,$$

$$\frac{Q(\mathrm{K}\,^2P_{3/2}\rightarrow\mathrm{Rb}\,^2P_{3/2})}{Q(\mathrm{K}\,^2P_{1/2}\rightarrow\mathrm{Rb}\,^2P_{3/2})}=1.0\pm0.2,\qquad \frac{Q(\mathrm{K}\,^2P_{1/2}\rightarrow\mathrm{Rb}\,^2P_{3/2})}{Q(\mathrm{K}\,^2P_{1/2}\rightarrow\mathrm{Rb}\,^2P_{1/2})}=2.2\pm0.6,$$

where the errors quoted are purely statistical. Possibilities of systematic errors are discussed. Combined with the absolute cross sections of Ornstein and Zare, these ratios give a complete set of cross-section values, namely,

$$Q(\mathrm{K}\,^2P_{1/2}\rightarrow\mathrm{Rb}\,^2P_{1/2})=2.3\pm0.6\ \text{Å}^2,\qquad Q(\mathrm{K}\,^2P_{1/2}\rightarrow\mathrm{Rb}\,^2P_{3/2})=5.3\pm0.8\ \text{Å}^2,$$

$$Q(\mathrm{K}\,^2P_{3/2}\rightarrow\mathrm{Rb}\,^2P_{1/2})=2.5\pm0.5\ \text{Å}^2,\qquad \text{and}\qquad Q(\mathrm{K}\,^2P_{3/2}\rightarrow\mathrm{Rb}\,^2P_{3/2})=5.5\pm1.2\ \text{Å}^2.$$

I. INTRODUCTION

The present investigation is concerned with the sensitized fluorescence processes

$$K^*(4p\,^2P_{1/2,3/2})+\mathrm{Rb}(5s\,^2S_{1/2})\rightarrow\mathrm{K}(4s\,^2S_{1/2})+\mathrm{Rb}^*(5p\,^2P_{1/2,3/2}),$$

whereby electronic excitation is exchanged between the lowest-lying excited states of potassium and rubidium. Previously, absolute cross-section measurements have been reported by Hrycyshyn and Krause[1] and by Ornstein and Zare[2] (hereafter referred to as I) for excitation transfer between the various multiplets of this system. In addition to the difficulty encountered in working with weak light signals from optically thin samples, these absolute measurements are subject to uncertainties in the determination of the vapor density. In the experiments reported here, which form an extension of I, the ratios between the cross sections of the four possible transfers from the K resonance levels to those of Rb have been measured. Since these determinations involve only cross-section ratios, the problem of the vapor density has been circumvented.

The ratios of the cross sections for two of the excitation transfer processes are in substantial disagreement with the ratios calculated from the results of Hrycyshyn and Krause. The description of the experiment and the results is followed by an examination of the possible errors, random and systematic, that may influence the ratios presented. No satisfactory explanation for the disagreement can be given.

II. THEORY OF EXPERIMENT

The four possible energy transfers from the K-resonance levels to those of Rb are

$$\mathrm{K}(^2P_J)+\mathrm{Rb}(^2S_{1/2})\rightarrow\mathrm{K}(^2S_{1/2})+\mathrm{Rb}(^2P_{J'})+\Delta E, \tag{1}$$

where J and J' can each have the values $\frac{1}{2}$ or $\frac{3}{2}$. Figure 1 shows the energy levels of K and Rb and the energy defects ΔE involved. These processes were studied by irradiating a mixture of K and Rb atoms with K-resonance radiation and observing the resulting Rb-resonance fluorescence.

In the following the index, $i=1,2$ refers to the resonance levels $^2P_{1/2}$, $^2P_{3/2}$ of K, respectively, while $j=1,2$ refers similarly to the resonance levels of Rb; g denotes the ground state of either alkali. In the steady state, the number I of photons emitted per unit time per unit volume from level j of the Rb atoms is given by

$$I^{\mathrm{Rb}}(j\rightarrow g;i)=N^{\mathrm{Rb}}(g)N^{\mathrm{K}}(i)\,\bar{v}\,Q(i,j), \tag{2}$$

where $Q(i,j)$ is the (temperature-dependent) cross section for the energy transfer from level i of K to level j of Rb. Experimentally, the radiation

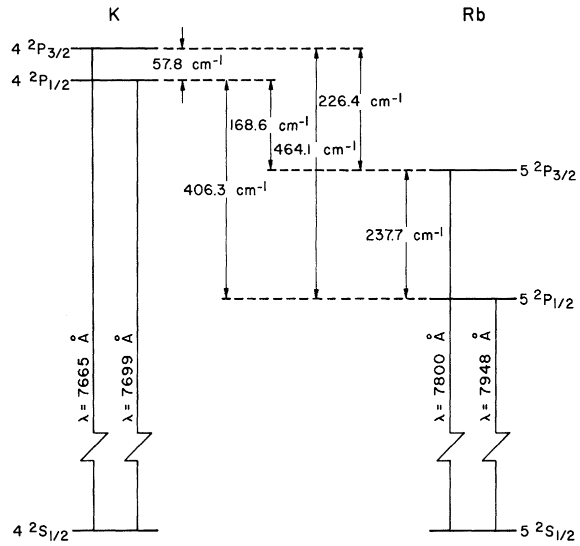

FIG. 1. Diagram of the resonance levels of K and Rb (drawn to scale), showing the energy defects of the four excitation transfer processes described by Eq. (1).

emerging from the system consisted of (a) K fluorescence, (b) Rb cross fluorescence, (c) radiation from the lamp scattered from the cell walls (independent of alkali density), and (d) other radiation sources, such as blackbody radiation, which have been discussed in I. In the present discussion it is assumed that (a) and (b) can be separated and investigated independently. Spectral impurities are discussed in Sec. V.

The signals S observed in the cross-fluorescence detection channels may therefore be written

$$S(i,j) = I^{\mathrm{Rb}}(j \to g; i) + C(i,j) \ , \tag{3}$$

where the constant C [resulting from the radiation source (c)] is labeled to denote that it has different values for different filter systems. To obtain ratios of cross sections, the signals may be expressed in the form

$$S(i,j) = mS(i',j') + b \ . \tag{4}$$

With the help of Eqs. (2) and (3), Eq. (4) may be rewritten

$$N^{\mathrm{Rb}}(g)\, N^{\mathrm{K}}(i)\, \bar{v}\, Q(i,j) + C(i,j)$$
$$= m[N^{\mathrm{Rb}}(g)\, N^{\mathrm{K}}(i')\, \bar{v}\, Q(i',j') + C(i',j')] + b \ . \tag{5}$$

By equating like coefficients, it is found that

$$m = N^{\mathrm{K}}(i)\, Q(i,j)/N^{\mathrm{K}}(i')\, Q(i',j') \ , \tag{6}$$

and

$$b = C(i,j) - mC(i',j') \ . \tag{7}$$

If $i = i'$, m is the ratio of two cross sections; if $i \neq i'$, m is the ratio of two cross sections multiplied by the ratio of the number of atoms in the K-resonance levels. In either case m is independent of vapor density. The latter ratio was measured by detecting the K fluorescence. The measured ratios were

$$R1 = \frac{N_2^{\mathrm{K}}}{N_1^{\mathrm{K}}} \ , \qquad R2 = \frac{N_2^{\mathrm{K}}\, Q(\mathrm{K2,\ Rb1})}{N_1^{\mathrm{K}}\, Q(\mathrm{K1,\ Rb1})} \ ,$$

$$R3 = \frac{N_2^{\mathrm{K}}\, Q(\mathrm{K2,\ Rb2})}{N_1^{\mathrm{K}}\, Q(\mathrm{K1,\ Rb2})} \ , \qquad R4 = \frac{Q(\mathrm{K2,\ Rb2})}{Q(\mathrm{K2,\ Rb1})} \ ,$$

$$R5 = \frac{Q(\mathrm{K1,\ Rb2})}{Q(\mathrm{K1,\ Rb1})} \ ,$$

giving three independent ratios between the cross sections and one consistency check.

Since ratios were measured, it can be seen from the above that moderate radiation trapping constitutes a problem only when its effect is different in the numerator and the denominator, i.e., Rb radiation trapping does not affect $R2$ or $R3$, and K radiation trapping does not affect $R4$ or $R5$. Therefore, in the measurement of $R1$, $R2$, and $R3$, the K should be optically thin whereas Rb may be optically thick; the reverse should be true when measuring $R4$ and $R5$. Note that in I, conditions of optical thinness were simultaneously important for both species.

III. EXPERIMENTAL METHOD

The apparatus is shown in Fig. 2. It is essentially the same as that used in I (see Fig. 4 of I), but with a K-absorption cell inserted in the emergent beam to increase the rejection of the K fluorescence. Since a comprehensive explanation of the experimental arrangement appears in I, the description given here will be brief.

The light from the K lamp was passed through an interference filter, and one K resonance line (with an impurity of less than 1 part in 10^3 of the second resonance line) was incident on the K-Rb cell. Light emitted from the cell at right angles to the incident beam was detected by an S-1 photomultiplier housed in a liquid-nitrogen–cooled Dewar. Placed in front of the photomultiplier was a filter system which either permitted the radia-

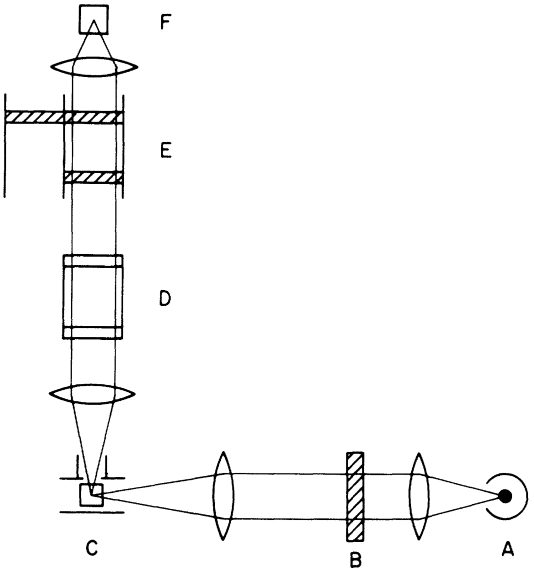

Fig. 2. Diagram of the apparatus: A is the K lamp, B is the interference filter passing one K line, C is the K-Rb cell, D is the K-absorption cell, E are the two interchangeable channels which hold interference filters, and F is the photomultiplier.

tion to pass through a neutral density filter or isolated the Rb cross fluorescence by means of the K-absorption cell in conjunction with interference filters passing the Rb lines. The absorption cell body was at 175 °C and the reservoir at 133 °C. The K fluorescence emerging from the K-Rb cell was approximately 10^6 times larger than the Rb cross fluorescence. Consequently, the measurement of all the radiation passed by the neutral density filter was equivalent to a measurement of the K fluorescence.

The temperature of the K-Rb cell was 97 °C; the K-doped Rb reservoir was varied between 34 and 55 or 85 °C, depending on the optical conditions required and the amount of K in the reservoir. Under these conditions the Rb densities were $\sim 10^{11}$ atoms per cm^3.

To measure the ratios $R1$, $R2$, and $R3$, the filters passing the K-resonance lines were interchanged in the incident beam. $R1$ was measured with a Wratten absorption neutral density filter to prevent saturation of the photomultiplier; $R2$ and $R3$ were measured using the K-absorption cell with one 7948 Å [100 Å full width at half-maximum (FWHM)] interference filter for $R2$, and two 7800 Å (90 Å FWHM) interference filters for $R3$. The ratio $R1$ was not measured simultaneously with $R2$ and $R3$ because moving the absorption cell caused temperature fluctuations in the K-Rb cell. To measure the ratios $R4$ and $R5$, the relative concentration of K to Rb was increased. In the course of a run measuring $R4$ or $R5$, one K resonance line was incident on the cell, and the 7948 and 7800 Å filter systems were interchanged.

In order to obtain the ratios from the measured signals, it was necessary to measure filter factors, and to correct $R1$ for the polarization of the K fluorescence. As in I, the filter factors were measured *in situ* to eliminate changes in geometry. The S-1 photomultiplier has a nearly constant quantum efficiency over the wavelength range used and no correction was made. Tests were carried out at high and low alkali densities to ascertain whether the filter apertures and the K-absorption cell affected the ratio of the intensity of the two Rb resonance lines. The transmission of the K-absorption cell was found to be the same for both Rb lines and consistent with the transmission expected through four glass windows. Therefore absorption by Rb contamination in the K-absorption cell was negligible. The absorption of K radiation by the K cell was found to be a function of the relative quantities of K fluorescence and K-lamp radiation scattered from the walls of the K-Rb cell. Since the latter was independent of alkali densities, it was a constant addition to the signals and contributed to a nonzero intercept. The transmission of the absorption cell was 2×10^{-2} for the K-lamp radiation and less than 2×10^{-3} for the K fluorescence. The K lamp was run cooler than in I to reduce the width of its radiation and thereby to obtain this rejection. (The cross sections involving transfer to the $\text{Rb}\,^2P_{3/2}$ level were not measured in I because the rejection of K fluorescence through the 7800 Å filters was at the time insufficient.)

The intensities were measured, as described in I, using a dc detection system and a chart recorder. The signals observed were $\sim 10^{-12}$ Å for $R2$ and $R3$, and $\sim 10^{-13}$ Å for $R4$ and $R5$. The integration time was determined by the characteristic time of the background noise which, together with blackbody radiation, was subtracted from the signals. During a run, which generally took 12 h, at least two measurements of each signal were made at every temperature of the K-doped Rb reservoir. Care was taken to alternate measurements between the two cross fluorescent signals at a given K-Rb–cell–reservoir temperature. To ensure that steady-state equilibrium conditions existed in the cell, the readings were taken 30 min after the temperature of the reservoir was increased. The radiation from the lamp scattered by the cell walls consisted of Ar lines in addition to the selected K line. The intercepts of the graphs shown in Figs. 3(b)–3(d) are caused predominantly by those Ar lines that fell within the passbands of the Rb filters.

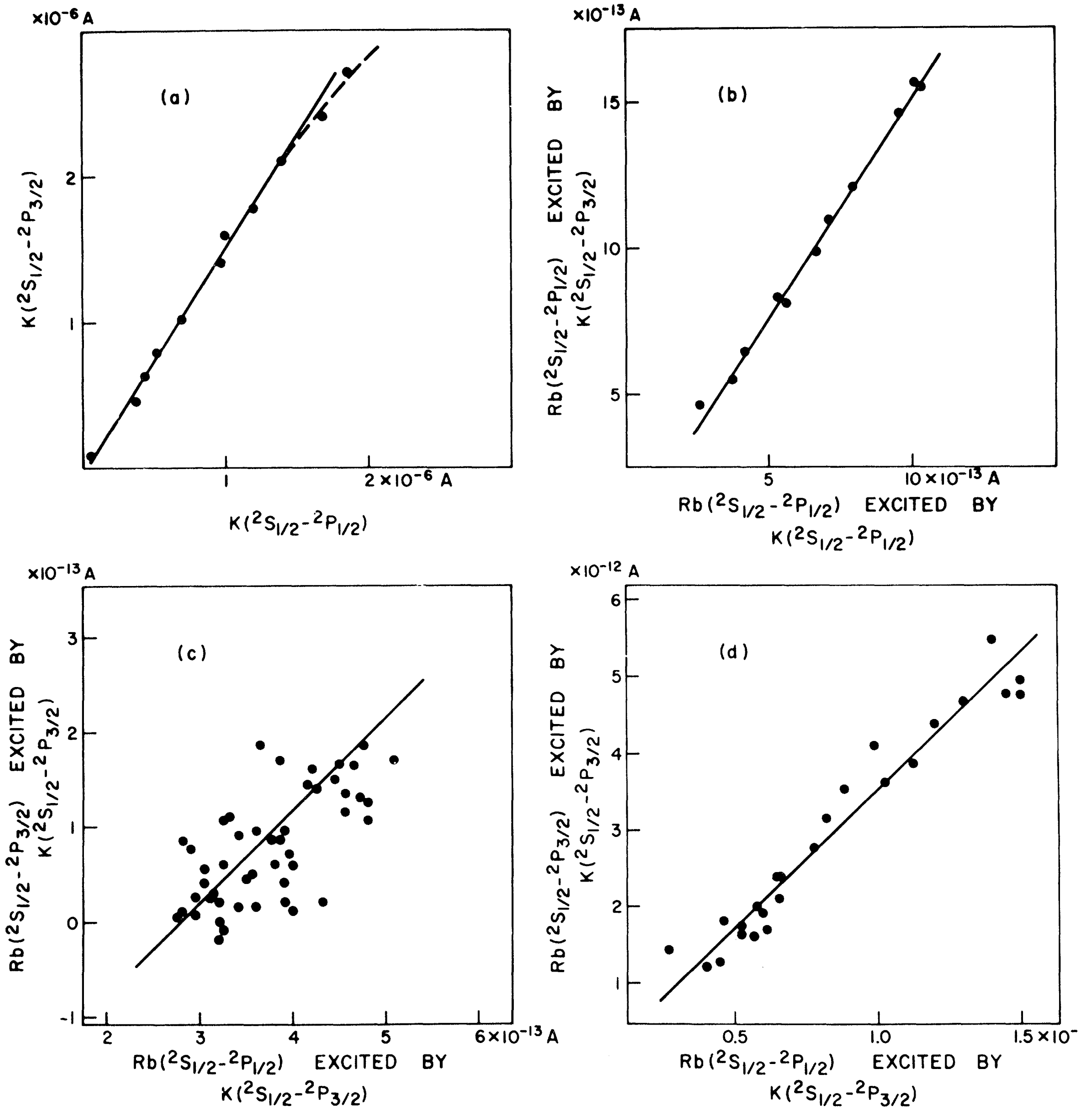

Fig. 3. Experimental data: measured ratios of various light signals. Note that (c) was obtained at low Rb optical depths and (d) at higher Rb optical depths for the same process.

IV. RESULTS

The graphs of four experimental runs are shown in Fig. 3. The ratios $R1$, $R2$, $R4$ (at low Rb densities), and $R4$ (at higher Rb densities) were found from a linear least-squares fit to the data in Fig. 3(a)–3(d), respectively. Runs yielding $R3$ and $R5$ were similar to Fig. 3(b) and 3(c). $R1$ was determined from three runs, $R2$ and $R4$ from four runs, $R3$ and $R5$ from two runs.

By combining the ratios of this work with the absolute values of the cross sections given in I (slightly adjusted for self-consistency[3]), a complete set of absolute values may be obtained. The absolute values of the cross sections and four ratios between them are given in Table I; the results of Hrycyshyn and Krause are also given for comparison. The quoted error for the present work is based on the scatter of the data (see Sec. V). The calculation of the ratio $R5$ from $R2$, $R3$, and $R4$ gives 2.4 ± 0.7, which is consistent with the measured value of $R5$ equal to 2.2 ± 0.6. It can be seen from Table I that there is good agreement between the absolute cross sections reported in I and the work of Hrycyshyn and Krause. However, while there is reasonable agreement between the ratios $Q3/Q1$ and $Q4/Q2$ reported by Hrycyshyn and Krause and those obtained in the present work,

TABLE I. Comparison of absolute cross sections and of ratios between them.

	Absolute cross sections (Å^2)			
	Q_1	Q_2	Q_3	Q_4
	$K\,^2P_{1/2} \to Rb\,^2P_{1/2}$	$K\,^2P_{1/2} \to Rb\,^2P_{3/2}$	$K\,^2P_{3/2} \to Rb\,^2P_{1/2}$	$K\,^2P_{3/2} \to Rb\,^2P_{3/2}$
Reference 2	2.2±0.6	...	2.6±0.5	...
Reference 1	2.7±0.6	40±8	1.9±0.6	27±7
This work	2.3±0.6	5.3±0.8	2.5±0.5	5.5±1.2
	Ratios between cross sections			
	$R2/R1 = Q3/Q1$	$R3/R1 = Q4/Q2$	$R4 = Q4/Q3$	$R5 = Q2/Q1$
Reference 2	1.2	...	...	...
Reference 1	0.7	0.7	14.2	14.8
This work	1.1±0.2	1.0±0.2	2.2±0.2	2.2±0.6

there is considerable disagreement between the values of the other two ratios.

V. DISCUSSION OF ERRORS

When detection of extremely low signals is unavoidable, as in this experiment, it is particularly important to scrutinize all possible sources of error. For example, if only 1 part in 10^6 of the K fluorescent radiation reached the detector, the present measurements would be invalidated. Since the signals were close to the limit of detectability, the checks designed to measure the presence of spurious contributions to the observed signals could not always be carried out entirely satisfactorily, and the possibility still cannot be excluded that some systematic error remains. However, it seems possible to conclude that the random error is due almost entirely to the statistical uncertainty in evaluating the low light signals reaching the detector and that any systematic effects remaining are likely to lead to even poorer agreement with the results of Hrycyshyn and Krause.

The various sources of uncertainty in this work are identified in Table II, together with the type of error and where each is discussed. Much of the error analysis in I (Sec. V) applies to this experiment and will not be repeated. The magnitude of the random error can be seen from the scatter shown in the graphs of Fig. 3; at the most, this leads to a 30% uncertainty in the cross-section ratios. Systematic effects, however, can influence the plots of Fig. 3 in three ways. (a) Signals independent of the alkali density cause an intercept to appear in the graphs; these signals contribute only to the random error in this experiment. (b) Certain effects, such as errors in the transmission factors of the filter system and spurious signals that depend on the second power of alkali density, alter only the slope of the graphs, and so are undetectable from a study of the data. (c) Signals that depend on some other power of the alkali density would manifest themselves by causing curvature in the graphs. Some of the effects listed in Table II are easily shown to be negligible; these are discussed briefly below. Effects requiring more careful consideration, e.g., radiation trapping and leakage of the K radiation through the Rb filters, are discussed at greater length.

Random changes in the lamp conditions were caused by variations of the voltage and of the air flow cooling the lamp. Such changes contribute to the scatter of the data and cause fluctuations in the intercept. Drifts in the lamp conditions were checked by decreasing as well as increasing the alkali densities during a run. No systematic changes were observed. Changes in the K-Rb-cell temperature during a run were also caused by voltage variations. The greatest differences were about 2 °C and developed over several hours. The cross sections are not expected to be rapidly varying functions of temperature; therefore, the systematic errors from this source should be small. Since ratios have been measured between signals of the same order of magnitude, the effect of any nonlinearity in the electronics was negligible.[4]

As mentioned above, the optical depth requirements of I were more stringent than those of the present work. In the theory discussion above, it

TABLE II. Error analysis.

Source	Type	Mechanism	Discussion
K lamp	random	short-term fluctuations	a
	systematic	long-term drift	a
K-Rb cell	random	temperature fluctuations	a
	systematic	temperature gradients	b
	systematic	polarization of K radiation	b
	systematic	polarization of Rb radiation	a
	systematic	radiation trapping	a
Filter system			
Interference filters	systematic	spectral purity	b, c
	systematic	polarization characteristics	a
	systematic	apertures	c
K-absorption cell	systematic	Rb contamination	c
Detection system	random and systematic	zero correction	b
	systematic	photomultiplier quantum efficiency	b, c
	random and systematic	nonlinearity	a

[a] Section V.

[b] Reference 2.

[c] Section III.

was shown that $R1$, $R2$, and $R3$ are primarily sensitive to the optical depth of K, and $R4$ and $R5$ to the optical depth of Rb, since cross-section ratios were measured. The first-order effects of radiation trapping are an increase in the concentration of atoms in the excited state and a change in spatial and angular distributions of the emitted radiation. In the $K^* + Rb$ system the increase in the effective number of excited K atoms causes more energy transfer collisions without increasing the K resonance fluorescent signal. Hence the ratio $N^K(i)/N^K(i')$ in $R2$ and $R3$ cannot be that measured by $R1$ when radiation trapping is present.

By comparing the resonance fluorescent radiations of K and Rb, shown in Figs. 5 and 6 of I, it can be seen that the onset of nonlinearity of the cross fluorescence (Fig. 7 of I) was determined by the optical depth of K, which was less than that of Rb. This demonstrates that at the Rb optical depths used in I, the changes in intensity due to the changes in radiation distribution were very small, but the effect of increasing the concentration of excited K atoms was more serious. As in I, care was taken to ensure that the K was optically thin for the ratios $R1$, $R2$, and $R3$; the lower optical depths of Rb $^2P_{3/2}$ used in determining $R4$ and $R5$ [Fig. 3(c)] were the same as those used in I for Rb $^2P_{1/2}$. The depths of Rb $^2P_{1/2}$ used were correspondingly a factor of 2 lower. The higher Rb density data for $R4$ [Fig. 3(d)] were taken beyond the range of density used for the absolute cross sections of I. They were consistent with the lower-density data. From this it is concluded that the effects of Rb-radiation trapping were still small at these optical depths. Thus the effects of radiation trapping were minimal.

The systematic error from the K leakage through the filters passing the Rb resonance lines was more difficult to assess. On the basis of separate tests of the K-absorption cell and the interference filters the leakage was calculated to be 0.02 of the Rb signals for $R2$ and $R3$, and 0.05 of the signals for $R4$ and $R5$. This however does not take into account the possibility of a "Lorentzian" type wing (>100 Å from line center) of the K resonance lines that falls in the passband of the filters. In view of the small signals, there appears to be no satisfactory method of distinguishing between the Rb resonance lines and the K wing in the same region. However, if more K signals were observed than were indicated by the tests, it would be manifested in a nonlinearity of the graphs. It can be plausibly argued that the cross sections involving Rb $^2P_{3/2}$ would be affected more than those involving Rb $^2P_{1/2}$, since the wavelength of the resonance line from the former is closer to the K resonance lines. In this case the measured ratios $R4$ and $R5$ would be larger than the true values, increasing the discrepancy between this work and that of Hrycyshyn and Krause. Indeed, most sources of systematic error tend to increase the observed signals rather than the reverse.

It should be noted that the cross fluorescence may be polarized.[5,6] No allowance was made for this since information is not presently available on polarization transfer in the K* + Rb system. However, the degree of polarization of the cross fluorescence is expected to be small.

During discussions with Hrycyshyn and Krause,[7] it was suggested that if the interference filters acted as polarizers, the pair that pass 7800 Å radiation might have been crossed, thus decreasing the signals observed. The filters were tested using an infrared linear polarizer and were not found to cause any polarization. As yet no satisfactory explanation for the discrepancy can be given.

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[1] E. S. Hrycyshyn and L. Krause, Can. J. Phys. 47, 215 (1969).

[2] M. H. Ornstein and R. N. Zare, Phys. Rev. 181, 214 (1969).

[3] Since the ratio $Q3/Q1$ calculated from the absolute values of I is not equal to the measured value of this work, the values of $Q1$, $Q3$, and the ratio were adjusted according to their statistical weights to give the results reported. To the significant figures given, the ratio was not altered; however, $Q1$ and $Q3$ were altered by $+0.1$ Å^2 and -0.1 Å^2, respectively.

[4] The photomultiplier response and related electronics were found to be linear to better than 5 % over the entire range used. This was calibrated with a variable distance light point source. See M. H. Ornstein, Ph. D. thesis, University of Colorado (unpublished).

[5] W. Gough, Proc. Phys. Soc. (London) 90, 287 (1967).

[6] G. W. Series, Proc. Phys. Soc. (London) 90, 1179 (1967).

[7] The authors would like to thank E. S. Hrycyshyn and Dr. L. Krause for useful discussions at the Sixth International Conference on the Physics of Electronic and Atomic Collisions, Boston, Mass. 1969.