9^2D fine-structure mixing in rubidium by collisions with ground-state Rb and noble-gas atoms

T. R. Mallory, W. Kedzierski, J. B. Atkinson, and L. Krause
Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4
(Received 6 June 1988)

The following cross sections for $9^2D_{3/2} \leftrightarrow 9^2D_{5/2}$ fine-structure mixing in Rb, induced in collisions with ground-state Rb and noble-gas atoms, have been measured using methods of atomic fluorescence spectroscopy: $Q(9^2D_{3/2} \rightarrow 9^2D_{5/2}) = 93$, 9, 6, 26, and 42; $Q(9^2D_{3/2} \leftarrow 9^2D_{5/2}) = 62$, 6, 3, 17, and 23, for Rb, He, Ne, Ar, and Kr, respectively, in units of 10^{-14} cm^2. The measured cross sections are in good agreement with recent theoretical calculations of Sirko and Rosiński.

I. INTRODUCTION

Inelastic collision of alkali-metal atoms excited to "intermediate" states that are higher than the resonance states but cannot be properly classified as Rydberg states, continue to be investigated in several laboratories. We have reported measurements of cross sections for fine-structure mixing in 6^2D, 7^2D, and 8^2D Rb atoms, induced in collisions with ground-state Rb atoms, noble-gas atoms, and N_2 molecules.[1-3] Total depopulation cross sections for nS and nD Rb atoms ($9 \leq n \leq 18$) colliding with He atoms have been measured by Hugon *et al.*[4] and fine-structure mixing cross sections for n^2D Cs atoms ($N = 11-13$) colliding with ground-state Cs atoms, were determined by Sirko and Rosiński.[5] Most recently, Sharma *et at.*[6] reported measurements of cross sections for $8^2S \rightarrow 6^2D$ excitation transfer in Rb, induced in collision with noble gases and ground-state Rb atoms. In this investigation we measured the cross sections for $9^2D_{3/2} - 9^2D_{5/2}$ fine-structure mixing in Rb by collisions with ground-state Rb and noble-gas atoms. The results (and those of previous experiments) are compared with values calculated by Sirko and Ronsiński[7] who used a semiclassical method to obtain the first theoretical rubidium and cesium ^2D fine-structure mixing cross sections.

Figure 1 shows a partial energy diagram of the Rb states involved in the radiative and collisional processes. The $9^2D_{3/2}$ or $9^2D_{5/2}$ state is selectively excited by two-photon absorption and the observed fluorescence arises from the three radiative transitions: $9^2D_{5/2} \rightarrow 5^2P_{3/2}$, $9^2D_{3/2} \rightarrow 5^2P_{3/2}$, and $9^2D_{3/2} \rightarrow 5^2P_{1/2}$. The $5P$ fine-structure splitting which amounts to 238 cm^{-1} could be easily resolved, though not the splitting of the ^2D states (0.70 cm^{-1}). Accordingly, the observed fluorescence spectrum consisted of two components, one at 5197 Å and the other, an unresolved doublet at 5262 Å, arising from both radiatively and collisionally populated substates. When the $^2D_{3/2}$ state was optically excited, the fluorescence consisted of component A which was due entirely to direct fluorescence, and component B which was due to a mixture of direct and sensitized fluorescence. When, on the other hand, the $^2D_{5/2}$ state was radiatively populated, the fluorescence consisted of component C consisting of sensitized fluorescence and D arising from a mixture of direct and sensitized fluorescence. Since sensitized fluorescence appears as the result of transfer between the ^2D states, induced in collisions with ground-state atoms, a variation in their density causes a corresponding change in the fluorescence intensity ratios. The equations which describe this relationship are[2,8]

$$\frac{A_{42}}{A_{31}}\left[\frac{I_B}{I_A}-\frac{A_{32}}{A_{31}}\right]^{-1}\frac{\tau_4 P}{C\sqrt{T}}=\frac{Q_{43}+Q_4}{Q_{34}}\frac{\tau_4 P}{C\sqrt{T}}+\frac{1}{Q_{34}}\,, \tag{1}$$

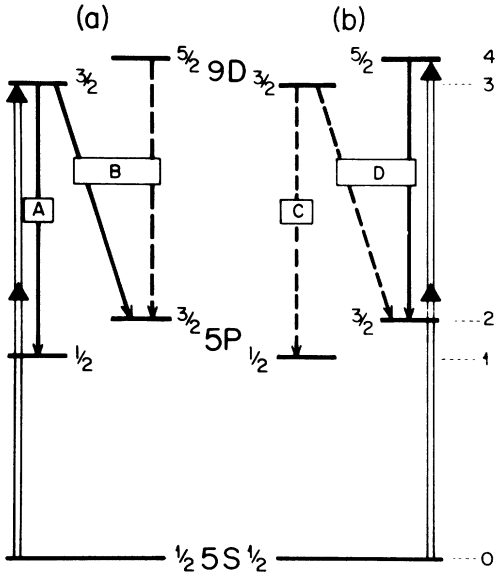

FIG. 1. Energy levels involved in the two-photon absorption and fluorescence emission process. (a) corresponds to optical excitation of the $9^2D_{3/2}$ state and (b) to optical excitation of the $9^2D_{5/2}$ state. A,B,C,D are the observed fluorescence components.

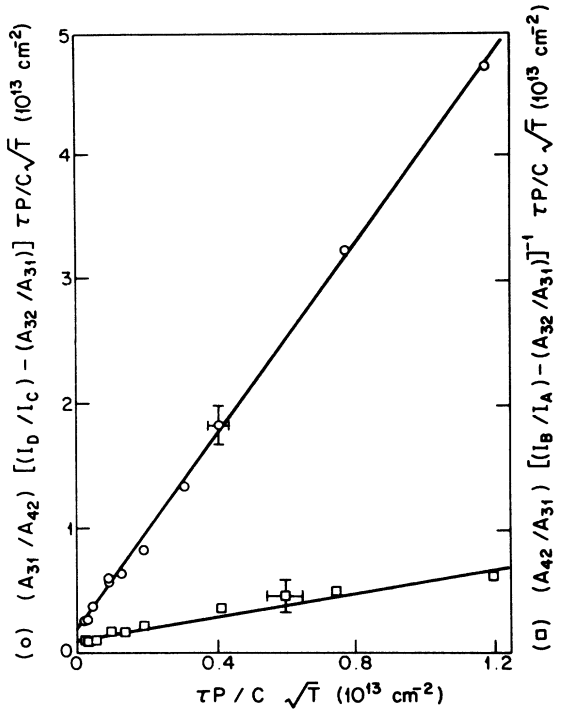

FIG. 2. Plots of the left-hand sides of Eqs. (1) and (2) against $\tau P/C\sqrt{T}$. The error bars are representative over the Rb-density range.

$$\frac{A_{31}}{A_{42}}\left[\frac{I_D}{I_C}-\frac{A_{32}}{A_{31}}\right]\frac{\tau_3 P}{C\sqrt{T}}=\frac{Q_{34}+Q_3}{Q_{43}}\,\frac{\tau_3 P}{C\sqrt{T}}+\frac{1}{Q_{43}}\,, \tag{2}$$

where τ_3 and τ_4 are the lifetimes of the $9D_{3/2}$ and $9D_{5/2}$ states, respectively, as determined by Waligórski *et al.*[9] ($\tau_3=\tau_4=618$ ns); P is the total pressure, T the temperature in the cell, and $C=\sqrt{\pi k\mu/8}$,. μ is the reduced mass of the colliding partners, Q_{34} and Q_{43} are the total (thermally averaged) cross sections for transfers $^2D_{3/2}\rightarrow{}^2D_{5/2}$ and $^2D_{3/2}\leftarrow{}^2D_{5/2}$, respectively, and Q_3 and Q_4 are the depopulation cross sections. The ratios of Einstein A coefficients were calculated from oscillator strengths given by Migdalek and Baylis.[10] They are $A_{32}/A_{31}=0.2085$; $A_{31}/A_{42}=0.8057$.

II. EXPERIMENTAL

The arrangement of the apparatus and the experimental method have been described previously.[1,2] A glass fluorescence cell containing Rb vapor, pure or mixed with a buffer gas, was irradiated with pulses of monochromatic light (6284 Å) from a N_2 laser-pumped dye laser operated with Rhodamine 640. The resulting fluorescence was resolved with a two-channel monochromator and registered with a gated photon counter. The cell was fitted with a side-arm and was mounted in a two-compartment oven which allowed accurate control of the Rb vapor pressure.

During the experiments with pure Rb vapor, the side-arm temperature was varied between 378 and 458 K which corresponded to the Rb vapor pressure range 0.26–20 mTorr.[8] During the experiments with Rb-buffer-gas mixtures, the side-arm temperature was kept constant at 353±0.5 K which produced a Rb vapor pres-

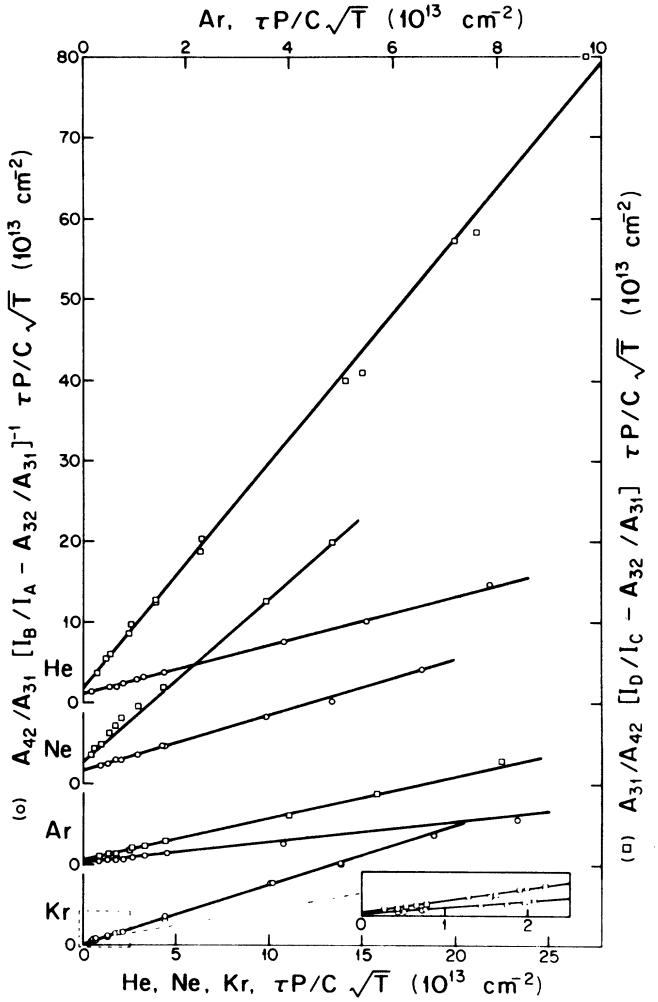

FIG. 3. Plots of the left-hand sides of Eqs. (1) and (2) against $\tau P/C\sqrt{T}$ for He, Ne, Ar, and Kr. The error bars are representative over the range of gas densities.

TABLE I. $9^2D_{3/2}$-$9^2D_{5/2}$ fine-structure mixing cross sections for Rb-Rb collisions (in units of 10^{-14} cm^2).

$Q_{34}(^2D_{3/2}\rightarrow{}^2D_{5/2})$	$Q_{43}(^2D_{3/2}\leftarrow{}^2D_{5/2})$	Q_{34}/Q_{43}	σ_g	Source
91±32	62±22	1.61	71.3	This work
65±20				Ref. 11
	26±5			Ref. 12

TABLE II. $9^2D_{3/2}$-$9^2D_{5/2}$ fine-structure mixing cross sections for Rb–noble-gas collisions (in units of 10^{-14} cm^2).

Collision partners	$Q_{34}(^2D_{3/2}\rightarrow{}^2D_{5/2})$	$Q_{43}(^2D_{3/2}\leftarrow{}^2D_{5/2})$	Q_{34}/Q_{43}
Rb-He	9±3	6±2	1.5
	5.1±1.0[a]		
Rb-Ne	6±2	3±1	1.9
Rb-Ar	26±9	17±6	1.5
Rb-Kr	42±15	23±8	1.8

[a] Reference 4.

sure of 4×10^{-5} Torr and provided a reasonable compromise between adequate fluorescence signals and sufficiently low Rb densities to render negligible the effects of Rb-Rb collisions. Noble-gas pressures ranged from 3 to 270 mTorr.

III. RESULTS AND DISCUSSION

Figure 2 shows plots of Eqs. (1) and (2) against $\tau P/C\sqrt{T}$ for pure Rb vapor and represents 9^2D fine-structure mixing induced in collisions between excited- and ground-state Rb atoms. As expected, the plots are linear; their slopes depend on the quenching cross sections Q_3 and Q_4 and the intercepts give the mixing cross sections Q_{34} and Q_{43}. The cross sections which were found to be independent of laser power[1] were calculated by a least-squares analysis of the data and are compared in Table I with the results reported by other groups. We believe the mixing cross sections to be accurate within ±35%. There are much larger errors associated with Q_3 and Q_4 and no useful purpose would be served in quoting values for these cross sections. The various sources of error have been discussed in some detail previously[1] and are also applicable to the present measurements whose results are affected by uncertainties in the 9^2D lifetime, the calculated Einstein A coefficients and, most of all, by the determination of the Rb vapor pressure from the side-arm temperature. The cross sections which are in the ratio close to the value 1.5 predicted by the principle of detailed balancing, agree within the stated limits of error with the values reported by Hugon *et al.*[11] and Q_{43} agrees quite well with σ_g, the geometrical cross section.[1] The cross section Q_{43} measured by Schuessler[12] is smaller than our value, in keeping with a general trend which has been noted previously.[3]

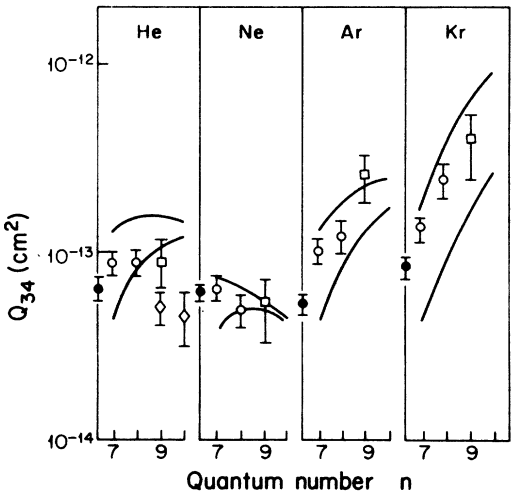

FIG. 4. Plots of $n^2D_{3/2}\rightarrow n^2D_{5/2}$ rubidium fine-structure mixing cross sections for He, Ne, Ar, and Kr collisions, in relation to n, the principal quantum number. The curves represent calculated cross sections (Ref. 7) and the points are experimental: ●, Ref. 3; ○, Ref. 1; □, this work; ◇, Ref. 4.

The experimental data representing 9^2D fine-structure mixing (and quenching) by collisions with He, Ne, Ar, and Kr, are shown in Fig. 3 and the resulting mixing cross sections are listed in Table II together with the single cross section for He determined by Hugon *et al.*[4] As expected, the noble-gas cross sections are smaller than the Rb-Rb cross sections because of the difference in the interaction.[1,2] As was the case with the 6^2D, 7^2D, and 8^2D mixing cross sections for collisions with noble gases, the cross sections exhibit a minimum at Ne and their relative sizes can be ascribed to several competing effects: relative speed of the colliding atoms, the increase of atomic polarizability from He to Kr, and the variation of the free electron-scattering cross section with the noble gases, which also shows a minimum at Ne, suggesting that the Rb ^2D orbital electron behaves as a quasifree particle,[1,8] though this model might not be applicable to the "intermediate" excited states to the same extent as it applies to Rydberg states.

A useful comparison may be made of the measured noble-gas cross sections for n^2D mixing in Rb with the calculations of Sirko and Rosiński.[7] Figure 4 shows the trends of the calculated cross sections in relation to n for the various noble gases, in juxtaposition with the experimental data obtained in this laboratory and elsewhere. It may be seen that our experimental values are in good agreement with the theoretical predictions; the values reported by Hugon *et al.*[4] agree less well, but their cross sections had been measured at $T=520$ K, a temperature at which the theoretical values of Rb-He cross sections are about 17% smaller than at 380 K.[5]

In comparing the Rb*-noble-gas cross sections for the $9D$ states with those for other n states, it should be noted that, for intermediate n values, the collision cross sections

tend to rise with n to a maximum and then gradually decrease as n increases.[13] The position of this maximum depends on the buffer gas. The measured cross sections for collisions of Rb with Ar and Kr, clearly show this increase of Q_{34} with n for $n=6-9$, while the Rb-He and Rb-Ne cross sections indicate only a possible increase between $n=6$ and $n=7$.

The internal consistency of the data can be checked using the principle of detailed balancing which predicts the ratio of the fine-structure mixing cross sections:

$$\frac{Q_{34}}{Q_{43}}=\frac{g_4}{g_3}\exp\left[\frac{-\Delta E}{kT}\right],$$

where $g_{3,4}=(2J+1)$ are the statistical weights equal to 4 and 6 for g_3 and g_4, respectively, $\Delta E=0.70\ \mathrm{cm}^{-1}$ is the 9^2D fine-structure splitting and $T=353$ K. The predicted value for the 9^2D cross sections is $Q_{34}/Q_{43}=1.50$. The ratios of the measured cross sections agree with this ratio within the stated limits of error.

ACKNOWLEDGMENT

This research was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

[1]J. Supronowicz, J. B. Atkinson, and L. Krause, Phys. Rev. A **30**, 112 (1984).

[2]J. Wolnikowski, J. B. Atkinson, J. Supronowicz, and L. Krause, Phys. Rev. A **25**, 2622 (1982).

[3]J. Supronowicz, J. B. Atkinson, and L. Krause, Phys. Rev. A **31**, 2691 (1985).

[4]M. Hugon, F. Gounand, P. R. Fournier, and J. Berlande, J. Phys. B **13**, 1585 (1980).

[5]L. Sirko and K. Rosiński, J. Phys. B **18**, L221 (1985).

[6]A. D. Sharma, H. A. Schuessler, and R. H. Hill, Jr., Phys. Rev A **37**, 4649 (1988).

[7]L. Sirko and K. Rosiński, J. Phys. B **19**, L279 (1986).

[8]T. R. Mallory, M. Sc. thesis, University of Windsor.

[9]G. Waligórski, P. Kowalczyk, and C. Radzewicz, Z Phys. D **3**, 79 (1986).

[10]J. Migdałek and W. E. Baylis, Can. J. Phys. **57**, 1708 (1979).

[11]M. Hugon, F. Gounand, and P. R. Fournier, J. Phys. B **13**, L109 (1980).

[12]J. W. Parker, H. A. Schuessler, R. H. Hill, and B. G. Zollars, Phys. Rev. A **29**, 617 (1984).

[13]M. Hugon, B. Sayer, P. R. Fournier, and F. Gounand, J. Phys. B **15**, 2391 (1982).